*p*H Values of the Clark and Lubs Buffer Solutions at 25°C

Vincent E. Bower and Roger G. Bates

The *p*H values of the well-known Clark and Lubs buffer solutions have been determined at 25° C on the conventional activity *p*H scale defined by the NBS standards. These solutions, which are useful for *p*H control in the range 1 to 10, are readily prepared by combining portions of four stock solutions with standard solutions of hydrochloric acid or sodium hydroxide. The four stock solutions contain potassium chloride, potassium hydrogen phthalate, potassium dihydrogen phosphate, or boric acid and potassium chloride. The compositions and buffer values of the solutions are listed at intervals of 0.1 *p*H. The estimated accuracy is ±0.02 *p*H unit.

1. Introduction

Among the best known series of buffer solutions for *p*H control are those of Sørensen [1] [1]; Palitzsch [2]; Clark and Lubs [3]; McIlvaine [4]; and Cohn, Heyroth, and Menkin [5]. Of these, perhaps the most widely used, particularly as standards in colorimetric *p*H determinations, are the solutions of Clark and Lubs. These are prepared by addition of standard solutions of hydrochloric acid or sodium hydroxide to portions of four stock solutions, followed by suitable dilution with water. In this way, buffer solutions of a predetermined *p*H value from 1 to 10 can be made.

The compositions and *p*H ranges of the solutions are as follows:[2]

*p*H 1.0 to 2.2: 25 ml 0.2 *M* KCl+*x* ml 0.2 *M* HCl, diluted to 100 ml.

*p*H 2.2 to 3.8: 50 ml 0.1 *M* KH phthalate+*x* ml 0.1 *M* HCl, diluted to 100 ml.

*p*H 4.0 to 6.2: 50 ml 0.1 *M* KH phthalate+*x* ml 0.1 *M* NaOH, diluted to 100 ml.

*p*H 5.8 to 8.0: 50 ml 0.1 *M* KH$_2$PO$_4$+*x* ml 0.1 *M* NaOH, diluted to 100 ml.

*p*H 7.8 to 10.0: 50 ml of a solution 0.1 *M* in both H$_3$BO$_3$ and KCl+*x* ml 0.1 *M* NaOH, diluted to 100 ml.

The exact compositions of solutions whose Sørensen *p*H values at 20° C vary in steps of 0.2 unit are to be found in monographs on *p*H measurement and in chemical handbooks.

In recent years there has been a gradual shift from the *p*H scale set forth by Sørensen to a conventional activity scale defined in such a way that measured *p*H values are consistent with the thermodynamic dissociation constants of the weak acids and bases that fix the *p*H [6]. The *p*H values assigned by Clark and Lubs to their buffer solutions are based on the earlier, virtually outmoded, scale. They are, therefore, about 0.04 unit lower between *p*H 3 and 11 than the values that would be assigned today. Near the ends of the *p*H scale the difference may be considerably greater.

Moreover, the *p*H values of these buffer solutions were determined by Clark and Lubs at 20° C rather than at 25° C, the temperature preferred for most experiments today. For these reasons, the *p*H of these useful buffers has been redetermined on the new scale at 25° C.

2. Method

The *p*H was calculated from the electromotive force, *E*, of cells of the type,

$$\text{Pt; H}_2 \text{ (g) solution X } | \text{ KCl (satd.) } | \text{ solution S, H}_2 \text{ (g); Pt.} \quad \text{(I)}$$

at 25° according to the relation

$$p\text{H}_\text{X}=p\text{H}_\text{s}+\frac{E}{0.059156}, \quad (1)$$

In cell I, solution X is the "unknown" buffer solution and solution S one of the NBS *p*H standards. In eq (1), 6.059156 is the value of 2.3026 RT/F at 25° C, if R is 8.31439 j deg^{-1} mole^{-1}, F is 96493.1 coulombs equiv.$^{-1}$, and T is 298.16° on the absolute temperature scale.

In accord with the usual convention, *E* was given the sign of the electrode on the right. It was thus positive when the *p*H of solution X exceeded that of solution S and negative when the *p*H of X exceeded that of S. Due to the symmetry of cell I, the value of *E* is unaffected by changes in the partial pressure of hydrogen, for equality of the latter at the two electrodes was maintained.

For a part of the measurements, the potentials of the two half-cells were measured separately with respect to a saturated calomel reference electrode that made electrolytic contact with the bridge solution of cell I. The *p*H of solution X was then calculated by eq (1), modified by the substitution of $E_\text{X}-E_\text{S}$ for *E*.

Four of the NBS standards were used in this study. In general, the standard with *p*H nearest that of the "unknowns" was selected for each particular series, as follows:

Series	Standard	*p*H$_\text{S}$ at 25° C
HCl, KCl (*p*H$_\text{X}$ 1.0 to 2.2)	0.05 *M* potassium tetroxalate	1. 68
KH phthalate, HCl (*p*H$_\text{X}$ 2.2 to 4.0)	0.05 *M* potassium hydrogen phthalate	4. 01
KH phthalate, NaOH (*p*H$_\text{X}$ 4.1 to 5.9)	0.05 *M* potassium hydrogen phthalate	4. 01
KH$_2$PO$_4$, NaOH (*p*H$_\text{X}$ 5.8 to 8.0)	0.025 *M* KH$_2$PO$_4$, 0.025 *M* Na$_2$HPO$_4$	6. 86
H$_3$BO$_3$, KCl, NaOH (*p*H$_\text{X}$ 8.0 to 10.2)	0.01 *M* borax	9. 18

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[1] Figures in brackets indicate the literature references at the end of this paper.
[2] In his monograph [3], Clark proposed a series of hydrochloric acid-potassium chloride mixtures of constant ionic strength 0.1 to replace the above series for the *p*H range 1.0 to 2.2.

The four standard solutions were freshly prepared for each series of measurements and were intercompared occasionally in cells of type I. The differences of pH among the three standards of pH above 4 were always consistent with the values assigned to these solutions. Because of the residual liquid-junction potential, which becomes significant at low and high pH [7], the measured difference between one of these three standards and the tetroxalate standard is found to be too large by about 0.02 pH unit. Therefore, uncorrected pH measurements with cell I in the range between pH 1.68 and pH 4.01 may be considered to be in error by $\pm 0.02n/(4.01-1.68) = \pm 0.009n$, where n is the difference of pH between the unknown and the standard. In applying this correction, due regard must be given the sign. If the assembly is standardized at pH 4 or above, the correction is added to the measured pH; if it is standardized at pH 1.68, the correction is subtracted. This correction has been applied to the values reported in this paper.

3. Experimental Procedures

The cell vessel has been described elsewhere [7]. Fresh hydrogen electrodes were prepared daily. For use in the phthalate solutions, the platinum foil bases were coated with palladium black [8]; in the other solutions, a coating of platinum black was satisfactory. The deposits were formed by electrolysis for about 2 min at a current of 300 ma. The palladium and platinum solutions were prepared as described elsewhere [9]. About 1 hr after the cell was immersed in the constant-temperature water bath and the flow of hydrogen begun, the liquid junctions were formed. The emf was measured immediately after establishment of the junctions and was found to remain constant within ± 0.1 mv for one-half to one hour.

The potassium hydrogen phthalate and potassium dihydrogen phosphate were NBS Standard Samples 185a and 186Ib, respectively. Boric acid was recrystallized twice from water and was dried in air at room temperature. The potassium chloride was a purified fused sample prepared in a manner described previously [10]. The standard solutions of hydrochloric acid were prepared from a distilled sample and were standardized by the gravimetric silver-chloride procedure. The solution of carbonate-free sodium hydroxide was standardized against NBS Standard Sample potassium hydrogen phthalate using phenolphthalein as the indicator. The standard solutions were not exactly 0.1 M or 0.2 M, but the results have been expressed on this basis. Calibrated volumetric glassware was used.

4. Results

The pH values obtained were plotted as a function of the quantity of standard acid or alkali added. The amounts of reagent read from the smoothed large-scale plots at even intervals of 0.1 pH are listed in the accompanying tables. The estimated accuracy of the pH values is ± 0.02 unit. When corrections for the differences in temperature and scale of reference are applied, the results of Clark and Lubs for the phthalate, phosphate, and borate solutions are found to be entirely consistent with those given here. The discrepancy is greater with the acid-chloride mixtures, for which the residual liquid-junction potential is appreciable.

The Van Slyke buffer value, β, is defined as db/dpH [11]. The quantity db represents the number of moles of strong alkali which increase the pH of 1 liter of the buffer solution by the amount dpH. The values of β given in the last columns of the tables were computed from the data for a finite increment, ΔpH $= 0.2$, by the relation $\beta \approx \Delta b/\Delta p$H. In this formula, then, Δb was the number of moles of strong alkali needed to raise the pH of 1 liter of the buffer solution from 0.1 unit below the point in question to 0.1 unit above. Both Δb and ΔpH are negative for additions of strong acid.

The pH values of the acid-chloride mixtures given in table 1 agree closely with the pH computed from the molar concentration, c, of hydrochloric acid and the ionic strength, μ, by the formula

$$p\mathrm{H} = -\log c + \frac{0.509 \sqrt{\mu}}{1 + 1.643 \sqrt{\mu}}$$

in which the activity coefficient of hydrogen ion is expressed by the Debye-Hückel equation with ion size of 5 A. This formula has also been used to calculate the pH values of mixtures of a constant total molarity (and ionic strength) of 0.1, which Clark [3] preferred. The results are given in table 6.

The buffer solutions should be prepared with a good grade of distilled water. Water for the preparation of the alkaline solutions should be boiled and protected from carbon dioxide while cooling, or should be purged with carbon dioxide-free air. The solutions will usually show satisfactory stability over a period of several weeks.

TABLE 1. *Compositions and buffer values of solutions of p*H *1.0 to 2.2: 25 ml 0.2 M KCl, x ml 0.2 M HCl, diluted to 100 ml*

pH	x	Buffer value, β
1.00	67.0	0.31
1.10	52.8	.24
1.20	42.5	.19
1.30	33.6	.16
1.40	26.6	.13
1.50	20.7	.10
1.60	16.2	.077
1.70	13.0	.060
1.80	10.2	.049
1.90	8.1	.037
2.00	6.5	.030
2.10	5.1	.026
2.20	3.9	.022

TABLE 2. *Compositions and buffer values of buffer solutions of pH 2.2 to 4.0: 50 ml 0.1 M KH phthalate, x ml 0.1 M HCl, diluted to 100 ml*

pH	x	Buffer value, β
2.20	49.5	----------
2.30	45.8	0.036
2.40	42.2	.035
2.50	38.8	.034
2.60	35.4	.033
2.70	32.1	.032
2.80	28.9	.032
2.90	25.7	.033
3.00	22.3	.034
3.10	18.8	.033
3.20	15.7	.030
3.30	12.9	.026
3.40	10.4	.023
3.50	8.2	.020
3.60	6.3	.018
3.70	4.5	.017
3.80	2.9	.015
3.90	1.4	.014
4.00	0.1	.014

TABLE 3. *Compositions and buffer values of buffer solutions of pH 4.1 to 5.9: 50 ml 0.1 M KH phthalate, x ml 0.1 M NaOH, diluted to 100 ml*

pH	x	Buffer value, β
4.10	1.3	0.016
4.20	3.0	.017
4.30	4.7	.018
4.40	6.6	.020
4.50	8.7	.022
4.60	11.1	.025
4.70	13.6	.027
4.80	16.5	.029
4.90	19.4	.030
5.00	22.6	.031
5.10	25.5	.031
5.20	28.8	.030
5.30	31.6	.026
5.40	34.1	.025
5.50	36.6	.023
5.60	38.8	.020
5.70	40.6	.017
5.80	42.3	.015
5.90	43.7	.013

TABLE 4. *Compositions and buffer values of buffer solutions of pH 5.8 to 8.0: 50 ml 0.1 M KH₂PO₄, x ml 0.1 M NaOH, diluted to 100 ml*

pH	x	Buffer value, β
5.80	3.6	----------
5.90	4.6	0.010
6.00	5.6	.011
6.10	6.8	.012
6.20	8.1	.015
6.30	9.7	.017
6.40	11.6	.021
6.50	13.9	.024
6.60	16.4	.027
6.70	19.3	.030
6.80	22.4	.033
6.90	25.9	.033
7.00	29.1	.031
7.10	32.1	.028
7.20	34.7	.025
7.30	37.0	.022
7.40	39.1	.020
7.50	40.9	.016
7.60	42.4	.013
7.70	43.5	.011
7.80	44.5	.009
7.90	45.3	.008
8.00	46.1	----------

TABLE 5. *Compositions and buffer values of buffer solutions of pH 8.0 to 10.2: 50 ml of a mixture 0.1 M with respect to both KCl and H₃BO₃, x ml 0.1 M NaOH, diluted to 100 ml*

pH	x	Buffer value, β
8.00	3.9	----------
8.10	4.9	0.010
8.20	6.0	.011
8.30	7.2	.013
8.40	8.6	.015
8.50	10.1	.016
8.60	11.8	.018
8.70	13.7	.020
8.80	15.8	.022
8.90	18.1	.025
9.00	20.8	.027
9.10	23.6	.028
9.20	26.4	.029
9.30	29.3	.028
9.40	32.1	.027
9.50	34.6	.024
9.60	36.9	.022
9.70	38.9	.019
9.80	40.6	.016
9.90	42.2	.015
10.00	43.7	.014
10.10	45.0	.013
10.20	46.2	----------

TABLE 6. *HCl–KCl mixtures of constant ionic strength, $\mu=0.1$; compositions and buffer values of solutions of pH 1.0 to 2.2: x ml 0.2 M HCl, y ml 0.2 M KCl, diluted to 100 ml*

Molarity of HCl	Molarity of KCl	pH	Buffer value, β
0.10	0	1.11	0.23
.09	0.01	1.15	.21
.08	.02	1.20	.18
.07	.03	1.26	.16
.06	.04	1.33	.14
.05	.05	1.41	.12
.04	.06	1.50	.092
.03	.07	1.63	.069
.02	.08	1.80	.046
.01	.09	2.11	.023
.005	.095	2.41	.012
.002	.098	2.80	.004
.001	.099	3.11	.002

pH	x	y	Buffer value, β
[a](1.00)	67.0	0	0.31
[b](1.10)	51.2	0	.24
1.20	40.7	9.3	.19
1.30	32.3	17.7	.15
1.40	25.7	24.3	.12
1.50	20.1	29.9	.093
1.60	16.0	34.0	.074
1.70	12.8	37.2	.059
1.80	10.2	39.8	.047
1.90	8.1	41.9	.037
2.00	6.5	43.5	.030
2.10	5.2	44.8	.024
2.20	4.2	45.8	.019

[a] $\mu=0.134$.
[b] $\mu=0.102$.

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