pH of Solutions of Potassium Tetroxalate from 0° to 60° C

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The National Bureau of Standards conventional activity scale of pH is defined in terms of a series of standard buffer solutions prepared from certified materials issued as NBS Standard Samples. In order to increase the accuracy of measurements at low and high pH, standards of high acidity and high alkalinity are needed to supplement the four now available, which cover adequately the intermediate range from 3.5 to 9.2.

Potassium tetroxalate dihydrate, chosen as the fifth pH standard, is a stable, crystalline substance composed, in addition to water, of equal molar amounts of oxalic acid and potassium acid oxalate. Its solutions are therefore well buffered in the concentration range 0.01 to 0.1 M and are highly acidic, with pH ranging from 1.5 to 2.2. Electromotive-force data were obtained for 12 mixtures of potassium tetroxalate and potassium chloride at 13 temperatures from 0° to 60° C, and pH values were assigned to 0.1-, 0.05-, 0.025-, and 0.01-M solutions of potassium tetroxalate without added chloride. The 0.05-M solution, which has a pH value of 1.68 from 15° to 35° C, is recommended as a standard for measurements at low pH.

1. Introduction

There are two primary reasons for the establishment of pH standards. The first and more important is to provide a reference for the adjustment of all pH equipment to a common basis, making possible true reproducibility of pH measurements from time to time and from place to place. The second purpose of pH standardization is to simplify the interpretation of the measured pH and to make it uniform over the entire range of the scale.

The first of these objectives can be met by the universal adoption of a single pH standard. The second is not so easily achieved. The unknown and variable potential at the liquid junction, indicated by the vertical line, in the practical pH cell

Pt; H_2 (or glass electrode), solution X| 3.5 M or
saturated KCl, Hg_2Cl_2; Hg   (1)

makes the interpretation of measured pH values in terms of concentrations or activities very difficult. Indeed, it is justifiable to assume that the practical pH lies on the scale defined by the standards only when solution X is a dilute aqueous solution of simple ionized solutes.

As is well known, the liquid-junction potential results from transfer of the positive and negative ions across the boundary in unequal numbers. Inasmuch as the transference numbers of all the ions are different, and possibly also the concentration gradients of the several ions through the boundary, the net charge transferred is rarely zero. It is impossible to make an exact correction for the variable liquid-junction potential. Hence, an unchanged liquid, junction potential on substitution of the standard (S) for the unknown solution in the cell is implied in the operational definition of the practical pH value:

$$pH = pH_S + \frac{(E - E_S)F}{RT \ln 10}.$$ (2)

In eq (2), E and E_S represent the electromotive force of cell 1 when the unknown and the standard solution (whose pH is pH_S), respectively, are in contact with the electrodes.

The hydrogen and hydroxyl ions have much greater mobilities than other ions. Furthermore, the mobilities of these other ions are all of the same order. For this reason, the liquid-junction potentials depart appreciably below pH 3 and above pH 11 from the relatively constant values maintained in the region of intermediate pH. At high acidities and high alkalinities, therefore, the measured pH may not be susceptible to the same simple interpretation given it near pH 7. When measurements below pH 3 and above pH 11 are to be made, this defect can be remedied to some degree by the choice of standards that are themselves highly acidic or highly alkaline [1].

To permit as far as possible a consistent interpretation of the pH over the entire scale, the National Bureau of Standards is establishing a series of standards extending from low to high pH. The standard pH is based upon emf measurements of cells free from a liquid junction and its attendant uncertainties. The standard pH scale is thus defined in terms of several fixed points in much the same manner as the International Temperature Scale.

The pH of the standards is defined formally by

$$pH_S \equiv -\log a_H,$$ (3)

where a_H is a conventional hydrogen-ion activity. Also by definition, $a_H \equiv f_H m_H$, in which f_H and m_H are the activity coefficient and molality of hydrogen ion. Inasmuch as the activity coefficient of a single ionic species cannot be determined, the numerical values of pH_S must have a conventional or defined basis. The NBS pH values rest upon the average of several reasonable estimates of the individual activity coefficient. At ionic strengths less than 0.1, the pH_S

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

values computed in these several ways are the same within about ±0.01 unit [2, 3, 4].

Potassium tetroxalate dihydrate, a stable acid salt, is a promising standard for the acid region. Its aqueous solutions, formed by weighing a single solid substance, contain equal molar amounts of oxalic acid and potassium binoxalate and are therefore well buffered. The pH is of the same order of magnitude as $-\log K_1$, where K_1 is the first dissociation constant of oxalic acid. This acid group is moderately strong, with $K_1 = 0.0536$ at $25°$, according to Darken [5]; hence, solutions of potassium tetroxalate with pH less than 2 can be prepared.

2. Method

The method by which the standard pH values (pH_S) were assigned to solutions of potassium tetroxalate has been described earlier.[2] There are three steps in the procedure. First, the emf, E, of cells of the type

$$\text{Pt; H}_2 \text{ (g, 1 atm), K tetroxalate } (m_1), \text{ KCl } (m_2),$$
$$\text{AgCl; Ag} \qquad (4)$$
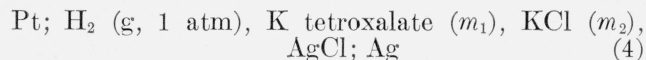
was measured and, with a knowledge of m_2, the molality of chloride ion in the buffer solution, values of the quantity pwH calculated by the equation

$$\text{pwH} \equiv -\log\ (f_H f_{Cl} m_H) = (E - E°)F/(2.3026RT) + \log m_2, \qquad (5)$$

where $E°$ is the standard potential of cell 4 and the other symbols have their usual significance.[3]

The second step was to determine $pwH°$, the limit approached by pwH for each buffer solution as the molality of added chloride was reduced. This was accomplished by the determination of pwH for chloride molalities of 0.015, 0.01, and 0.005, plotting pwH as a function of m_{Cl} (that is, m_2), and extrapolating to $m_{Cl} = 0$.

The third step was to compute pH_S from $\overline{pwH°}$. From the definitions of pH_S and pwH, we have]

$$pH_S = pwH° + \log f°_{Cl}, \qquad (6)$$

where $f°_{Cl}$ is the limit approached by the activity coefficient of chloride ion as the composition of the buffer-chloride mixture approaches that of the pure buffer solution. A nonthermodynamic assumption must be introduced at this point to permit the ionic activity coefficient to be evaluated.

The several reasonable conventional definitions of this coefficient that have been employed earlier for the computation of pH_S [6, 10, 11, 12] are all con-

sistent with the Debye-Hückel equation

$$-\log f°_{Cl} = \frac{A\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \qquad (7)$$

in which μ is the ionic strength, a_i is the ion-size parameter, and A and B are constants for aqueous solutions at a particular temperature.[4] These assumptions differ essentially only in the value of a_i and the manner in which this value was chosen. By combination of eqs (6) and (7),

$$pH_S = pwH° - A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}). \qquad (8)$$

From an examination of the mean activity coefficients of hydrochloric acid and chloride salts, it may be concluded that a_i for chloride ion probably lies between 3 and 6. When the concentration of the tetroxalate is 0.05 M, this uncertainty (± 1.5) in a_i amounts to less than 0.01 unit in the assigned pH_S.

3. Experimental Procedures and Results

The potassium tetroxalate dihydrate $(KH_3(C_2O_4)_2 \cdot 2H_2O)$ was a composite sample of a 250-lb lot purchased for issuance as NBS Standard Sample 189. The material was slightly moist. Before it was dried it was found to assay 99.6 to 99.7 percent by titration with a carbonate-free 0.17-M solution of sodium hydroxide to the endpoint of phenolphthalein. After drying three samples for 2 to 3 hours in air at $50°$ C, they assayed 99.93 ± 0.02 percent. The salt should not be heated above $60°$ C [1]. The results of other standard tests [14] were as follows:

Chloride: Less than 0.002 percent.
Sodium: Less than 0.02 percent.
Calcium: Less than 0.005 percent.
Iron: Less than 0.001 percent.
Ammonia: Less than 0.002 percent.
Sulfur compounds: None perceptible.
Heavy metals: Less than 0.002 percent (as Pb).
Substances darkening sulfuric acid: None.

The potassium chloride was a bromide-free fused sample prepared in the manner described earlier [15]. The specific conductance of the water used was, on the average, 0.8×10^{-6} ohm^{-1}cm^{-1}. Dissolved air was removed from the solutions by passing nitrogen through them for 2 hours.

Four concentrations of potassium tetroxalate, namely 0.1, 0.05, 0.025, and 0.01 ml, were studied. The emf values, corrected in the usual way to a partial pressure of 1 atm of hydrogen, are summarized in table 1. Each recorded figure represents the average for two pairs of electrodes in the same cell. These potentials are in good agreement with similar but less extensive measurements made in an earlier investigation [1].

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[2] See, for example, the assignment of pH_S values to solutions of potassium hydrogen tartrate [6].

[3] The values of $E°$ and $2.3026RT/F$ in absolute volts are listed in [7]. The values of the standard potential were derived from the measurements of Harned and Ehlers [8] as recalculated by Hamer, Burton, and Acree [9].

[4] Values of the Debye-Hückel constants from $0°$ to $100°$ C will be found in [13]. In the formula for B (bottom of p. 1765), "10^{-8}" should read "10^{8}".

TABLE 1. *Electromotive-force values for cell 4 from 0° to 60° C.*

KH tetrox- alate m^1	Potas- sium chloride m^2	Electromotive force at (° C.)—												
		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.1	0.015	------	------	------	0.42610	0.42673	0.42740	0.42783	0.42826	0.42860	0.42888	0.42908	0.42914	0.42922
							.42724	.42779	.42821	.42858	.42883	.42906	.42911	.42916
							.42732	.42767	.42813	.42852				
	.010	------	------	.43616	.43718		.43767	.43905	.43971	.44014	.43959	.44035	.44069	.44088
				.43559	.43654		.43769	.43797	.43888	.43925	.44003	.44044	.44082	.44107
							.43763	.43822	.43884					
	.005	------	------	------	.45313	.45407	.45564	.45618	.45719	.45809	.45915	.45986	.46048	.46102
							.45539	.45637	.45728	.45811	.45888	.45971	.46031	.46094
0.05	.015	0.43137	0.43262	0.43377	.43453	.43517	.43598	.43649	.43700	.43740	.43778	.43808	.43826	.43842
		.43133	.43248	.43349	.43438	.43518	.43582	.43646	.43694		.43775	.43803	.43814	.43816
							.43584	.43637	.43654	.43725	.43760	.43779	.43792	.43793
	.010	.44077	.44207	.44325	.44427	.44526	.44620	.44692	.44758	.44817	.44873	.44920	.44957	.44989
		.44077	.44216	.44330	.44435	.44535	.44620	.44697	.44764	.44813	.44870	.44901	.44939	.44935
		.44081	.44209	.44324	.44429	.44529	.44614	.44697	.44760	.44828	.44881	.44923	.44954	.44962
							.44602	.44678	.44736	.44801	.44862	.44905	.44949	.44981
							.44618	.44686	.44753	.44814	.44862	.44897	.44933	.44963
	.005		.45700	.45856	.46003	.46138	.46263	.46398	.46487	.46581	.46667	.46737	.46806	.46870	.46912
			.45703	.45864	.46010	.46149	.46267	.46399	.46497	.46598	.46687	.46757	.46836	.46903	.46961
							.46377	.46494	.46593	.46682	.46764	.46837	.46877	.46937
0.025	.015	.44064	.44193	.44309	.44413	.44524	.44612	.44661	.44728	.44780	.44813	.44840	.44837	.44831
		.44099	.44232	.44348	.44457	.44545	.44629	.44698	.44754	.44797	.44844	.44874	.44899	.44883
							.44602			.44762		.44840		.44867
	.010	.45014	.45162	.45302	.45423	.45532	.45639	.45723	.45800	.45866	.45923	.45974	.46021	.46052
		.45013	.45161	.45302	.45422	.45528	.45635	.45721	.45798	.45871	.45894	.45946	.45986	.46013
		.45024	.45167	.45306	.45430	.45539	.45638		.45776	.45834	.45904	.45953	.45999	.46013
										.45816		.45922		.46007
	.005		.46614	.46814	.46798	.47129	.47271	.47398	.47516	.47627	.47716	.47818	.47897	.47963	.48023
			.46625	.46796	.46962	.47117	.47252	.47389	.47500	.47604	.47704	.47796	.47883	.47952	.48013
								.47378	.47504	.47621	.47718	.47800	.47850	.47925	.47989
											.47657		.47829		.47971
0.010	.015	.45572	.45732	.45870	.45993	.46114	.46243	.46317	.46409	.46481	.46515	.46542	.46572	.46604
		.45550	.45709	.45851	.45966	.46098	.46210	.46275	.46352					
							.46237	.46312	.46388	.46468	.46537	.46586	.46626	.46648
							.46250	.46337	.46416	.46483	.46535	.46591	.46626	.46671
	.010	.46494	.46662	.46805	.46952	.47092	.47230	.47368	.47463	.47540	.47628	.47696	.47747	.47785
		.46507	.46684	.46849	.46990	.47121	.47237	.47725	.47408	.47493	.47580	.47636	.47694	.47730
							.47233	.47357	.47444	.47502	.47607	.47675	.47723	.47767
							.47228	.47350	.47434	.47531		.47606	.47681	.47731	.47777
								.47323	.47416			.47568	.47633	.47674	.47716
	.005	.48082	.48292	.48485	.48667	.48838	.48997	.49120	.49243	.49361	.49487	.49577	.49661	.49712
		.48098	.48303	.48490	.48670	.48830	.48975	.49112	.49239	.49355	.49461	.49557	.49639	.49709
		.48097	.48302	.48490	.48664	.48827	.48971	.49117	.49246		.49469	.49563	.49628	.49697

4. Determination of pwH°

The pwH was calculated by eq (5) from each emf value recorded in table 1. In order to obtain pwH°, the value of pwH for each tetroxalate solution in the absence of chloride, two types of extrapolation, illustrated in figure 1, were tried. The pwH values for the 0.1-m solution of potassium tetroxalate were first plotted as a function of the molality of chloride. A straight line, the lower line of figure 1, was drawn and extended to zero molality of chloride. The upper line was drawn through the pwH values for solutions containing the three different amounts of chloride but of lower tetroxalate content, so that the three points correspond to a constant ionic strength equal to that of the chloride-free buffer solution. The pwH, obtained by interpolation, is plotted as a function of m_{Cl}/μ, the fractional contribution of the potassium chloride to the ionic strength.

The two types of extrapolation gave the same result, within the error of the determination. Hence, the simpler and more convenient treatment, illustrated by the lower curve, was used. The plots of pwH as a function of the molality of added potassium chloride at 0°, 25°, and 60° C are shown in figures 2, 3, and 4, respectively. The positions of the lines were determined by the method of least squares. The values of pwH° obtained are summarized in table 2. The accuracy of pwH° is judged to be about ±0.003 at 0° and 25° C and ±0.005 at 60° C.
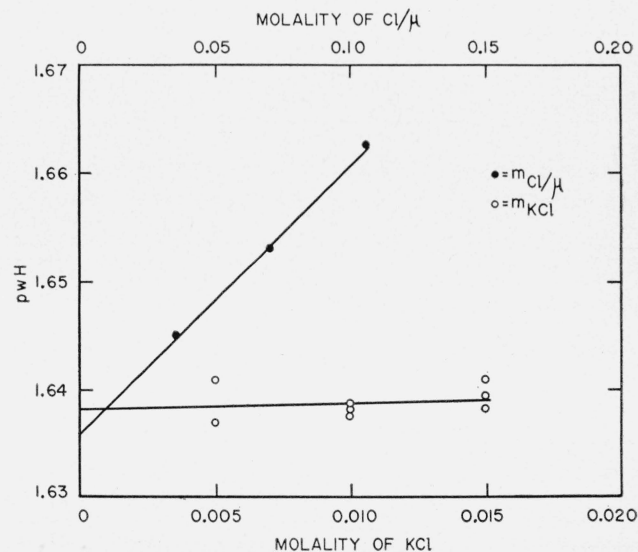
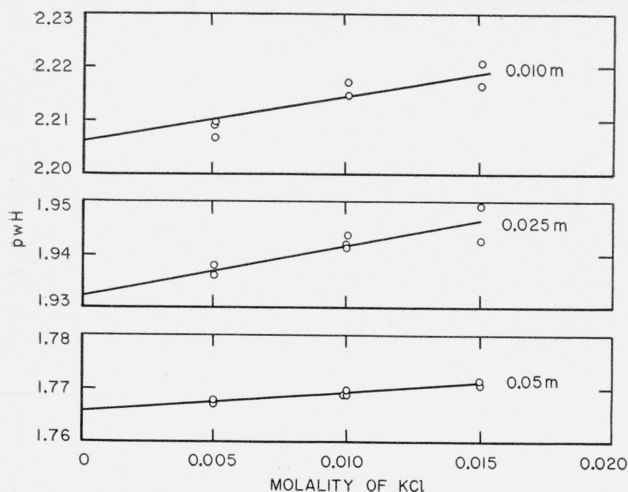FIGURE 1. *Extrapolation of* pwH *to zero concentration of potassium chloride by two different methods.*

FIGURE 2. pwH *of solutions of potassium tetroxalate as a function of the molality of added potassium chloride at 0° C.*
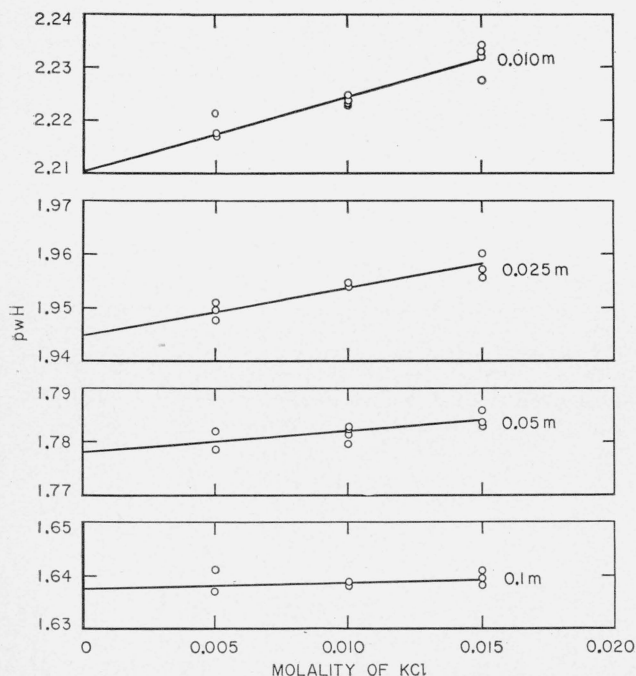

FIGURE 3. pwH *of solutions of potassium tetroxalate as a function of the molality of added potassium chloride at 25° C.*
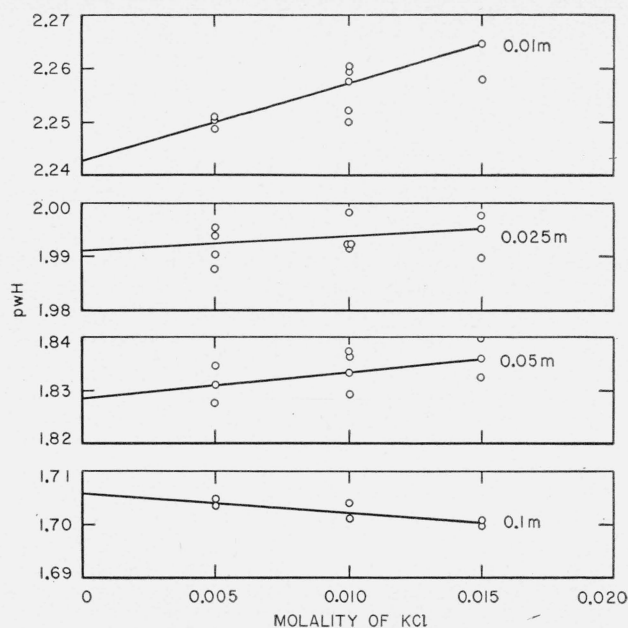

FIGURE 4. pwH *of solutions of potassium tetroxalate as a function of the molality of added potassium chloride at 60° C.*

5. Calculation of pH$_s$

The ionic strength of a solution of potassium tetroxalate of molality m_1 is given by

$$\mu = m_1 + m_H. \tag{9}$$

The dissociation of the second acid group of oxalic acid in tetroxalate solutions is so slight that its contribution need not be considered [16]. The hydrogen-ion concentration, m_H, was obtained with sufficient accuracy by the method of successive approximations directly from pwH° with activity coefficients estimated by the Debye-Hückel equation

$$-\log m_H = pwH° + \log (f_H f_{Cl})° = pwH° - \frac{2A\sqrt{\mu}}{1 + 4B\sqrt{\mu}}. \tag{10}$$

The values of the ionic strength at 0°, 25°, and 60° C obtained in this manner are given in table 3.

TABLE 2. *pwH° for four solutions of potassium tetroxalate from 0° to 60°C*

t	0.1 m	0.05 m	0.025 m	0.01 m
° C				
0	--------	1. 766	1. 933	2. 207
5	--------	1. 766	1. 936	2. 204
10	--------	1. 765	1. 938	2. 207
15	1. 624	1. 770	1. 941	2. 211
20	1. 627	1. 773	1. 942	2. 212
25	1. 638	1. 778	1. 945	2. 212
30	1. 641	1. 783	1. 950	2. 216
35	1. 650	1. 791	1. 956	2. 220
40	1. 659	1. 796	1. 961	2. 219
45	1. 671	1. 804	1. 969	2. 231
50	1. 683	1. 813	1. 972	2. 236
55	1. 694	1. 821	1. 983	2. 240
60	1. 706	1. 828	1. 991	2. 243

TABLE 3. *Ionic strengths of four solutions of potassium tetroxalate*

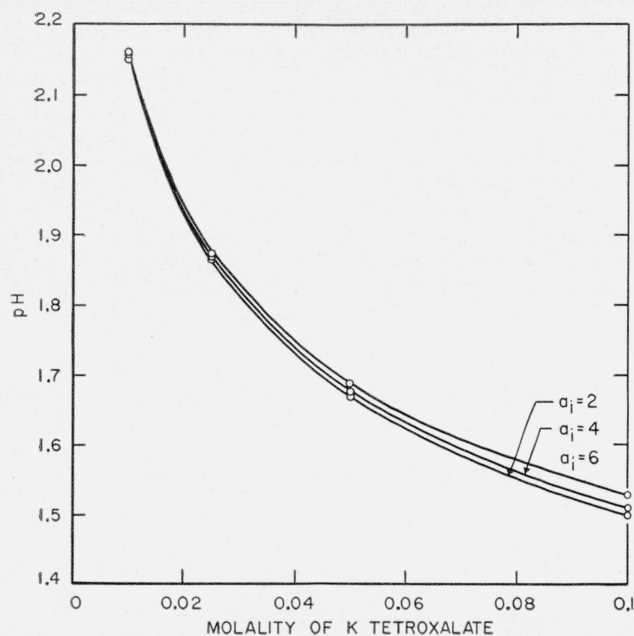| Molality of tetroxalate	Ionic strength at (° C)—		
	0°	25°	60°
0. 01	0. 0181	0. 0180	0. 0175
. 025	. 0417	. 0413	. 0401
. 05	. 0772	. 0760	. 0744
. 1	a. 1433	. 1400	. 1383

a At 15° C.

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FIGURE 5. pH *of solutions of potassium tetroxalate at 25° C.*
as a function of molality.

The three curves represent pH obtained by eq (8), with a_i values of 6, 4, and 2, as marked.

The pH_S at 25°, calculated by eq (8) for three values of a_i, namely, 2, 4, and 6, is plotted in figure 5. The curves converge as the ionic strength decreases. Hence, it is possible, for molalities of tetroxalate not exceeding 0.05, to select an average pH_S that will represent the values on all three curves within ±0.01 unit. Nevertheless, when the mean activity coefficients of hydrochloric acid in its pure aqueous solutions and in solutions with added potassium salts are fitted to equations of type (7), the ion-size parameter is usually found to lie between 4 and 6. For this reason, the pH_S given in table 4 is the average of those computed by eq (8) with $a_i = 4$ and $a_i = 6$. In view of the arbitrary selection of a_i, an uncertainty of ±0.01 is assigned to the values for 0.01-, 0.025-, and 0.05-M solutions and ±0.015 to those for the 0.1-M solution.

The pH of buffer solutions is not normally very sensitive to changes in the total concentration of

buffer substance, although the change of pH upon dilution increases near the ends of the pH scale. It is possible, therefore, to take advantage of the convenience of volumetric methods for the preparation of buffer solutions. It is evident from figure 5 that the pH of tetroxalate solutions at 25° changes about 0.2 unit when the molality drops from 0.05 to 0.025. Two determinations with a 50-ml picnometer showed the density of the 0.05-molal solution to be 1.00320 at 25° C; hence, the 0.05-molal (m) solution is 0.0496 molar (M). This difference of 0.8 percent in the tetroxalate concentration between 0.05-m and 0.05-M solutions corresponds to 0.001 to 0.002 pH unit, an entirely negligible amount in comparison with the uncertainty in the assignment of pH_S. It is therefore justifiable to assign the pH_S values determined as described above for 0.01-, 0.025-, 0.05-, and 0.1-m solutions also to the solutions of numerically the same molarity, as has been done in table 4.

6. Tetroxalate Buffer Standards

The 0.05-M solution is recommended for use as a standard for pH measurements in the acid range.[5] In common with other strongly acidic solutions, it has a high buffer value and a high dilution value. In other words, its pH is little influenced by chance contamination with acid or base but is relatively sensitive, in comparison with buffer solutions of moderate acidity, to dilution or concentration of the buffer components. Nevertheless, the dilution value is not high enough to impair the usefulness of tetroxalate buffer solutions in any significant degree.

The Van Slyke buffer value, β, is defined as the differential ratio dB/dpH [18] and represents the number of equivalents of strong base (B) required, without volume change, to increase the pH of 1 liter of a particular solution by 1 pH unit. Approximate buffer values are obtained experimentally by measuring the pH change produced by the addition of small volumes of solution, each of which contains ΔB equivalents of concentrated, strong alkali. In this way, the buffer value of 0.05-M potassium tetroxalate at 25° C was found to be

$$\frac{dB}{d\text{pH}} \approx \frac{\Delta B}{\Delta \text{pH}} = 0.07. \qquad (11)$$

The pH change was determined with the glass electrode.

The dilution effect is conveniently expressed as the increase of pH on dilution of the buffer solution with an equal volume of pure water. For the 0.05-M solution of potassium tetroxalate, this quantity, designated $\Delta\text{pH}_{1/2}$ is

$$\Delta\text{pH}_{1/2} = +0.19. \qquad (12)$$

TABLE 4. pH_S *of four solutions of potassium tetroxalate from*
0° to 60° C

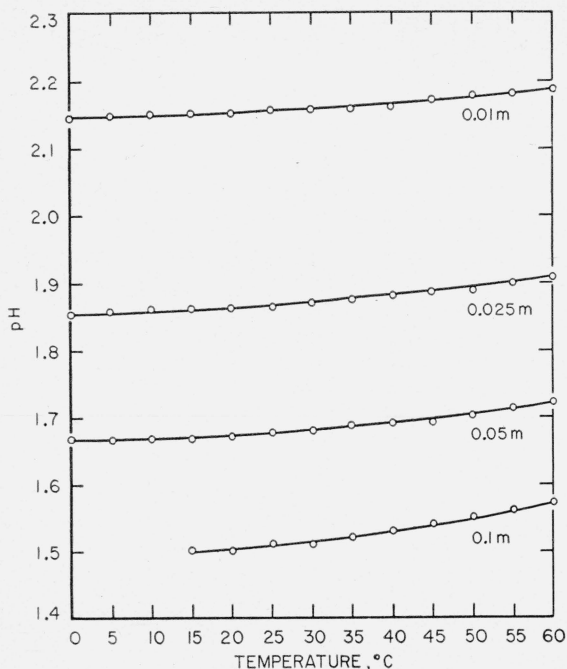| t	0.1 M	0.05 M	0.025 M	0.01 M
° C				
0	-----	1.671	1.858	2.153
5	-----	1.671	1.860	2.150
10	-----	1.669	1.862	2.152
15	1.508	1.674	1.864	2.156
20	1.509	1.676	1.865	2.156
25	1.520	1.681	1.867	2.156
30	1.521	1.685	1.872	2.160
35	1.530	1.693	1.877	2.162
40	1.538	1.697	1.882	2.162
45	1.549	1.704	1.890	2.174
50	1.560	1.712	1.892	2.179
55	1.570	1.719	1.902	2.182
60	1.580	1.726	1.909	2.185

FIGURE 6. pH *of four tetroxalate solutions as a function of temperature.*

The buffer value of the 0.05-M solution of potassium acid phthalate is about 0.02, and its dilution value is $+0.05$; hence, the pH of the tetroxalate solution is altered less than that of the phthalate solution by addition of acid or alkali but is more sensitive to dilution.

As shown in figure 6, the temperature coefficient of pH is small and positive for all four tetroxalate solutions in the range of the measurements. The pH of the 0.05-M solution is 1.68 ± 0.01 at all temperatures between 15° and 35° C.

A solution of potassium tetroxalate saturated at at 0° C was used by Schomaker and Brown [19] in their standard quinhydrone half-cell. Hitchcock and Taylor [20] selected the 0.1-M solution of this salt as a useful pH standard and assigned to it pH values of 1.480 at 25° and 1.495 at 38° C. These pH values are 0.040 unit lower than those given in table 4, or about two and one-half times the estimated uncertainty of the latter. This difference corresponds to 2.4 mv.

The determination of Hitchcock and Taylor was based on the emf of cells with a liquid junction, and the primary reason for the difference between the values of the two investigations is probably the residual liquid-junction potential, which becomes appreciable at low pH values. In other words, the potential across the boundary between the bridge solution (saturated potassium chloride) and 0.1-M potassium tetroxalate differs from that between the bridge and other buffer solutions whose pH values lie closer to neutrality.

Potassium tetroxalate dihydrate can be dried in air at 1-atm pressure at temperatures up to about 60° C without loss of crystal water. The 0.05-M solution is prepared by dissolving 12.70 g (air weight) in water and diluting to 1 liter. In an experiment designed to reveal the effect of drying the salt, two solutions were prepared by adding the same weight of wet and dry salt to equal amounts of a solution of potassium chloride. Although the wet sample contained about 0.5 percent of water, the emf of cells prepared from the two solutions displayed no significant differences. Hence, it appears that drying is usually unnecessary. Tetroxalate solutions are satisfactorily stable without the addition of preservatives. In order to minimize the effects of evaporation and accidental contamination, however, it is recommended that the standard be replaced every 2 months.

7. References

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