PROVISIONAL pH VALUES FOR CERTAIN STANDARD BUFFER SOLUTIONS

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ABSTRACT

For use in the calibration of electrometric pH assemblies, 17 standard buffer solutions have been investigated, and pH values at 20°, 25°, and 30° C have been assigned to them. The pH values of these solutions range from 2.27 to 11.68 and are considered accurate to ±0.02 pH unit.

Hydrogen–silver-chloride cells without liquid junctions were used for establishing the precise pH values of the buffer mixtures. The assumptions made to determine the activity coefficients of the ions in the mixtures are discussed. The method of assigning an accurate pH value to a buffer mixture is outlined.

Directions for preparing the mixtures from purified anhydrous salts, standard solutions of acid and alkali, and pure water are given. Changes of temperature have a larger effect on the pH values of the buffers of pH greater than 7 than on those of the acid buffers. In all cases the effect of dilution is small; an error of 1 percent in the volume of solvent added results in a change of less than 0.001 pH unit.

The use of a pH meter of the glass-electrode–calomel-electrode type calibrated by means of a standard buffer may often involve greater uncertainties than those inherent in the pH value assigned to the buffer mixture. It should be recognized that errors arising from liquid junction, hysteresis, temperature, and salt effects may combine to give an uncertainty of 0.01 and 0.03 unit or more in practical pH tests.

CONTENTS

I. RECOMMENDED BUFFER SOLUTIONS

In the practice of determining pH (the negative common logarithm of the hydrogen-ion activity) by electrometric methods, the electrode system is usually standardized by means of buffer solutions of known acidity. Standard reference solutions used in the calibration of such pH equipment must be easily reproducible in composition, and stable, so that the pH values accurately established for them by means of the hydrogen electrode can be used with confidence.

The pH Standards Section of the National Bureau of Standards has in progress the selection and standardization of suitable substances of requisite purity and stability. The thermodynamic ionization constants of the weak acids which form useful buffer mixtures are being determined at temperatures between 0° and 60° C from electro-motive-force measurements of hydrogen–silver-chloride cells without liquid junction. These measurements likewise yield information regarding the activity coefficients of the ions which compose the mixture. The evaluation of the pH numbers from the electromotive-force measurements for each buffer solution is then possible. The

description of the method and its application to the determination of the pH values of malonate-chloride mixtures have been given in detail by Hamer and Acree [1]* and by Hamer, Burton, and Acree [2]. It is expected that pure crystalline buffer salts to cover the useful pH range in intervals of 0.2 pH unit will ultimately be available.

In table 1 are listed pH values of 17 mixtures at 20°, 25°, and 30° C. All of the values are thought to be accurate within ±0.02 unit. Compositions are given in table 1 in molalities (moles per kilogram of water); those of table 2 are given in terms of moles of alkali or acid and weight of water and of anhydrous buffer salt required for the accurate preparation of the solutions. For work which requires more than one ionic strength, different concentrations of certain buffers having nearly the same pH values are given. In the articles giving the precise data on which the tabulated values are based, the pH values at 0° to 60° C in 5° steps will be given to within 0.001 to 0.002 unit for concentrations of buffers from 0.1 to 0.001 M.

TABLE 1.—pH *values of standard buffer mixtures at 20°, 25°, and 30° C*

Solution No.	Standard buffer mixture	Molalities			pH value		
		m_1	m_2	m_3	20°	25°	30°
1	}KH$_2$PO$_4$ (m_1), HCl (m_2)_____	0.01549	0.01221	_____	2.262	2.270	2.280
2		.01105	.008710	_____	2.358	2.366	2.373
3	HKC$_8$H$_4$O$_4$ (acid potassium phthalate) (m_1), HCl (m_2)_____	.03600	.01800	_____	3.002	3.009	3.017
4	HKC$_8$H$_4$O$_4$ (acid potassium phthalate) (m_1)_____	.05000	_____	_____	4.001	4.008	4.015
5	}HKC$_8$H$_4$O$_4$ (acid potassium phthalate) (m_1) KOH (m_2), KCl (m_3)_____	.1000	.0600	0.04000	4.633	4.629	4.628
6		.03000	.02000	.01000	5.071	5.069	5.071
7	}CH$_2$(COOH)$_2$ (malonic acid) (m_1), NaOH (m_2) NaCl (m_3)_____	.02000	.03000	.01000	5.434	5.444	5.454
8		.01400	.02100	.007000	5.466	5.476	5.487
9	}KH$_2$PO$_4$ (m_1), Na$_2$HPO$_4$ (m_2), NaCl (m_3)_	.02877	.01834	.02877	6.658	6.640	6.630
10		.02000	.03000	.02000	7.012	6.994	6.983
11	NaH$_2$PO$_4$ (m_1), Na$_2$HPO$_4$ (m_2), NaCl (m_3)_____	.002943	.004501	.002943	7.218	7.202	7.195
12	}p-HOC$_6$H$_4$SO$_3$K (potassium p-phenol-sulfonate) (m_1), NaOH (m_2), NaCl (m_3)_	.01896	.009539	.009419	8.902	8.848	8.798
13		.01168	.005875	.005801	8.933	8.879	8.828
14	}Na$_2$B$_4$O$_7$ (m_1), NaCl (m_2)_____	.006045	.01210	_____	9.210	9.165	9.124
15		.004731	.009465	_____	9.212	9.168	9.127
16	}Na$_2$HPO$_4$ (m_1), NaOH (m_2), NaCl (m_3)__	.01213	.009303	.003022	11.76	11.62	_____
17		.01796	.01377	.004474	11.82	11.68	_____

TABLE 2.—*Compositions of the standard buffer mixtures*

Solution No.	Composition [1] (Amounts to be added to 1 kg of H$_2$O)
1_____	2.108 g KH$_2$PO$_4$; 0.01221 mole HCl.
2_____	1.504 g KH$_2$PO$_4$; 0.008710 mole HCl.
3_____	7.352 g HKC$_8$H$_4$O$_4$ (acid potassium phthalate); 0.018 mole HCl.
4_____	10.211 g HKC$_8$H$_4$O$_4$ (acid potassium phthalate).
5_____	20.422 g HKC$_8$H$_4$O$_4$ (acid potassium phthalate); 0.06 mole KOH; 2.982 g KCl.
6_____	6.126 g HKC$_8$H$_4$O$_4$ (acid potassium phthalate); 0.02 mole KOH; 0.746 g KCl.
7_____	2.081 g CH$_2$ (COOH)$_2$ (malonic acid); 0.03 mole NaOH; 0.585 g NaCl.
8_____	1.457 g CH$_2$(COOH)$_2$ (malonic acid); 0.021 mole NaOH; 0.409 g NaCl.
9_____	3.915 g KH$_2$PO$_4$; 2.604 g Na$_2$HPO$_4$; 1.682 g NaCl.
10_____	2.722 g KH$_2$PO$_4$; 4.260 g Na$_2$HPO$_4$; 1.169 g NaCl.
11_____	0.3530 g NaH$_2$PO$_4$; 0.6390 g Na$_2$HPO$_4$; 0.172 g NaCl.
12_____	4.025 g p-HOC$_6$H$_4$SO$_3$K (potassium p-phenolsulfonate); 0.009539 mole NaOH; 0.551 g NaCl.
13_____	2.479 g p-HOC$_6$H$_4$SO$_3$K (potassium p-phenolsulfonate); 0.005875 mole NaOH; 0.339 g NaCl.
14_____	1.217 g Na$_2$B$_4$O$_7$; 0.707 g NaCl.
15_____	0.9520 g Na$_2$B$_4$O$_7$; 0.553 g NaCl.
16_____	1.456 g Na$_2$HPO$_4$; 0.009303 mole NaOH; 0.177 g NaCl.
17_____	2.155 g Na$_2$HPO$_4$; 0.01377 mole NaOH; 0.262 g NaCl.

[1] For practical work, these amounts can be used in a liter of solution.

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

II. PREPARATION OF REAGENTS AND SOLUTIONS

All of the salts required for the preparation of these buffer solutions can be purified by recrystallization from water. Purified potassium dihydrogen phosphate, potassium p-phenolsulfonate, p-$HOC_6H_4SO_3K$, sodium chloride, and potassium chloride can be powdered and dried to the anhydrous state at 110° C. Sodium dihydrogen phosphate and disodium hydrogen phosphate should be dried at room temperature, or slightly above, for a day or more before complete dehydration at 110° is attempted. In this way fusion of the hydrated salts can be avoided. Borax can be dehydrated by fusion in platinum. Acid potassium phthalate, o-$HKC_8H_4O_4$, is supplied by the National Bureau of Standards as Standard Sample 84a. It is suggested that malonic acid, $CH_2(COOH)_2$, be purified by washing it with carbon tetrachloride and by recrystallizing it from ether. To avoid decomposition, the acid and its solutions should not be heated above 66° C.

A carbonate-free stock solution of sodium hydroxide can be prepared by the dilution of a 50-percent solution of sodium hydroxide of reagent quality (filtered to remove the insoluble carbonate) with freshly boiled distilled water. Carbonate can be removed from a 50-percent solution of potassium hydroxide by the dropwise addition of a strong solution of barium hydroxide until no more precipitate is formed. The barium carbonate precipitate should be allowed to settle overnight in a stoppered bottle and the clear solution siphoned off and diluted with carbon-dioxide-free water. The alkali solutions should be standardized against benzoic acid or acid potassium phthalate (NBS Standard Samples 39e and 84a). A solution of hydrochloric acid may then be standardized by titration against one of the standard alkalies. Phenolphthalein will serve as an indicator in each of these titrations. Precautions should be taken to prevent carbon dioxide from the air from gaining access to the titration vessel or to the bottle in which the standard alkali is stored.

The buffer solutions should be prepared with freshly boiled distilled water. It may be boiled in a large flask which can be closed during cooling by means of a stopper which bears a soda-lime tube. In this way the danger of contamination of the water with carbon dioxide is avoided.

Buffers having pH values near the neutral point or on the acid side should be stored in glass-stoppered bottles of resistant glass. It is suggested that alkaline buffers be kept in alkali-resistant bottles or flasks equipped with a siphon, and with a soda-lime guard tube at the air intake, which permits withdrawal of the solution without the introduction of carbon dioxide.

Six-tenths gram of thymol dissolved in each liter of buffer solution prevents mold growth, but the pH values of the alkaline buffers will be altered slightly. The magnitude of the pH change attendant on the addition of thymol to the standard buffer may be determined by comparing, by means of a pH meter, the pH value of the untreated buffer solution with that of a portion of the mixture to which has been added the proper quantity of preservative. The meter need not be accurately standardized for the measurement of this small change of pH.

III. SOURCES OF ERROR IN THE USE OF pH METERS CALIBRATED WITH STANDARD BUFFERS

Measurements of pH with the glass electrode are ordinarily made at temperatures between 20° and 40° C. The instrument must be calibrated at the temperature of use. These standard buffers are intended only for comparison with dilute aqueous solutions, and the pH value of an alcohol-water mixture or of a nonaqueous solution cannot be determined reliably with an apparatus calibrated by their means.

It is apparent from an inspection of table 1 that the temperature must be controlled if the highest reproducibility in the pH of the standard solution is to be attained. Most of the acid buffer solutions increase in pH, and the alkaline buffers decrease in pH, with rise in temperature from 20° to 30° C. It may be noted that at room temperature those buffers having pH values on the acid side of the neutral point show a smaller change with temperature than do those of high pH. For a precision of 0.02 pH unit, the measurement of pH values above 7.3 must be made at temperatures controlled within 2 degrees, and to within 1 degree when the most alkaline phosphate solutions are being employed. For measurements on the acid side, control to 5 degrees is sufficient for the attainment of the same degree of precision. A correction must be made for the electromotive force of the reference electrode at its temperature [5], including the liquid-junction potential (see p. 188). The change in pH with rise in temperature of each buffer can be computed from table 1.

The pH value of a buffer mixture composed of a weak acid and its salt is a function of (a) the ionization constant of the weak acid, (b) the ratio of acid to salt, and (c) a "salt-effect" term which depends upon the total amount and type of ionized substance present. The change of the pH value with temperature is largely the result of the change in the ionization constant. The salt-effect term is small for dilute solutions. On the other hand, accidental errors which alter the ratio of acid to salt are serious. Of these, contamination of the alkaline mixtures with carbon dioxide is the most common source of error. A carbon dioxide-free atmosphere should be employed when possible, but use of the buffer in air within 10 minutes after its removal from the bottle will ordinarily be permissible.

The addition of water in too large or too small a quantity has a relatively small effect, as an inspection of the data of table 1 will indicate. A dilution of 1 percent corresponds to a change of the order of 0.001 pH unit. For this reason, the standard buffers may be prepared with an error less than 0.002 pH unit by dilution to a total volume of 1 liter instead of by the addition of a kilogram of water.

The electromotive-force values of the buffers were determined with a precision corresponding to 0.001 to 0.002 pH in cells without liquid junctions, and the pH values assigned to them probably have an accuracy well within ± 0.02 unit. In the practical use of these buffers, however, in the calibration of vacuum-tube pH meters that have calomel and glass electrodes, the following additional sources of error may be present:

(1) The liquid-junction potentials between the unknown solutions and the reference electrode, such as the saturated KCl-Hg_2Cl_2-Hg system, may differ considerably from those between the standard

buffer solution and the same reference electrode. This error may range from 0.01 to 0.03 pH. When strong acid or alkaline solutions are being measured, however, this error may amount to 0.1 to 0.3 pH unit.

(2) The uncertainties in the temperature equilibrium and the hysteresis in the calomel and glass-electrode systems. Even with normal precautions these errors may range from 0.01 to 0.03 pH.

(3) Slow attainment of equilibrium in the double layer at the surface of the glass electrode under certain conditions. This disturbing hysteresis is manifested in a calibration "drift" after the glass electrode is removed from a buffer solution of known pH, rinsed once with distilled water or a second buffer, and then placed in the second buffer, which may or may not have the same hydrogen-ion activity. The electrode should be tested in consecutive small portions of the standard buffer or unknown solution until the drift disappears. This electromotive-force drift may be caused by adsorption of ions from the preceding solution, and to some extent by reactions of the 015 glass with the Na^+, OH^- or other ions in solution, and is especially disturbing when the electrode is calibrated in 0.01 to 0.05 M buffer and then used in very dilute unknown solutions.

An apparent reproducibility of 0.01 in pH readings may indicate that the factors (1), (2), and (3) are temporarily constant. The error of the measurement, however, may be much larger than 0.01 pH unit, even though the instrument has been calibrated with precise buffer standards.

For the calibration of glass-electrode assemblies, it is important to choose buffers which have pH values and compositions close to those of the unknown mixtures. This precaution is of particular importance at pH values above 9.5, where the "alkali error" of the 015 glass electrode is large. It is hoped that the pH values assigned to the borate and phosphate standards will be especially valuable in calibrations of glass electrodes for tests of alkaline solutions such as boiler waters. For a precision of 0.05 pH, the 015 glass electrode, when calibrated with standard borax buffer, may be used up to pH 9.5 and 10.5 in solutions containing 1 N and 0.1 N sodium ions, respectively. For the same precision, the standard buffer and an unknown mixture containing 0.1 N sodium ion should have pH values differing by 0.1 or less above pH 11.7 to minimize the effects of hysteresis of the glass electrode.

The pH value as read from a pH meter of the glass-electrode–calomel type with liquid junction is expressed approximately by

$$\text{pH} = \frac{(E - E^\circ - Ej)F}{2.3026RT},$$

where E is the electromotive force between the electrodes of the assembly consisting of inner reference electrode, glass, unknown solution, liquid junction, saturated KCl, Hg_2Cl_2, and Hg; E° is the standard potential of the cell; E_j is the potential of the liquid junction between saturated KCl and the solution of unknown pH; and R, T, and F are recognized constants.

It is assumed that the asymmetry potential of the glass electrode has been compensated by calibration of the instrument with a known

buffer and that it remains constant. At 25° C the above equation becomes

$$pH = (E - E° - E_j)/0.05914.$$

According to almost universal practice, the instrument is calibrated with a standard solution of known pH value, and $E°$ and E_j are assumed to remain constant for the subsequent measurement of unknown solutions. The instrument is adjusted to the "theoretical slope," that is, 0.05914 at 25° C. Thus it is assumed that any solution whose electromotive-force value differs from that of the standard solution by 0.05914 volt at 25° C will have a pH value 1 unit larger or smaller than that of the standard. Adjustments may be made for other theoretical slopes corresponding to the value of 2.3026 RT/F at any temperatures at which the instrument may be used. In most commercial instruments this adjustment is made either automatically or by a temperature-control knob.

Fairly concordant values of $E° - E_j$ have been obtained from measurements of several weak acid buffers having pH values ranging from 2.6 to 9.2 [3, 4]. Measurements of strong acid-salt mixtures, however, suggest that E_j for these solutions may differ by 1 to 3 millivolts (0.01 to 0.05 pH unit) from the value established by calibration with a standard buffer [3, 5]. In such cases, the simple theoretical relation between pH and electromotive force at that temperature is in error, and the measured pH value will differ from the true value. This error may be minimized by calibrating the instrument with the use of a standard buffer having pH value and ion mobilities and concentrations as close as possible to those of the unknown. The fact that the theoretical slope is practically that found experimentally gives assurance for the future of accurate pH measurements, when standards are available for calibration at pH values near those of the unknown solutions.

Until these sources of error are evaluated by extensive precision work, it is better to recognize uncertainties of 0.01 to 0.03 pH unit or more in practical pH tests. This uncertainty is always present in measurements of solutions whose ion concentrations, dielectric constants, liquid-junction potentials, etc., are not known.

IV. ACCURACY OF THE STANDARD pH VALUES

To obtain the pH of a standard buffer mixture containing known quantities of chlorides, as illustrated in table 2, use is made of the fact that the electromotive force (E) between the hydrogen and silver-silver-chloride electrodes is related to the pH value [1, 2] by four equations which involve the ionization constant of the buffer acid, HAn; the concentration of the acid and of its salts; and the activity coefficients of the various ions involved in the reactions:

$$pH = \frac{(E - E°)F}{2.3026\ RT} + \log m_{Cl} + \log f_{Cl}, \tag{1}$$

$$\frac{(E - E°)F}{2.3026\ RT} + \log m_{Cl} + \log (m_{HAn}/m_{An}) = pK - \log(f_{Cl} f_{HAn}/f_{An}), \tag{2}$$

$$\log f_i = \frac{-A z_i^2 \sqrt{\mu}}{1 + B a_i \sqrt{\mu}} + \beta\mu, \tag{3}$$

$$pH = pK - \log (m_{HAn}/m_{An}) + \log (f_{An}/f_{HAn}). \tag{4}$$

The symbol m represents the molality of chloride and of buffer acid and ions indicated in the subscripts; K is the ionization constant; z_i is the valence and f_i is the activity coefficient of each ion indicated in subscripts; μ is the ionic strength;[1] a_i is the "ionic size"; β is an empirical term; and R, T, and F have their usual significance. E° is the standard potential for the reaction $\frac{1}{2}$ H_2(1 atm)$+$AgCl (solid) $=$H$^+$$+Cl^-$$+$Ag (solid), forming HCl at an activity (fm) of unity. The values of E° at 20°, 25°, and 30° are taken as 0.22550, 0.22238, and 0.21911 volt, respectively [2, 6].

For monobasic acid buffers, the last term of eq 2 is very small. For such buffers the parameters a_i and β of eq 3 must be evaluated from differences between several series of measurements of solutions with varying ratios of chloride ion to buffer acid and anion.

It may be emphasized that by means of precise work it is comparatively easy to obtain the pK value of the buffer acid within ± 0.001. The use of pK in eq 4 to obtain the true pH of the buffer acid-salt mixture may, however, involve comparatively large uncertainties. The procedure of computing the pH value involves either the substitution in eq 1 of values of f_i (from eq 3) or substitution in eq 4 of values of f_i and of pK (from eq 2). The best values of a_i and β (eq 3) for computing f_i for the mixtures are obtained from the observed change of the last term of eq 2 when the buffer is diluted. When a_i and β values for the buffers have been ascertained from electromotive-force measurements of the solutions at several concentrations, the pH value may be computed with a high degree of certainty. Thus the pH values for the phthalate buffers, the malonate buffers, and the disodium-phosphate–dihydrogen-phosphate mixtures (solutions 3 to 11, inclusive) listed in table 1 are thought to be correct to well within 0.005 unit, for extensive measurements of these particular buffer mixtures have been made over wide ranges of temperature and concentration in the determination of the pK values of the buffer acid by means of eq 2. The a_i and β values so obtained, however, apply only to the individual ions which compose the mixture and probably do not form a very sound basis for estimating the activity coefficients of mixtures of other salts of the buffer acid and other chlorides.

The pH values of the borate and phenolsulfonate buffers and of phosphate solutions 1, 2, 16, and 17 were derived from electromotive-force measurements without the use of the most precise a_i and β values for the mixtures themselves. Since the total activity-coefficient contribution (last term of eq 4) for these dilute buffers is of the order of 0.09 unit or less, an uncertainty of not over ± 0.02 can safely be ascribed to the salt-effect term in the values listed.

A plot of the known buffer concentrations against the left side of eq 2, involving the measured electromotive-force data for a series of dilutions of a stock buffer-chloride solution of known ratio $m_{Cl}:m_{An}:m_{HAn}$, gives $-\log K$ (pK) at the extrapolated zero concentration of the buffer. This is true because the right-hand term, $-\log$ ($f_{Cl} f_{HAn}/f_{An}$), becomes zero at the extrapolated zero concentration of the buffer-chloride mixture, in which all of the activity coefficients (f_i) are unity. The same limiting value of pK is reached as a convergence point when any reasonable individual values of a_i and β are used in

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[1] The ionic strength, μ, is defined by $\mu = \Sigma m_i z_i^2/2$. For the computation of the molality of each ion species, strong electrolytes are considered to be completely ionized. The ionization of the weak acid is computed from the ionization constant of eq 2 and 4.

eq 3 for computing log f_i for each ion.   These plots may, however, have widely different slopes, both negative and positive, when different values of a_i and β are chosen.   It is possible then to choose values of a_i and β to keep pK in eq 2 constant for all concentrations of the buffer [2].   With these "best" values for a_i, β, and pK, it is then possible to compute the pH value within the experimental error of 0.001 to 0.002 unit for any concentration of the buffer-chloride mixture at the same buffer ratio.   As the sodium, potassium, and other salts in identical concentrations give slightly different electromotive-force data and may require different a_i and β values, it is obvious that much work, on all kinds of salts of the same buffer and on their mixtures with various chlorides and other salts, will be required before a_i values for particular combinations of ions can be estimated to cover all buffer-salt mixtures.   It is hoped that the activities of the buffers may also be measured by other more direct methods to obtain a_i and β values.

All of the pH values of table 1 are to be considered provisional. Further work on phthalate, phosphate, borate, and phenolsulfonate buffers is in progress and will be reported in detail at its completion.

V. REFERENCES

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