

# Second Dissociation Constant of Oxalic Acid from 0° to 50° C, and the pH of Certain Oxalate Buffer Solutions

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The second dissociation constant of oxalic acid was determined at intervals of 5 degrees from 0° to 50° C by measurement of the electromotive force of cells without liquid junction. Hydrogen and silver-silver-chloride electrodes were employed. The solutions were composed of potassium binoxalate, sodium oxalate, and sodium chloride. The value of the second dissociation constant,  $K_2$ , in the temperature range studied is given by the equation

$$-\log K_2 = \frac{1423.8}{T} - 6.5007 + 0.020095T,$$

where  $T$  is the absolute temperature. The thermodynamic quantities associated with the second dissociation step were calculated. The pH values of 8 solutions of potassium binoxalate and sodium oxalate in the ratio 1:5 were determined at 11 temperatures.

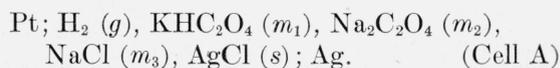
## I. Introduction

As fixed points of reference on a standard scale of pH, it is desirable to have available several standard buffer solutions that differ not only in pH but in chemical character and ionic type. If these solutions are all of comparable stability and give rise to about the same liquid-junction potential when brought into contact with a saturated solution of potassium chloride, they will serve equally well for the calibration of the pH meter with glass electrode. For control purposes, however, some will be preferred on account of a higher buffer capacity. Others may be unsuitable for use with indicators or with the quinhydrone electrode because of specific unfavorable reactions or because the multivalent anions of which they are composed cause unusually large salt errors. Other buffer substances may poison the platinum-hydrogen electrode or may undergo catalytic reduction in contact with it. Hence, new standards of pH will usually find use. These may eventually be classified, on the basis of comparative studies, as either primary or secondary standards.

In the search for buffer mixtures that might partially bridge the gap in pH between acid potas-

sium phthalate (pH 3.9 to 4.2 [1]<sup>1</sup>) and mixtures of primary and secondary alkali phosphates (pH 6.7 to 7.0 [2]), the oxalate system was considered. Aqueous mixtures of a primary and a secondary alkali oxalate in equal molal amounts have pH values near 4. If the same two salts are used in the molal ratio of 1:5, however, buffer solutions with pH from 4.5 to 4.8 can be obtained. These solutions are stable in contact with the platinum hydrogen electrode. Furthermore, pure sodium oxalate is available as an NBS Standard Sample. Although the relatively large concentration of bivalent anions may detract from the usefulness of these buffer solutions in some instances, oxalate mixtures can often be employed advantageously for control and standardization.

The second dissociation constant of oxalic acid at intervals of 5 degrees from 0° to 50° C was determined by the method of Harned and Ehlers [3] from the electromotive force of cells of the type



<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

The changes of free energy, heat content, entropy, and heat capacity that occur when the process



takes place in the standard state were computed from the dissociation constants and their temperature coefficients. The activity pH values (paH) of several buffer solutions composed of potassium binoxalate and sodium oxalate in the ratio of 1 to 5 moles were calculated. The activity coefficient of chloride ion in the chloride-free buffer solutions was evaluated by five different methods, all of which were found to yield nearly the same paH.

## II. Experimental Procedures and Results

Oxalic acid, the neutral and acid oxalates of sodium and potassium, and potassium tetroxalate were compared in an effort to determine which were best suited to the preparation of standard buffer solutions. Solubility, drying characteristics, hygroscopicity, degree of hydration, thermal stability, and ease of purification were considered. Each of the salts, with the exception of potassium tetroxalate, was dried to constant weight at 105° C. The temperature was then raised in steps of 10 degrees and constant weight attained at each temperature. This procedure was continued until the increase of 10 degrees in temperature produced a loss in weight no greater than 0.01 percent of the weight of the sample, or until the substance decomposed. The dried samples were then exposed for 24 hours to air of 45-percent relative humidity at 25° C. The results of these experiments are listed in table 1, together with some other properties of these materials.

Potassium tetroxalate dihydrate could not be dried to constant weight, and when the temperature was raised sufficiently to drive off the water of hydration, the component oxalic acid began to sublime. Sodium oxalate is considerably less soluble than potassium oxalate. Nevertheless, sodium oxalate was selected because it is less hygroscopic and is available in pure form as an NBS Standard Sample. Inasmuch as sodium binoxalate could not be dried to constant weight, potassium binoxalate was chosen as the primary salt used in preparing the buffer solutions.

Reagent-grade potassium binoxalate was purified by two recrystallizations from water to which a small amount of potassium carbonate had been

TABLE 1. *Properties of oxalic acid and its sodium and potassium salts*

Material	Hydration	Decomposition temperature of anhydrous material	Drying temperature	Moisture taken up by anhydrous material
Oxalic acid.....	2 H <sub>2</sub> O.....	° C ( <sup>b</sup> )	° C ( <sup>b</sup> )	% of total weight -----
Sodium oxalate...	Anhydrous...	350 [4].....	105.....	-----
Potassium oxalate.	H <sub>2</sub> O.....	370 (vac.) [5]..	105.....	2.6
Sodium binoxalate.	H <sub>2</sub> O.....	210 to 220 [4]..	( <sup>c</sup> )	4.4
Potassium binoxalate.	Anhydrous...	300 [4].....	130.....	0.02

<sup>a</sup> Exposed for 24 hr to air having 45-percent relative humidity.

<sup>b</sup> Sublimes.

<sup>c</sup> Does not come to constant weight.

added [6]. Seven weight titrations of the product gave a mean of 100.03 percent, with an average departure from the mean of 0.03 percent. Phenolphthalein was used as indicator, and the endpoint was established by comparison with a buffer-indicator mixture adjusted to about pH 8.3. The sodium chloride used had been recrystallized from water. It was tested [7] and found to contain about 0.002 mole percent of bromide. The specific conductance of the water used to prepare the buffer solutions ranged from 0.4 to  $0.7 \times 10^{-6}$  mho.

An upward drift in the electromotive force of some of the earlier cells, most pronounced at temperatures above 25° C, was observed. It was discovered that this drift could be eliminated almost completely by guarding the buffer solutions from contact with the rubber stoppers. The intervening space was filled with pure hydrogen. The cause of the drift is as yet unexplained. Traces of sulfide, such as might be dissolved from the rubber, have been found not to have a large effect on the potential of the silver-silver-chloride electrode [7].

In view of the relatively low pH of the oxalate mixtures, no attempt was made to exclude atmospheric carbon dioxide while the solutions were being prepared. Dissolved air was subsequently removed, however, by passing pure hydrogen through the solutions. Other experimental details will be found in an earlier publication [8].

The electromotive force, in international volts, of cell (A) at 11 temperatures from 0° to 50° C is given in table 2. Each cell contained two hydrogen electrodes and two silver-silver-chloride

electrodes. Hence, each electromotive force value represents, in general, the mean of two results. The electromotive force has been corrected in the usual way to a partial pressure of 760 mm of hydrogen. In the first four series of solutions, the relative proportions of potassium binoxalate,

sodium oxalate, and sodium chloride were 1 : 5 : 2.5. In the next two series, the molalities of sodium chloride were respectively the same as, and one-half of, the molalities of the acid salt. The solutions comprising the last series contained equal molal amounts of the three salts.

TABLE 2. *Electromotive force of cells of type (A) containing*  $\text{KHC}_2\text{O}_4$  ( $m_1$ ),  $\text{Na}_2\text{C}_2\text{O}_4$  ( $m_2$ ), and  $\text{NaCl}$  ( $m_3$ ) *from*  $0^\circ$  *to*  $50^\circ$  *C*

$m_1$	Temperature, ° C										
	0	5	10	15	20	25	30	35	40	45	50
$m_2=5m_1; m_3=2.5m_1$ . Series 1											
0.03914	0.53738	0.54039	0.54344	0.54646	0.54953	0.55275	0.55624	0.55946	0.56276	0.56607	0.56942
.03010	.54469	.54785	.55110	.55427	.55755	.56113	.56479	.56825	.57171	.57521	.57871
.02019	.55606	.55952	.56302	.56644	.56999	.57372	.57780	.58153	.58529	.58912	.59295
.009545	.57643	.58038	.58420	.58818	.59233	.59655	.60081	.60491	.60910	.61334	.61757
.008654	.57933	.58336	.58741	.59136	.59544	.59963	-----	-----	-----	-----	-----
.007858	.58182	.58591	.59002	.59409	.59829	.60264	.60691	.61117	.61547	.61982	.62417
.006936	.58524	.58937	.59354	.59769	.60205	.60637	.61068	.61500	.61938	.62376	.62820
.005651	.59085	.59515	.59947	.60381	.60814	.61260	.61707	.62153	.62604	.63059	.63514
.004557	.59664	.60118	.60563	.60996	.61431	.61881	.62348	.62800	.63268	.63735	.64203
.003448	.60445	.60902	.61366	.61819	.62282	.62747	.63220	.63691	.64169	.64651	.65136
$m_2=5m_1; m_3=2.5m_1$ . Series 2											
0.04037	0.53654	0.53963	0.54268	0.54573	0.54889	0.55206	0.55515	0.55817	0.56164	0.56446	0.56778
.02909	.54549	.54879	.55209	.55547	.55893	.56236	-----	-----	-----	-----	-----
.02390	-----	-----	-----	-----	-----	.56864	-----	-----	-----	-----	-----
.02192	.55354	.55704	.56048	.56400	.56755	.57117	.57469	.57827	.58178	.58544	.58914
.01733	.56001	.56363	.56723	.57093	.57466	.57843	.58211	.58585	.58966	.59348	.59735
.01113	.57229	.57616	.58005	.58401	.58793	.59192	.59582	.59987	.60389	.60797	.61204
.01032	.57438	.57826	.58221	.58622	.59023	.59427	.59839	.60237	.60625	.61064	.61482
.008392	.58010	.58411	.58816	.59228	.59646	.60073	.60479	.60900	.61325	.61749	.62181
.006037	.58939	.59357	.59783	.60217	.60652	.61081	.61537	.61970	.62417	.62865	.63318
.004162	.59927	.60373	.60816	.61269	.61722	.62180	.62638	.63095	.63561	.64026	.64500
$m_2=5m_1; m_3=2.5m_1$ . Series 3											
0.03966	0.53696	0.53992	0.54305	0.54619	0.54938	0.55262	-----	-----	-----	-----	-----
.02586	.54892	.55210	.55552	.55896	.56236	.56600	0.56921	0.57226	0.57606	0.57983	0.58338
.01955	-----	.56020	.56380	.56732	.57091	.57473	-----	-----	-----	-----	-----
.01751	.55974	.56328	.56694	.57062	.57431	.57807	.58167	.58527	.58910	.59295	.59667
.01493	-----	.56800	.57177	.57556	.57924	.58312	.58682	.59057	.59436	.59828	.60226
.01232	.56942	.57324	.57713	.58102	.58491	.58888	.59268	.59654	.60060	.60459	.60862
.009901	.57559	.57947	.58348	.58736	.59144	.59559	.59947	.60346	.60747	.61178	.61592
.007886	.58181	.58580	.58984	.59397	.59816	.60245	.60666	.61091	.61526	.61963	.62394
.003934	.60082	.60523	.60976	.61426	.61877	.62335	.62794	.63253	.63727	.64205	.64684

TABLE 2. Electromotive force of cells of type (A) containing  $\text{KHC}_2\text{O}_4$  ( $m_1$ ),  $\text{Na}_2\text{C}_2\text{O}_4$  ( $m_2$ ), and  $\text{NaCl}$  ( $m_3$ ) from  $0^\circ$  to  $50^\circ$  C—  
Continued

$m_1$	Temperature, ° C										
	0	5	10	15	20	25	30	35	40	45	50
$m_2=5m_1; m_3=2.5m_1$ . Series 4.											
0.03031	0.54476	0.54798	0.55118	0.55449	0.55782	0.56112	0.56452	0.56794	-----	-----	-----
.02527	.54978	.55312	.55646	.55984	.56326	.56677	.57020	.57374	0.57714	0.58092	0.58457
.02027	.55588	.55934	.56270	.56625	.56987	.57354	.57702	.58070	.58445	.58820	.59202
.01715	.56057	.56410	.56771	.57137	.57505	.57884	.58266	.58641	.59026	.59413	.59798
.01416	.56588	.56958	.57329	.57698	.58077	.58468	.58848	.59232	.59630	.60032	.60430
.01147	.57166	.57558	.57942	.58331	.58727	.59121	.59521	.59926	.60334	.60739	.61151
.009697	.57632	.58028	.58419	.58818	.59216	.59620	.60032	.60449	.60864	.61282	.61703
.007591	.58321	.58730	.59145	.59553	.59984	.60388	.60814	.61241	.61676	.62106	.62544
.005787	.59059	.59482	.59916	.60336	.60765	.61199	.61644	.62097	.62551	.63006	.63458
.003146	.60706	.61166	.61632	.62090	.62558	.63028	.63490	.63963	.64453	.64937	.65430
$m_2=5m_1; m_3=m_1$											
0.04392	0.55627	0.55964	0.56313	0.56660	0.57014	0.57376	0.57753	0.58096	0.58469	-----	0.59187
.04054	-----	.56220	.56554	.56911	.57272	.57627	.57978	.58343	.58718	0.59090	.59463
.02644	-----	-----	-----	.58197	.58577	.58965	.59390	.59783	.60185	.60580	.60977
.01330	.58943	.59367	.59776	.60212	.60641	.61062	.61508	.61939	.62380	.62831	.63262
$m_2=5m_1; m_3=0.5m_1$											
0.03882	0.57643	0.58025	0.58409	0.58800	0.59184	0.59574	0.59958	0.60347	0.60750	0.61162	0.61577
.02908	.58423	.58832	.59233	.59656	.60068	.60481	.60893	.61307	.61726	.62146	.62569
.01979	.59506	.59933	.60361	.60794	.61224	.61656	.62101	.62543	.62988	.63437	.63896
.01252	.60760	.61210	.61663	.62130	.62593	.63051	.63534	.64000	.64478	.64952	.65431
.01010	.61353	.61824	.62289	.62762	.63233	.63714	.64203	.64687	.65178	.65674	.66174
.008771	.61741	.62216	.62690	.63171	.63649	.64144	.64626	.65117	.65618	.66114	.66625
.007190	.62256	.62750	.63235	.63727	.64217	.64718	.65209	.65710	.66215	.66723	.67241
.006896	-----	-----	-----	-----	-----	.64874	-----	-----	-----	-----	-----
.006046	-----	-----	-----	-----	-----	.65230	-----	-----	-----	-----	-----
.005167	.63160	.63667	.64171	.64674	.65181	.65694	.66227	.66751	.67274	.67807	.68343
.004186	.63748	.64267	.64784	.65305	.65825	.66352	.66881	.67413	.67949	.68491	.69039
$m_1=m_2=m_3$											
0.09729	0.50111	0.50372	0.50622	0.50853	0.51112	0.51374	0.51625	0.51885	0.52150	0.52431	0.52707
.07340	.50911	.51182	.51452	.51716	.51992	.52262	.52539	.52842	.53107	.53399	.53695
.05902	.51519	.51800	.52083	.52357	.52632	.52935	.53232	.53528	.53830	.54135	.54448
.05485	.51716	.52006	.52295	.52575	.52864	.53156	.53455	.53755	.54060	.54365	.54678
.04188	.52487	.52791	.53096	.53392	.53702	.54016	.54319	.54634	.54952	.55282	.55611
.02945	.53457	.53787	.54112	.54428	.54751	.55076	.55437	.55773	.56110	.56460	.56813
.02065	.54419	.54767	.55114	.55452	.55779	.56128	.56514	.56871	.57231	.57599	.57973
.01039	.56326	.56704	.57085	.57463	.57846	.58226	-----	-----	-----	-----	-----

The most accurate and extensive results were obtained for the first four series, where the ratio of concentration of sodium chloride to that of potassium binoxalate was somewhat higher than in the other three series. For this reason, the second dissociation constant was evaluated from the electromotive force data for the first four series alone.

All of the cells were brought to initial equilibrium at  $25^\circ$  C. Another measurement at  $25^\circ$  C was made at the completion of the measurements at the lower temperatures and before the measurements at the higher temperatures were begun. In addition, a final value at  $25^\circ$  C was obtained. The initial and final values for the solutions of the first four series, from which the

dissociation constant was determined, differed on the average by about 0.10 mv. The electromotive-force values given for series 4 are the averages of two complete series of measurements, the mean deviations of which were about 0.10 mv.

### III. Calculation of the Second Dissociation Constant

The dissociation constant is expressed in terms of the measured electromotive force,  $E$ , by the equation

$$pK'_2 = -\log K_2 - \beta^* \mu = \frac{(E - E^\circ) F}{2.3026RT} + \log m_{C_1^-} + \log \frac{m_{HC_2O_4^-}}{m_{C_2O_4^{2-}}} + \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}}, \quad (2)$$

where  $E^\circ$  is the standard potential of the cell [3,9],  $A$  and  $B$  are constants for the water medium at each temperature [10],  $a^*$  and  $\beta^*$  are adjustable parameters, and  $F$ ,  $R$ ,  $T$ , and  $\mu$  have their usual significance. Equation 2 results from combining the equation for the electromotive force of the cell with the mass-law expression for the dissociation of binoxalate ion and with the Hückel formula [11] for the activity coefficients. The activity-coefficient term, for convenience designated  $\log f_r$ , takes the form

$$\log f_r = \log \frac{f_{HC_2O_4^-} f_{C_1^-}}{f_{C_2O_4^{2-}}} = \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} + \beta^* \mu. \quad (3)$$

As a result of the appreciable acidic dissociation of the binoxalate ion, the penultimate term of eq 2 is not given with sufficient accuracy by  $\log (m_1/m_2)$ . Consideration of the equilibrium represented by eq 1 leads to the equality,

$$\frac{m_{HC_2O_4^-}}{m_{C_2O_4^{2-}}} = \frac{m_1 - m_H}{m_2 + m_H}. \quad (4)$$

The hydrogen-ion concentration,  $m_H$ , was computed in one of two ways: from the electromotive force by the expression

$$-\log m_H = \frac{(E - E^\circ) F}{2.3026RT} + \log m_{C_1^-} - \frac{2A\sqrt{\mu}}{1 + 5B\sqrt{\mu}}, \quad (5)$$

or from the mass-law expression with the aid of a first estimate of  $pK_2$ ,

$$-\log m_H = pK_2 - \log \frac{m_{HC_2O_4^-}}{m_{C_2O_4^{2-}}} - \frac{4A\sqrt{\mu}}{1 + 5B\sqrt{\mu}}. \quad (6)$$

The value of  $m_H$  obviously depends upon the choice of  $a^*$  (that is, 5) in the last terms of eq 5 and 6. The error in  $m_H$  from this cause diminishes as the ionic strength decreases and disappears in the extrapolation to infinite dilution. Hence both methods were found to yield the same value of  $pK_2$ .

When the right side of eq 2 at 25° C was plotted as a function of ionic strength, the three curves of figure 1 were obtained. From top to bottom, these

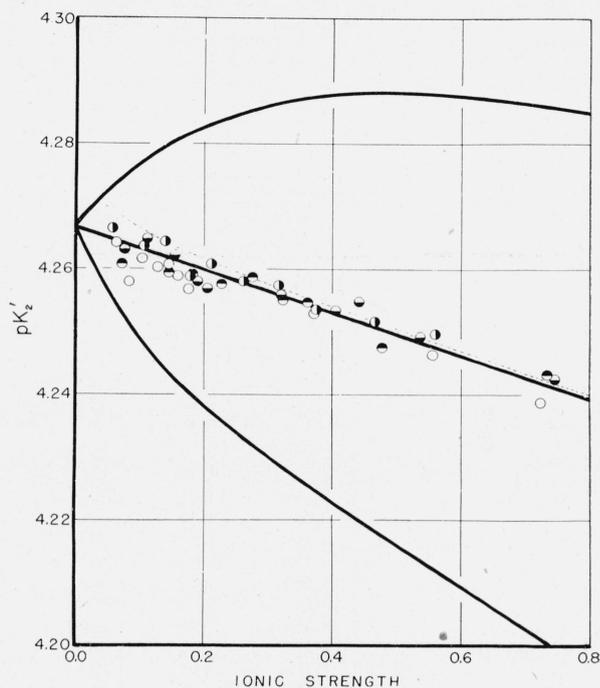


FIGURE 1.  $pK'_2$  at 25° C as a function of ionic strength for solutions in which  $m_2 = 5m_1$  and  $m_3 = 2.5m_1$ .

○, Series 1; ◐, series 2; ●, series 3; and ◑, series 4.

three curves correspond to  $a^*$  values of 4.0, 5.0, and 6.0. An  $a^*$  value of 5.0 was found to yield values of  $-\log K_2 - \beta^* \mu$  that were a linear function of ionic strength at each temperature studied. The slope,  $-\beta^*$ , of these straight lines was determined, and hence  $-\log K_2$  ( $pK_2$ ). The values of  $\beta^*$  are summarized in table 3, and those of  $-\log K_2$  and  $K_2$  are found in table 4. The dotted line in the figure represents  $pK'_2$  obtained for  $a^* = 5.0$  when the acidic dissociation of the binoxalate ion was disregarded and  $m_1/m_2$  employed as the ratio of the oxalate anions in eq 2. The last column of table 3 lists  $\beta^\circ$ , the limit of  $\beta^*$  for 1:5 oxalate buffer solutions without sodium chloride. These values were obtained by linear extrapolation of  $\beta^*$  plotted with respect to  $m_{NaCl}/\mu$ , the fractional contribution of sodium chloride to the total ionic strength [2]. No

TABLE 3. Values of  $\beta^*$  from  $0^\circ$  to  $50^\circ$  C.

Temperature  $^\circ\text{C}$	Relative proportions of $\text{KHC}_2\text{O}_4$ , $\text{Na}_2\text{C}_2\text{O}_4$ , and $\text{NaCl}$							
	1:1:1	1:5:2.5				1:5:1	1:5:0.5	1:5:0 ( $\beta^*$ )
		Series 1	Series 2	Series 3	Series 4			
0.....	0.023	0.006	0.010	0.009	0.006	0.005	-0.002	-0.002
5.....	.027	.013	.013	.015	.012	.012	+.001	+.002
10.....	.032	.021	.018	.023	.026	.015	.008	.006
15.....	.038	.026	.024	.022	.026	.017	.009	.006
20.....	.042	.035	.026	.030	.031	.018	.009	.008
25.....	.051	.038	.032	.034	.037	.024	.018	.014
30.....	.056	.031	.038	.045	.041	.031	.024	.021
35.....	.064	.041	.045	.054	.046	.035	.032	.026
40.....	.070	.044	.054	.059	.056	.037	.036	.028
45.....	.074	.046	.058	.058	.064	.042	.042	.032
50.....	.078	.050	.062	.070	.063	.049	.045	.038

TABLE 4. Values of  $\text{p}K_2$  and  $K_2$  from  $0^\circ$  to  $50^\circ$  C.

Temperature  $^\circ\text{C}$	Series 1		Series 2		Series 3		Series 4		Average $\text{p}K_2$	$K_2 \times 10^5$
	$\text{p}K_2$	Average deviation								
0.....	4.1987	0.0017	4.2006	0.0013	4.1999	0.0006	4.2037	0.0007	4.201	6.30
5.....	4.2057	.0014	4.2067	.0012	4.2062	.0009	4.2093	.0011	4.207	6.21
10.....	4.2164	.0018	4.2164	.0011	4.2176	.0012	4.2220	.0013	4.218	6.05
15.....	4.2292	.0015	4.2313	.0009	4.2298	.0011	4.2339	.0011	4.231	5.87
20.....	4.2456	.0012	4.2460	.0009	4.2457	.0012	4.2489	.0012	4.247	5.67
25.....	4.2654	.0013	4.2663	.0012	4.2657	.0014	4.2683	.0011	4.266	5.41
30.....	4.2863	.0015	4.2870	.0011	4.2861	.0010	4.2889	.0016	4.287	5.16
35.....	4.3124	.0021	4.3115	.0011	4.3094	.0018	4.3136	.0019	4.312	4.88
40.....	4.3385	.0017	4.3383	.0029	4.3360	.0012	4.3410	.0018	4.338	4.59
45.....	4.3690	.0022	4.3675	.0015	4.3656	.0015	4.3721	.0015	4.369	4.28
50.....	4.3993	.0020	4.3978	.0019	4.3973	.0021	4.4013	.0015	4.399	3.99

significant trend of  $a^*$  with ratio of chloride to oxalate was detected. The uncertainty in  $\beta^0$  appears to be about  $\pm 0.005$ .

These values of  $\text{p}K_2$  are compared in table 5 with previous determinations of the second constant. It will be seen that the values of  $\text{p}K_2$  given by Harned and Fallon [17] are higher by 0.02 to 0.03 than the results reported here. The same method and type of cell were employed in both investigations. Sodium binoxalate was used instead of the potassium salt, and the buffer solutions were composed of the three salts in the approximate molal proportions 1.9:1:1.5. In an effort to explain this discrepancy, two oxalate-chloride mixtures of the same compositions as two of the solutions used by Harned and Fallon were pre-

pared. The electromotive force of cells of type (A) containing these solutions was measured at  $25^\circ$  C and found to agree fairly well with the results given in their paper. Furthermore, calculation of  $\text{p}K_2 - \beta^*\mu$  at  $25^\circ$  C from the data of Harned and Fallon without consideration of the dissociation of binoxalate ion led to values apparently identical, when  $a^* = 4.3$  was used, with those obtained by Harned and Fallon without a correction for hydrogen ion. As these authors have pointed out, their "uncorrected"  $\text{p}K_2$  also agrees with the results of Parton and Gibbons [16], whose data were not corrected for acidic dissociation.

The discrepancy therefore seems to have arisen in the correction applied for the acidic dissociation

TABLE 5. Comparison of values for the second dissociation constant

Year	Observer	Temperature	Method	$K_2 \times 10^5$	$pK_2$
		° C.			
1908	Chandler [12]		Partition	4.1	4.39
			Conductance	4.9	4.31
1920	Drucker [13]	18	Emf conductance freezing point	6.9	4.16
1925	Britton [14]	18	H <sub>2</sub> calomel cells	13.4	3.87
1929	Dawson and Smith [15]		Catalysis of acetone-iodine reaction	7.2	4.14
1939	Parton and Gibbons [16]	25	Emf of cells without liquid junction, quinhydrone and Ag-AgCl electrodes.	5.012	4.300
			Recalculated <sup>a</sup>	5.41	4.267
1939	Harned and Fallon [17]	25	Emf of cells without liquid junction, H <sub>2</sub> and Ag-AgCl electrodes.	5.18	4.286
			Recalculated <sup>a</sup>	5.41	4.267
1941	Darken [18]	25	Conductance	5.3	4.28
1947	Present investigation	25	Emf of cells without liquid junction, H <sub>2</sub> and Ag-AgCl electrodes.	5.42	4.266

<sup>a</sup> Computed from the earlier data by the authors of this paper.

of the primary anion. Harned and Fallon state that the correction amounts to 0.007 in  $pK_2'$  for their lowest concentration ( $m_1=0.004516$ ,  $m_2=$

0.008589) and is negligible for the highest ( $m_1=0.04945$ ,  $m_2=0.02600$ ). The corresponding corrections from the present calculation are 0.0253 and 0.0081. When  $pK_2$  is calculated by the same procedure from the data of Harned and Fallon, of Parton and Gibbons, and of this investigation, substantially the same result is obtained.

The  $pK_2$  value obtained in this investigation is plotted in figure 2 as a function of ionic strength and compared with corresponding values (crosses) computed from the data of Harned and Fallon [17]. The triangles indicate  $pK_2$  computed from the electromotive force of the 1:1:1 series of solutions (see table 2). It is apparent that substantially the same dissociation constant is obtained from the three series of measurements, although the buffer ratio changes tenfold. The horizontal lines represent the average value of  $pK_2$  listed in the next to the last column of table 4.

The variation of the dissociation constant with absolute temperature,  $T$ , is represented, with an average deviation of 0.0004, by

$$pK_2 = \frac{1423.8}{T} - 6.5007 + 0.020095T. \quad (7)$$

The use of an equation of this form was suggested by Harned and Robinson [19]. The change of  $-\log K_2$  with change of temperature is illustrated in figure 3.

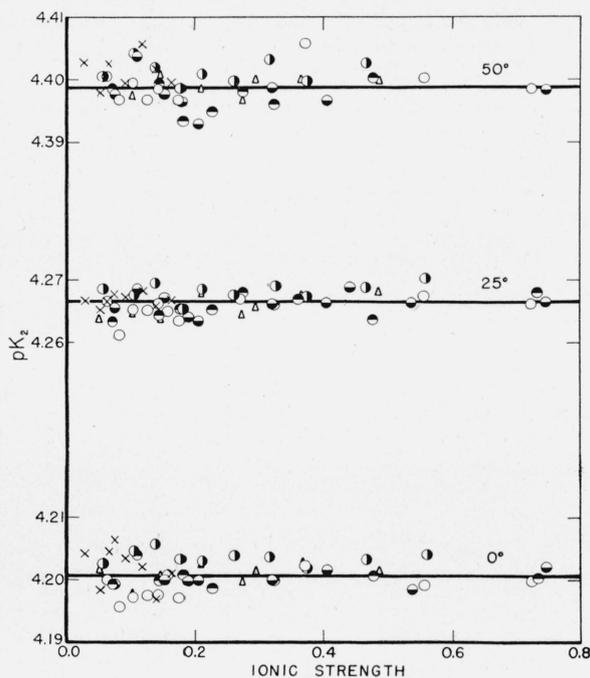


FIGURE 2.  $pK_2$  as a function of ionic strength.

○,  $m_2=5m_1$ ;  $m_3=2.5m_1$ ; series 1. ●,  $m_2=5m_1$ ;  $m_3=2.5m_1$ ; series 2. ●,  $m_2=5m_1$ ;  $m_3=2.5m_1$ ; series 3; ●,  $m_2=5m_1$ ;  $m_3=2.5m_1$ ; series 4. △,  $m_1=m_2=m_3$ . x, Data of Harned and Fallon [17].

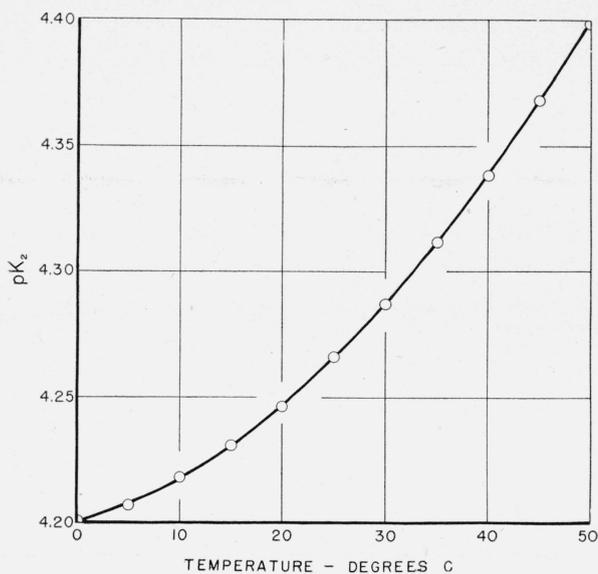


FIGURE 3. Plot of  $pK_2$  with respect to temperature.

#### IV. Thermodynamic Quantities

From the parameters of eq 7, a calculation was made of the changes of free energy, of heat content, of entropy, and of heat capacity that accompany the process  $\text{HC}_2\text{O}_4^- = \text{H}^+ + \text{C}_2\text{O}_4^{2-}$  in the standard state. The equations relating these quantities to  $A$ ,  $B$ , and  $C$  (which are respectively 1423.8,  $-6.5007$ , and  $0.020095$ ; compare eq 7) are given in an earlier paper [8]. The results of the calculation are listed in table 6.

#### V. Activity Coefficients and $\text{p}a\text{H}$ Values

It is evident from eq 3 that an expression for  $\log f_r^\circ$ , that is, the limit of  $\log (f_{\text{HC}_2\text{O}_4^-} f_{\text{C}_2\text{O}_4^{2-}})$  in 1:5 oxalate buffer solutions without chloride, can be

TABLE 6. Thermodynamic quantities for the process  $\text{HC}_2\text{O}_4^- = \text{H}^+ + \text{C}_2\text{O}_4^{2-}$

Temperature °C	$\Delta F^\circ$		$\Delta H^\circ$		$\Delta S^\circ$		$\Delta C_p^\circ$	
	int j	cal	int j	cal	int j/deg	cal/deg	int j/deg	cal/deg
0	21,964	5,250	-1,447	-346	-85.7	-20.5	-210	-50
5	22,403	5,355	-2,508	-600	-89.6	-21.4	-214	-51
10	22,859	5,464	-3,587	-857	-93.4	-22.3	-218	-52
15	23,336	5,578	-4,686	-1,120	-97.2	-23.2	-222	-53
20	23,832	5,697	-5,804	-1,387	-101.1	-24.2	-226	-54
25	24,347	5,820	-6,941	-1,659	-104.9	-25.1	-229	-55
30	24,882	5,948	-8,098	-1,936	-108.8	-26.0	-233	-56
35	25,436	6,080	-9,274	-2,217	-112.6	-26.9	-237	-57
40	26,008	6,217	-10,468	-2,502	-116.5	-27.8	-241	-58
45	26,600	6,359	-11,683	-2,793	-120.3	-28.8	-245	-58
50	27,211	6,505	-12,916	-3,088	-124.2	-29.7	-249	-59

TABLE 7.  $\log f_r^\circ$  for solutions of  $\text{KHC}_2\text{O}_4$  (m) and  $\text{Na}_2\text{C}_2\text{O}_4$  (5m) from 0° to 50° C

Temperature °C	Molality of potassium binoxalate							
	0.001	0.002	0.004	0.005	0.006	0.008	0.010	0.015
0	0.103	0.135	0.175	0.189	0.201	0.221	0.237	0.266
5	.103	.136	.177	.191	.203	.223	.239	.269
10	.104	.138	.178	.193	.205	.225	.241	.272
15	.105	.139	.180	.194	.206	.227	.243	.274
20	.106	.140	.181	.196	.208	.229	.245	.276
25	.107	.141	.183	.198	.210	.231	.248	.280
30	.108	.142	.185	.200	.212	.234	.251	.283
35	.109	.144	.186	.202	.215	.236	.254	.287
40	.110	.145	.188	.203	.217	.238	.256	.289
45	.111	.146	.190	.205	.219	.241	.259	.293
50	.112	.148	.192	.208	.221	.244	.262	.296

written in terms of the limiting values of  $a^*$  and  $\beta^*$ , namely, 5.0 and  $\beta^*$ :

$$\log f_r^\circ \equiv \log \frac{f_{\text{HC}_2\text{O}_4} f_{\text{Cl}^-}}{f_{\text{C}_2\text{O}_4}} = \frac{2A\sqrt{\mu}}{1+5B\sqrt{\mu}} + \beta^\circ \mu. \quad (8)$$

Log  $f_r^\circ$  for eight oxalate buffer solutions is listed in table 7.

The quantity  $-\log (f_{\text{H}^+} f_{\text{Cl}^-} m_{\text{H}^+})$ , readily obtainable from the electromotive force of cells of type (A), has been proposed by Guggenheim [20] and by Hitchcock [21] as a unit of acidity. Its value for eight 1:5 oxalate buffer solutions without

chloride was computed from a combination of eq 8 with the mass-law expression:

$$\text{pwH} \equiv -\log (f_{\text{H}^+} f_{\text{Cl}^-} m_{\text{H}^+})^\circ = -\log K_2 - \log \frac{m_{\text{HC}_2\text{O}_4}}{m_{\text{C}_2\text{O}_4}} - \frac{2A\sqrt{\mu}}{1+5B\sqrt{\mu}} - \beta^\circ \mu, \quad (9)$$

where the superscript zero indicates that chloride is absent. It should be noted that  $-\log (f_{\text{H}^+} f_{\text{Cl}^-} m_{\text{H}^+})^\circ$ , which will be called pwH whether chloride is present or not, is a quantity with exact thermodynamic meaning. Its value in the oxalate buffer solutions is summarized in table 8.

TABLE 8. pwH for solutions of  $\text{KHC}_2\text{O}_4$  ( $m$ ) and  $\text{Na}_2\text{C}_2\text{O}_4$  ( $5m$ ) in the absence of chloride from  $0^\circ$  to  $50^\circ$  C

Temperature  ° C	Molality of potassium binoxalate							
	0.001	0.002	0.004	0.005	0.006	0.008	0.010	0.015
0	4.808	4.770	4.728	4.714	4.701	4.681	4.665	4.634
5	4.813	4.775	4.732	4.718	4.706	4.685	4.669	4.638
10	4.823	4.786	4.743	4.727	4.715	4.694	4.678	4.646
15	4.835	4.796	4.754	4.739	4.726	4.705	4.689	4.657
20	4.848	4.810	4.768	4.752	4.739	4.718	4.702	4.670
25	4.869	4.830	4.786	4.771	4.758	4.737	4.720	4.688
30	4.888	4.849	4.806	4.789	4.779	4.754	4.737	4.703
35	4.910	4.872	4.828	4.812	4.798	4.776	4.760	4.725
40	4.936	4.896	4.853	4.834	4.822	4.800	4.782	4.748
45	4.963	4.925	4.881	4.863	4.850	4.828	4.810	4.775
50	4.992	4.953	4.908	4.892	4.878	4.855	4.837	4.802

The definition of pH and the relative advantages of several possible scales of acidity have been discussed recently [22]. The pwH differs from paH by the logarithm of the activity coefficient of a single ionic species, a quantity that cannot be measured:

$$\text{paH} = \text{pwH} + \log f_{\text{Cl}^-}. \quad (10)$$

Hence, some assumption must be made in order to relate  $f_{\text{Cl}^-}$  to measurable combinations of activity coefficients or to theoretical equations. Since no single assumption has as yet been assimilated into a generally accepted definition of paH, five scales based upon five different assumptions have been considered.<sup>2</sup> For the 1:5 oxalate buffers, these scales are defined by the following equations:

$$\text{p}_1\text{H} = \text{pwH} - \frac{A\sqrt{\mu}}{1+Ba_i\sqrt{\mu}}, \quad (11)$$

where the value for  $a_i$  is arbitrarily chosen;

$$\text{p}_2\text{H} = \text{pwH} + \log f_{\text{HCl}}, \quad (12)$$

where  $f_{\text{HCl}}$  is the mean activity coefficient of hydrochloric acid;

$$\text{p}_3\text{H} = \text{pwH} - \frac{A\sqrt{\mu}}{1+5B\sqrt{\mu}} - \frac{1}{2} \beta^\circ \mu; \quad (13)$$

$$\text{p}_4\text{H} = \text{pwH} - \frac{A\sqrt{\mu}}{1+5B\sqrt{\mu}} + \beta^\circ \mu; \quad (14)$$

and

$$\text{p}_5\text{H} = \text{pwH} - \frac{A\sqrt{\mu}}{1+5B\sqrt{\mu}}. \quad (15)$$

In table 9, pwH and the five paH values, all at  $25^\circ$  C, are compared with the paH determined with a pH meter of the glass-electrode type calibrated at 4.01 with a 0.05- $m$  solution of acid potassium phthalate [1]. For the computation of  $\text{p}_2\text{H}$ , the average of  $f_{\text{HCl}}$  in pure solutions of sodium chloride and potassium chloride of the appropriate ionic strength was chosen in preference to its value in solutions of hydrochloric acid, in recognition of the probable specific influences of different cations

<sup>2</sup> These five assumptions have been discussed elsewhere [22, 23].

upon  $f_{Cl}$  in the buffer medium. This activity coefficient was computed from published electromotive force data [24, 25] with the use of Harned's equations for the activity coefficient of hydrochloric acid in mixtures with alkali chlorides [25]. A graphical comparison of  $p_2H$ ,  $p_3H$ ,  $p_4H$ , and  $p_5H$  as a function of ionic strength is made in figure 4. The upper and lower dotted lines locate  $p_1H$  when  $a_i$  is respectively 6 and 4. It is evident from table 9 and figure 4 that the five assumptions yield equivalent results at low concentrations and that the scales diverge to the extent of only 0.02 unit at an ionic strength of 0.24.

Tables 10 and 11 list the values of  $p_3H$  and  $p_5H$  for eight 1:5 oxalate buffer solutions at 11 temperatures from 0° to 50° C. The change of  $paH$  (taken as the mean of the closely agreeing  $p_3H$  and  $p_5H$ ) with change of temperature is shown in figure 5.

The densities of three solutions of potassium binoxalate ( $m$ ) and sodium oxalate ( $5m$ ), in which  $m$  had the values 0.002, 0.008, and 0.015, were determined at 25° C with a picnometer that had a volume of approximately 57 ml. The ratio of the molar concentration of binoxalate,  $M$ , to molality,

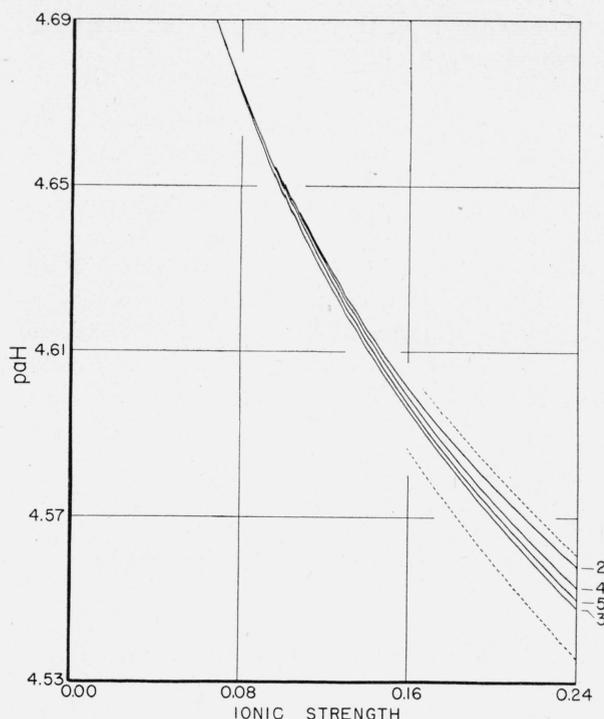


FIGURE 4.  $p_2H$ ,  $p_3H$ ,  $p_4H$ , and  $p_5H$  of oxalate buffer solutions as a function of ionic strength.

Dotted lines represent  $p_1H$  for  $a_i=4$  (lower curve) and  $a_i=6$  (upper curve).

TABLE 9. pH at 25° C of solutions of  $KHC_2O_4$  ( $m$ ) and  $Na_2C_2O_4$  ( $5m$ ) on several scales

$m$	pWH	p <sub>1</sub> H		p <sub>2</sub> H	p <sub>3</sub> H	p <sub>4</sub> H	p <sub>5</sub> H	paH (glass electrode <sup>a</sup> )
		$a_i=4$	$a_i=6$					
0.001	4.869	4.814	4.817	4.812	4.815	4.816	4.815	4.81
.002	4.830	4.757	4.763	4.758	4.760	4.760	4.760	4.77
.004	4.786	4.690	4.701	4.695	4.695	4.696	4.696	4.68
.005	4.771	4.666	4.679	4.673	4.673	4.674	4.673	4.67
.006	4.758	4.646	4.660	4.654	4.653	4.655	4.654	4.64
.008	4.737	4.613	4.630	4.625	4.621	4.624	4.622	4.59
.010	4.720	4.586	4.606	4.601	4.596	4.599	4.597	4.54
.015	4.688	4.536	4.561	4.558	4.548	4.553	4.550	4.54

<sup>a</sup> Calibrated at pH 4.01 with 0.05- $m$  acid potassium phthalate.

$m$ , is expressed with an average deviation of 0.00002 by

$$M/m = 0.99707 - 0.1708m, \quad (16)$$

when  $m$  is equal to or less than 0.015. Molality and molarity therefore differ by only 0.5 percent

for the most concentrated of the buffer solutions whose  $\text{pH}$  is given in tables 10 and 11. Hence, the  $\text{pH}$  listed differs by less than 0.0008 from that for solutions of molarity numerically equal to the molality given at the head of each column, and the two scales of concentration can be used interchangeably below  $m = 0.015$ .

TABLE 10.  $\text{pH}$  of solutions of  $\text{KHC}_2\text{O}_4$  ( $m$ ) and  $\text{Na}_2\text{C}_2\text{O}_4$  ( $5m$ ) from  $0^\circ$  to  $50^\circ \text{C}$

Temperature  $^\circ \text{C}$	Molality of potassium binoxalate							
	0.001	0.002	0.004	0.005	0.006	0.008	0.010	0.015
0	4.756	4.703	4.640	4.619	4.601	4.570	4.547	4.502
5	4.761	4.707	4.644	4.623	4.605	4.574	4.550	4.504
10	4.771	4.717	4.654	4.631	4.613	4.582	4.558	4.510
15	4.783	4.727	4.665	4.642	4.623	4.592	4.568	4.520
20	4.795	4.740	4.678	4.655	4.635	4.604	4.579	4.532
25	4.815	4.760	4.695	4.673	4.653	4.621	4.596	4.548
30	4.834	4.778	4.713	4.689	4.677	4.638	4.612	4.563
35	4.856	4.801	4.735	4.711	4.691	4.659	4.633	4.582
40	4.881	4.824	4.759	4.734	4.714	4.681	4.654	4.604
45	4.908	4.852	4.786	4.761	4.740	4.708	4.680	4.629
50	4.937	4.880	4.812	4.788	4.768	4.734	4.706	4.654

TABLE 11.  $\text{pH}$  of solutions of  $\text{KHC}_2\text{O}_4$  ( $m$ ) and  $\text{Na}_2\text{C}_2\text{O}_4$  ( $5m$ ) from  $0^\circ$  to  $50^\circ \text{C}$

Temperature  $^\circ \text{C}$	Molality of potassium binoxalate							
	0.001	0.002	0.004	0.005	0.006	0.008	0.010	0.015
0	4.756	4.703	4.640	4.619	4.600	4.570	4.546	4.501
5	4.761	4.707	4.644	4.623	4.605	4.574	4.550	4.504
10	4.771	4.717	4.654	4.631	4.613	4.582	4.558	4.511
15	4.783	4.727	4.665	4.642	4.623	4.592	4.568	4.521
20	4.795	4.740	4.678	4.655	4.635	4.604	4.580	4.533
25	4.815	4.760	4.696	4.673	4.654	4.622	4.597	4.550
30	4.834	4.778	4.714	4.690	4.678	4.639	4.613	4.564
35	4.856	4.801	4.736	4.712	4.692	4.660	4.635	4.585
40	4.881	4.824	4.760	4.735	4.715	4.683	4.656	4.607
45	4.908	4.852	4.787	4.762	4.742	4.710	4.683	4.633
50	4.937	4.880	4.813	4.790	4.770	4.736	4.709	4.658

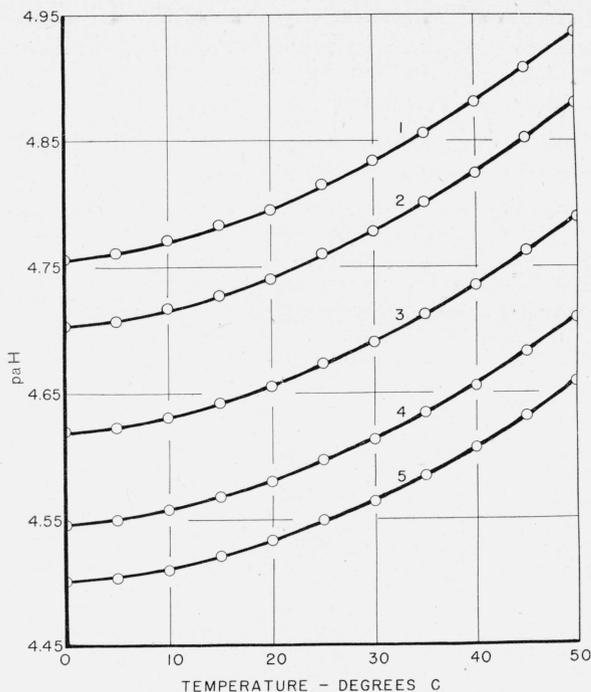


FIGURE 5. pH of oxalate buffer solutions:  $\text{KHC}_2\text{O}_4$  ( $m$ ),  $\text{Na}_2\text{C}_2\text{O}_4$  ( $5m$ ), as a function of temperature.

Curves 1 to 5 represent solutions for which  $m$  has the values 0.001, 0.002, 0.005, 0.01, and 0.015, respectively.

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