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Standardization of pH Measurements Made with
the Glass Electrode

Measurement and control of acidity and alkalinity are frequently essential in both industrial and research work. Commercial pH meters of the glass-electrode type, some of which are claimed to measure pH values with a reproducibility of 0.005 unit, are used in nearly every laboratory where chemical analyses and control tests are performed. These instruments are used to compare the acidity or alkalinity of unknowns and standard buffer solutions with which the electrode systems are calibrated from time to time. It is therefore quite important to have universal agreement on a standard scale of pH and to adopt standard reference buffers to define fixed points on this scale.

The National Bureau of Standards proposes that the scale of pH be defined in terms of certain pH standards whose assigned pH values correspond as closely as possible to the negative of the common logarithm of the activity of hydrogen (hydronium) ion, $-\log a_{\text{H}^+}$, in the respective solutions. For several years the materials from which 3 of these standards are prepared have been issued in the form of certified pH standard samples. Provisional values for 5 additional standards which will shortly extend the range of the standard scale to cover the region from pH 2 to pH 12 have been obtained. The NBS standards have received wide acceptance as reference buffers for adjusting glass-electrode pH meters so that all readings shall have a common basis.

1. Definition of pH

In the early days of pH measurements the usual object of measuring acidity was the estimation of the hydrogen-ion concentration of a buffer solution or a solution of an acid or base. However, development of the glass-electrode pH meter brought hydrogen-ion measurements out of the laboratory and put them to work in all phases of commerce and industry. The pH is now customarily regarded as a property of many diverse materials that possess some acidic or basic character. These may even include solids and solutions in non-aqueous or partially aqueous solvents. The technologic importance of pH is based to a large degree on this point of view. With this change of emphasis the pH unit has necessarily lost some of its fundamental meaning.

The practical scale of pH is now defined operationally in terms of the assigned pH (pH_S) of one or more standard solutions by the formula

$$pH = pH_S + (E - E_S)F/(2.3026 RT), \quad (1)$$

where E is the electromotive force of the cell

H₂; Solution | Satd. KCl, reference electrode

and E_S is the electromotive force of the same cell when the unknown is replaced by the standard; F is the faraday, 96,496 coulombs equiv.⁻¹ (1); R is the gas constant, 8.3144 joules deg⁻¹ mole⁻¹ (1); and T is the temperature on the Kelvin scale, T = t °C + 273.16. The vertical line indicates a liquid junction between two different solutions. Values of F/2.3026 RT in volts⁻¹ are listed in Table 1.

Table 1. Values of E° for the Hydrogen-Silver Chloride Cell and F/(2.3026 RT) from 0° to 60° C.

t	E°	F/(2.3026 RT)
°C	Volts	Volts ⁻¹
0	0.23652	18.452
5	.23404	18.120
10	.23140	17.800
15	.22854	17.492
20	.22557	17.193
25	.22245	16.905
30	.21918	16.626
35	.21571	16.356
38	.21358	16.199
40	.21214	16.095
45	.20829	15.942
50	.20439	15.597
55	.20040	15.359
60	.19625	15.129

Although the hydrogen electrode is the primary indicator for hydrogen ions, the glass electrode is much more convenient and versatile and is usually used for practical pH determinations. However, correction terms must be applied to measurements made in strongly acid and strongly alkaline solutions where the response of the glass electrode no longer parallels that of the standard hydrogen electrode. Although the saturated calomel electrode is most commonly chosen as the reference electrode, the difference of potential, E-E_S, is unaffected by substitution of another reference if proper precautions are observed.

The interpretation of the pH numbers computed by eq 1 evidently depends to a large extent upon the significance of the number assigned to the standard solution. If imperfections in this method of comparison could be ignored, the pH unit would derive its character exclusively from that of pH_S . A consideration of various possible standard scales reveals that none can be thermodynamically exact if pH is to be a measurable quantity.

The choice of a unit for expressing the degree of acidity of the standard solutions is most properly made in the light of (1) the nature of the response of physicochemical phenomena to changes of acidity and (2) of the techniques and methods of measurement. The term pH was originally proposed by Sørensen (2) and defined as

$$\text{pH} = -\log c_{\text{H}}, \quad (2)$$

where c_{H} is the concentration of the hydrogen ion. Later, as modern theories of electrolytic solutions developed, it became clear that, except in special cases, it is not possible to ascertain the concentration of hydrogen ions in buffer solutions and that the numerical values of acidity determined by the experimental procedure of Sørensen bear no simple direct relation to chemical equilibria.

Inasmuch as the effective concentration or activity, a_{H} , is fundamental in chemical equilibria, a definition of pH on the activity basis has much to recommend it (3). Furthermore, the well established electrometric method of pH measurement furnishes a number related more closely to a_{H} than to c_{H} . For these reasons pH_S is defined in terms of activity:

$$\text{pH}_S \equiv -\log a_{\text{H}} = -\log (f_{\text{H}}m_{\text{H}}) \quad (3)$$

where m is molality and f is the activity coefficient on the molal scale.

The activity and activity coefficient of a single ionic species such as hydrogen have no precise thermodynamic meaning. This objection to the form of eq 3 could be removed by substituting the mean activity coefficient, f_{\pm} , of a typical uni-univalent electrolyte for f_{H} . However, there is nothing to be gained by such a sacrifice of simplicity, for the estimated values of f_{H} may be identical with f_{\pm} at all concentrations.

Under ideal experimental conditions the measured pH is regarded as approaching the true $-\log a_{\text{H}}$ in the unknown solution. These conditions are realized most closely for buffer solutions of concentrations between 0.01 and 0.1 Molar (4) and pH between 3 and 11. Concentrated solutions, particularly those containing strong acids and bases, display larger deviations. Measurements in mixed solvents or non-aqueous media must be treated as numbers only, as the interpretation of pH in solvents other than pure water is difficult if not impossible at the present time.

2. Assignment of pH Values to Standards.

Inasmuch as there is no known physical method for separating the activity of a single ionic species from measurable combinations of ionic activities or activity coefficients, the assignment of pH values to any solution must rest upon an unproved assumption. Standard pH_s values are either made consistent with the known dissociation constants of the weak electrolytes (4, 5) or with the known behavior of activity coefficients in dilute solutions (6, 7, 8). For the second approach, a galvanic cell without liquid junction containing hydrogen electrodes and silver-silver chloride electrodes is preferred.

The electromotive force, E , of the hydrogen-silver chloride cell at a partial pressure of 1 atm of hydrogen measures a quantity which, for convenience, has been termed pWH :

$$pWH \equiv (E - E^\circ)F/(2.3026 RT) + \log m_{Cl} = -\log (f_{H^+} f_{Cl^-} m_H). \quad (4)$$

In eq 4, E° is the standard potential of the cell and m_{Cl} the molality of chloride ion in the buffer solution. Values of E° in absolute volts based upon the measurements of Harned and Ehlers (9) and the calculations of Hamer, Burton, and Acree (10) are given in Table 1. The limit of pWH in the chloride-free buffer solution, namely pWH° , is readily obtained by extrapolation of pWH values determined at two or more chloride concentrations. Unlike pH , pWH° is a definite physical quantity that retains its significance at all concentrations. The two units are related by

$$pH = pWH^\circ + \log f_{Cl}^\circ, \quad (5)$$

where f_{Cl}° is the limit approached by the activity coefficient of the chloride ion as the chloride molality is reduced to zero.

Several means of estimating f_{Cl}° in a pure buffer solution for the calculation of pH from pWH° by eq 5 have been considered (11, 12). All of these, and others as well, can qualify as reasonable in the light of the condition that the ions shall approach ideal behavior in infinitely dilute solutions. Consequently the value of pH at ionic strengths below 0.01 is little influenced by the particular assumption chosen for the computation. Such is not the case, however, in the range of ionic strengths from 0.01 to 0.1, where differences characteristic of the individual buffer ions become apparent. Fortunately it is possible, for ionic strengths as high as 0.1, to assign a mean pH that will represent, within about 0.01 unit, the separate pH values furnished by several reasonable methods of computation.

5. Recommended Standards

The National Bureau of Standards recommends eight standards, namely 0.01-M potassium tetroxalate; a solution of potassium hydrogen tartrate saturated at room temperature; 0.05-M acid potassium phthalate; a solution 0.025 M with respect to both sodium hydrogen succinate and sodium succinate;

a solution 0.025 M with respect to both potassium dihydrogen phosphate and disodium hydrogen phosphate; 0.01-M borax (sodium tetraborate); a solution 0.025 M with respect to both sodium bicarbonate and sodium carbonate; and 0.01-M trisodium phosphate. Six of these solutions are prepared by dissolving the proper weights of the pure materials (indicated in table 2) in water and diluting to 1 liter. The solution of potassium hydrogen tartrate is made by shaking vigorously an excess of the pure crystalline salt with 100 to 300 ml of water contained in a glass-stoppered bottle. The temperature of the water should be $25 \pm 3^\circ$. The most alkaline solution, 0.01-M trisodium phosphate, is prepared by dissolving 0.01 mole (1.419 g in air) of anhydrous disodium hydrogen phosphate in 100 ml of a 0.1-N solution of carbonate-free sodium hydroxide and diluting to 1 liter.

Freshly boiled water protected from atmospheric carbon dioxide while cooling should be used for all of the standard solutions. The pH of the water should be 6.7 to 7.3. When preparation of the standard requires the weighing of two salts, the weights of the primary and secondary salts are listed under A and B, respectively, in the table.

Table 2. Compositions of Standard Buffer Solutions (Air weights of salt per liter of buffer solution)

Standard	A	B
$\text{KH}_2(\text{C}_2\text{O}_4)_2 \cdot 2 \text{H}_2\text{O}$, 0.01 M	8. 2.54	6.
KH Phthalate, 0.05 M	10.21	
NaH Succinate (A) Na ₂ Succinate (B); each 0.025 M	3.50	4.05
KH_2PO_4 (A), Na_2HPO_4 (B); each 0.025 M	3.40	3.55
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, 0.01 M	3.81	
NaHCO_3 (A), Na_2CO_3 (B); each 0.025 M	2.10	2.65

None of the salts is appreciably hygroscopic. Potassium tetroxalate dihydrate should not be dried at temperatures higher than 55° , nor should borax be heated above normal room temperatures. Sodium carbonate should be heated for 2 hours at 300° before use. The other salts can safely be dried at 110° .

The pH values of these eight standards at several temperatures are given in Table 3. The approximate buffer value, dB/dpH, appears on the next to the bottom line. This quantity is defined (15) as the number of moles, B, of strong base required to change the pH of a liter of the buffer solution by one pH unit. Since the buffer value conveys no information concerning the change of pH with changes of concentration, the approximate change of pH at 25° on

Table 5. pH of Standard Buffer Solutions. Buffer Values and Dilution Effects.

t	0.01-M Tetroxalate	satd. Tartrate	0.05-M Phthalate	0.025-M Succinate	0.025-M Phosphate	0.01-M Borax	0.025-M Carbonate	0.01-M Trisodium Phosphate
0	2.14	-	4.01	5.46	6.98	9.46	10.52	-
10	2.15	-	4.00	5.42	6.92	9.53	10.18	-
20	-	-	4.00	-	6.88	9.22	-	-
25	2.15	5.56	4.01	5.40	6.86	9.18	10.02	11.72
50	-	-	4.01	-	6.85	9.14	-	-
58	2.16	5.55	-	5.41	-	-	9.91	11.58
40	-	-	4.05	-	6.84	9.07	-	-
50	-	-	4.06	-	6.85	9.01	-	-
60	-	-	4.10	-	6.84	8.96	-	-
$\frac{dB}{d\mu} \times 10^3$	22	27	24	57	24	20	26	27
Dilution ΔpH	+0.50	+0.06	+0.06	+0.06	+0.09	+0.02	+0.09	-0.10

diluting the solution with an equal volume of water has been chosen as an arbitrary measure of the dilution effect. The values of this quantity, designated Dilution ΔpH , are given on the bottom line of Table 5. A positive ΔpH signifies an increase of pH on dilution.

The saturated solution of potassium hydrogen tartrate is subject to molding and should be used only during the first day after preparation. Mold may also appear in the succinate buffer solution several weeks after preparation. This and the other solutions should be replaced every two months.

Only acid potassium phthalate, potassium dihydrogen phosphate, disodium hydrogen phosphate, and borax are presently available in purified form as Standard Samples issued by the National Bureau of Standards with certificates giving the pH values of their solutions at various concentrations and at temperatures from 0 to 60° C. Supplement to NBS Circular C398, which will be sent free on request, lists the Standard Samples prepared and sold by the National Bureau of Standards. The acid potassium phthalate (Sample No. 185) is priced at \$3.00 for 60 grams. The potassium dihydrogen phosphate and disodium hydrogen phosphate (Sample No. 186 I and No. 186 II, respectively), which are to be used together in equal molar proportions, are furnished in separate bottles containing 30 grams each at \$6.00 for the pair. The borax (Sample No. 187) is priced at \$3.00 for 30 grams. Orders, made payable to the National Bureau of Standards, should give both the number and name of the sample and must be paid for in advance with the order. Terms for foreign shipments and other details are described in the Supplement to Circular C398.

Potassium tetroxalate of the theoretical composition is obtained by recrystallization from water under such conditions that no crystals separate above 50° (14). Potassium hydrogen tartrate and the sodium succinates are readily recrystallized from water.

4. The pH Meter with Glass Electrode

A troublesome feature of electrometric pH determinations is the unknown magnitude of the potential across the liquid junction. Equation 1 assumes that replacement of the standard by the unknown results in no change in either the sign or magnitude of the liquid-junction potential. It is known that this assumption is only partially correct. The potential at the junction between saturated potassium chloride and a variety of buffer solutions of intermediate acidities (pH 5 to 11) appears to be fairly uniform. However, when appreciable amounts of strong acids and bases are present and the pH is less than 5 or greater than 11 the highly mobile hydrogen or hydroxyl ions carry an excess of electric charge across the boundary and give rise to a potential different from that given by the buffer standard. There is some evidence that the error of measurement caused by the difference of liquid-junction potentials may be either positive or negative in strongly acid solutions. In strongly alkaline ones, however, the measured pH is almost invariably too low. Unfortunately, the alkaline error of the glass electrode is in the same direction.

The magnitude of the residual liquid-junction potential is dependent on the geometry of the boundary as well as on the types of ions, their mobilities, and their activities. Because the number of variables is so great, it is not possible to tabulate corrections to be applied to individual measurements. The only practical means of dealing with these errors is through the use, for calibration of pH instruments, of standard solutions whose pH and ionic compositions match those of the unknowns fairly closely.

Inasmuch as the sodium-ion error of the ordinary glass electrode fabricated from Corning 015 glass is large, the high-alkalinity electrode should be used for all pH measurements above pH 9.5. The 015 glass electrode gives a measurement that is 0.6 unit low at a scale reading of 11.0 in solutions 1 N with sodium ion, whereas the high-alkalinity electrode gives correct results in the same solution. Furthermore, the latter type of electrode reads low by only 0.18 unit at pH 15.5 in solutions of this same sodium-ion concentration. The high-alkalinity electrode is not recommended for use below pH 9 and should be standardized with the borax, carbonate, or trisodium phosphate buffer solutions.

The pH meter should always be standardized at or near the temperature of the solutions to be measured, with the temperature dial properly adjusted. This dial permits the electromotive force-pH slope, that is, $F/2.3026 RT$ in eq 1, to be adjusted to its proper value for various electrode temperatures. Where necessary, the buffer solutions must be cooled or heated to match the temperature of the unknowns. If changes of temperature are not suitably compensated, correct pH values cannot be read directly from the scale. It is still possible to measure the electromotive force, however, and to compute the correct pH by eq 1. It is advisable always to standardize the instrument with two standards bracketing the pH of the unknown. Chance errors from improper temperature compensation are lessened by making the difference of pH between unknown and standard as small as possible.

Neither the 015 electrode nor the high-alkalinity electrode should be used consistently at temperatures above 45°. However, special electrodes are available for continuous operation at 95°, and these can be used for short periods at 100°. Little is known about the errors of these electrodes. The problem of measuring pH at high temperatures is further complicated by the lack of standards of which the pH is known above 60°. For approximate results, the pH of the phthalate, phosphate, and borax standards given in Table 3 can be plotted as a function of temperature and the line extended to the desired temperature. If measurements are to be made below pH 4 at elevated temperatures, approximately correct results will be obtained by standardizing the assembly with 0.01-M hydrochloric acid. The pH of this solution is about 2.05 at 60°, and its change with temperature is negligible. Approximate pH values for these 4 standards at temperatures from 60° to 95° are listed in Table 4. The estimated accuracy is 0.05 to 0.10 unit.

Table 4. Estimated pH of Standards for Use Between 60° and 95° C

t	0.01-M Hydrochloric acid	0.05-M Phthalate	0.025-M Phosphate	0.01-M Borax
°C				
60	2.05	4.10	6.84	8.96
65	2.05	4.13	6.85	8.94
70	2.05	4.16	6.86	8.92
75	2.05	4.19	6.88	8.90
80	2.05	4.22	6.90	8.89
85	2.05	4.26	6.92	8.88
90	2.05	4.30	6.95	8.87
95	2.05	4.35	6.98	8.87

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