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COMPARATIVE LIQUID-JUNCTION POTENTIALS OF SOME pH BUFFER STANDARDS AND THE CALIBRATION OF pH METERS

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ABSTRACT

By application of the equation $\mathrm{pH}=(E-E_{ref}-E_j)/k$ to solutions whose pH values were known accurately, the sum of the potentials of the reference electrode and of the liquid-junction potential, $E_{ref}+E_j$, was obtained at 25° C by the method of cells with liquid junction for seven solutions suitable for standards of pH. The solutions used were 0.1018-*m* hydrochloric acid, pH 1.081; 0.01-*m* hydrochloric acid+0.09-*m* sodium chloride, pH 2.101; 0.05-*m* potassium acid phthalate +0.02-*m* potassium chloride, pH 3.989; 0.02-*m* potassium dihydrogen phosphate+0.02-*m* disodium hydrogen phosphate+0.02-*m* sodium chloride, pH 6.863; 0.02-*m* potassium phenolsulfonate+0.02-*m* potassium sodium phenolatesulfonate +0.02-*m* sodium chloride, pH 8.795; 0.02-*m* boric acid+0.02-*m* sodium borate (added together as sodium tetraborate)+0.02-*m* sodium chloride, pH 9.155; and 0.01727-*m* calcium hydroxide+0.01819-*m* sodium chloride, pH 12.38. Silver-silver-chloride electrodes immersed in saturated potassium chloride solution were used rather than the calomel electrodes customarily employed.

As E_{ref} remains constant when the buffer is changed, values for the *differences* in the liquid-junction potentials of various buffers in contact with saturated potassium chloride solution were obtained from the data. These differences were then used to calibrate seven Type 015 and three "low-alkali error" glass electrodes of commercial manufacture. The average agreement between the true pH of the buffer-chloride solution (determined from cells without liquid junctions) and that read on various commercial pH meters when corrected for the difference in the liquid-junction potentials and the alkali error of the electrode was ±0.01 pH unit. The data also furnish a critical test of the consistency of the pH values assigned to the various buffer solutions recommended by this Bureau for the calibration of the pH scale and for checking pH meters.

Recommendations are made for checking pH meters.

CONTENTS

I. INTRODUCTION

Recent publications from this Bureau have given provisional pH values for certain standard buffer solutions [1] [1] and detailed information concerning phthalate [2], phosphate [3], phenolsulfonate [4], and borax buffers [5]. The precision of each standard, established by the method of cells without liquid junctions [6], is considered to be 0.002 pH unit.

In the establishment of the pH scale by electrometric methods, it is assumed that any solution in which the emf of a hydrogen electrode differs from that in a second solution by 59.14 mv at 25° C ($2.3026RT/F$ at other temperatures) has a pH value 1 unit higher or lower than that of the first. The establishment of the pH scale therefore involves the use of one or more standard buffer solutions of known pH to obtain reference points and the subdivision of the scale into desired fractions (e.g. 0.1) of the theoretical pH unit.

It is evident that as many independent sets of calibrations of the scale of a pH meter can be made as there are available buffer standards. As the number of reference materials increases, it becomes important to determine how well the corresponding calibrations agree. Because the potential at the junction between the buffer solution and the electrolyte of the reference electrode (the so-called liquid-junction potential) enters into practically all measurements of pH, data on the comparative values for these liquid-junction potentials are needed. One of the purposes of this paper is to present data on the comparative liquid-junction potentials at 25° C for seven standard buffers that range in pH from 1.081 to 12.38. The method is independent of the potential and of the type of reference electrode.

As glass and hydrogen electrodes agree closely over the range of pH values from 1 to 9 [7], it is possible to use glass electrodes in pH meters, together with the values for the comparative liquid-junction potentials, to determine the accuracy with which the scale of the pH meter can be calibrated by the use of different buffers; that is, how closely the theoretical relation of 59.14 mv (at 25° C) for 1 pH unit is followed. Conversely, if it is assumed that the standards are spaced correctly with relation to one another along the pH scale, it is possible to determine accurately the performance of various types of glass electrodes immersed in different buffer solutions.

II. EXPERIMENTAL TECHNIC

1. METHOD

The pH of a buffer or unknown solution can be obtained by measurement of the electromotive force of the cell

$$-\mathrm{H_2(g)}\underset{E_1}{|}\text{buffer or unknown solution}\underset{E_j}{||}\text{saturated KCl}\underset{E_{ref}}{|}\text{reference electrode}+ \qquad (1)$$

and the equation

$$\mathrm{pH}=(E-E_{ref}-E_j)/k, \qquad (2)$$

in which E is the measured emf, $(E_1+E_j+E_{ref})$ of the cell between the hydrogen and the reference electrodes, E_1 and E_5 in figure 1:

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

E_{ref} is the potential of the reference electrode toward the hydrogen electrode in a solution of unit hydrogen ion activity when E_j is zero. E_j is the potential at the liquid junction between the buffer solution and the saturated potassium chloride, and k is the value for $2.3026RT/F$ at the temperature of the measurements [8]. Conversely, if solutions are available whose pH values are known accurately, a measurement of E permits a simple calculation of $E_{ref}+E_j$ for each buffer. Since the value for E_{ref} does not change with the buffer, it is possible to obtain accurate values for the *differences* in E_j for various buffers by a method that is independent of the nature of the reference electrode.

If the data pertaining to two buffers of known pH are designated by the subscripts I and II, the difference in the liquid-junction potentials is given by the expression

$$E_{j_{\mathrm{I}}}-E_{j_{\mathrm{II}}}=(E_{\mathrm{I}}-E_{\mathrm{II}})-k(\mathrm{pH}_{\mathrm{I}}-\mathrm{pH}_{\mathrm{II}}), \tag{3}$$

directly in terms of the measured quantities.

Independently, values for $E_{ref}+E_j$ can be obtained from the emf of two silver–silver-chloride electrodes, E_2 and E_5, immersed, respectively, in solutions of the buffer (I) containing known concentrations of chloride ions and in saturated potassium chloride (III). The emf of such a cell is given by the equation

$$(E_{ref}+E_j-E_2)=k\log\left(a_{\mathrm{Cl}_{\mathrm{I}}}/a_{\mathrm{Cl}_{\mathrm{III}}}\right)+E_j. \tag{4}$$

If the ratios of the activities of the chloride ions in solutions I and III were known, eq 4 would yield directly values for E_j for each buffer. It is not possible to obtain this ratio, however, and the data permit only the calculation of $E_{ref}+E_j$.

The activity of the chloride ion in the two solutions can be expressed by the following equations:

$$k\log a_{\mathrm{Cl}_{\mathrm{I}}}=k\ \mathrm{pH}-(E_1+E_2)+E^\circ \tag{5}$$

and

$$k\log a_{\mathrm{Cl}_{\mathrm{III}}}=E^\circ-E_{ref}, \tag{6}$$

where E° is the normal potential of the silver–silver-chloride electrode, 0.22238 v at 25° C [9]. Equations 4, 5, and 6 can be combined to give

$$E_{ref}+E_j=(E_1+E_2)+(E_{ref}+E_j-E_2)-k\ \mathrm{pH}. \tag{7}$$

Comparison of the sum of (E_1+E_2) and $(E_{ref}+E_j-E_2)$ with the values for $(E_1+E_j+E_{ref})$ obtained by direct measurement indicate a consistency of 0.07 mv (0.001 pH unit) in the two sets of data for each buffer. This comparison is important because the emf between E_2 and E_5 involves electrodes reversible to the same ion, whereas the emf between E_1 and E_2 and between E_1 and E_5 involve electrodes reversible to different ions.

It should be emphasized that it is actually the difference in E_j for various buffers in contact with the saturated potassium chloride which is used in the calibration of pH meters rather than the absolute values for E_j for each buffer. The following example will make this point clear. When a pH meter is calibrated with buffer I and the dial set to read the corresponding pH value, the setting of the "zero control" knob, E_{zero}, compensates for the liquid-junction potential of the first buffer in contact with the reference electrolyte and for the departure,[2] ΔE_{ref}, of the emf of the reference electrode from its normal value. The emf impressed upon the potentiometer system is then given correctly by the equation

$$E_{obs_{\mathrm{I}}}=E_{ref}+E_{j_{\mathrm{I}}}+E_{g_{\mathrm{I}}}+E_{zero}+\Delta E_{ref}, \tag{8}$$

where $E_{g_{\mathrm{I}}}$ is the potential of the glass (or hydrogen) electrode in contact with buffer I. When buffer I is replaced by buffer II and the setting E_{zero} left unchanged, the observed emf is given by

$$E_{obs_{\mathrm{II}}}=E_{ref}+E_{j_{\mathrm{II}}}+E_{g_{\mathrm{II}}}+E_{zero}+\Delta E_{ref}. \tag{9}$$

The true difference in the pH of the two buffers is given by

$$\mathrm{pH}_{true_{\mathrm{II}}}-\mathrm{pH}_{true_{\mathrm{I}}}=(E_{g_{\mathrm{II}}}-E_{g_{\mathrm{I}}})/k, \tag{10}$$

whereas the observed difference (as read on the meter) is

$$\begin{aligned}\mathrm{pH}_{obs_{\mathrm{II}}}-\mathrm{pH}_{obs_{\mathrm{I}}}&=(E_{obs_{\mathrm{II}}}-E_{obs_{\mathrm{I}}})/k\\&=(E_{g_{\mathrm{II}}}-E_{g_{\mathrm{I}}}+E_{j_{\mathrm{II}}}-E_{j_{\mathrm{I}}})/k.\end{aligned} \tag{11}$$

Since $\mathrm{pH}_{obs_{\mathrm{I}}}$ and $\mathrm{pH}_{true_{\mathrm{I}}}$ are equal, the correction to be applied to the reading of the meter is

$$\mathrm{pH}_{true_{\mathrm{II}}}=\mathrm{pH}_{obs_{\mathrm{II}}}+(E_{j_{\mathrm{I}}}-E_{j_{\mathrm{II}}})/k. \tag{12}$$

Because most meters use saturated potassium chloride solution as the reference electrolyte, the measurements reported here were confined to this solution.

2. ELECTRODES

The hydrogen and the silver-silver-chloride electrodes were prepared by methods described previously [5]. Palladinized electrodes were used in solutions of potassium acid phthalate [2]. The silver-silver-chloride electrodes were of greater utiliy than the calomel electrodes generally used, because they were less affected by air and showed considerably smaller thermal hysteresis. When the potassium chloride solution was saturated with silver chloride, successive batches of electrodes agreed in 24 hours to within 0.02 mv (0.0003 pH unit) and remained stable within this limit for several months. If the potassium chloride was not saturated with silver chloride, the emf drifted and became increasingly electropositive with time as the silver chloride dissolved from the surface of the electrode. Drifts as high as 17 mv were observed. It is thus possible to introduce serious errors when microelectrodes are immersed directly in comparatively large volumes of the solution.

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[2] This departure can be caused by exposure of the calomel to air [10] or by use of potassium chloride containing traces of bromides [11]. The zero control knob also compensates for the asymmetry potential of the glass electrode, but this is assumed to remain constant when the buffer is changed.

3. CHEMICALS

Potassium chloride of reagent-grade quality stated to contain 0.01 percent bromides was recrystallized twice from conductivity water. The recrystallized material and the corresponding mother liquor were tested by the following method at each stage of the purification process. Two electrodes that previously agreed to within 0.02 mv in a saturated solution of the purest potassium chloride were immersed, respectively, in (a) a solution of the crop of crystals and (b) the corresponding mother liquor, both saturated at 25° C. Oxygen was excluded from the cell system, and the solutions were saturated with silver chloride. The compartments containing the two solutions were connected by a rubber tube with a pinchcock. Measurements were made of the emf of such a cell, the potential of which is due solely to the presence of different quantities of bromide ion in the two solutions. When tested as above, a solution saturated with potassium chloride containing 0.05-mole percent of potassium bromide and 99.95-mole percent of the purest potassium chloride was found to give an emf 1.46 mv higher than the purest potassium chloride alone. From measurements of this type it was concluded that each recrystallization removed approximately 90 percent of the bromides. The final product contained less than 0.0002-mole percent of bromides, which would produce a difference in potential of less than 0.01 mv. The hydrochloric acid used for the preparation of the silver–silver-chloride electrodes was also freed from bromides [5]. Although the values for $E_{j_{\mathrm{I}}}-E_{j_{\mathrm{II}}}$ are independent of the emf and of the nature of the reference electrode, the above precautions were employed in order that the values for $E_{ref}+E_j$ for each buffer would not include a systematic error because of the presence of potassium bromide or air in the reference electrolyte.

The solutions were prepared in quantities of 10 liters from weighed amounts of conductivity water and specially purified chemicals. The conductivity water was prepared by C. G. Malmberg and had a specific conductance of 0.2×10^{-6} mho/cm^3 at 25° C. It was stored in an atmosphere of hydrogen until needed. The phosphates and phenolsulfonate were purified by R. G. Bates [4]. Particular care was taken to prevent contamination with atmospheric carbon dioxide. The solutions were transferred when necessary by a vacuum-hydrogen technic [5]. The calcium hydroxide was prepared by carefully washing pure calcium carbonate (low-alkali grade) with distilled water, after which the material was ignited at 1,000° C. The resulting oxide was allowed to react with an excess of water in a stoppered, paraffin-lined bottle and the calcium hydroxide washed several times with conductivity water. The final solution was diluted slightly with water to avoid precipitation at higher temperatures, and the concentration determined by titration with standard hydrochloric acid. This procedure for the preparation of solutions of pure calcium hydroxide was recommended by Flint and Wells [12].

4. EQUIPMENT

The apparatus is shown in figure 1. Reservoir *A* was filled with a solution of potassium chloride and silver chloride saturated at a temperature slightly higher than 25° C and kept free from air by bubbling hydrogen through the solution. Chamber *B* contained two silver-silver-chloride electrodes, E_4 and E_5, and was provided with a liquid-junction compartment, *C*, of the type used previously [13, 14] and a stopcock, *D*, leading to a waste jar, *E*. A second chamber, *F*, served to prevent accidental contamination of the main body of the buffer solution in *G* by possible diffusion of the saturated potassium chloride solution from the liquid-junction compartment *C*. Bubbler *H* was used to saturate the hydrogen gas with water vapor and was filled with the same solution used in *F* and *G*. The buffer solution under study was transferred to *F* and *G* without exposure to the air. Cell *G* contained two silver-silver-chloride electrodes, E_2 and E_3, and a double hydrogen electrode, E_1, [14] immersed in the buffer solution. The apparatus was then immersed in a water thermostat, the temperature of which was controlled at 25° C to within 0.01 degree.

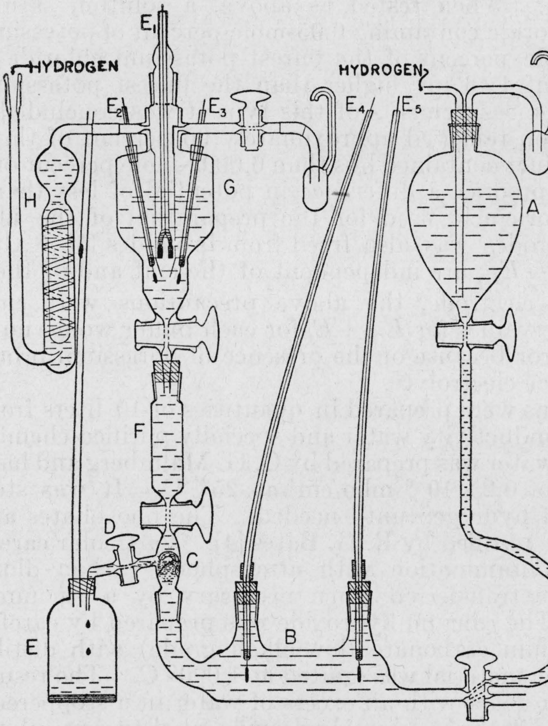

FIGURE 1.—*Apparatus used for the determination of $E_{ref}+E_j$ for buffer-chloride solutions by the method of cells with liquid-junctions.*

A, Reservoir for the saturated potassium-chloride solution; *B*, chamber containing the two silver-silver-chloride electrodes E_4 and E_5; *C*, the liquidjunction compartment with stopcock *D* leading to waste jar *E*; *F*, chamber to prevent contamination of the buffer chloride solution in *G* by accidental mixing of the saturated potassium chloride solution from *B*; *H*, the bubbler which saturates the hydrogen with water vapor before the gas enters the double hydrogen electrode chamber E_1; E_2 and E_3, silver-silver-chloride electrodes immersed in the buffer-chloride solution.

III. MEASUREMENTS OF ELECTROMOTIVE FORCE

The stopcock between *F* and *G* was closed, and hydrogen gas was bubbled over the hydrogen electrodes in *G*. Measurements were made of the emf (E_1+E_2) and of the agreement between the pairs of electrodes, E_3 and E_2, E_5 and E_4, and of the double hydrogen electrode. The hydrogen electrodes agreed to within 0.01 mv in a number of preliminary trials, and for the balance of the measurements the two hydrogen electrodes were connected by a pool of mercury with a common terminal E_1, as shown in figure 1. Equilibrium was attained in a few hours, after which the emf did not vary by more than 0.05 mv for several days. All values were corrected to 1-atmosphere pressure of hydrogen gas. The values for (E_1+E_2) reported here for hydrochloric acid, hydrochloric acid–sodium chloride, phthalate, phenolsulfonate, and borax agreed within 0.05 mv with data published previously for these buffers; the emf for the phosphate buffer was 0.11 mv (0.0018 pH unit) higher than that subsequently found by Bates in an extension of his work [3], but is within the precision claimed for these measurements. The pH value for the phenolsulfonate buffer was recalculated by a somewhat more detailed method and is 0.006 unit higher than that previously reported [4a]. The pH for the hydrochloric acid-sodium chloride solution was calculated from the data of Harned and Ehlers [9] and differs slightly from that used by Hitchcock and Taylor [15].

After measurements of (E_1+E_2) had been obtained for a buffer solution, cock *D* was opened, and the liquid junction between the potassium chloride and the buffer solution was made in *C*. The emf $(E_1+E_j+E_{ref})$ and $(E_{ref}+E_j-E_2)$ were measured at frequent intervals for various combined rates of flow and for various ratios of potassium chloride and buffer solution. The liquid junction for each buffer was quite sharp even at the highest rates of flow and the steadiness of the emf justified measurements to the nearest 0.01 mv. In table 1 is given a portion of the observed data and the calculated value for $E_{ref}+E_j$ for a typical buffer, potassium acid phthalate.

TABLE 1.—*Electromotive force and other data at 25°C for the cell:*

$-\text{Pt, H}_2 \mid$ 0.05-*m* KHPhthalate, 0.02-*m* KCl (pH 3.989) $\parallel$ saturated KCl $\mid$ AgCl, Ag+ Ag, AgCl $\mid$

Rate of flow, drops per minute		Time in minutes after a change in flow rate	Electromotive force in international volts				
Buffer	KCl		$(E_1+E_j+E_{ref})$	$(E_{ref}+E_j-E_2)$	(E_1+E_2)	(E_3+E_2)	(E_5+E_4)
12	0	2	0.43435	−0.13023	0.56443	0.00002	0.00001
		5	.43435	.13021	------	------	------
12	14	2	.43434	.13021	------	------	------
		4	.43434	.13021	------	------	------
12	36	2	.43434	.13021	------	------	------
		4	.43436	.13019	------	------	------
48	36	2	.43429	.13023	.56442	.00000	−.00003
		4	.43432	.13021	------	------	------
72	36	2	.43429	.13024	------	------	------
		6	.43429	.13026	------	------	------
8	36	2	.43429	.13026	.56445	.00002	+.00001
		5	.43430	.13026	------	------	------
Average values:					Values of $E_{ref}+E_j$:		
Flow of buffer > flow of KCl			0.43432	−0.13023	From $E_1+E_j+E_{ref}$		0.19839
Flow of buffer ≃ flow of KCl			.43432	−.13022	From $E_{ref}+E_j-E_2$		.19827
Flow of buffer < flow of KCl			.43432	−.13024	------		------
Grand average			0.43432	−0.13023	------		0.19833

For comparison with other data in the literature involving calomel electrodes, 0.0455 v should be added to $E_{ref}+E_j$ for each of the buffers given in table 2.

TABLE 2.—*Electromotive force and other data at 25° C for the cell:*

$$\begin{array}{l} -\text{Pt, H}_2 \\ \text{Ag, AgCl} \end{array}\Big|\textit{buffer}\text{, NaCl } \textit{or} \text{ KCl}\Big\|\textit{saturated}\text{ KCl}\Big|\text{AgCl, Ag}+$$

Buffer [a]	pH	Electromotive force in international volts			Values of $E_{ref}+E_j$ from	
		(E_1+E_2)	$(E_1+E_j+E_{ref})$	$(E_{ref}+E_j-E_2)$	$(E_1+E_j+E_{ref})$	$(E_{ref}+E_j-E_2)$
Hydrochloric acid	1. 081	0. 35149	[b] 0. 26292 [c] . 26296 [d] . 26318	[b] −0. 08850 [c] . 08849 [d] . 08829	0. 19909	0. 19913
		Average	0. 26302	−0. 08843		
Hydrochloric acid+chloride.	2. 101	0. 41209	[b] 0. 32147 [c] . 32145 [d] . 32155	[b] −0. 09065 [c] . 09068 [d] . 09061	. 19724	. 19719
		Average	0. 32149	−0. 09065		
Phthalate+chloride	3. 989	0. 56443	[b] 0. 43432 [c] . 43432 [d] . 43430	[b] −. 013023 . 13022 [d] . 13024	. 19841	. 19829
		Average	0. 43432	−0. 13023		
Phosphate+chloride	6. 863	0. 73499	[b] 0. 60375 [c] . 60374 [d] . 60373	[b] −0. 13124 [c] . 13119 [d] . 13122	. 19786	. 19789
		Average	0. 60374	−0. 13122		
Phenolsulfonate+chloride.	8. 795	0. 84811	[b] 0. 71783 [c] . 71725 [d] . 71726	[b] −0. 13080 [c] −. 13081 [d] −. 13081	. 19711	. 19716
		Average	0. 71725	−0. 13081		
Borax+chloride	9. 155	0. 86919	[b] 0. 73976 [c] . 73975 [d] . 73976	[b] −0. 12956 [c] . 12954 [d] . 12954	. 19833	. 19822
		Average	0. 73976	−0. 12954		
Calcium hydroxide+chloride.	12. 38	1. 06350	[b] 0. 92900 [c] . 92900 [d] . 92892	[b] −0. 13445 [c] . 13447 [d] . 13450	. 1968	. 1969
		Average	0. 92897	−0. 13447		

[a] Composition of buffer solutions:
0.1018 *m* HCl.
0.01 *m* HCl+0.09 *m* NaCl.
0.05 *m* $KHC_8H_4O_4$+0.02 *m* KCl.
0.02 *m* KH_2PO_4+0.02 *m* Na_2HPO_4+0.02 *m* NaCl.
0.02 *m* KHPs+0.02 *m* KNaPs+0.02 *m* NaCl; (Ps=paraphenolatesulfonate ion).
0.02 *m* H_3BO_3+0.02 *m* $NaBO_2$+0.02 *m* NaCl.
0.01727 *m* $Ca(OH)_2$+0.01819 *m* NaCl.

[b] Flow of buffer > flow of KCl.

[c] Flow of buffer ≅ flow of KCl.

[d] Flow of buffer < flow of KCl.

The data reported here for the emf and the pH of calcium hydroxide–sodium chloride solutions are believed to be the first obtained by the method of cells without liquid junctions. The values 4.5A for a_i and 0.1 for β for this solution were estimated from data for other buffer-chloride mixtures. Reasonable departures therefrom (±0.5 in a_i and ±0.05 in β) are unlikely to give rise to uncertainties larger than 0.02 pH unit, a quantity which is negligible in the calibration of the majority of pH meters. A comparison with the available pH data of other workers is given in table 3. The measurements of Wells [12a] and of Flint and Wells [12b, c] made at 30° C compare favorably with those of Lea and Bessey at 25° C [16] when correction is made for the change in pH with temperature for highly alkaline solutions. Measurements of the emf and the pH at 30° C by the method of cells without liquid junctions indicate that $d\mathrm{pH}/dT = -0.035$ pH unit per degree in this region.

TABLE 3.—pH *values interpolated for 0.01727-m calcium hydroxide solution at 25°*C

Year	Method	pH at 25° C	Investigator
1907	Conductivity	12.45	Noyes and Eastman [17].
1928	Electromotive force, H_2-calomel	12.36	Wells [12a] [a].
1933	do	12.41	Flint and Wells [12b] [a].
1934	do	12.36	Flint and Wells [12c] [a].
1937	do	12.43	Lea and Bessey [16].
1938	do	12.45	Fritsch [19] [b].
1943	do	12.40	Kalousek, Jumper, and Tregoning [18].
1944	Electromotive force, cells without liquid junctions.	12.38	This investigation.

[a] Corrected to 25° C by means of $d\,\mathrm{pH}/dT = -0.035$ pH/degree at pH 12.4.

[b] Temperature varied from 24° to 27° during the investigation.

IV. COMPARATIVE LIQUID-JUNCTION POTENTIALS

Values of $E_{j_{\mathrm{I}}} - E_{j_{\mathrm{II}}}$ can be obtained for various pairs of buffers by application of eq 3 and 7 to the data in table 2. The entries in table 4 represent the average values of $(E_{j_{\mathrm{I}}} - E_{j_{\mathrm{II}}})/k$ in terms of pH units. In each case, $E_{j_{\mathrm{I}}}$ designates the buffer listed at the top of columns 2 to 8 and $E_{j_{\mathrm{II}}}$ is the corresponding buffer in column 1. The consistency of the data presented in tables 1 and 2 indicates that the values for $(E_{j_{\mathrm{I}}} - E_{j_{\mathrm{II}}})/k$ in table 4 have the same degree of precision as claimed for the pH measurements themselves, ±0.002 unit. In general, the acid and the alkaline buffers have liquid-junction potentials which are, respectively, positive and negative to the saturated potassium chloride solution.

TABLE 4.—*Experimental values for $(E_{j_{\mathrm{I}}} - E_{j_{\mathrm{II}}})/k$ at 25° C for various pairs of buffers in contact with saturated potassium chloride solution*

Buffer I	Hydrochloric acid	Hydrochloric acid+chloride	Phthalate+chloride	Phosphate+chloride	Phenolsulfonate+chloride	Borax+chloride	Calcium hydroxide+chloride
Buffer II:							
Hydrochloric acid	0.000	−0.032	−0.013	−0.020	−0.033	−0.014	−0.03
Hydrochloric acid+chloride	+.032	+.000	+.019	+.012	−.001	+.018	−.01
Phthalate+chloride	+.013	−.019	+.000	−.007	−.020	−.001	−.02
Phosphate+chloride	+.020	−.012	+.007	+.000	−.013	+.006	−.02
Phenolsulfonate+chloride	+.033	+.001	+.020	+.013	+.000	+.019	−.01
Borax+chloride	+.014	−.018	+.001	−.006	−.019	+.000	−.02
Calcium hydroxide+chloride	+.03	+.01	+.02	+.02	+.01	+.02	+.00

It is beyond the scope of this paper to discuss the actual value of E_{ref} to be used in pH measurements performed with the hydrogen or the glass electrode. It is recommended instead that the meter be calibrated with two or more buffers at the start of the work. In most cases these extra measurements form but a small part of the total effort expended. More important, however, such a calibration eliminates the errors otherwise present which may be caused by insufficient purification of the potassium chloride, improperly prepared reference electrodes including the effect of air on their potentials, hysteresis, and the possibility of undersaturation of the potassium chloride solution. For purposes of comparison, however, it is of interest to observe the values for $E_{ref}+E_j$, which have been assigned to the saturated calomel electrode by various workers. These data are given in table 5. It should be noted that the value 243.4 ±0.4 mv (±0.007 pH unit) for the use with average buffers (pH 4 to 9) is identical with that estimated by Hamer [22], 243.4, for buffers of pH 4 to 5. The variations in $E_{ref}+E_j$ given in table 5 are not surprising in view of the possible sources of error. For example, 0.05-mole percent of bromides in the potassium chloride of the reference electrolyte increases the potential by 1.5 mv; an additional increase of 1.5 mv is found if the electrolyte is saturated with air.

TABLE 5.—*Comparison of the potential of the saturated calomel electrode at 25° C obtained by various investigators*

Year	Investigator	$E_{ref}+E_j$ in millivolts		
		Strong acids	Average buffers	Strong bases
1925	Scatchard [20]	245.4	245.4	
1928	Clark [21]	245.8	245.8	
1937	Hamer [22]	245.7	243.4	
1937	Hitchcock and Taylor [15]	245.0	244.1	
1938	MacInnes, Belcher, and Shedlovsky [23]		244.6	
1944	This research [a]	244.6	[b] 243.4	242.4

[a] Corrected for the difference of 45.5 mv in $E_{ref_{\mathrm{Hg_2Cl_2}}}-E_{ref_{\mathrm{Ag\text{-}AgCl}}}$.

[b] ±0.4 mv.

V. COMPARISON OF AVAILABLE BUFFER STANDARDS

The buffer solutions in table 2 and the values of $(E_{j_{\mathrm{I}}}-E_{j_{\mathrm{II}}})/k$ in table 4 were used to calibrate a total of seven Type 015 and three "low alkali-error" glass electrodes. The apparent pH values at 25° C were measured in a constant-temperature room by means of the Beckman model G, the Coleman model 3C, the Hellige model 7040, and the Leeds & Northrup model 7661–A1 commercial vacuum-tube pH meters.

The results showed that the sum of the dial readings on the meter and the corresponding value of $(E_{j_{\mathrm{I}}}-E_{j_{\mathrm{II}}})/k$, together with the alkali-error correction of the glass electrode whenever this was significant, equalled the true pH of the buffer solution to within an average of ±0.01 unit, regardless of the order in which the buffers were selected for use in the initial calibration of the meter. The averages of the data for the Type 015 and for the "low alkali-error" electrodes in which a 0.05-*m* solution of potassium acid phthalate (NBS Standard Sample 84 b) was used for the initial calibration are given in table 6. The correction for the alkali error in 0.01727–*m* calcium hydroxide +0.01819–*m* sodium chloride solution, 0.21 pH unit, was obtained by subtracting the corrected pH reading from the true pH. This procedure is considered preferable to the use of the value 0.26 obtained by Fritsch [19], because the temperature was not carefully controlled during his experiments.

VI. RECOMMENDATIONS FOR THE CALIBRATION OF pH METERS

The buffer standards listed in table 6 can be used for calibrating pH meters at 25° C when appropriate corrections are made for differences in the liquid-junction potentials and the alkali errors of the glass electrode. The maximum difference found in the calibration of four commerical meters by the use of these buffers was 0.01 unit and is the limit of readability of most of these instruments. In the analysis of unknown solutions, it is recommended that a standardizing buffer be selected that most nearly approximates the unknown in pH and in composition.

TABLE 6.—*Comparison of the calibrations of type 015 and "low-alkali error" glass electrodes in various buffer solutions at 25° C*

[0.05-*m* potassium acid phthalate (pH 4.008) was used for the initial calibration of the pH meters]

Buffer [a]	Known pH value	pH reading observed on meter	$(E_{j\mathrm{I}}-E_{j\mathrm{II}})/k$	Correction for alkali error	Corrected value for the observed pH (sum of columns 3, 4, and 5)	$\mathrm{pH}_{known}-\mathrm{pH}_{obs\,(corr.)}$
AVERAGE TYPE 015 GLASS ELECTRODE						
Phthalate	4.008	[b] (4.01)	0.00	0.00	4.01	(0.00)
Hydrochloric acid	1.081	1.09	−.01	.00	1.08	.00
Hydrochloric acid+chloride	2.101	2.08	+.02	.00	2.10	.00
Phthalate+chloride	3.989	3.99	.00	.00	3.99	.00
Phosphate+chloride	6.863	6.86	+.01	.00	6.87	−.01
Phenolsulfonate+chloride	8.795	8.77	+.02	.00	8.79	+.01
Borax+chloride	9.155	9.14	.00	.02	9.16	.00
Calcium hydroxide+chloride	[c] 12.38	12.15	+.02	[d] .21	12.38	.00
					Average difference.	0.00
AVERAGE "LOW-ALKALI ERROR" GLASS ELECTRODE						
Phthalate	4.008	[b] (4.01)	0.00	0.00	4.01	(0.00)
Hydrochloric acid	1.081	1.08	−.01	.00	1.07	+.01
Hydrochloric acid+chloride	2.101	2.09	+.02	.00	2.11	−.01
Phthalate+chloride	3.989	3.99	.00	.00	3.99	.00
Phosphate+chloride	6.863	6.86	+.01	.00	6.87	−.01
Phenolsulfonate+chloride	8.795	8.78	+.02	.00	8.80	.00
Borax+chloride	9.155	9.16	.00	.00	9.16	.00
Calcium hydroxide+chloride	[c] 12.38	12.35	+.02	.00	12.37	+.01
					Average difference.	0.00

[a] Composition of the buffer solutions:
0.05 *m* $KHC_8H_4O_4$.
.1018 *m* HCl.
.01 *m* HCl+0.09 *m* NaCl.
.05 *m* $KHC_8H_4O_4$+0.02 *m* KCl.
.02 *m* KH_2PO_4+0.02 *m* Na_2HPO_4+0.02 *m* NaCl.
.02 *m* KHPs+0.02 *m* $KNaPs$+0.02 *m* NaCl.
.02 *m* H_3BO_3+0.02 *m* $NaBO_2$+0.02 *m* NaCl.
.01727 *m* $Ca(OH)_2$+0.01819 *m* NaCl.

[b] The dial of the pH meter was set to read this value, and the instrument was balanced with the "zero control" knob.

[c] Provisional value, ±0.02 pH unit.

[d] Obtained by difference.

The concentrations of the solutions that can be used for the calibration of pH meters are not limited to those given in table 6 but may include others that are either more dilute or more concentrated (references 1 to 5). Since the experimental values for $(E_{j_{\mathrm{I}}}-E_{j_{\mathrm{II}}})/k$ in table 4 were determined for buffer-chloride solutions at 25° C, it is of interest to ascertain how much these quantities are changed when chloride-free buffers and other temperatures are employed. From the considerations given below, it can be said that the changes are considerably less than 0.01 pH unit.

Because $(E_1+E_j-E_{ref})$ and $(E_{ref}+E_j-E_2)$ for all buffers studied were affected on the average to less than 0.1 mv by wide variations in the rate of flow and in the ratios of the buffer and saturated potassium chloride solution forming the liquid junction, the differences in $(E_{j_{\mathrm{I}}}-E_{j_{\mathrm{II}}})/k$ for the same pairs of buffers with and without chloride are probably less than 0.002 pH unit. A degree of turbulence in the formation of the junction sufficient to cause a mixing of only 4 parts of the saturated potassium chloride solution with 996 parts of the chloride-free buffer would raise the chloride content of the latter to 0.02 *m*. Furthermore, at the concentrations used the difference in the effective mobilities of the positive and the negative ions of a chloride-free buffer is not altered appreciably when the solution is then made 0.02 *m* in sodium or potassium chloride. When the Henderson equation [24] is used to calculate the differences in the potentials of the liquid junction between the reference electrolyte and the buffer solution with and without chloride, the major assumptions made in the initial derivation of this equation are found to cancel; such a procedure should therefore be expected to give reasonably trustworthy values for these differences. The average difference calculated in this manner for the solutions listed in table 4, with and without chloride (hydrochloric acid and hydrochloric acid–sodium chloride excepted), is −0.003 pH unit.[3] Since this average difference is applied to each of the entries for $E_{ref}+E_j$ in table 2, no net change results in the values for $(E_{j_{\mathrm{I}}}-E_{j_{\mathrm{II}}})/k$ in table 4.

Likewise, the temperature coefficients for the liquid-junction potentials do not vary greatly. The calculated average liquid-junction potential for the buffers studied here is approximately 0.010 pH unit higher at 35° than at 25° C.[4] Again, the use of this average difference causes no net change in the values in table 4. Until more accurate data for the conductance of mixtures of ions become available, it is recommended that the values in table 4 be used for chloride-free buffers as well as for those that are 0.02 *m* in chloride and for temperatures up to or slightly beyond 35° C. The pH of these solutions varies with the concentration of the chloride ion and the temperature, and the appropriate pH values (references 1 to 5) must be used in addition to the corrections given in table 4.

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[3] The individual differences for phthalate, phosphate, phenolsulfonate, borax, and calcium hydroxide buffers are, respectively, −0.004, −0.003, −0.003, −0.005, and −0.002 pH unit. The mobilities of HPs^- and of Ps^{--} were estimated from data on other sulfonic acids.

[4] The individual differences for the buffers listed in table 4 are, respectively, 0.002, 0.006, 0.008, 0.009 0.009, 0.013, and 0.008 pH unit.

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