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pH OF AQUEOUS MIXTURES OF POTASSIUM DIHYDROGEN PHOSPHATE AND DISODIUM HYDROGEN PHOSPHATE AT 0° TO 60° C

By Roger G. Bates and S. F. Acree

ABSTRACT

A method is suggested for computing the pH of phosphate buffers from electromotive-force measurements of cells without liquid junction. Each of the 33 buffer solutions studied was prepared from equal molal quantities of potassium dihydrogen phosphate and disodium hydrogen phosphate. The solutions were divided into five series with respect to the amount of sodium chloride added. The ratios of the molality of each buffer salt to that of sodium chloride in the five series were about 1, 2, 3, 8, and 10. The pH values were computed from measurements of cells with hydrogen electrodes and silver-silver-chloride electrodes by a procedure that involves extrapolation of a function of the emf to zero concentration of sodium chloride.

The values of the second dissociation constant of phosphoric acid given in an earlier paper (RP1524) were confirmed. The mean values of pK, the negative of the common logarithm of the second dissociation constant, are given as a function of absolute temperature, T, by the equation

$$\mathrm{p}K = 2073.0/T - 5.9884 + 0.020912\,T$$

between $T=273.16$ and $T=323.16$ (0° to 50° C). Equations are given to express the change of pH with molality of sodium chloride. The pH values from 0° to 60° C of eight phosphate buffers without chloride are listed. The densities of the buffers were determined. At 25° C, the pH of buffers containing equal molal quantities of potassium dihydrogen phosphate and of disodium hydrogen phosphate is given by the equations

$$\mathrm{pH} = 7.162 + 2.18\,m - 2.237\sqrt{m}$$

and

$$\mathrm{pH} = 7.169 + 2.39\,c - 2.324\sqrt{c},$$

where m and c, the molality and the molar concentration of each buffer salt, lie between 0.005 and 0.1.

CONTENTS

I. INTRODUCTION

Aqueous mixtures of primary and secondary phosphates have found extensive use for the control of pH in the region near neutrality. When the molal amounts of the two phosphates are approximately equal, buffer solutions with pH between 6.5 and 7.0 are obtained. The pH is relatively insensitive to contamination of the solution with carbon dioxide from the air, or with small amounts of alkali, and changes only 0.1 unit when the solution is diluted to twice its volume with pure water.

It was shown in an earlier paper [1][1] that potassium dihydrogen phosphate and disodium hydrogen phosphate are well suited by ease of purification, stability, and lack of pronounced hygroscopicity to the preparation of standard buffers of constant and reproducible pH. The equimolal mixture of these two salts was chosen for detailed study. The purpose of this investigation was twofold: to determine the pH of a series of phosphate buffer standards, and to study the effect of sodium chloride on the thermodynamic properties of the phosphate buffer system. The study of salt effects on the behavior of indicators and buffers has been the subject of earlier communications from this Bureau [2, 3, 4, 5].

In the past, pH values assigned to phosphate buffers have been based upon emf measurements of cells which involved liquid junctions [6, 7, 8]. The experimental and theoretical difficulties caused by the liquid junction have been well recognized, and it has been suggested [9, 10, 11] that pH be defined in terms of cells without liquid junction. The experimental difficulties are thereby removed to a large extent, but the uncertainty in evaluating the potential at the liquid junction remains in the guise of its counterpart, the enigma of the single-ion activity. In either case, a non-thermodynamic assumption must be made, and the pH scale is somewhat arbitrary in character. When strong acids and bases as well as buffered solutions are to be used, however, a consistent scale based on cells with liquid junction is not readily achieved [8, 11a].

In previous work by the authors, the second dissociation constant of phosphoric acid was evaluated from emf measurements of cells without liquid junction. Certain assumptions were made to relate the activity coefficient of chloride ion to an observed activity function, and pH values were computed for the mixtures of phosphate and chloride salts. A change in the ratio of chloride to buffer salt alters the pH of the buffer, however, in a hitherto unknown manner. In this investigation, the effect of the sodium chloride on the activity coefficients has been studied, and the pH of phosphate buffers in the absence of sodium chloride has been estimated.

II. EXPERIMENTAL PROCEDURE

The solutions were prepared by the dilution of eight stock solutions with conductivity water. Each stock solution was prepared from the proper weights of pure potassium dihydrogen phosphate, disodium hydrogen phosphate, sodium chloride, and water. The dilutions were made in an atmosphere from which carbon dioxide had been removed.

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

The concentration of each component was expressed on the weight basis and was thought to be correct to 0.01 percent. Dissolved oxygen was removed from each solution by means of nitrogen, which had been purified by passage through a tower of soda-lime and over copper heated to 500° C. The gas was bubbled through each solution for 3 hours before the final weighings were made.

The silver–silver-chloride electrodes were of the thermal-electrolytic type (Harned's type 2 [12]). About 15 mg of the silver formed on each electrode (usually about 70 mg) was converted to silver chloride. Both the hydrogen electrodes and the silver–silver-chloride electrodes were freshly prepared before each series of experiments was begun. The latter were intercompared in a 0.05-*m* solution of hydrochloric acid and only those differing from the mean value by 0.06 mv or less were used. Experience showed that a similar intercomparison of hydrogen electrodes was unnecessary.

Each series of experiments ordinarily was completed within 72 hours after the cells were filled. Initial and final measurements were made at 25° C. The thermometer, standard cell, and potentiometer had been calibrated recently. The ice point of the thermometer was usually redetermined before each series of experiments was started. Other experimental details are given in an earlier paper [1].

1. MATERIALS

Potassium dihydrogen phosphate and disodium hydrogen phosphate were purified by recrystallization from water, dried at 110° and 130° C, respectively, and used as the anhydrous salts. The secondary salt was first dried for a time at room temperature in air and in vacuum. In this way, fusion of the hydrated salt at 130° C was avoided. Samples of these two salts, prepared by triple crystallization of reagent grade salts which conformed to specifications of the American Chemical Society, were analyzed by the Reagents and Platinum Metals Section of this Bureau. The assays of potassium dihydrogen phosphate and of disodium hydrogen phosphate were, respectively, 100.003 and 99.995 percent. The secondary salt was shown to contain less than 0.01 percent of carbonate.

Sodium chloride, "special grade," was precipitated from a saturated aqueous solution with dry hydrogen chloride, prepared according to the directions of Sweeney [13], and fused in platinum to remove water and occluded acid, as recommended by Richards and Wells [14]. It was broken into large lumps and bottled without grinding. The salt was not strictly neutral, as Richards and Wells found theirs to be. A measure of its alkalinity was made by titration of a sample of 11 g of the salt to both the phenolphthalein and methyl-orange end points with a solution of hydrochloric acid. The amount of acid required indicated the presence of 0.008 percent of sodium hydroxide by weight. As this impurity would cause an error in electromotive force of less than 0.01 mv, or considerably less than the experimental error, no further purification of the salt was undertaken.

The conductance of the water used in the preparation of the solutions was approximately 0.5×10^{-6} mho. Before the water was used, a stream of air freed of carbon dioxide was bubbled through it for 18 to 24 hours. In an experiment to test the removal of dissolved carbon dioxide by this method, eight liters of water having an initial conductance of 0.44×10^{-6} mho remained in the receiver for 2 months. The conductance rose to 0.97×10^{-6} mho during this time but fell to 0.57×10^{-6} mho when carbon dioxide-free air was bubbled through the water overnight.

2. RESULTS OF EMF MEASUREMENTS

The electromotive forces, E_t, of the cell $\mathrm{Pt} | \mathrm{H_2} | \mathrm{KH_2PO_4}, (m_1); \mathrm{Na_2HPO_4}, (m_1); \mathrm{NaCl}, (m_2) | \mathrm{AgCl} | \mathrm{Ag}$ are given in table 1. These values have been corrected as usual to 1 atm of hydrogen. In each solution, the stoichiometric molalities (m_1) of the primary and secondary phosphate salts were equal. Furthermore, it can be shown that the concentrations of primary and secondary phosphate anions are substantially equal (within 0.01 percent) to the stoichiometric molalities of the corresponding phosphate salts. The molalities of the components of the solution are given in the second and third columns of the table. The solutions are divided into five series. In series A, B, C, D, and E the ratios of the molality of each buffer salt to the molality of sodium chloride were respectively 1.00, 1.92, 3.21, 8.20, and 9.90. The molalities of solutions A5 and A5a were identical. Solution A5 was saturated with hydrogen, however, before the cells were filled, and A5a was saturated with nitrogen in the same manner as was each of the other buffers. The emf values agree satisfactorily. The data recorded for solutions D2 and D6 are the average values of two cells. The mean differences between the two cells were 0.03 mv (for D2) and 0.08 mv (for D6).

The values at 25° C, in general, are somewhat more reliable than those listed for the other temperatures, by virtue of the threefold check obtained at this reference temperature. The initial equilibrium values at 25° C were uniformly in agreement with those recorded at the conclusion of the low-temperature series. When the molality of the buffer was less than 0.005 or that of the chloride less than 0.002, however, the final values at the same temperature often differed from the initial data by 0.02 to 0.03 percent of the emf (about 0.2 mv). In such cases, the final measurement was disregarded in assigning the value to the cell at 25° C. It was recognized, further, that at least a part of this error possibly resides in the values at the highest temperatures. It will be seen later that the deviations from the mean of the second dissociation constant calculated from the experimental results at 50°, 55°, and 60° C are somewhat larger than those at the lower temperatures.

TABLE 1.—*Electromotive forces of cells containing mixtures of phosphate buffers with sodium chloride*

Solution number	$KH_2PO_4=Na_2HPO_4$ (m_1)	NaCl (m_2)	E_{0°	E_{5°	E_{10°	E_{15°	E_{20°	E_{25°	E_{30°	E_{35°	E_{40°	E_{45°	E_{50°	E_{55°	E_{60°
	Molality	*Molality*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*	*Int. v*
A1	0.06568	0.06568						0.69706							
A2	.03898	.03898		0.69697		0.70538		.71392		0.72247		0.73114		0.73979	
A3	.02873	.02875	0.70191		0.71030		0.71898	.72342	0.72778		0.73666		0.74562		0.75468
A4	.02820	.02822	.70235	.70678	.71100	.71523	.71966	.72407	.72844	.73293	.73748	.74204	.74675	.75144	.75594
A5	[a].02157	[a].02158		.71451		.72339		.73246		.74161		.75089		.76021	
A5a	[b].02157	[b].02158		.71451		.72334		.73248							
A6	.02000	.02000						.73481							
A7	.019412	.019422	.71303		.72187		.73094	.73559	.74021		.74954		.75889		.76835
A8	.018981	.018999	.71366	.71827	.72274	.72728	.73170	.73635	.74102	.74571	.75048	.75517	.75994	.76468	.76946
A9	.013668	.013672		.72753		.73685		.74638		.75618		.76600		.77591	
A10	.012317	.012328	.72586	.73058	.73526	.74005	.74484	.74950							
A11	.009647	.009651	.73245		.74207		.75184	.75683	.76178		.77188		.78209		.79237
A12	.007584	.007591	.73905	.74400	.74892	.75392	.75895	.76398	.76917	.77433	.77953	.78461	.78996	.79517	.80044
A13	.007040	.007043	.74107		.75095		.76103	.76616	.77133		.78171		.79219		.80277
A14	.004657	.004660	.75212		.76236		.77278	.77819	.78361		.79442		.80533		.81639
B1	.09928	.05170	.68172	.68576	.68967	.69359	.69766	.70158	.70560	.70962	.71375	.71785	.72192	.72600	.73018
B2	.05478	.02853	.69848	.70385	.70806	.71228	.71663	.72087	.72526	.72976	.73420	.73870	.74315	.74762	.75213
B3	.03073	.016003	.71627	.72084	.72533	.72987	.73454	.73912	.74376	.74866	.75346	.75829	.76309	.76789	.77275
B4	.019053	.009921	.72968	.73454	.73925	.74403	.74897	.75381	.75869	.76393	.76900	.77407	.77913	.78420	.78935
C1	.09928	.03087	.69422	.69851	.70264	.70683	.71109	.71528	.71947	.72389	.72828	.73263	.73702	.74136	.74581
C2	.05143	.016069	.71374	.71826	.72252	.72711	.73170	.73637	.74104	.74566	.75040	.75514	.75993	.76464	.76948
C3	.02691	.008411	.73217	.73709	.74183	.74669	.75165	.75654	.76144	.76667	.77176	.77687	.78197	.78708	.79227
D1	.08250	.010026	.72249	.72715	.73186	.73649	.74118	.74597	.75083	.75558	.76043	.76524	.77005	.77495	.77980
D2	.06265	.007614	.73065	.73545	.74026	.74506	.74991	.75489	.75979	.76471	.76971	.77469	.77968	.78465	.78962
D3	.05571	.006771	.73401	.73871	.74362	.74850	.75338	.75845	.76344	.76844	.77346	.77851	.78355	.78857	.79363
D4	.04935	.005998	.73751	.74240	.74738	.75230	.75722	.76227	.76740	.77248	.77761	.78273	.78785	.79292	.79810
D5	.04277	.005199	.74159	.74654	.75157	.75658	.76162	.76680	.77197	.77714	.78233	.78753	.79272	.79791	.80309
D6	.03079	.003742	.75109	.75623	.76146	.76664	.77184	.77715	.78238	.78772	.79309	.79843	.80381	.80915	.81455
D7	.017007	.002067	.76745	.77285	.77833	.78380	.78936	.79496							
D8	.010457	.0012709	.78083	.78646	.79219	.79792	.80367	.80954							
E1	.09928	.010012	.72144	.72616	.73073	.73544	.74017	.74491	.74964	.75445	.75930	.76415	.76902	.77389	.77880
E2	.03802	.003834	.74937	.75461	.75970	.76480	.77006	.77531	.78052	.78593	.79133	.79673	.80215	.80752	.81297
E3	.017598	.0017745	.77074	.77639	.78180	.78732	.79296	.79881	.80438	.81002	.81580	.82159	.82737	.83313	.83895

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[a] Solution saturated with hydrogen.
[b] Solution saturated with nitrogen.

3. SECOND DISSOCIATION CONSTANT OF PHOSPHORIC ACID AND RELATED THERMODYNAMIC QUANTITIES

The calculation of the second dissociation constant of phosphoric acid from the data of table 1 was made in the manner outlined in the earlier paper.[2] As shown in figure 1, a value of 4.4 A for a^*, the ion-size parameter, gave the best straight-line extrapolation of pK', the negative of the common logarithm of the "apparent" dissociation constant, to zero ionic strength for series D as well as for series A at 25° C, although the ratio of chloride molality to molality of buffer salt was only one-eighth as large. The computation of pK' was made, as before, by use of the equation

$$\mathrm{p}K'=(E-E^\circ)/k+\log\,(m_{\mathrm{H_2PO_4}}m_{\mathrm{Cl}}/m_{\mathrm{HPO_4}})+2A\sqrt{\mu}/(1+Ba^*\sqrt{\mu}),\quad (1)$$

where E° is the standard potential of the cell, μ is the ionic strength, and a^* and β^* are considered to be related to the ion-size parameters, a_i, and β values characteristic of the chloride and phosphate anions. This expression has been found to yield values of pK' that are a linear function of ionic strength.

The uncertainty in establishing a^* for series D is about 0.2 A. The uniform character of the measurements of the series A solutions at 25° C, however, makes possible a more accurate evaluation of a^* for this series than can be made for the others. Fortunately, however, the pH values calculated for the phosphate buffer are but slightly affected by a change of 0.2 A in a^*, as will be shown in the following section. This value of a^* is considerably larger than 3.8 A found to give the best representation for mixtures of sodium phosphates and also for a mixture of potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride in which the molal proportions were 3:2:3 [1].

In accord with previous experience with mixtures of sodium phosphates, it was found that the value of a^* increased slowly with rise of temperature, whereas β^*, the slope of the plot of pK' as a function of ionic strength, remained substantially constant or decreased slowly. As can be seen in figure 2, where pK' from all five series at 25° C is plotted as a function of ionic strength, the β^* slope decreases as the ratio of molalities of sodium chloride to buffer salt is decreased. Since too few solutions in series B, C, and E were studied to provide sufficient data for unambiguous extrapolation, their lines have been drawn to a common intercept which represents the mean value of pK computed analytically from the 10 experimental points.

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[2] The newer values of $k=2.3036RT/\mathrm{F}$ and of the constants A and B of the Debye-Hückel equation were employed [15]. In this paper, K represents the thermodynamic second dissociation constant, and K' the false, "apparent" constant computed with the use of any arbitary activity-coefficient term.

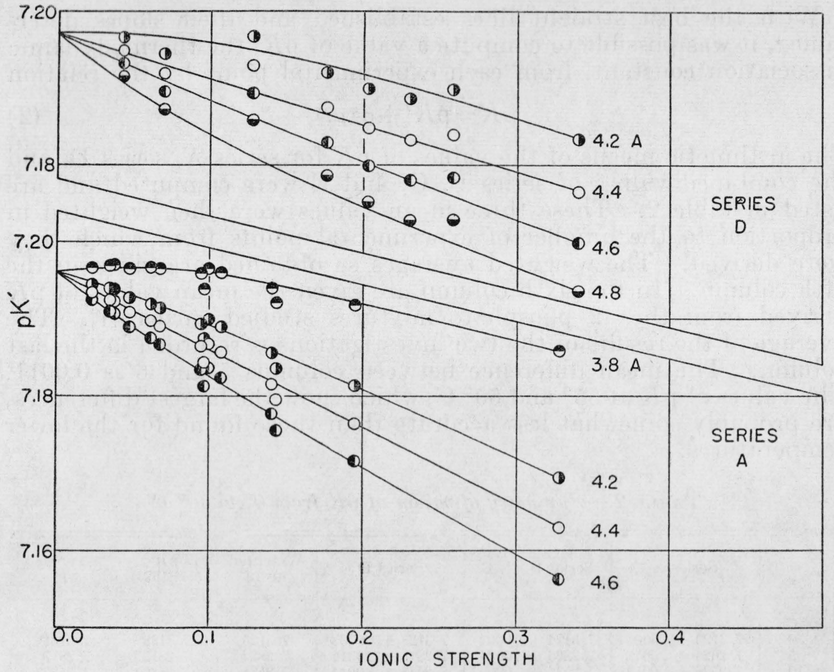

Figure 1.—pK at 25° C for various values of a^* plotted as a function of ionic strength.

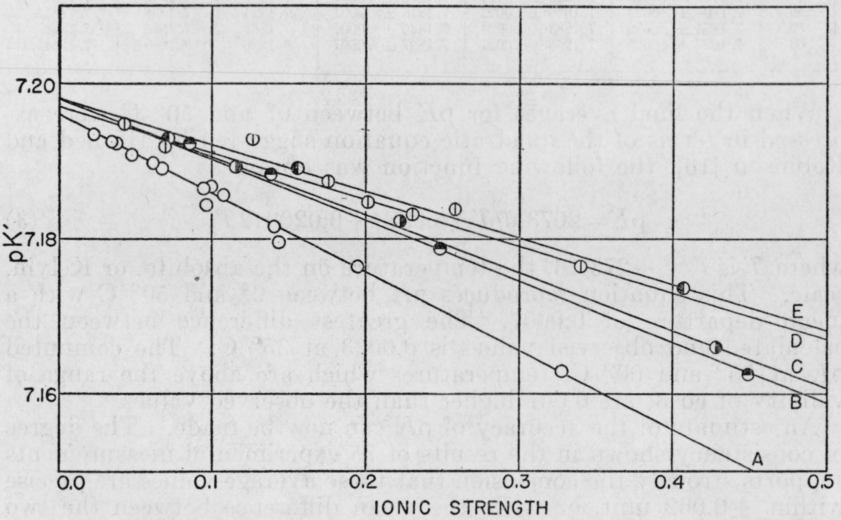

Figure 2.—pK' at 25° C for buffers of series A, B, C, D, and E plotted as a function of ionic strength.

With the best straight lines established and their slopes determined, it was possible to compute a value of pK, the thermodynamic dissociation constant, from each experimental point by the relation

$$\mathrm{p}K=\mathrm{p}K'+\beta^*\mu. \tag{2}$$

The arithmetic means of the values of pK for series A, series D, and the combined values of series B, C, and E were computed and are listed in table 2. These three mean values were then weighted in proportion to the number of experimental points from which they were derived. The weighted averages so obtained are given in the fifth column. In the sixth column are given the mean values of pK derived from the 42 phosphate mixtures studied earlier [1]. The average of the results of the two investigations is recorded in the last column. The mean difference between columns 5 and 6 is 0.0011. The values of pK at 55° and 60° C, which show the largest differences, are probably somewhat less accurate than those found for the lower temperatures.

TABLE 2.—*Summary of values of* pK *from 0° to 60° C*

t	Series A	Series B, C, E	Series D	Weighted mean	pK (RP1524)	Average pK
°C						
0	7.3123 ±0.0007	7.3124 ±0.0007	7.3128 ±0.0008	7.3125	7.3138	7.3131
5	7.2824 ± .0011	7.2826 ± .0004	7.2815 ± .0014	7.2822	7.2812	7.2817
10	7.2526 ± .0013	7.2536 ± .0009	7.2543 ± .0014	7.2535	7.2540	7.2537
15	7.2321 ± .0010	7.2317 ± .0006	7.2321 ± .0011	7.2320	7.2304	7.2312
20	7.2125 ± .0014	7.2141 ± .0008	7.2129 ± .0010	7.2132	7.2128	7.2130
25	7.1959 ± .0005	7.1985 ± .0006	7.1978 ± .0011	7.1972	7.1980	7.1976
30	7.1880 ± .0009	7.1886 ± .0007	7.1889 ± .0005	7.1885	7.1897	7.1891
35	7.1844 ± .0009	7.1850 ± .0013	7.1840 ± .0005	7.1845	7.1854	7.1850
40	7.1787 ± .0017	7.1821 ± .0022	7.1794 ± .0007	7.1802	7.1816	7.1809
45	7.1799 ± .0012	7.1820 ± .0019	7.1799 ± .0007	7.1808	7.1810	7.1809
50	7.1804 ± .0023	7.1846 ± .0023	7.1818 ± .0007	7.1824	7.1838	7.1831
55	7.1874 ± .0019	7.1883 ± .0024	7.1830 ± .0007	7.1865	7.1875	7.1870
60	7.1927 ± .0025	7.1955 ± .0027	7.1897 ± .0007	7.1930	7.1958	7.1944

When the final averages for pK between 0° and 50° C were expressed in terms of the quadratic equation suggested by Harned and Robinson [16], the following function was obtained:

$$\mathrm{p}K=2073.0/T-5.9884+0.020912T, \tag{3}$$

where T is t° C+273.16, the temperature on the absolute, or Kelvin, scale. This equation reproduces pK between 0° and 50° C with a mean departure of 0.0007. The greatest difference between the calculated and observed values is 0.0023 at 35° C. The computed pK at 55° and 60° C, temperatures which are above the range of validity of eq 3, are 0.007 higher than the observed values.

An estimate of the accuracy of pK can now be made. The degree of consistency shown in the results of 75 experimental measurements supports strongly the conclusion that these average values are precise within ±0.002 unit, or twice the mean difference between the two sets of pK values given in columns 5 and 6. The purity of the phosphate salts was such that no appreciable uncertainty can justifiably be attributed to that source. The slight alkalinity of the sodium chloride would cause all of the values to be too high by only 0.0001 unit. The $E°$ values of Harned and Ehlers [17] seem to be reliable to about 0.05 mv, which corresponds to 0.0009 in pK. A more recent calculation of $E°$ from their data [18] confirms this view, as far as the extrapolation is concerned. It is important to note that the same type of silver–silver-chloride electrode [12] was used in this investigation and in the work of Harned and Ehlers. By summation of these possible errors, a maximum uncertainty of ±0.003 unit can be assigned to pK.

Since eq 3 differs somewhat from the equation which represented most successfully the series of pK values given in column 6 as a function of absolute temperature [1],[3] the quantities derived from the temperature coefficient of the dissociation constant were recalculated from the parameters of the revised equation. They are compared in table 3 with the corresponding quantities obtained from the emf measurements of Nims [19], and with a direct calorimetric determination of $\Delta H°$ by Pitzer [20]. The constants are given in international joules and in calories;[4] one calorie is 4.1833 int. j. The entropy value in the third column was computed from Pitzer's value for $\Delta H°$, together with $\Delta F°$ from this investigation.

TABLE 3.—*Thermodynamic constants for the dissociation of* $H_2PO_4^-$ *at 25° C*

	Nims (emf)	Pitzer (calorimetry)	This investigation
pK	7.205_8	------------	7.197_6
$\Delta F°$ cal/mole	9,830	------------	9,822
int. j/mole	41,122	------------	41,088
$\Delta H°$ cal/mole	825	800 ±80	979
int. j/mole	3,451	3,347 ±335	4,095
$\Delta S°$ cal/deg mole	−30.2	−30.3	−29.6
int. j/deg mole	−126.3	−126.8	−123.8
$\Delta C_p°$ cal/deg mole	−45	------------	−57
int. j/deg mole	−188	------------	−238

In the absence of unforeseen reactions at the electrodes which may alter the emf in an abnormal manner as the temperature is changed, $\Delta H°$ should have an uncertainty of about 300 int. j/mole, $\Delta S°$ might be in error by 0.9 int. j/degree mole, and $\Delta C°_p$ by 25 int. j/degree mole.[5] It is apparent, however, that the difference between $\Delta H°$ from calorimetric data and from the emf measurement given in the last column is greater than the sum of the uncertainties assigned to the two values. This discrepancy has not been explained.

III. CALCULATION OF THE pH OF PHOSPHATE BUFFERS

If the mass-law expression for the equilibrium between primary and secondary phosphate ions is written in its exact form, the following

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[3] This equation was $pK=1979.5/T-5.3541+0.019840T$. The values found by Nims [19] from 20° and 50° C are expressed by $pK=1651.9/T-3.2703+0.016555T$.

[4] Quantities of energy in chemical thermodynamics are measured in joules, and the arbitrary conversion to artificial calories has little to recommend it. The eventual abandonment of the calorie as a unit of energy has been urged by Smith and Taylor [21], Mueller and Rossini [22], and others.

[5] These uncertainties were estimated from the probable limit of error (0.002 unit) assigned to pK. If pK at 15° C were too low by 0.002 unit and pK at 35° too high by the same margin, the stated errors would be included in the values of the thermodynamic constants at 25° C.

equation for the pH of any mixture of potassium dihydrogen phosphate and disodium hydrogen phosphate is obtained:

$$\mathrm{pH} = \mathrm{p}K - \log \frac{m_{\mathrm{H_2PO_4}}}{m_{\mathrm{HPO_4}}} - \log \frac{f_{\mathrm{H_2PO_4}}}{f_{\mathrm{HPO_4}}}. \tag{4}$$

In order to estimate the last term of eq 4, an equation of the Hückel form was assumed to express the change of each ionic activity coefficient in the mixture with respect to ionic strength, as follows:

$$-\log f_i = \frac{Az_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} - \beta_i\mu. \tag{5}$$

In eq 5, z_i is the valence of the ion, and a_i and β_i are parameters characteristic of the ionic species i in the mixture.

If eq 5 correctly represents the change of each ionic activity coefficient with respect to the ionic strength, it is possible to derive the relationship between a^* and a_1, a_2, and a_3, where the subscripts 1, 2, and 3 refer respectively to the anions $\mathrm{H_2PO_4}$, $\mathrm{HPO_4}$, and Cl.

$$a^* = \frac{(4a_2 - a_1 - a_3) + (3a_1a_2 - 2a_1a_3 + 3a_2a_3)B\sqrt{\mu} + 2a_1a_2a_3B^2\mu}{2 + (3a_1 - 2a_2 + 3a_3)B\sqrt{\mu} + (4a_1a_3 - a_1a_2 - a_2a_3)B^2\mu}. \tag{6}$$

This derivation is accomplished by combining expressions of the form of eq 5 for the activity coefficients of the three anions according to the formula $(\log f_{\mathrm{H_2PO_4}} - \log f_{\mathrm{HPO_4}} + \log f_{\mathrm{Cl}})$, and equating the result to $2A\sqrt{\mu}/(1+Ba^*\sqrt{\mu}) + \beta^*\mu$, which is found by experiment to represent satisfactorily the quantity $\log\,(f_{\mathrm{H_2PO_4}}\,f_{\mathrm{Cl}}/f_{\mathrm{HPO_4}})$.

Consideration of eq 6 shows that a^* is totally independent of ionic strength only when $a_1 = a_2 = a_3 = a^*$. When the values of the ion-size parameter for the three ions are different, a^* is an insensitive function of μ. As the ionic strength approaches zero, a^* approaches $(4a_2 - a_1 - a_3)/2$ as a limit. At infinite ionic strength, a^* is $2a_1a_2a_3/(4a_1a_3 - a_1a_2 - a_2a_3)$. When the ratios of the ions were fixed, no variation of a^* with ionic strength larger than the experimental error could be detected. This invariance would be observed if the ion-size parameters for the three ions were equal. For many combinations of different values of a_i lying between 3 and 5 A, however, the change of a^* over very large ranges of ionic strengths can be shown to be so small as not to be discernible.

Examination of eq 6 in the light of the behavior of the term log $(f_{\mathrm{H_2PO_4}}f_{\mathrm{Cl}}/f_{\mathrm{HPO_4}})$ with changing buffer ratio, however, reveals no explanation of the observed change of a^* as the relative amounts of the primary and secondary phosphates are varied at a constant ionic strength, provided that the individual a_i values are considered to be constants. It seems reasonable to assume that the ionic parameters are not equal and that their contributions to a^* are weighted in some manner, not shown in eq 6, according to the contributions of the respective ions to the ionic strength. The limiting value of a^*, or a°, as m_{NaCl}/μ approaches zero at a constant ratio of the phosphate salts would then be little influenced by the individual characteristics of the chloride ion and determined chiefly by those of the phosphate anions.

In the light of eq 5, the slope β^* can be considered to be a combination of the values of β_i for primary phosphate ion, secondary phosphate ion, and chloride ion: $\beta^* = \beta_{\mathrm{H_2PO_4}} - \beta_{\mathrm{HPO_4}} + \beta_{\mathrm{Cl}}$. If the contribution of β_{Cl} varies in some direct manner with the fractional contribution of sodium chloride to the total ionic strength, the limit of β^* for the equimolal phosphate buffer in the absence of sodium chloride, $(\beta_{\mathrm{H_2PO_4}} - \beta_{\mathrm{HPO_4}} + \beta_{\mathrm{Cl}})^\circ$ is largely determined by the properties of the equimolal mixture of primary and secondary phosphates.[6] [7]

In view of these considerations, the last term of eq 4 is computed with the use of eq 5. The limiting value of the ion-size parameter, a°, is employed, and $(\beta_{\mathrm{H_2PO_4}} - \beta_{\mathrm{HPO_4}} + \beta_{\mathrm{Cl}})^\circ$ is used for $\beta_{\mathrm{H_2PO_4}} - \beta_{\mathrm{HPO_4}}$. The equation for pH then becomes

$$\mathrm{pH} = \mathrm{p}K - \log \frac{m_{\mathrm{H_2PO_4}}}{m_{\mathrm{HPO_4}}} - \frac{3A\sqrt{\mu}}{1 + Ba^\circ\sqrt{\mu}} - (\beta_{\mathrm{H_2PO_4}} - \beta_{\mathrm{HPO_4}} + \beta_{\mathrm{Cl}})^\circ \mu. \tag{4a}$$

The calculation of the pH of the buffer without sodium chloride thus rests upon the following assumptions:

1. The activity coefficients of the two phosphate anions and of chloride ion in a mixture containing all three ionic species are given as a function of total ionic strength by expressions of the Hückel type (eq 5). At a given temperature, each of these three ions has its characteristic a_i and β_i which remain unaltered with changing ionic strength. When the kinds or ratios of the ions in the mixture are changed, however, the value of β_i may change also, but a_i does not.
2. The limiting values of a^* and $(\beta_{\mathrm{H_2PO_4}} - \beta_{\mathrm{HPO_4}} + \beta_{\mathrm{Cl}})$ as the ratio of the molality of sodium chloride to that of each phosphate salt approaches zero can be employed to compute $(f_{\mathrm{H_2PO_4}}/f_{\mathrm{HPO_4}})$ in equimolal phosphate buffers without added salt.

When eq 1 and 2 are combined, the following expression is obtained:

$$\frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} + \beta^*\mu = \mathrm{p}K - \frac{E - E^\circ}{k} - \frac{m_{\mathrm{H_2PO_4}}}{m_{\mathrm{HPO_4}}} - \log m_{\mathrm{Cl}}. \tag{7}$$

It is apparent that a^* and β^* can be obtained from two or more determinations of the right side of eq 7 for constant ratios of ions but changing ionic strength, provided pK is known. If the dissociation constant is to be evaluated, however, it is convenient to obtain these parameters from the extrapolation plots, as described in the previous section. Within the error of establishing a^*, the value of this parameter for all five series (m_{NaCl}/μ between 0.2 and 0.025), and hence also for the limit, was 4.4 A at 25° C.

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[6] These limiting values of the parameters actually describe the change of log $(f_{\mathrm{H_2PO_4}} f_{\mathrm{Cl}}/f_{\mathrm{HPO_4}})$ with changing ionic strength when sodium chloride is absent. Use of the assumption that these parameters also describe the change of log $(f_{\mathrm{H_2PO_4}}/f_{\mathrm{HPO_4}})$ with ionic strength (when the appropriate alteration of the valence coefficient in the first term of the Hückel equation is made) implies that β_{Cl} is zero in the absence of sodium chloride but does not suggest that f_{Cl} is unity. Thus, at 25° C, f_{Cl} is 0.775 in an equimolal phosphate buffer of ionic strength 0.1 containing no sodium chloride.

[7] In earlier papers [1, 4, 23] it was assumed for the calculation of pH that $\beta_{\mathrm{HA}} = \beta_{\mathrm{A}} = \beta_{\mathrm{Cl}} = \beta^*$. Although the effect of sodium chloride on mixtures of sodium phosphates has not been studied, a comparison of β^* for series A in the earlier article [1] with that for series A reported here indicates that the corrections to be subtracted from the pH values of 25° C of series A buffers studied in the earlier work are about 0.003, 0.007, and 0.013 at ionic strengths of 0.1, 0.2, and 0.4, respectively.

The experimental values of a^* and β^* are given in table 4. As mentioned above, a^* and a° are identical. The table also lists the values of $3A$ and Ba° [15] for convenience in the use of eq 4a.

TABLE 4.—*Parameters of the Hückel equation for phosphate buffers composed of equal molalities of potassium dihydrogen phosphate and disodium hydrogen, phosphate with and without sodium chloride.*

t	$a^*=a^\circ$	$3A$	Ba°	β^* for series—					$(\beta_{H_2PO_4}-\beta_{HPO_4}+\beta_{Cl})^\circ$
				A	B	C	D	E	
	A								
0	4.2	1.4649	1.3612	0.137	0.086	0.080	0.067	0.068	0.060
5	4.2	1.4763	1.3646	.143	.077	.076	.065	.062	.058
10	4.3	1.4880	1.4009	.131	.081	.076	.067	.066	.060
15	4.3	1.5000	1.4044	.119	.075	.072	.061	.058	.055
20	4.4	1.5126	1.4401	.128	.081	.076	.066	.063	.057
25	4.4	1.5255	1.4436	.102	.081	.075	.060	.059	054
30	4.4	1.5390	1.4476	.132	.079	.077	.061	.060	.053
35	4.4	1.5525	1.4507	.129	.080	.073	.065	.061	.056
40	4.5	1.5663	1.4873	.141	.094	.075	.070	.064	.058
45	4.5	1.5810	1.4913	.126	.083	.073	.072	.062	.057
50	4.5	1.5957	1.4945	.121	.081	.068	.070	.056	.055
55	4.6	1.6113	1.5313	.133	.088	.075	.070	.062	.058
60	4.6	1.6275	1.5355	.146	.083	.071	.071	.057	.057

As was found to be the case with phenolsulfonate buffers [4], the variation of β^* with the contribution of the sodium chloride to the ionic strength (m_{NaCl}/μ) was approximately linear. Since the pH is relatively insensitive to the limiting value of β^*, an adequate value of $(\beta_{H_2PO_4}-\beta_{HPO_4}+\beta_{Cl})^\circ$ (within 0.005, which corresponds to 0.002 in the pH of the 0.1-*m* phosphate buffer) can readily be obtained. These extrapolated values are given in the last column of table 4. At temperatures other than 25° C, β^* for series A lies above the straight line drawn through the other four points. As figure 3 shows, however, the linear relationship is valid at 25° C.

Since the means of evaluating a^*, by choice of the function which yields the best straight line (see fig. 1), is incapable at these relatively low concentrations of furnishing values of this parameter that are more accurate than 0.1 to 0.2 A, a corresponding uncertainty is inherent in a°. It is thus important to consider what error in the pH is introduced by an error of 0.2 A in a°. At first this uncertainty appears to be a serious limitation to the accuracy of all pH values computed from eq 4a, for the term that contains a° is 0.010 less at $a^\circ=4.6$ than at $a^\circ=4.4$, when the molality of each buffer salt is 0.1. It must be remembered, however, that a change in the value of a^* for any series would cause β^* also to be different.[8] The upper (dashed) line in figure 3 shows the changes of β^* when a^* for series A, B, C, D, and E is, respectively, 4.4, 4.5, 4.5, 4.6, and 4.6. The limiting values of a^* and β^* would then be 4.6 and 0.074 instead of 4.4 and 0.054, and the difference of pH would be 0.002 unit for the most concentrated buffer and correspondingly less for the more dilute ones.

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[8] This interdependence of the two parameters of the Hückel equation has led to the formulation of single-parameter equations for activity coefficients. Van Rysselberghe and Eisenberg [24] express the $\beta\mu$ term as a function of a by considering it to be a measure of the van der Waals (or covolume) correction to the activity coefficient. Robinson and Harned [25] derived an empirical relation between a and β for 12 uniunivalent electrolytes, finding β to be proportional to the fourteenth power of a. A critical discussion of these equations is given in the monograph of Harned and Owen [26].

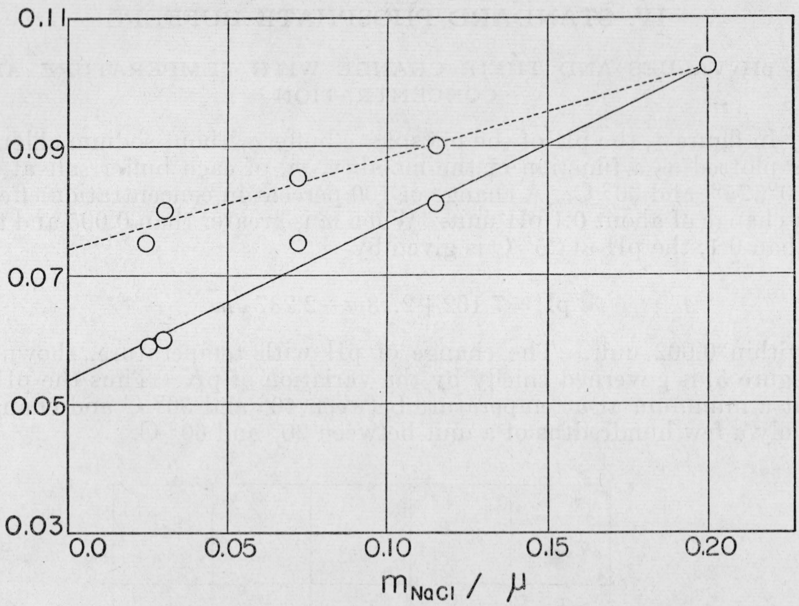

FIGURE 3.—*Plot of β^* at 25° C as a function of the contribution of sodium chloride to the ionic strength.*

Table 4 shows that $(\beta_{H_2PO_4} - \beta_{HPO_4} + \beta_{Cl})^\circ$ is practically the same for all 13 temperatures. The mean value is 0.057 ± 0.002. Inasmuch as the maximum departure from the mean is 0.004 at 30° C, or 0.0016 in the pH of the most concentrated buffer, the mean value was employed in eq 4a for the calculation of the pH at all temperatures. The pH values of phosphate buffers composed of equal molal quantities of potassium dihydrogen phosphate and disodium hydrogen phosphate without sodium chloride are given in table 5. The average values of p*K* given in the last column of table 2 were used. It is estimated that the pH has a precision of ±0.003.

TABLE 5.—pH *of equimolal phosphate buffers without sodium chloride*

t	pH for buffer of molality—							
	0.005	0.01	0.02	0.025	0.04	0.05	0.075	0.1
° *C*								
0	7.138	7.081	7.012	6.983	6.925	6.895	6.836	6.792
5	7.106	7.048	6.976	6.950	6.891	6.861	6.802	6.758
10	7.077	7.019	6.948	6.922	6.864	6.832	6.776	6.732
15	7.053	6.995	6.922	6.896	6.838	6.808	6.750	6.706
20	7.034	6.976	6.904	6.878	6.820	6.791	6.733	6.690
25	7.018	6.959	6.886	6.860	6.802	6.772	6.714	6.671
30	7.007	6.948	6.875	6.849	6.790	6.760	6.702	6.658
35	7.001	6.942	8.868	6.842	6.782	6.752	6.694	6.650
40	6.996	6.937	6.863	6.837	6.778	6.748	6.690	6.647
45	6.994	6.934	6.860	6.834	6.775	6.745	6.686	6.642
50	6.995	6.934	6.859	6.833	6.773	6.743	6.684	6.640
55	6.997	6.935	6.862	6.836	6.777	6.747	6.688	6.645
60	7.002	6.941	6.866	6.840	6.780	6.749	6.691	6.647

IV. STANDARD PHOSPHATE BUFFERS

1. pH VALUES AND THEIR CHANGE WITH TEMPERATURE AND CONCENTRATION

In figure 4, the pH of the phosphate buffer without sodium chloride is plotted as a function of the molality, m, of each buffer salt at 0°, 10°, 25°, and 60° C. A change of 100 percent in concentration effects a change of about 0.1 pH unit. When m is greater than 0.005 and less than 0.1, the pH at 25° C is given by

$$\mathrm{pH}=7.162+2.18m-2.237\sqrt{m}, \tag{8}$$

within 0.002 unit. The change of pH with temperature, shown in figure 5, is governed chiefly by the variation of pK. Thus the pH is at a minimum at a temperature between 40° and 50° C and changes only a few hundredths of a unit between 20° and 60° C.

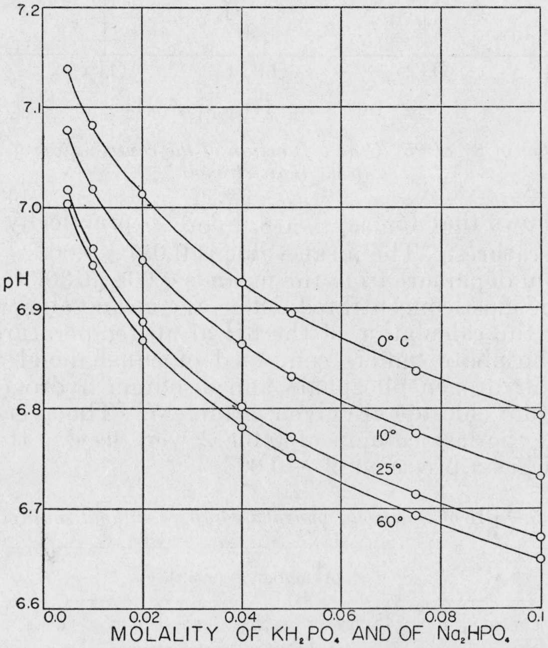

FIGURE 4.—pH *of phosphate buffers as a function of molality at 0°, 10°, 25° and 60° C*

The densities of four phosphate buffers, of molalities 0.01, 0.02, 0.05, and 0.1, were determined at 25° ±0.01° C with a picnometer that had a volume of approximately 57 ml. The results are given by the equation

$$c/m=0.99707-0.0477m-0.024m^2, \tag{9}$$

where c represents the concentration of each buffer salt expressed in moles per liter of solution. The mean departure of the values of c/m calculated by this equation from those computed from the measured densities is ±0.00001, or 0.001 percent. The upper limit of validity of eq 9 is $m=0.1$.

It is now possible to express the pH as a function of the molarity of the buffer[9] by eq 10

$$\mathrm{pH}=7.169+2.39c-2.324\sqrt{c}. \tag{10}$$

In the concentration range 0.005 c to 0.1 c, eq 10 reproduces the pH with an accuracy of 0.002 unit.[10]

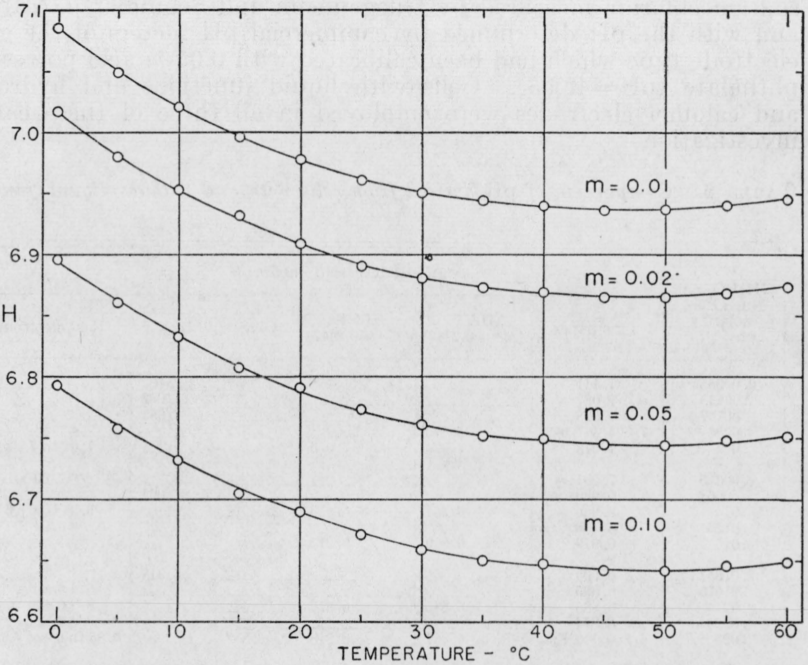

FIGURE 5.—pH *of four phosphate buffers as a function of temperature.*

By differentiation of eq 10, one obtains

$$\mathrm{d(pH)}/\mathrm{d}c=2.39-1.162/\sqrt{c}, \tag{11}$$

from which the change of pH that accompanies small changes in c can be computed. With the use of eq 9, the difference, dc, in molar concentration between buffer solutions which are, respectively, x molal and x molar in each salt can be found. From eq 11 it can be shown that the pH of a 0.01-molar phosphate buffer differs from that of a 0.01-molal buffer by only 0.0003 unit, whereas the difference

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[9] The pH given by eq 10 is referred to the same standard state as that used throughout this paper: $\mathrm{pH}=-\log a_H$, where a_H is the activity of hydrogen ion on the molal or weight basis. Since the infinitely dilute solution is normally chosen as the standard state on both the molal (m) and molar (c) scales, $\mathbf{a}_c=\mathbf{a}_m d°$, where $d°$ is the density of the solvent. Hence, the pH is the same at 4° C on the molar and molal scales and differs at 25° and 60° C by 0.0013 and 0.0073 unit, respectively.

[10] Obviously, eq 8 and 10 are merely formalized representations of the pH in the range of molalities (and molarities) between 0.005 and 0.1, for unlimited dilution of the buffer must yield the pH of pure water. Since the pH is rather close to neutrality, the buffer effect will persist to fairly low concentrations. On the other hand, a solution of which the pH is far removed from neutrality will begin to lose its regulating power at relatively high concentrations.

is 0.0010 unit when the buffers are 0.1 molar and 0.1 molal. Since this larger difference is within the limits of accuracy assigned to the pH in table 5, the pH of a buffer the molar concentration of which is known can be considered the same as that of the solution of numerically equal molality.

The pH values at 25° C of the phosphate buffer derived from measurements of cells without liquid junction are compared in table 6 with the pH of five buffers studied by Hitchcock and Taylor (H&T) [8], with six measured by Michaelis and Krüger (M&K) [27], with those of three buffers composed of sodium phosphates and sodium chloride measured by Guggenheim and Schindler (G&S) [7], and with the pH determined by commercial pH meters of the glass electrode type which had been calibrated with 0.05-*m* acid potassium phthalate (pH=4.005). Cells with liquid junctions and hydrogen and calomel electrodes were employed in all three of these earlier investigations.

TABLE 6.—*Comparison of* pH *derived from cells with and without liquid junction at 25° C*

KH_2PO_4 and Na_2HPO_4, molarity	pH from measurements of—					
	This paper	H&T (E_o'=0.2442)	H&T (E_o'=0.2447)	G&S	M&K [a]	Glass electrodes
0.000665	7.111	----------	----------	----------	7.102	----------
.00133	7.087	----------	----------	----------	7.082	----------
.00167	7.078	----------	----------	----------	7.083	----------
.0025	7.064; [b] 7.050	----------	----------	[c] 7.072	----------	[d] 7.06
.005	7.018	7.024	7.016	----------	----------	7.01 to 7.02
.00625	7.001	----------	----------	----------	----------	[d] 7.00
.00667	6.993	----------	----------	----------	7.004	----------
.01	6.959	6.961	6.953	----------	----------	6.94 to 6.96
.0125	6.938	----------	----------	----------	----------	[d] 6.93
.015	6.919	6.919	6.911	----------	----------	----------
.01667	6.909	----------	----------	----------	6.918	----------
.01875	6.895	----------	----------	----------	----------	[d] 6.89
.02	6.886	6.885	6.877	----------	----------	6.87
.0225	6.874	----------	----------	----------	----------	[d] 6.86
.025	6.860; [b] 6.833	6.857	6.848	[c] 6.837	----------	6.85 to 6.86; [d] 6.86
.03333	6.825	----------	----------	----------	[e] 6.827	----------
.04	6.802	----------	----------	----------	----------	6.79
.05	6.772; [b] 6.741	----------	----------	[c] 6.735	----------	6.76 to 6.78
.1	6.671	----------	----------	----------	----------	6.68 to 6.69

[a] Recalculated with the use of 0.3358 v for the potential of the *N*/10 calomel electrode at 18° C; the pH at 25° C was obtained by subtracting 0.024 unit from the pH at 18° C.

[b] pH of the buffer that contains sodium chloride equal in concentration to that of each phosphate.

[c] Buffers prepared with sodium dihydrogen phosphate instead of the corresponding potassium salt. Sodium chloride in concentration equal to that of each phosphate.

[d] Measurement of Glaubiger [29] with the Young "Electron-Ray" pH meter.

[e] Measurement of Serensen [28] leads to the same value for this buffer.

The solutions studied by Guggenheim and Schindler are not strictly comparable with the others listed in the table, for they contained sodium chloride and the primary sodium salt. The results for these solutions have been included, however, in recognition of the fact that this substitution of the sodium salt for the potassium salt may not introduce an uncertainty any greater than that involved in the estimation of the potential at the liquid boundary. Cohn [6] has reexamined the data obtained by Sørensen [28] and Michaelis and Krüger at 18° C. We have made a further adjustment of these values to conform to a potential of 0.3358 for the *N*/10-calomel electrode at 18° C and have obtained the pH at 25° C by subtracting 0.024 unit from the pH at 18° C.

The agreement of the results of this investigation with all three sets of earlier values is quite satisfactory. The pH measurements with the glass electrode agree with the computed pH within the limits of accuracy of the commercial instruments [30, 34]. The measurements of Glaubiger [29] show agreement of a higher order than can normally be expected of a cell with glass electrode and a liquid junction. His results are, on the average, 0.006 unit lower than those given in the second column of table 6. The instrument used by Glaubiger was calibrated at 4.00 with 0.05–*m* phthalate buffer. If a value of 4.005, 4.008, or 4.01 had been chosen for this standard, as is usually recommended, the agreement would have been even more complete.

The measurements of Hitchcock and Taylor [8] are of particular interest. These authors approached the problem of standardizing the determination of pH from measurements of cells with liquid junction in a manner suggested by the work of Cohn, Heyroth, and Menkin [31] and MacInnes and coworkers [32, 33]. In this treatment, the simple emf equation is used for the computation of pH,

$$\mathrm{pH}=(E-E^{\circ}-E_j)/k=(E-E^{\circ\prime})/k, \tag{12}$$

and $E^{\circ\prime}$ is adjusted to make the equation conform as closely as possible to thermodynamic quantities. Guggenheim and Schindler, on the other hand, computed E_j, the liquid-junction potential, from the Henderson equation and employed a selected value of E°, the standard potential of the calomel reference half-cell.

Hitchcock and Taylor assigned a value of 0.2442 v at 25° C to $E^{\circ\prime}$ for their saturated calomel electrode, as a result of extrapolations to infinite dilution of a function of the dissociation constant of primary phosphate ion [19] and the emf of cells containing phosphate buffers. An average value of 0.2441 v was chosen from measurements of acetate, phosphate, borate, and glycolate buffers, together with the dissociation constants of the corresponding buffer acids. Comparison of the second and third columns of table 6 demonstrates the essential agreement between the Hitchcock and Taylor pH scale and that defined by our method which utilizes measurements of cells without liquid junction.

In order that the results of the two investigations might relate to the same value of the dissociation constant, the measurements made with phosphate buffers by Hitchcock and Taylor at 25° and 38° C have been recalculated with the use of the Hückel equation and with pK and a° listed in this paper. The extrapolation plot was a straight line of small slope for each temperature. At 25° C, $E^{\circ\prime}$ from the measurements with phosphate buffers becomes 0.2447 v. If this value is used in eq 12, the pH of each solution measured by Hitchcock and Taylor is lowered by 0.008 unit, as shown in the fourth column. MacInnes, Belcher, and Shedlovsky [33], from extrapolation of their measurements of cells containing acetate and chloroacetate buffers, concluded that $E^{\circ}+E_j$ has a value of 0.2446 v at infinite dilution.[11] The emf data of Hitchcock and Taylor at 38° C were obtained from measurements of the cell, $H_2|\text{Buffer}||\text{KCl (saturated)}||\text{HCl } (0.1\ c)|H_2$, for which they chose $E°+E_j=-0.0668$ v. Recalculation with $pK=7.182$ yields -0.0666 v for $E+E_j$ at 38° C. The two sets of pH values are given in table 7. The last column gives data obtained by Glaubiger (G) [29] with the glass electrode.

TABLE 7.—*Comparison of* pH *derived from cells with and without liquid junction at 38° C*

KH_2PO_4 and Na_2HPO_4, molarity	pH from measurements of—			
	This paper	H&T ($E°'=-0.0668$)	H&T ($E°'=-0.0666$)	Glass electrodes (G)
0.0025	7.045	7.048	7.045	7.03
.00625	6.981	6.983	6.980	6.97
.0125	6.917	6.918	6.915	6.90
.01875	6.874	6.871	6.868	6.86
.0225	6.854	----------	----------	6.83
.025	6.840	6.837	6.834	6.83

The mean differences between the pH at 25° C obtained by Hitchcock and Taylor from measurements of cells with liquid junction and the pH derived here from measurements of cells without liquid junction are only 0.002 unit ($E°'=0.2442$) and 0.005 unit ($E°'=0.2447$). At 38° C, the differences are 0.002 unit ($E°'=-0.0668$) and 0.003 unit ($E°'=-0.0666$).

When the pH values are made to conform to the same thermodynamic constant, complete agreement is found for the dilute buffers on the two scales. The pH on the scale of Hitchcock and Taylor falls farther below the values reported in this paper as the ionic strength increases. For a fivefold increase in concentration of the buffer, the values of Hitchcock and Taylor and of Michaelis and Krüger both exhibit a decrease of 0.009 unit relative to the pH given in the second column. It is, perhaps, not surprising to discover that the potential at the liquid junction does not remain constant with changing concentration of the buffer, as is assumed in their method. With the values of this article as a reference, a difference of 0.6 mv between E_j for phosphate buffers of 0.005- and 0.025-molar concentration is computed from eq 12. In this manner $E°+E_j$ at 25° C can be found for each of the phosphate buffers. To reproduce the pH values of table 5, $E°+E_j$ for the saturated calomel electrode used by Hitchcock and Taylor must change with concentration of buffer. The potentials for buffers of molar concentrations 0.005, 0.01, 0.015, 0.02, and 0.025 would be, respectively, 0.2446, 0.2443, 0.2442, 0.2442, and 0.2440 v. Although such a change is to be expected, it cannot be stated definitely that the error does not reside in the method of computing pH from measurements of cells without liquid junction.

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[11] A value of 0.2434 v for $E°+E_j$ at ionic strengths of 0.04, 0.07, and 0.1 was found by Manov, DeLollis, and Acree [34] from measurements at 25° C of hydrogen-calomel cells with liquid junctions. Their calculation was made, with the use of eq 12, from the pH values and emf obtained in this Bureau for phthalate, phosphate, phenolsulfonate, and borate buffers and a mixture of hydrochloric acid and sodium chloride, from all of which oxygen was rigorously excluded. In the presence of air 0.2446 v was obtained for $E°+E_j$. It must be remembered that intercomparison of the values of $E°+E_j$ obtained by various investigators is not always justifiable, for this quantity is dependent not only upon the kinds and concentrations of ions at the boundary but upon the manner of forming the junction as well.

The measurements of Glaubiger [29], on the other hand, do not reveal a similar change of liquid-junction potential with a change in the concentration of equimolal phosphate buffer. The agreement of his results with the pH reported here leads to the conclusion that the potential at the liquid junction between saturated potassium chloride and 0.05-*m* phthalate buffer does not differ greatly from that at the boundary between saturated potassium chloride and phosphate buffers of concentrations that range from 0.0025 *m* to 0.025 *m*. Since the total change in potential is not much greater than the precision of Glaubiger's measurement, this discrepancy need cause little concern.

2. PREPARATION OF PHOSPHATE BUFFERS

These buffers are best prepared from freshly boiled distilled water and weighed amounts of each anhydrous salt, or of a carefully prepared mixture of the solid phosphates. The compositions of eight useful buffer solutions are given in table 8. Inasmuch as anhydrous disodium hydrogen phosphate will take up moisture when the relative humidity exceeds about 41 percent at 25° C, it is considered good practice always to dry this salt, or the mixture of solid salts, at 110° to 130° C for at least 2 hours.

TABLE 8.—*Compositions of standard phosphate buffers*

Moles of each phosphate per liter of solution	pH	KH_2PO_4	Na_2HPO_4	Equimolal mixture of buffer salts
	(25° C)	*g/liter*	*g/liter*	*g/liter*
0.005	7.018	0.6805	0.7099	1.390
.01	6.959	1.361	1.420	2.781
.02	6.886	2.722	2.840	5.562
.025	6.860	3.402	3.550	6.952
.04	6.802	5.444	5.680	11.12
.05	6.772	6.805	7.099	13.90
.075	6.714	10.21	10.65	20.86
.1	6.671	13.61	14.20	27.81

It is evident from a consideration of the properties of a buffer composed of two salts that departures of the buffer ratio from unity will cause larger errors in the pH of the buffer than will inaccuracies in total composition. If the ratio, moles KH_2PO_4/ moles Na_2HPO_4, is between 0.996 and 1.004, however, the pH will not differ by more than 0.002 unit from that calculated for equal molal quantities of the two salts. It is well to strive for an accuracy of 0.1 percent in the weight of each salt used in the preparation of a standard phosphate buffer. The total volume of the buffer should be correct within 8 ml/ liter, or 0.8 percent, if an accuracy in composition corresponding to 0.001 pH unit is desired.

Inasmuch as all of these standard buffers are prepared from equal molal amounts of the two phosphates, it would be a convenience to the user to have at hand a mixture of the pure anhydrous salts in the proper proportions. An experiment was therefore performed to ascertain whether such a mixture of solid salts would be mechanically stable in shipment and storage.

One bottle, half filled with a powdered mixture of the two salts in equal molal proportions, and one full bottle of the same mixture, were shipped by mail twice from Washington, D. C., to San Diego, Calif., and back to Washington. Five buffer solutions, each 0.02 m in sodium chloride and 0.02 m with respect to both primary and secondary phosphate salts if segregation had not occurred, were prepared with the use of the top 4 g of salt mixture in each of these two bottles and three controls. Eight cells with hydrogen electrodes and silver–silver-chloride electrodes were prepared from these solutions and emf measurements made at 25° C. The average emf, corrected to a pressure of hydrogen of 760 mm, was 0.73473 v, and the average deviation was 0.03 mv. Inasmuch as the emf of this cell was found to be 0.73478 v from a plot of the data given earlier in this paper, it was concluded that little or no segregation had taken place. The possibility that prolonged exposure to the normal vibrations of the laboratory shelf might effect appreciable segregation cannot, however, be ignored.

V. EFFECT OF SODIUM CHLORIDE ON THE pH

The pH of an equimolal phosphate buffer containing sodium chloride cannot be calculated from measurements of cells of the type used in this work and the two assumptions made earlier in this paper. In order to do so, it would be necessary to evaluate $\beta_{H_2PO_4}-\beta_{HPO_4}$ in the presence of the chloride. The decrease of β^* as the molality of sodium chloride is lowered at constant ionic strength (see fig. 3) is partitioned in an unknown manner among the values of β for the three ions concerned. Whereas it was assumed that $\beta_{H_2PO_4}-\beta_{HPO_4}$ in the absence of chloride can be identified with the limiting value of β^*, this term must logically be considered, in the light of the first assumption made earlier, to change when sodium chloride is added to the buffer solution. If this were not the case, there would be no "specific salt effect," and the pH of a buffer solution with salt and one without salt could both be calculated from eq 4a without a change in the ionic parameters.

In an unpublished investigation of the effect of neutral salts of different valence types upon the pH of the equimolal phenolsulfonate buffer, the authors of this paper concluded that potassium nitrate, sodium sulfate, and trisodium citrate displayed only slight specific effects in their influence upon the pH. As a first approximation, each salt lowered the pH by the same amount as did an equimolal mixture of the buffer salts which contributed the same amount to the ionic strength. In view of the fact that a knowledge of the approximate pH of phosphate buffers with added sodium chloride is often desired, such a calculation has been made on the assumption that the influence of sodium chloride is, in this instance also, a "normal salt effect." It seems improbable, by analogy with the equimolal phenolsulfonate buffer, that this assumption should introduce an error greater than 0.005 unit when the ionic strength is 0.5 and the molalities of sodium chloride and of buffer are equal.

If equations of the form of eq 4a are written for the pH of a 1:1 phosphate buffer with no chloride at the ionic strength μ, and for the pH of the same buffer, pH′, to which sodium chloride has been added to a molality m_2, an expression is obtained, by the subtraction of one equation from the other, for pH′ in terms of the pH of the buffer without chloride:

$$pH' = pH - \frac{3A\sqrt{\mu+m_2}}{1+Ba^\circ\sqrt{\mu+m_2}} + \frac{3A\sqrt{\mu}}{1+Ba^\circ\sqrt{\mu}} - (\beta_{\mathrm{H_2PO_4}} - \beta_{\mathrm{HPO_4}} + \beta_{\mathrm{Cl}})^\circ m_2, \quad (13)$$

or

$$pH' = pH - \phi(m_2). \quad (13a)$$

Within 0.002 pH unit, $\phi(m_2)$ is given empirically by

$$\phi(m_2) = (1+at)(bm_2 + cm_2^2) \quad (14)$$

for temperatures, t, between 0° and 60° C.

The constants of eq 14 were determined by the method of least squares and lead to the following expressions for the effect of sodium chloride on eight phosphate buffers, each of which contain equal molal concentrations (m) of potassium dihydrogen phosphate and of disodium hydrogen phosphate:

0.005-m buffer: $\mathrm{pH'} = \mathrm{pH} - (1+0.0009t)(3.06m_2 - 13.2m_2^2)$. (15a)
0.01-m buffer: $\mathrm{pH'} = \mathrm{pH} - (1+0.0006t)(2.13m_2 - 7.6m_2^2)$. (15b)
0.02-m buffer: $\mathrm{pH'} = \mathrm{pH} - (1+0.0004t)(1.36m_2 - 3.6m_2^2)$. (15c)
0.025-m buffer: $\mathrm{pH'} = \mathrm{pH} - (1+0.0003t)(1.16m_2 - 2.8m_2^2)$. (15d)
0.04-m buffer: $\mathrm{pH'} = \mathrm{pH} - 0.84m_2 + 1.6m_2^2$. (15e)
0.05-m buffer: $\mathrm{pH'} = \mathrm{pH} - 0.66m_2 + 0.8m_2^2$. (15f)
0.075-m buffer: $\mathrm{pH'} = \mathrm{pH} - 0.48m_2 + 0.4m_2^2$. (15g)
0.1-m buffer: $\mathrm{pH'} = \mathrm{pH} - 0.40m_2 + 0.4m_2^2$. (15h)

The pH value of each buffer without sodium chloride at each of 13 temperatures appears in table 5. These equations apply strictly only when the molality of sodium chloride (m_2) is equal to, or less than, the molality, m, of each buffer salt.

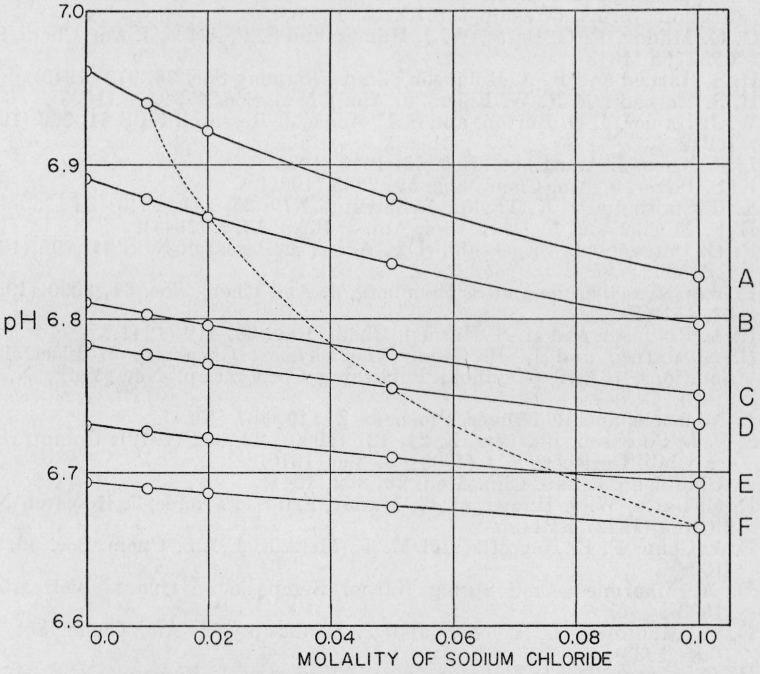

FIGURE 6.—*Effect of sodium chloride on the* pH *of six phosphate buffers.*

Curves A, B, C, D, E, and F represent buffers in which both phosphates are respectively 0.01, 0.02, 0.04, 0.05, 0.075, and 0.1 molal.

In figure 6, the pH of six of these buffers is plotted as a function of molality of added sodium chloride for values of m_2 up to 0.1. The dashed line which intersects all of the curves separates that portion of each curve (on the left) which lies in the range of concentrations of the experimental measurements from that portion (on the right) which was computed from 15a to 15h beyond the region of their validity.

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