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pH STANDARDS AT VARIOUS TEMPERATURES: AQUEOUS SOLUTIONS OF ACID POTASSIUM PHTHALATE

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ABSTRACT

pH values of aqueous solutions of acid potassium phthalate, National Bureau of Standards Standard Sample 84a, are given for concentrations from 0.001 to 0.2 *m* and for temperatures between 0° and 60° C. They were calculated from the values of the two dissociation constants of *o*-phthalic acid and the activity coefficients of the acid phthalate and phthalate ions. The pH values range from 3.88 to 4.42. They may be computed for any temperature from 0° to 60° C, inclusive, by the equation

$$\text{pH} = A^*/T + B + CT$$

or by the equation

$$\text{pH} = \text{pH}_{15} + k(t - 15)^2$$

where A^* , B , C , and k are constants whose numerical values are dependent upon the molality of the solutions, pH_{15} is the pH value at 15° C, and $T = t^\circ\text{C} + 273.16$.

A 0.05-*m* solution of acid potassium phthalate, the one used most extensively in the calibration of pH assemblies, has a pH value of 4.005 at 25° C. Its pH value at any temperature from 0° to 60° C, inclusive, may be computed by the equation

$$\text{pH} = 1336.08/T - 5.2678 + 0.016069T,$$

or by the equation

$$\text{pH} = 4.000 + 0.0000479(t - 15)^2.$$

The pH values of a 0.05-*m* solution of acid potassium phthalate prepared with Standard Samples 84a and 84b were found to agree within 0.001 pH unit at the various temperatures.

Directions are included for preparations of the solutions on a molal and a molar scale of concentration. A critique of the method of evaluating the pH values and comparisons with older values reported for 0.05-*M* and 0.2-*M* solutions are given.

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I. INTRODUCTION

Values of the two dissociation constants of *o*-phthalic acid have been reported previously [1, 2]¹ for temperatures 0° to 60° C, inclusive. With their use, it is possible to calculate the hydrogen-ion concentration and the pH of solutions of acid potassium phthalate of different concentrations and to compare the values with those determined by a short method previously described [3].

The hydrogen-ion concentration, m_{H} , of an aqueous solution of acid potassium phthalate is represented by the equation

$$m_{\text{H}}^3 + [a + (K_1 f_{\text{H}_2\text{Ph}})/(f_{\text{H}} f_{\text{HPh}})]m_{\text{H}}^2 + [(K_1 K_2 f_{\text{H}_2\text{Ph}})/(f_{\text{H}}^2 f_{\text{Ph}})]m_{\text{H}} - (a K_1 K_2 f_{\text{H}_2\text{Ph}})/(f_{\text{H}}^2 f_{\text{Ph}}) = 0, \quad (1)$$

or by

$$m_{\text{H}} = \left(\frac{K_1 K_2 / (f_{\text{H}}^2 f_{\text{Ph}}) (a - m_{\text{H}})}{K_1 / (f_{\text{H}} f_{\text{HPh}}) + a + m_{\text{H}}} \right)^{1/2}, \quad (2)$$

with the reasonable assumption that the effects of hydrolysis are negligible. In these equations a is the stoichiometric concentration of the solution of acid potassium phthalate, K_1 and K_2 are, respectively, the first and second dissociation constants of *o*-phthalic acid, and f is the activity coefficient of the species denoted by subscripts.²

The hydrogen-ion activity, a_{H} , is given by³

$$a_{\text{H}} = f_{\text{H}} m_{\text{H}}, \quad (3)$$

and the pH value by

$$\text{pH} = -\log a_{\text{H}} = -\log f_{\text{H}} m_{\text{H}}. \quad (4)$$

The activity coefficients [1, 2] of the various ions in a solution of acid potassium phthalate with or without dipotassium phthalate, *o*-phthalic acid, or potassium chloride are given by the Hückel [6] form of the Debye-Hückel equation, or by⁴

$$-\log f_{\text{H}} = A\sqrt{\mu}/(1 + 3.76 B\sqrt{\mu}) - \beta_{\text{H}} m_{\text{H}}, \quad (5)$$

$$-\log f_{\text{Cl}} = A\sqrt{\mu}/(1 + 3.76 B\sqrt{\mu}) - \beta_{\text{Cl}} m_{\text{Cl}}, \quad (6)$$

$$-\log f_{\text{HPh}} = A\sqrt{\mu}/(1 + 3.76 B\sqrt{\mu}) - \beta_{\text{HPh}} m_{\text{HPh}}, \quad (7)$$

and

$$-\log f_{\text{Ph}} = 4A\sqrt{\mu}/(1 + 3.76 B\sqrt{\mu}) - \beta_{\text{Ph}} m_{\text{Ph}}. \quad (8)$$

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

² Equations 1, 2, 9, and 10 are based on the mass-action equations for the dissociation of *o*-phthalic acid, the equation $a = m_{\text{H}_2\text{Ph}} + m_{\text{HPh}} + m_{\text{Ph}}$, and the equation $a + m_{\text{H}} = m_{\text{H}_2\text{Ph}} + 2m_{\text{Ph}}$, expressing electrical neutrality of the solutions. Equation 12 is derived in a similar manner except the concentration of the hydroxyl ion, m_{OH} , is included, so that $a + m_{\text{H}} = m_{\text{H}_2\text{Ph}} + 2m_{\text{Ph}} + m_{\text{OH}}$. Acid potassium phthalate is considered to be completely dissociated into potassium and acid phthalate ions. For more details and references to earlier work, see references [1 to 3]. In equations 1 or 2, the symbols H_2Ph , HPh , and Ph designate, respectively, undissociated *o*-phthalic acid, acid phthalate ion, and diphtalate ion. For convenience, the charges on the ions are omitted throughout the paper.

³ The activity coefficient of an individual ion cannot be determined by thermodynamics alone without assumption. In the work on pH standards at this Bureau the assumption is made that the activity coefficients of ions are given by the Hückel equation and that the "salting-out" terms of the chloride and hydrogen ions are equal. The parameters of the Hückel equation are determined from a study of the thermodynamic properties of mixtures of acid potassium phthalate, dipotassium phthalate, *o*-phthalic acid, and potassium chloride. For details in regard to this procedure, see references [1 to 5].

⁴ The equation of Hückel was derived for the activity coefficient of a single salt. Hückel assumed that the dielectric constant, D , of a solution varied with the salt concentration according to the equation $D = D_0(1 - \beta c)$, where D_0 is the dielectric constant of the solvent and β is a proportionality constant. In this paper and previous ones [1, 2] the assumption was made that the Hückel equation may also be applied to a solution containing a mixture of salts. This assumption leads to eq 5, 6, 7, and 8. Frequently, experimenters assumed that the salting-out term is proportional to the ionic strength of the solutions. When this assumption is made, it follows that solutions of a particular buffer mixture of different compositions but of the same ionic strength have the same pH value [1]. Hamer and Acree [1], however, have shown that solutions of a particular buffer mixture of different compositions and of the same ionic strength have different pH values.

The activity coefficient of the undissociated *o*-phthalic acid, H_2Ph , is assigned a value of unity, as is customary for neutral molecules. The data of Scatchard, Hamer, and Wood [7] show that this is not strictly true for concentrated solutions but is a very close approximation for most solutions below 0.2 *m*.⁵

It is the purpose of this paper to present values of the pH of NBS Standard Sample 84a of acid potassium phthalate of concentrations ranging from 0.001 to 0.2 *m* and for temperatures from 0° to 60° C, based upon the above equations and the values of K_1 , K_2 , β_{Cl} , β_{HPh} , and β_{Ph} given in former reports [1, 2]. Values of A and B at various temperatures for use in the above equations are given in a previous publication [5].⁶ The ionic strength of the solutions is given by $(m_K + m_{HPh} + 4m_{Ph} + m_H)/2$ and the values of the molalities of the acid phthalate and diphtalate ions by the equations

$$m_{HPh} = [(K_1 f_{H_2Ph}) / (f_H f_{HPh})] (a - m_H) / [2m_H + (K_1 f_{H_2Ph}) / (f_H f_{HPh})] \quad (9)$$

and

$$m_{Ph} = [m_H (a - m_H)] / [2m_H + (K_1 f_{H_2Ph}) / (f_H f_{HPh})], \quad (10)$$

where a represents the molality of acid potassium phthalate and the other terms have their usual significance. The value of m_K is equal to a , as acid potassium phthalate is completely dissociated into potassium and acid phthalate ions.

II. CALCULATION OF THE pH VALUES OF AQUEOUS SOLUTIONS OF ACID POTASSIUM PHTHALATE

The method of calculation of pH values is illustrated by the data given in table 1 for a 0.05-*m* solution of acid potassium phthalate at 25° C. First, the solution is considered to consist only of K^+ and HPh^- ions. The ionic strength is then equal to the molality. The hydrogen-ion concentration is calculated by eq 2, taking m_H as zero on the right side of the equation. This value of m_H is then used on the right side of eq 2 and a new value is determined for m_H . This procedure is repeated until consistent values of m_H are obtained. Generally only three approximations are required. Values of m_{HPh} and m_{Ph} are then obtained by eq 9 and 10, and a new value of the ionic

TABLE 1.—Values of molecular and ionic species and ionic strength in moles per 1,000 g of water, and the pH for 0.05-*m* solution of acid potassium phthalate corresponding to the several steps in the arithmetical procedure of successive approximations

	Assumed values	Number of successive approximations						
		I	II	III	IV	V	VI	VII
HAn^- -----	0.05				0.043657	0.043637	0.043637	0.043637
H^+ -----	.0	0.00012068	0.00012039	0.00012039	.00012039	.00012213	.00012214	.00012214
An^- -----	.0				.0032315	.0032424	.0032423	.0032423
H_2An -----	.0				.0031111	.0031203	.0031202	.0031202
μ -----	.05				.053412	.053426	.053426	.053426
pH-----	7	4.008	4.009	4.009	4.009	4.005	4.005	4.005

⁵ In this paper the symbol m is used to denote molality and the symbol M to denote molarity.

⁶ These values have since been revised [8]. The use of the new values, however, will not change the values of pH given in this paper, as the older values of A and B [5] were employed consistently throughout this investigation in the determination of the dissociation constants [1, 2], the concentrations of the various ions, and the value of the standard potential of the silver-silver-chloride electrode [5].

strength is calculated by using the values of m_{HPH} and m_{Ph} . The various quantities are given in table 1 under the column designated as approximation IV. The new ionic strength is used to calculate a new m_{H} , which in turn is used to calculate new values of m_{HPH} and m_{Ph} , and so on until self-consistent values of m_{H} , m_{HPH} , and m_{Ph} are obtained. Data in table 1 show the results of approximations V, VI, and VII. Values obtained in approximations VI and VII agree; hence no further arithmetical computations are required. The pH value of 0.05- m solution of acid potassium phthalate prepared with NBS Standard

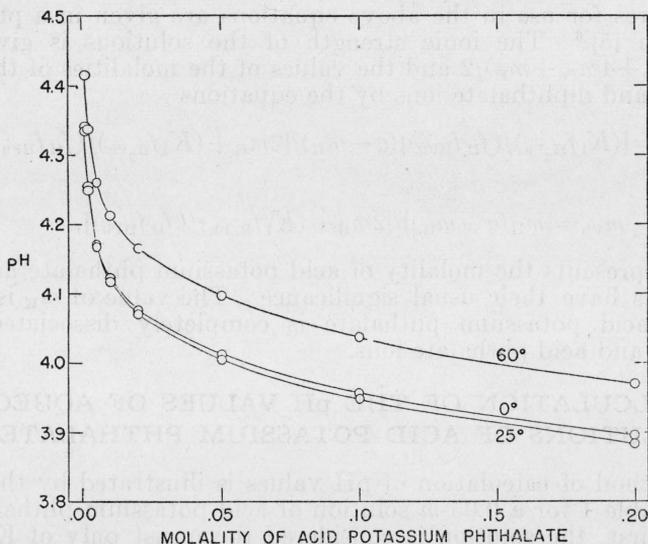


FIGURE 1.—Plots of the pH values of aqueous solutions of acid potassium phthalate, National Bureau of Standards Standard Sample 84a, at 0°, 25°, and 60° C as a function of the molality of the solution.

Sample 84a is therefore 4.005 at 25° C. The pH values of other concentrations at the various temperatures were determined in like fashion.

In table 2, values are given of m_{H} , m_{HPH} , m_{Ph} , and $m_{\text{H}_2\text{Ph}}$ from 0° to 60° C for aqueous solutions of acid potassium phthalate from 0.001 to 0.2 m . The amount of m_{Ph} and m_{HPH} is larger for the more concentrated solutions than for the more dilute ones. On a percentage basis, however, the reverse is true because of the increased ionization of the acid phthalate ion on dilution.

The pH values of acid potassium phthalate from 0.001 to 0.2 m are given in table 3 for temperatures from 0° to 60° C, inclusive. In figure 1 the values are shown as a function of the molality of acid potassium phthalate at 0°, 25°, and 60° C. From 0.05 to 0.2 m the pH values do not change very much. The pH of any intermediate concentration can be interpolated from the data of table 3 or read from the curves of figure 1.

TABLE 2.—Concentrations (molality $\times 10^4$) of molecular and ionic species in solutions of acid potassium phthalate of various molalities at temperatures from 0° to 60° C

Temperature	<i>m</i> =0.001 KHPH ^a				<i>m</i> =0.002 KHPH				<i>m</i> =0.005 KHPH				<i>m</i> =0.01 KHPH			
	H+	HPh-	Ph-	H ₂ Ph	H+	HPh-	Ph-	H ₂ Ph	H+	HPh-	Ph-	H ₂ Ph	H+	HPh-	Ph-	H ₂ Ph
0.....	0.4736	8.871	0.8013	0.3277	0.5848	17.83	1.377	0.7922	0.7276	44.59	3.069	2.341	0.8380	88.97	5.932	5.094
5.....	.4808	8.851	.8150	.3342	.5938	17.79	1.401	.8075	.7388	44.49	3.124	2.385	.8514	88.77	6.042	5.191
10.....	.4847	8.837	.8241	.3394	.5983	17.76	1.418	.8195	.7444	44.42	3.164	2.420	.8581	88.62	6.122	5.263
15.....	.4862	8.826	.8302	.3440	.5998	17.74	1.430	.8298	.7460	44.36	3.194	2.448	.8601	88.49	6.184	5.324
20.....	.4852	8.819	.8334	.3482	.5982	17.73	1.436	.8380	.7437	44.32	3.213	2.469	.8575	88.41	6.225	5.367
25.....	.4820	8.817	.8326	.3506	.5937	17.71	1.438	.8438	.7376	44.29	3.222	2.484	.8505	88.35	6.249	5.399
30.....	.4765	8.818	.8291	.3526	.5862	17.72	1.434	.8476	.7275	44.29	3.219	2.491	.8388	88.34	6.250	5.411
35.....	.4685	8.823	.8227	.3542	.5755	17.72	1.425	.8500	.7133	44.30	3.207	2.494	.8223	88.35	6.235	5.413
40.....	.4585	8.831	.8134	.3549	.5623	17.74	1.413	.8510	.6960	44.33	3.185	2.489	.8022	88.40	6.200	5.398
45.....	.4465	8.842	.8024	.3559	.5466	17.76	1.395	.8483	.6756	44.37	3.155	2.479	.7785	88.49	6.145	5.367
50.....	.4324	8.860	.7867	.3543	.5282	17.79	1.372	.8439	.6519	44.43	3.110	2.458	.7508	88.61	6.072	5.321
55.....	.4169	8.879	.7688	.3519	.5081	17.82	1.345	.8365	.6257	44.51	3.058	2.433	.7204	88.76	5.981	5.261
60.....	.4007	8.899	.7507	.3500	.4872	17.85	1.317	.8293	.5988	44.59	3.004	2.405	.6891	88.92	5.886	5.196

Temperature	<i>m</i> =0.02 KHPH				<i>m</i> =0.05 KHPH				<i>m</i> =0.1 KHPH				<i>m</i> =0.2 KHPH			
	H+	HPh-	Ph-	H ₂ Ph	H+	HPh-	Ph-	H ₂ Ph	H+	HPh-	Ph-	H ₂ Ph	H+	HPh-	Ph-	H ₂ Ph
0.....	0.9654	177.3	11.85	10.88	1.192	440.0	30.59	29.40	1.438	873.7	63.87	62.44	1.7748	1732.3	134.74	132.96
5.....	.9815	176.8	12.07	11.09	1.214	438.8	31.19	29.97	1.465	871.2	65.15	63.68	1.8114	1726.7	137.56	135.74
10.....	.9898	176.5	12.23	11.24	1.225	438.0	31.63	30.41	1.481	869.2	66.13	64.65	1.8334	1722.3	139.78	137.95
15.....	.9927	176.3	12.36	11.37	1.231	437.2	32.00	30.76	1.489	867.6	66.94	65.45	1.8466	1718.6	141.64	139.80
20.....	.9903	176.1	12.45	11.46	1.229	436.7	32.25	31.02	1.490	866.4	67.52	66.03	1.8494	1715.8	143.01	141.16
25.....	.9827	175.9	12.52	11.54	1.221	436.4	32.42	31.20	1.482	865.6	67.94	66.46	1.8432	1713.7	144.09	142.25
30.....	.9697	175.9	12.53	11.56	1.207	436.2	32.50	31.30	1.467	865.1	68.17	66.70	1.8269	1712.4	144.72	142.89
35.....	.9510	175.9	12.51	11.56	1.185	436.2	32.49	31.31	1.442	865.0	68.20	66.76	1.7997	1711.9	144.97	143.17
40.....	.9282	176.0	12.45	11.52	1.158	436.4	32.39	31.23	1.412	865.3	68.05	66.64	1.7649	1712.1	144.84	143.07
45.....	.9010	176.2	12.35	11.45	1.126	436.8	32.16	31.04	1.374	866.1	67.65	66.28	1.7207	1713.4	144.16	142.44
50.....	.8694	176.4	12.22	11.35	1.088	437.3	31.87	30.78	1.330	867.1	67.11	65.78	1.6680	1715.2	143.22	141.56
55.....	.8344	176.7	12.05	11.22	1.046	438.1	31.47	30.43	1.280	868.6	66.34	65.06	1.6089	1718.1	141.73	140.12
60.....	.7985	177.0	11.88	11.08	1.002	438.9	31.07	30.06	1.229	870.1	65.58	64.35	1.5476	1720.8	140.40	138.85

^a KHPH denotes acid potassium phthalate.

TABLE 3.—pH values of various molalities of acid potassium phthalate, Standard Sample 84a of the National Bureau of Standards, from 0° to 60° C

Temperature °C	pH values							
	<i>m</i> =0.001	<i>m</i> =0.002	<i>m</i> =0.005	<i>m</i> =0.01	<i>m</i> =0.02	<i>m</i> =0.05	<i>m</i> =0.1	<i>m</i> =0.2
0	4.341	4.255	4.171	4.122	4.076	4.012	3.956	3.895
5	4.334	4.248	4.165	4.115	4.069	4.005	3.949	3.887
10	4.331	4.245	4.162	4.112	4.066	4.001	3.945	3.883
15	4.330	4.244	4.161	4.111	4.065	4.000	3.944	3.881
20	4.331	4.246	4.163	4.113	4.067	4.001	3.945	3.882
25	4.334	4.249	4.167	4.117	4.070	4.005	3.948	3.884
30	4.339	4.255	4.173	4.124	4.077	4.011	3.953	3.890
35	4.346	4.263	4.182	4.133	4.086	4.019	3.962	3.897
40	4.356	4.273	4.193	4.144	4.097	4.030	3.972	3.907
45	4.367	4.286	4.206	4.157	4.111	4.043	3.985	3.920
50	4.381	4.301	4.222	4.174	4.127	4.059	4.000	3.934
55	4.397	4.318	4.240	4.192	4.145	4.077	4.018	3.952
60	4.415	4.337	4.260	4.212	4.165	4.097	4.037	3.970

In figure 2 the pH values are plotted with respect to temperature in degrees centigrade. This variation, which is quite small, may be expressed by an equation similar to that used by Harned and Robinson [9] for the variation of dissociation constants with temperature, namely,

$$\text{pH} = A^*/T + B + CT. \quad (11)$$

The numerical values of the constants A^* , B , and C were determined by the method of least squares, using the pH data of table 3. The numerical values of the constants are given in table 4 for the various molalities of acid potassium phthalate.

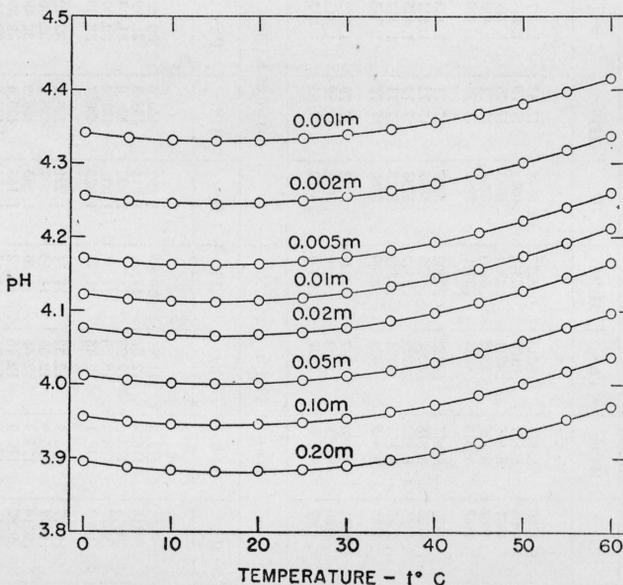


FIGURE 2.—Plots of the pH values of aqueous solutions of acid potassium phthalate, National Bureau of Standards Standard Sample 84a, of various molalities as a function of the temperature in degrees centigrade.

The variation of the pH values with temperature may also be expressed by the equation

$$\text{pH} = \text{pH}_{15} + k(t - 15)^2, \quad (11a)$$

where pH_{15} is the value for 15° C, and k is a constant whose numerical value depends on the stoichiometric concentration of acid potassium phthalate. The numerical values of the constant, k , are given in the last column of table 4 for various molalities of acid potassium phthalate.

TABLE 4.—Numerical values of the constants of equations 11 and 11a for the variation of the pH values of various molalities of acid potassium phthalate with temperature

Molality of acid potassium phthalate	A* (eq 11)	B (eq 11)	C (eq 11)	k (eq 11a)
0.001	1185.35	-3.8849	0.014230	0.0000423
.002	1251.83	-4.4517	.015099	.0000467
.005	1292.83	-4.8377	.015657	.0000491
.01	1321.45	-5.0867	.016003	.0000505
.02	1329.56	-5.1814	.016073	.0000503
.05	1336.08	-5.2678	.016069	.0000479
.10	1312.11	-5.1459	.015739	.0000464
.20	1312.12	-5.1824	.015648	.0000432

III. COMPARISONS OF THE pH VALUES WITH OLDER VALUES

In table 5 the values calculated for a 0.05-*m* solution are compared with ones obtained by previous investigators [3, 10, 11, 12, 13]. The values of Clark and Lubs are lower by 0.027 at 20° C than the ones reported in this paper, and those of Kolthoff and Tekelenburg are

TABLE 5.—Comparison of the pH values of 0.05-*m* solution of acid potassium with values determined by different investigators

Temperature	Clark and Lubs	Kolthoff and Tekelenburg	Hitchcock and Taylor	MacInnes, Belcher, and Shedlovsky	Hamer and Acree	Present values	Δ*
	[10]	[11]	[12]	[13]	[3]		
<i>t</i> ° C							
0					4.007	4.012	+0.005
5					4.002	4.005	+ .003
10					3.999	4.001	+ .002
12.5				4.000	4.000	^b 4.000	±.000
15					4.000	4.000	+ .000
18		3.94° (3.92)			4.001	^b 4.000	-.001
20	3.974				4.001	4.001	-.002
25			4.008	4.000	4.008	4.005	-.003
30		3.96 (3.92)			4.016	4.011	-.005
35					4.025	4.019	-.006
38			4.025	4.015	4.032	^b 4.027	-.005
40		3.99 (3.93)			4.036	4.030	-.006
45					4.050	4.043	-.007
50		4.02 (3.94)			4.068	4.059	-.009
55					4.084	4.077	-.007
60		4.05 (3.94)			4.101	4.097	-.004

* Differences between present values and former ones determined by Hamer and Acree [3].

^b Values were calculated by equation 11.

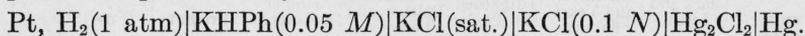
^c Values in parentheses were determined with a hydrogen electrode, whereas the other values of Kolthoff and Tekelenburg were determined with a quinhydrone electrode. They considered the hydrogen-electrode values less reliable because of possible reduction of the acid potassium phthalate.

lower by 0.06, 0.05, 0.04, 0.04, and 0.05, respectively, for temperatures of 18°, 30°, 40°, 50°, and 60° C. These differences may be attributed partially to the neglect of corrections for liquid-junction potentials and partially to their use of hydrogen-ion concentration rather than hydrogen-ion activity as the basis of the definition of the pH scale. Good agreement is obtained, however, with the results of Hitchcock and Taylor and of MacInnes, Belcher, and Shedlovsky.

The present values and those previously reported by Hamer and Acree [3] agree within 0.005, on the average, which is the limit of precision set by them. Hamer and Acree used a method in which a comparison was made of the emf of a cell containing 0.05-*m* acid potassium phthalate with the emf of two different cells, one containing 0.05-*m* hydrochloric acid and the other 0.05-*m* potassium hydroxide. Although the ionic strength of the hydrochloric acid and potassium hydroxide is 0.05, the ionic strength of acid potassium phthalate is somewhat higher, because of several ionic reactions that occur when the salt is dissolved in water. Hamer and Acree used an ionic strength of 0.0533 at each temperature. The true ionic strength may be calculated from the data of table 4. It is found to be 0.053378 at 25° C. Therefore, the value used for the ionic strength cannot account for the difference of 0.005 in pH cited above. Hamer and Acree used the activity coefficients of potassium hydroxide determined by Harned and Cook [14]. Harned and Cook determined the activity coefficients only for temperatures from 0° to 35° C, inclusive. Values of the activity coefficients of potassium hydroxide from 40° to 60° C were obtained by extrapolation of the data of Harned and Cook. The difference of 0.005 in pH, may, therefore, be attributed to the uncertainties in the values of the activity coefficients of potassium hydroxide, especially above 35° C.

The short method of Hamer and Acree, therefore, gives substantially the correct values of pH. This method also has added advantage in that it partially circumvents the theoretical difficulty of evaluating salting-out terms and "ion size" values of individual ions.

Clark and Lubs determined the pH of a 0.05-*M* solution of acid potassium phthalate by means of the cell



They obtained 0.5689 v for the emf of this cell at 20° C. Using 0.3379 v for the 0.1-*N* calomel half-cell and neglecting the potential of the liquid junction between the saturated solution of potassium chloride and the phthalate solution, they obtained a pH value of 3.974. Recent data make possible a recalculation of the potential of the half-cell, including corrections for the potential of the liquid junction. MacInnes, Belcher, and Shedlovsky [13] obtained 0.3358 v and Hamer [15] found 0.3365 v for the 0.1-*N* calomel half-cell at 25° C. If the temperature coefficient of the 0.1-*N* calomel half-cell given by MacInnes [16] is used, the values of the potential of the half-cell become 0.3360 v and 0.3367 v, respectively, at 20° C. These potentials, together with the emf of Clark and Lubs give, respectively, 4.005 and 3.998 for the pH value at 20° C, or an average value of 3.999, which agrees well with 4.001 found in this investigation.⁷

⁷ Clark and Lubs expressed their concentrations on a molar scale, whereas the concentrations used in this work were expressed on the molal scale. For concentrations below 0.2 *m*, differences in pH values introduced by differences in the concentration scale are negligible. A 0.05-*m* solution is 0.04946 *M*. (See table 7 for densities of KHPH.)

Kolthoff and Tekelenburg based their measurements upon Sorensen's [17] value of 2.038 for the pH of a solution composed of 0.01-*N* hydrochloric acid and 0.09-*N* potassium chloride at 18° C. This value was based upon conductivity measurements involving the Arrhenius isohydric principle. However, use of the activity concept alters this value. Harned and Hamer [18] obtained a value of 0.789 for the activity coefficient of 0.01-*m* hydrochloric acid in 0.09-*m* potassium chloride at 18° C, or 0.794 on a normal scale of concentration. As this solution has an activity of 0.00794, its pH value is 2.100 at 18° C. When used in conjunction with a salt bridge of saturated potassium chloride this solution should be assigned a pH value 0.02 pH unit lower, or a value of 2.080, because of the difference in the liquid-junction potentials of strong acids and weak buffers when used in contact with potassium chloride [15]. Hence, the values of Kolthoff and Tekelenburg become 3.98, 3.99, 4.00, 4.03, 4.05, and 4.08, respectively, for temperatures of 18°, 25°, 30°, 40°, 50°, and 60° C, all of which agree fairly closely with the pH values given in this paper.

TABLE 6.—Comparison of the pH values of 0.05-*m* solution of acid potassium phthalate at 25° C after corrections of literature data have been made

Experimenters	Year	Uncorrected pH values	pH values	Estimated uncertainty ^a
Clark and Lubs	1916	3.974	4.003	0.01
Kolthoff and Tekelenburg	1927	3.95	3.99	.01
Hitchcock and Taylor	1937	4.008	4.008	.005
MacInnes, Belcher, and Shedlovsky	1938	4.000	4.000	.005
Hamer and Acree	1944	4.008	4.008	.005
Hamer, Pinching and Acree	1946	4.005	4.005	.002
Average value			4.004 ± 0.005	0.006
Recommended value for National Bureau of Standards Standard Sample 84a or 84b, or Standard Samples of comparable purity.			4.005 ± 0.002	0.002

^a ±0.1 mv corresponds to ±0.0017 pH unit at 25° C.

In table 6 the various values, with corrections, for a 0.05-*m* solution of acid potassium phthalate are given for 25° C. The value of 4.005 obtained in this investigation agrees very well with the average value of 4.004. When it is realized that 0.1 mv in the emf corresponds to 0.0017 pH unit, the agreement is excellent. The differences between the two sets of values of MacInnes, Belcher, and Shedlovsky and of Hitchcock and Taylor correspond to 0.3 mv, which is an appreciable error for cells without liquid junction but not for cells with liquid junction, which they used in their determinations. The agreement of the pH values obtained in this investigation with those found by MacInnes, Belcher, and Shedlovsky, and by Hitchcock and Taylor, indicates that either pH method may be used. The method of MacInnes and Hitchcock is simpler and more direct, whereas the method herein described is more precise in that cells without liquid junction can be more accurately reproduced and lend themselves to thermodynamic treatment. Presumably, the different samples of acid potassium phthalate used by the various experimenters were of like purity and the various discrepancies may be attributed to the use of liquid junctions that are difficult to reproduce, to the use of

different types of hydrogen electrodes [19],⁸ or to accidental errors. Nevertheless, the various values are in quite good agreement, and the pH value of a solution of acid potassium phthalate of a molality of 0.05 may be said to be established as 4.005 ± 0.002 at 25° C.

Wood and Murdick [20] obtained 3.86 for the pH of a 0.2-*M* solution of acid potassium phthalate at 25° C from measurements with a saturated type of calomel half-cell, to which they assigned a value of 0.2437 v. Their pH value is 0.024 pH unit lower than the one obtained in this investigation. Recent data give 0.2434 v [15] and 0.2441 v [12] for the potential of the saturated calomel half-cell. The average value of 0.2438 v with the emf of Wood and Murdick gives 3.86 for the pH value. The difference of 0.024 between their value and the one reported here therefore must be due to either the difference in the pH methods, which becomes more pronounced at higher concentrations, or to the type of liquid junction used by Wood and Murdick.⁹ The potential of a liquid junction between solutions of these types depends on the way it is constructed [15]. Unfortunately, no data are available for other concentrations with which comparisons may be made.

IV. PREPARATION OF THE pH STANDARDS OF ACID POTASSIUM PHTHALATE

Solutions of acid potassium phthalate of molalities from 0.001 to 0.2 are well suited for use as standards of pH. They possess good buffer capacities between 0.05 and 0.2 *m*, vary little in magnitude with changes in temperature, especially between 0° and 30° C, and may be readily prepared from a single salt and freshly boiled distilled water. It is recommended that they be prepared as follows: Add a known weight of dry acid potassium phthalate of high purity to 1,000 g of

TABLE 7.—Quantities of acid potassium phthalate required to prepare solutions of various molalities.^a

Molality	Grams per 1000 grams of water	Density at 20° C	Density at 25° C	Grams per liter of solution	
				20° C	25° C
0.001	0.2042	0.99833	0.99716	0.2038	0.2036
.002	.4084	.99842	.99725	.4076	.4071
.005	1.0211	.99871	.99753	1.0187	1.0175
.01	2.0422	.99919	.99799	2.0364	2.0339
.02	4.0844	1.00014	.99892	4.0653	4.0633
.05	10.2108	1.00295	.00171	10.1374	10.1249
.1	20.4216	1.00750	1.00616	20.1630	20.1362
.2	40.8432	1.01628	1.01484	39.8793	39.8228

^a The weights given in the table are the weights of the substances in vacuum. International atomic weights of 1941 were used.

⁸ Hamer and Acree [19] observed that hydrogen electrodes prepared with platinum or palladium sponge behave differently in solutions of acid potassium phthalate. They found that both types gave the same potential during the first 5 or 6 hours after the electrodes were immersed in the solutions. However, they found that the potentials of the electrodes prepared with platinum sponge constantly increased after 5 or 6 hours, whereas the potentials of the electrodes prepared with palladium sponge remained constant in many cases for well over 100 hours. The good agreement in the pH values of acid potassium phthalate reported by various experimenters and given above indicates that most of the measurements with hydrogen electrodes must have been made within a relatively short time.

⁹ Wood and Murdick expressed their concentrations on a molar scale, whereas the concentrations used in this work are expressed on the molal scale. A 0.2-*m* solution corresponds to a 0.195-*M* solution (see table 7 for densities). Extrapolation to 0.2-*M* gives a pH of 3.881, which is 0.021 pH unit higher than the value of Wood and Murdick.

distilled water of pH 6.7 to 7.3. No preservative is necessary, and the solutions will keep in a glass-stoppered Pyrex bottle for at least 6 months with no change in pH. The requisite weights corrected to vacuum of acid potassium phthalate to be added to 1,000 g of water are given in the second column of table 7.

The purity (effective neutralizing power) of acid potassium phthalate may be determined by titrating a known weight of the salt with a standard solution of potassium hydroxide. Reagents and apparatus should be free of carbon dioxide or carbonates. The end point, which corresponds to a solution of dipotassium phthalate, may be determined by a pH meter or with a solution of phenolphthalein. The pH of solutions of dipotassium phthalate may be calculated by using values of K_1 , K_2 , β_{Ph} , β_{HPh} , and β_{H} given previously [1, 2] and eq 4, 5, 6, 7, and 8 and the eq

$$m_{\text{H}}^4 + (K'_1 + 2a)m_{\text{H}}^3 + (aK'_1 + K'_1K'_2 - K'_w)m_{\text{H}}^2 - (K'_wK'_1)m_{\text{H}} - K'_wK'_1K'_2 = 0 \quad (12)$$

giving the hydrogen-ion concentration of dipotassium phthalate. K'_1 , K'_2 , and K'_w refer, respectively, to $K_1f_{\text{H}_2\text{Ph}}/f_{\text{H}}f_{\text{HPh}}$, $K_2f_{\text{HPh}}/f_{\text{H}}f_{\text{Ph}}$, and $K_w a_{\text{H}_2\text{O}}/f_{\text{H}}f_{\text{OH}}$ where K_w is the dissociation constant of water [18], $a_{\text{H}_2\text{O}}$ is the activity of water, f_{OH} is the activity coefficient of the hydroxyl ion, and the other terms have the same significance as given above. At 25° C, the pH values of solutions of dipotassium phthalate having molalities of 0.01, 0.04, 0.05, 0.06, and 0.10 are, respectively, 8.55, 8.74, 8.77, 8.79, and 8.83. The pH values of a 0.05-*m* solution are 8.94, 8.85, 8.77, 8.69, and 8.61, respectively, at temperatures of 15°, 20°, 25°, 30°, and 35° C. Therefore, if about 1 g of acid potassium phthalate in 50 ml of distilled water is titrated with 0.1-*N* potassium hydroxide, the concentration of dipotassium phthalate at the end point will be approximately 0.05-*m* and the pH will be 8.8 at 25° C and 8.7 at 30° C. Frequently, sodium hydroxide is used as the titrant. In this case the solution at the end point will be sodium potassium phthalate, and the pH will be somewhat different than when potassium hydroxide is used as the titrant. Unfortunately, the values of the activity coefficients of the sodium salts of *o*-phthalic acid are not known. In general, however, the activity coefficients of sodium salts are higher than potassium salts. Therefore, it is to be expected that the pH of a solution of sodium potassium phthalate will be lower than that of a solution of dipotassium phthalate of equivalent concentration. Results given in the NBS certificate for Standard Sample 84c of acid potassium phthalate indicate that this is the case. A 0.05-*m* solution of sodium potassium phthalate has a pH value of 8.6 at 25° to 28° C.

In order that the solutions of acid potassium phthalate may be prepared on a volumetric basis, the densities of 0.02-, 0.05-, 0.10-, and 0.20-*m* solutions were determined at 20° and 25° C with the usual type of Ostwald picnometer of 50-ml capacity, using a tare of the same volume. Four independent determinations of the densities were made at each temperature. Average values are given in columns 3 and 4 of table 7. The data for solutions more dilute than 0.02-*m* were obtained from a smooth curve drawn through the densities of water and of solutions of higher concentrations. The requisite

weights of acid potassium phthalate for a liter of solution at 20° and 25° C are given in the last two columns of table 7.

For high accuracy, it is suggested that acid potassium phthalate, NBS Standard Sample 84a, having a certified purity of 100.00 percent, determined by titration, be used. It should be prepared for use as specified on the certificate. Standard Sample 84b may also be used. It has a purity of 100.04 percent, however. In order to ascertain if this small amount of acid impurity would appreciably affect the pH value of a 0.05-*m* solution, a series of measurements of the emf of hydrogen-silver-chloride cells without liquid junction were made with this sample. Experimental details have been described previously by Hamer and Acree [1, 2, 4]. Results are given in table 8 for measurements at 0°, 15°, 25°, 35°, 45°, and 60° C for solutions containing different amounts of potassium chloride. From these measurements, values of $-\log (f_{\text{H}}f_{\text{Cl}}m_{\text{H}})$ were calculated for each concentration of potassium chloride by the method previously described [3]. In figure 3 the values are plotted as a function of the molality of potassium chloride. The values for Standard Sample 84a given in a former paper [3] are included for comparison. Extrapolation to zero concen-

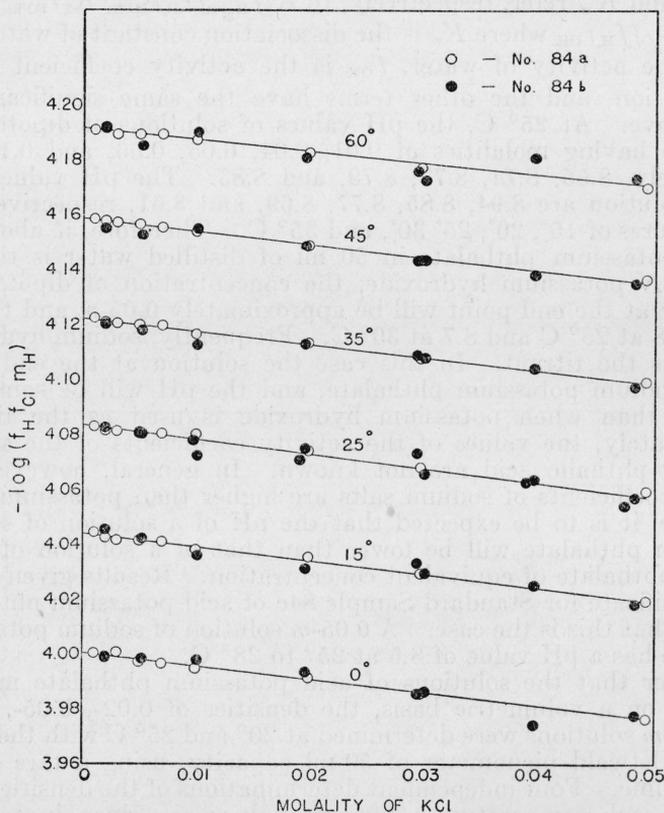


FIGURE 3.—Plots of $-\log (f_{\text{H}}f_{\text{Cl}}m_{\text{H}})$ as a function of the molality of potassium chloride for 0.05-*m* solutions of acid potassium phthalate, Standard Samples 84a and 84b issued by the National Bureau of Standards.

tration of potassium chloride gives the values of $-\log (f_{\text{H}}f_{\text{Cl}}m_{\text{H}})^{\circ}$ for a solution of acid potassium phthalate containing no chloride ion.

The pH value is then calculated from this value by means of the equation

$$\text{pH} = [-\log (f_{\text{H}}f_{\text{Cl}}m_{\text{H}})^{\circ} - P]/Q, \quad (13)$$

the derivation and constants of which are given by Hamer and Acree [3]. Values of the pH for a 0.05-*m* solution of acid potassium phthalate, Standard Sample 84b, calculated by means of eq 13 are given at the bottom of table 8 for the various temperatures and are compared with the values for Standard Sample 84a [3]. The slight differences of 0.001 to 0.002 pH unit between solutions prepared with Standard Samples 84a and 84b are well within the experimental error of the two series of measurements. Consequently, either sample may be used in the preparation of a solution of acid potassium phthalate for use as a pH standard. It is to be expected that other Standard Samples of acid potassium phthalate having purities comparable with Standard Samples 84a and 84b will have pH values equal to those of Standard Samples 84a and 84b.¹⁰

TABLE 8.—*Electromotive forces of the galvanic cell Pd, H₂|(g)KHPH(0.05 m), |KCl(m)|AgCl(s)|Ag(s) for acid potassium phthalate, NBS Standard Sample 84b*

Molality of potassium chloride	Temperature in degrees centigrade					
	0°	15°	25°	35°	45°	60°
0.002000	<i>v</i> 0.60422	<i>v</i> 0.61619	<i>v</i> 0.62403	<i>v</i> 0.63182	<i>v</i> 0.63952	<i>v</i> 0.65153
.005196	.58171	.59231	.59938	.60634	.61319	.62371
.01011	.56597	.57544	.58181	.58896	.59517	.60493
.01970	.55009	.55861	.56484	.57067	.57643	.58518
.02965	.54004	.54858	.55424	.55958	.56490	.57312
.03037	.53952	.54777	.55318	.55888	.56425	.57228
.04015	.53284	.54059	.54589	.55123	.55626	.56475
.04898	.52780	.53526	.54039	.54554	.55061	.55854
.005052			.60011			
.009816			.58290			
.02921			.55447			
.03945			.54669			
.04811			.54068			
pH values of 0.05- <i>m</i> acid potassium phthalate *						
Standard Sample 84a..	4.007	4.000	4.008	4.025	4.050	4.101
Standard Sample 84b..	4.007	4.001	4.009	4.025	4.049	4.099

* Calculated by the abbreviated method given in a previous report [3].

In order to ascertain the consistency of the pH values given in table 3 for use in the calibration of commercial pH meters, a pH meter was calibrated with 0.05-*m* solution of acid potassium phthalate which had a pH value of 4.01. The meter was then used to determine the pH value of other concentrations of acid potassium phthalate. All the measurements were made in a constant temperature room at

¹⁰ Since this work was done, Standard Samples 84a and 84b have been superseded by equivalent Standard Samples, Standard Sample 84c and 185. A 0.05-*m* solution of acid potassium phthalate has been found to have the same pH value, whether it is prepared with Standard Samples 84a, 84b, 84c, or 185.

25° C. In table 9, the pertinent data are given. The agreement between the standard pH values given in table 3 and the values determined by the commercial pH meter is good except for the 0.10-*m* solution. The glass electrode gives a value which is 0.01 greater than the standard value. However, this is well within the limits of accuracy of a commercial pH meter [21].

TABLE 9.—Comparison of pH values of acid potassium phthalate obtained with hydrogen and glass (commercial) electrodes

Molality of acid potassium phthalate	pH (hydrogen electrode)	pH (glass electrode) ^a			
		No. 1	No. 2	No. 3	Average
0.005	4.167	4.17	4.17	4.17	4.17
.01	4.117	4.11	4.11	4.11	4.11
.02	4.070	4.07	4.07	4.07	4.07
.05	4.005	^b (4.01)	(4.01)	(4.01)	4.01
.10	3.948	3.97	3.95	3.97	3.96

^a Measurements obtained with the commercial glass electrode were made by Elizabeth E. Sager and Alice S. Carr.

^b Glass electrodes were calibrated with a solution of this strength.

V. A CRITIQUE OF THE METHOD USED IN THE EVALUATION OF THE pH OF AQUEOUS SOLUTIONS OF ACID POTASSIUM PHTHALATE

The pH values of acid potassium phthalate given in this report were calculated from the dissociation constants of *o*-phthalic acid and the activity coefficients of the H⁺, HPh⁺, and Ph⁻ ions determined from the emf of hydrogen—silver-chloride cells without liquid junction. In the determination of these quantities, mixtures of phthalates and chlorides were used. The activity coefficients of the various ions were determined by the method of least squares, using the relationship: $\beta\mu = -\beta_{Cl}m_{Cl} - \beta_{HPh}m_{HPh} + \beta_{Ph}m_{Ph}$, where β is the "salting-out" term of the Hückel equation [6], given in equations above, and determined experimentally from the emf. It was necessary to assume that $\beta_H = \beta_{Cl}$, or that the activity coefficients of the hydrogen and chloride ions were equal except for the salting-out term. Only mean activity coefficients are obtained from the emf equation. The equations of Debye and Hückel are used to evaluate activity coefficients of ions. If instead, mixtures of phthalates and bromides had been used with silver bromide electrodes or if mixtures of phthalates and sulfates had been used with mercury-mercurous sulfate electrodes, the individual β values would have been determined, respectively, by $\beta\mu = -\beta_{Br}m_{Br} - \beta_{HPh}m_{HPh} + \beta_{Ph}m_{Ph}$ and $\beta\mu = -\beta_{SO_4}m_{SO_4} - \beta_{HPh}m_{HPh} + \beta_{Ph}m_{Ph}$, and β_H would be assumed to be equal in each case to β_{Br} or β_{SO_4} . As the β terms are independent of each other, the pH value is the same for acid potassium phthalate in the absence of chloride, bromide, or sulfate ion, but not in their presence because of the differences in their salting-out terms. Therefore, the pH values of acid potassium phthalate presented in this paper do not depend upon the reference electrode used but do depend upon the assumption used in the evaluation of the hydrogen ion. However, as the molality of H⁺ ions in

acid potassium^{*}phthalate is only about 0.0001, the term $\beta_{\text{H}}m_{\text{H}}$ contributes only a very small (negligible) fraction to the value of f_{H} as β is generally less than unity. It will not matter, therefore, whether β_{H} is assumed equal to β_{Cl} , β_{Br} , or β_{SO_4} .

Certain theoretical difficulties are encountered in the evaluation of the salting-out terms and ion sizes of individual ions as given above. Experimentally, only mean activity coefficients are obtained, and recourse was taken to the equations of Debye and Hückel to evaluate the activity coefficients of the individual ions. However, this procedure should give a very close approximation to the activity of ions in solutions, especially in dilute solutions ($<0.1m$). It does not imply that the activities of individual ions have been evaluated. Theoretical difficulties attendant on the evaluation of the salting-out terms and ion sizes of individual ions may be partially circumvented by using the short method of Hamer and Acree [3], which is independent of the Debye-Hückel theory. This method gives substantially the same pH values for solutions of acid potassium phthalate as the more involved method described in this paper. In the method of Hamer and Acree the activity coefficient of the hydrogen ion is taken equal to the mean activity coefficient of hydrochloric acid alone or in salt solutions.

It has been reported that observed activity coefficients of mixtures may be reproduced within 0.001 for ionic strengths as high as 0.5 if the assumption is made that $\beta_{\mu} = -\beta_{\text{Cl}}m_{\text{Cl}} - \beta_{\text{HPh}}m_{\text{HPh}} + \beta_{\text{Ph}}m_{\text{Ph}}$. An error of 0.001 in the activity coefficient of the hydrogen ion introduces an error of 0.0005 in pH. Hamer and Acree [4] have shown that probable uncertainties of 0.05 mv in the emf and the potential of the silver-silver-chloride electrode in its standard state, an error of 0.1 percent in the concentration, and the probable uncertainties in the natural constants for use in the emf equations given by Wensel [22] combine to give an uncertainty of 0.001 in pH values. Hence, with due consideration to possible accidental errors and to the assumptions made in evaluating the activity coefficient of the hydrogen ion, the pH values reported in this paper and previous ones in the series dealing with phthalate mixtures are considered to be accurate to 0.002 pH unit.

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