copper would be distributed on the leather than, would be if the dye bath was applied only to the fur surface.

Another reason the seal fur did not deteriorate as much as might be expected from the copper content, as compared to the Karakuls, may be that the oil tannage is inherently more resistant than the predominantly alum-type dressing of the lambskins.

The rate with which the metal salts are leached or removed from the lambskin pelts holds no relationship to the extent of deterioration. In other words the degree of the fixation of metal salts does not follow the aging. The results of water extraction of the metal salts from the skins are shown in table 7.

TABLE 7. *Aluminum, iron, and copper content of water-soluble extractives*

Constituent	Year of crop					
	Group I				Group II	
	1930	1931	1932	1933	1945	1946
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Al_2O_3	0.387	0.129	0.290	0.112	0.295	0.165
Fe_2O_3	.006	.007	.046	.020	.080	.030
CuO	.065	.006	.030	.012	.058	.010
Total	0.458	0.142	0.366	0.144	0.433	0.205

VI. Summary

Aged crossbred Karakul lamb furs appear to have different physical properties than aged purebred Karakul lamb furs.

Purebred Karakul lamb furs in storage 15 years or more are considerably weaker in strength than similar pelts in storage approximately 4 years. Differences in strength between the age groups are not attributed to a change in tannage procedure over the consecutive years of processing.

Comparable losses in strength occurred in Alaskan seal furs after a storage period of 10 years.

Evidences of acid deterioration were not found.

The presence of small quantities of copper salts, which are introduced into the furs during dyeing, relates significantly with the extents of deterioration, and provides evidence that the metal acting catalytically promotes deterioration. Iron salts apparently do not promote deterioration appreciably.

The findings are in accord with a previously published report on the influence of copper and iron on vegetable-tanned leather deteriorated under accelerated conditions. The findings are novel in that the leathers described herein were of an alum or oil tannage, which were aged under normal shelf storage conditions.

The extents of deterioration are conveniently measured by determining either burst, breaking strength, or stitch tear (furrier-sewn) values. Losses in strength are accompanied by lower petroleum ether extractives, increased water solubles, increased soluble proteinaceous and other water-extractable organic matter.

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Second Dissociation Constant of Succinic Acid from 0° to 50° C

By Gladys D. Pinching and Roger G. Bates

The second dissociation constant of succinic acid at intervals of 5 degrees from 0° to 50° C was determined from measurements of the electromotive force between hydrogen and silver-silver chloride electrodes in cells without liquid junction. The 19 solutions studied were divided into two series. The first series was made up of aqueous mixtures of sodium acid succinate, sodium succinate, and sodium chloride in the molar proportions 1 : 3 : 3. The solutions of the second series contained only sodium acid succinate and sodium chloride, in the molar ratio 1:1. The measurements of the second series were used to compute an approximate value for the first dissociation constant of the acid to be employed in correcting the results of the first series for the amount of free succinic acid formed by hydrolysis.

The second dissociation constant, K_2, for the temperature range studied can be expressed by

$$-\log K_2 = 1679.13/T - 5.7043 + 0.019153\ T,$$

where T is the temperature on the Kelvin scale. Thermodynamic quantities for the dissociation of acid succinate ion were calculated from the temperature coefficient of the second dissociation constant. At 25° C, the standard free-energy change was found to be 32,182 abs j mole^{-1}, and the changes of heat content and entropy for the dissociation process in the standard state were -450 abs j mole^{-1} and -109.4 abs j deg^{-1} mole^{-1}, respectively.

I. Introduction

The simultaneous dissociation of two or more acid groups of nearly equal strength complicates the determination of the dissociation constants of many dibasic and polybasic organic acids. Accurate values may indeed be impossible to obtain when the degree of dissociation is large in each overlapping step. Consequently, the thermodynamic quantities, such as heat-content and entropy changes, associated with the ionization of acids with more than one carboxyl group have received little careful study.

The three dissociation constants, K_1, K_2, and K_3, of citric acid have been determined from electromotive-force measurements with hydrogen and silver-silver chloride electrodes in cells without liquid junction [1].[1] There was a considerable amount of overlapping, inasmuch as K_1/K_2 and K_2/K_3 are both about 44 at 25° C. It was possible, however, to facilitate the separation by choice of favorable buffer ratios and by a supplementary determination of the products K_1K_2 and K_2K_3 according to a method recently described [2].

These methods have now been applied to a determination of the second dissociation constant of succinic acid from 0° to 50° C at intervals of 5 degrees. The ratio K_1/K_2 for succinic acid, a dibasic acid, is about 26. Hence, the overlapping of these two dissociation steps is somewhat greater than that of the corresponding steps in the ionization of citric acid. The changes of free energy, heat content, entropy, and heat capacity accompanying the dissociation of one mole of acid succinate ion in the standard state of 0° to 50° C have been evaluated from the dissociation constant and its temperature coefficient.

II. Experimental Procedures and Results

Sodium acid succinate and sodium succinate were both prepared from reagent-grade succinic acid and standardized sodium hydroxide solution. The sodium succinate was recrystallized twice from water and dried at 125° C. Ignition of the purified salt to sodium carbonate indicated a purity of 99.99±0.02 percent. The sodium acid succinate was analyzed by titration with standard alkali and found to contain a small amount of free acid. It was therefore recrystallized from water with the addition of the amount of sodium hydroxide required to bring the salt to the proper composition. The anhydrous salt was obtained by drying at 110° C. The purity was found by titration to be 100.03±0.02 percent. Sodium chloride, practically free from bromide, was recrystallized from water. The product contained less than 0.001 percent of bromide, as shown by the uranine test [3].

Neither of the succinate salts is appreciably hygroscopic. Exposed at 25° C to air of 45-percent relative humidity, sodium succinate took up only 0.012 percent of moisture in 10 days, and the acid salt gained only 0.006 percent in 24 hours.

Four stock solutions were prepared by weight from the purified salts and water having a specific conductance of approximately 0.5×10^{-6} reciprocal ohm. Each stock solution was diluted with water to form a series of four or five cell solutions. Dissolved air was removed by passage of nitrogen through each solution before the cells were filled.

The hydrogen electrodes were formed by depositing platinum black upon bases of platinum foil. Each foil was electrolyzed for 2 minutes at a current of 300 ma in a 3-percent solution of chloroplatinic acid that was 0.002 M with respect to lead acetate. The preparation of the silver chloride electrodes has been described [4]. The cells were those heretofore employed for studies of systems of weak acids and their salts in which the solubility of silver chloride is negligible [5]. Each cell, with electrodes in place, was twice filled with solution and emptied by pressure of pure hydrogen before the final portion was admitted. The cells were allowed about 5 hours to attain initial equilibrium at 25° C, after which the temperature was lowered overnight to near 0° C. Measurements of the electromotive force were made from 0° to 25° C on the second day and from 25° to 50° C on the third day. At the conclusion of the series, final values at 25° were obtained. These usually agreed with the initial values within 0.00010 v.

The platinum-hydrogen electrodes were mounted just beneath the surface of the solution, and the mean total pressure at each electrode was assumed to equal that of the atmosphere. Hills and Ives [6] have recently found that the effective pressure, that is, the pressure that fixes the concentration of dissolved hydrogen in equilibrium with the electrode, is determined by the depth of the jet as well as by the gas-phase pressure. The solution becomes saturated with gas at the jet level and is thoroughly mixed by the bubbling. The free surface apparently is slow to relieve supersaturation. The excess pressure is, according to Hills and Ives, about two-fifths of the hydrostatic pressure at the jet. The jet in the cells used here is located about 5 cm below the surface of the solution. At a hydrogen pressure of 1 atm, a change of 1 mm Hg (13.6 mm water) in the partial pressure of hydrogen changes the potential of the hydrogen electrode by about 16 μv at 25° C and 21 μv at 50° C. Hence, a jet depth of 5 cm, or an excess pressure of 2 cm water, would cause an error of 0.00002 v at 25° C and 0.00003 v at 50° C. This error is somewhat less than the observed differences between duplicate cells. No attempt has been made to apply a correction for this effect. It is presumably largely compensated by a comparable error in the values for the standard potential of the hydrogen-silver chloride cell, which were derived from measurements of hydrochloric-acid solutions contained in cell vessels of a similar design [7].

The electromotive force of the cell

$$\text{Pt; H}_2(g,\ 1\ \text{atm}),\ \text{NaHSuc}\ (m),\ \text{Na}_2\text{Suc}(3m),\ \text{NaCl}\ (3m),\ \text{AgCl}(s);\ \text{Ag}$$

from 0° to 50° C is listed in table 1 (series 1). Each recorded value is the mean of the potentials between two pairs of electrodes in the same cell. Here, as elsewhere in this paper, $\text{Suc}^=$ is written for succinate anion ($^-\text{OOCCH}_2\text{CH}_2\text{COO}^-$) and HSuc^- for acid succinate ion. Similarly, succinic acid will be abbreviated H_2Suc. Indication of the charges of hydrogen and chloride ions will be omitted. The data of table 1 (series 2) are for the cell

$$\text{Pt; H}_2(g, 1\ \text{atm}), \text{NaHSuc}\ (m), \text{NaCl}\ (m), \text{AgCl}\ (s);\ \text{Ag}.$$

---

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

Table 1. *Electromotive force of hydrogen-silver chloride cells containing succinate-chloride solutions at 0° to 50° C.*

m_{NaHSuc}	Temperature, °C										
	0	5	10	15	20	25	30	35	40	45	50
Series 1. NaHSuc:Na$_2$Suc:NaCl=1:3:3											
0.05012	0.60112	0.60417	0.60722	0.61036	0.61341	0.61645	0.61977	0.62292	0.62612	0.62939	0.63278
.04951	.60142	.60447	.60750	.61066	.61376	.61686	.62002	.62307	.62638	.62958	-------
.04555	.60364	.60674	.60988	.61303	.61622	.61935	.62259	.62583	.62913	.63243	.63574
.03985	.60696	.61012	.61335	.61648	.61977	.62304	.62635	.62972	.63313	.63647	.63982
.03715	.60891	.61214	.61536	.61869	.62195	.62526	.62840	.63191	.63535	.63874	.64233
.03556	.60998	.61325	.61655	.61988	.62323	.62649	.62992	.63331	.63677	.64023	.64371
.02511	.61896	.62242	.62594	.62950	.63306	.63648	.64020	.64380	.64745	.65112	.65477
.02509	.61900	.62248	.62601	.62956	.63306	.63666	.64020	.64384	.64752	.65121	.65483
.02493	.61925	.62278	.62625	.62981	.63329	.63675	.64054	.64415	.64778	.65143	.65530
.014886	.63277	.63655	.64035	.64421	.64806	.65189	.65579	.65973	.66369	.66767	.67165
.014853	.63291	.63671	.64050	.64433	.64807	.65195	.65599	.65988	.66381	.66777	.67199
.010184	.64262	.64662	.65065	.65467	.65875	.66267	.66695	.67105	.67520	.67925	.68330
.007573	.65035	.65456	.65878	.66300	.66725	.67139	.67578	.68003	.68441	.68871	.69263
.005074	.66083	.66523	.66965	.67408	.67849	.68287	.68740	.69196	.69652	.70113	.70574
Series 2. NaHSuc:NaCl=1:1											
0.10000	0.55454	0.55673	0.55898	0.56121	0.56350	0.56557	0.56781	0.57007	0.57225	0.57445	0.57663
.07296	.56248	.56484	.56724	.56957	.57194	.57434	.57666	.57899	.58136	.58377	.58610
.05012	.57187	.57443	.57702	.57956	.58223	.58469	.58727	.58986	.59244	.59492	.59734
.03155	.58345	.58627	.58909	.59188	.59484	.59730	.60036	.60323	.60599	.60880	.61154
.019390	.59569	.59874	.60183	.60484	.60793	.61069	.61390	.61695	.61993	.62294	.62590

III. Calculation of the Dissociation Constant

When the two acid groups of a dibasic acid are of widely different strengths, the second dissociation constant can readily be computed from a single series of measurements of buffer solutions such as those of series 1.[2] To accomplish this, the mass-action expression is combined with the equation that relates the electromotive force to the activities of the reactants and products of the cell reaction. When exact values of the activity coefficients are unknown, the semi-empirical Hückel formula [14] can be used to facilitate the determination of the true thermodynamic dissociation constant, K, by extrapolation to zero ionic strength. The resulting expression for the apparent dissociation constant, K', (obtained with the use of inexact activity coefficients) is

$$-\log K_2' \equiv -\log K_2 - \beta\mu = \text{pwH} - \log \frac{m_{\text{Suc}^=}}{m_{\text{HSuc}^-}} + \frac{2A\sqrt{\mu}}{1+Ba^*\sqrt{\mu}}, \qquad (1)$$

where A and B are constants of the Hückel equation,[3] a^* and β are adjustable parameters, and μ is the ionic strength.

The quantity pwH is defined by

$$\text{pwH} \equiv -\log (f_H f_{Cl} m_H) = (E-E^o)F/(2.3026RT) + \log m_{Cl}, \qquad (2)$$

where f is an activity coefficient on the molal scale, E and E^o are the electromotive force and standard potential,[3] respectively, of the hydrogen-silver chloride cell, F is the faraday, R the gas constant, and T the temperature on the Kelvin scale.

Equation 1 also applies when the two dissociation steps overlap, as do those of succinic acid. However, the terms in m represent the actual ionic molalities and cannot be assumed to be equal to the stoichiometrical molalities of the primary and secondary succinate salts. Instead, the detailed ionic composition of each solution must be considered.

1. The Hydrogen-Ion Correction

In order to compute the actual concentrations of the succinate ions and the second term on the right of eq 1, the equilibria among these ions must be considered. The equilibria involving acid succinate ion in aqueous solution may be represented by

$$\text{HSuc}^- = \text{H}^+ + \text{Suc}^= \qquad (3)$$

and

$$2\ \text{HSuc}^- = \text{H}_2\text{Suc} + \text{Suc}^=. \qquad (4)$$

In series 1, where the stoichiometric molality of sodium succinate is $3m$ and that of acid succinate m,

$$m_{\text{HSuc}^-} = m - m_H - 2\ m_{\text{H}_2\text{Suc}} \qquad (5)$$

and

$$m_{\text{Suc}^=} = 3\ m + m_H + m_{\text{H}_2\text{Suc}}. \qquad (6)$$

The ionic strength of each solution of series 1 is given by

$$\mu = 13\ m + 2\ m_H + m_{\text{H}_2\text{Suc}}. \qquad (7)$$

---

[2] For the application of this method to the determination of second dissociation constants when overlapping is negligible ($K_1/K_2 > 1{,}000$), and for the derivation of eq 1, the reader is referred to the following papers on the respective acids: carbonic [8, 9], malonic [10], oxalic [11, 12], phenolsulfonic [4], phosphoric [5, 13].

[3] The constants A and B at 0° to 100° C are given in [15] and E^o and $2.3026RT/F$ in abs v in [16].

The hydrogen-ion concentration is small relative to m and is estimated with sufficient accuracy by

$$-\log m_{\mathrm{H}} = \mathrm{pwH} + \log f_{\mathrm{H}} f_{\mathrm{Cl}} = \mathrm{pwH} - \frac{2A\sqrt{\mu}}{1+Ba^*\sqrt{\mu}}. \quad (8)$$

The quantity $f_{\mathrm{H}} f_{\mathrm{Cl}}$ represents the square of the mean activity coefficient of hydrochloric acid in the succinate buffer solutions. Although this is unknown, $f_{\mathrm{H}} f_{\mathrm{Cl}}$ in pure hydrochloric acid solutions at ionic strengths of 0.05 to 0.2 [7, 17] is represented by the last term of eq 8 with a^* values of 5.8 to 6.2. Also $f_{\mathrm{H}} f_{\mathrm{Cl}}$ in pure solutions of sodium chloride of the same concentrations [18] can be expressed similarly with values of 5 to 5.6 for a^*. Although the correct value of a^* thus appears to lie near 6 in solutions containing chiefly sodium salts, a change from 4 to 7 produces a negligible change in the second dissociation constant, for the hydrogen-ion correction is small. Inasmuch as the best extrapolation was obtained when a value of 7 was used for a^* in eq 1, it was found convenient to employ this value in eq 8 as well.

2. Correction for the First Dissociation Step

As a result of overlapping of the first and second acid groups, a part of the acid succinate ion is converted into molecular succinic acid. The concentration of succinic acid in the solutions of series 1 was only about 2 percent of m, since the excess of the normal succinate over the acid salt was effective in suppressing reaction 4. Because the residual overlapping was small, a precise knowledge of the first dissociation constant, K_1, and the activity coefficients was not needed to obtain sufficiently accurate figures for the molality of succinic acid in eq 5 and 6. If $f_{\mathrm{H}} f_{\mathrm{HSuc^-}}$ is approximately equal to $f_{\mathrm{H}} f_{\mathrm{Cl}}$ in the same solutions, a not unreasonable assumption, we have from the definition of pwH (eq 2) and the mass law for the first dissociation step,

$$m_{\mathrm{H_2Suc}} = m_{\mathrm{HSuc^-}} / (K_1 \text{ antilog pwH}). \quad (9)$$

For an accuracy of ±0.002 in log K_2, it was necessary to know log K_1 only to ±0.05. Values in the literature are quite adequate at and near 25° C but do not extend to 0° and 50° C. Hence, five solutions of sodium acid succinate and sodium chloride (series 2) were studied in order to obtain an approximate value of K_1 throughout the temperature range. For the solutions of series 2,

$$-1/2 \log (K_1K_2)' = \mathrm{pwH} - 1/2 \log \frac{mx + m_{\mathrm{H}}}{mx - m_{\mathrm{H}}} + \frac{A\sqrt{\mu}}{1+Ba^*\sqrt{\mu}}, \quad (10)$$

where the prime indicates again the "apparent" value and

$$x \equiv \frac{\sqrt{4k_2/k_1}}{1+\sqrt{4k_2/k_1}}. \quad (11)$$

The symbols k_1 and k_2 represent the concentration constants. The details of the application of eq 10 and 11 to the calculation of K_1K_2 have been given elsewhere [1, 2] and need not be repeated. The solution of eq 1 and 10 was most conveniently accomplished by successive approximations, of which only two were usually necessary. The extrapolation of $-1/2 \log (K_1K_2)'$ is shown in figure 1. The limiting values of $-1/2 \log K_1K_2$ and of $-\log K_1$ at each temperature are given in table 2. Inasmuch as these are based upon too few points to provide an unambiguous extrapolation, they are to be regarded as approximate. Nevertheless, log K_1 is probably correct to ±0.01 and, hence, more than adequate for the purpose.

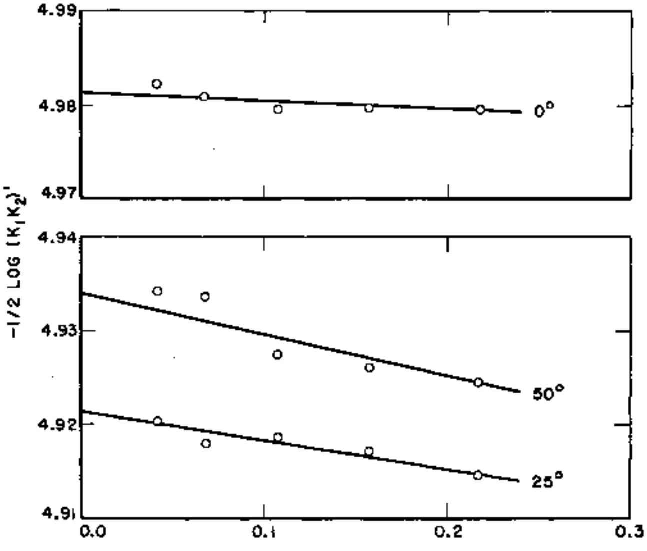

FIGURE 1. *Determination of the product K_1K_2 by extrapolation to zero ionic strength.*

TABLE 2. *Values of log K_1K_2 and log K_1 at 0° to 50° C*

Temperature	$-1/2 \log K_1K_2$	$-\log K_1$	Temperature	$-1/2 \log K_1K_2$	$-\log K_1$
°C			°C		
0	4.981	4.28_6	30	4.921	4.20_0
5	4.963	4.26_5	35	4.921	4.19_4
10	4.948	4.24_7	40	4.924	4.19_4
15	4.937	4.23_2	45	4.930	4.19_0
20	4.931	4.22_5	50	4.934	4.18_8
25	4.921	4.20_6			

3. The Extrapolation

Figure 2 demonstrates the effect of three different values of a^* (eq 1) upon pK_2' (that is, $-\log K_2'$) at 25° C. From top to bottom of the figure, the three solid lines correspond to a^* values of 6, 7, and 8, respectively. The upper dashed line, computed for $a^*=7$, illustrates the effect of omitting entirely the correction for the first dissociation, that is, of ignoring $m_{\mathrm{H_2Suc}}$ in eq 5 and 6. Although K_1/K_2 is only 26, it appears that the 3:1 buffer ratio has materially reduced the extent of overlapping, for the K_1 correc-

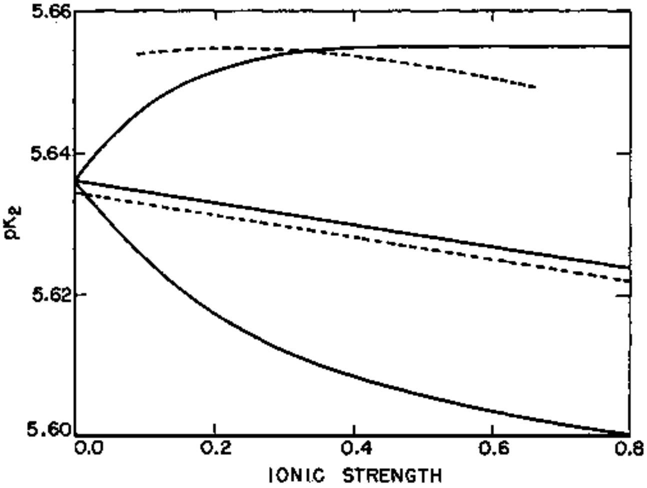

Figure 2. *Effect of a^* on the course of the extrapolation line.*

Solid lines represent (top to bottom) $a^*=6$, 7, and 8. The dashed lines show the course of the extrapolation when the correction for the overlapping first dissociation is ignored (upper dashed line) or made with a value of log K_1 that is in error by 0.05 unit (lower dashed line).

tion contributes only about 0.02 to log K_2. The lower dashed line indicates the change of position of the center extrapolation line that would result from an error of 0.05 in log K_1.

When a^* was taken to be 7, log K_2' was found to be a linear function of ionic strength at each temperature, as shown in figure 3, although the slopes of the lines changed considerably with temperature. These slopes ($-\beta$ in eq 1) were measured and log K_2 calculated from each experimental point with the aid of eq 1. The average values are given in the second column of table 3, together with the mean deviation from the average at each temperature. The corresponding K_2 appears in the last column. The uncertainty in log K_2 is believed to be less than ±0.003 unit.

Table 3. *Values of log K_2 and K_2 from 0° to 50° C*

Temperature	$-\log K_2$	$K_2 \times 10^6$	Temperature	$-\log K_2$	$K_2 \times 10^6$
° C			° C		
0	$5.674_1 \pm 0.0013$	2.12	30	$5.641_8 \pm 0.0014$	2.28
5	$5.660_8 \pm .0012$	2.18	35	$5.647_7 \pm .0011$	2.25
10	$5.649_0 \pm .0009$	2.24	40	$5.654_0 \pm .0012$	2.22
15	$5.642_5 \pm .0011$	2.28	45	$5.669_6 \pm .0013$	2.14
20	$5.639_0 \pm .0008$	2.30	50	$5.680_2 \pm .0026$	2.09
25	$5.635_8 \pm .0012$	2.31			

Table 4 is a summary of the published values for the second dissociation constant grouped according to the method used for the determination. The constant found by Jones and Soper [33] should be most nearly comparable with that reported here, for their measurements were also made with a hydrogen-silver chloride cell without liquid junction. However, a different method of calculation was used. Unfortunately, no electromotive-force data are listed in their paper, so it is impossible to explain the differences of about 0.03 and 0.04 between their log K_2 and that of this investigation at 25° and 50° C, respectively.

Table 4. *Summary of determinations of log K_2*

Reference	Method [a]	Temperature	$-\log K_2$
CONDUCTANCE			
		° C	
1908, Chandler [19]		25	5.57
1921, Duboux [20]	(Recalculation)	25	5.60
DISTRIBUTION			
1908, McCoy [21]		25	5.37
1908, Chandler [19]		25	5.66
REACTION RATE			
1927, Duboux and Frommelt [34]	Decomposition of diazoacetic ester.	25	5.55
SOLUBILITY			
1915, Datta and Dhar [35]	Of CO_2	25	5.54
1926, Larsson [36]	Of benzoic acid	25	5.6
ELECTROMOTIVE FORCE, CELLS WITH LIQUID JUNCTION			
1922, Larsson [22]	Q-cal	18	5.620
1924, Auerbach and Smolczyk [23].	Q-cal	20	5.401
1925, Britton [24]	H-cal	18	5.28
1926, Mizutani [25]	H-cal	18	5.43
1928, Simms [26]	H-cal	25	5.570
1928, Kolthoff and Bosch [27]	H-cal	18	5.57
1928, Gane and Ingold [28]	H-cal	25	5.347
1929, Ölander [29]	H-Q; Q at 18° C	50	5.733
1931, Gane and Ingold [30]	H-cal	25	5.478
1934, Ashton and Partington [31]	H-cal	25	5.322
1936, German and Vogel [32]	Q-cal	25	5.595
ELECTROMOTIVE FORCE, CELLS WITHOUT LIQUID JUNCTION			
1936, Jones and Soper [33]	H-AgCl	25 50 74	5.607 5.638 5.726
1950, This investigation	H-AgCl	20 25 50	5.639 5.636 5.680

[a] H=hydrogen electrode, Q=quinhydrone, cal=calomel.

IV. Thermodynamic Functions

The dissociation constants given in table 3 are adequately represented by either

$$-\log K_2 = 1679.13/T - 5.7043 + 0.019153\ T \qquad (12)$$

or

$$-\log K_2 = 3756.1/T - 79.2716 + 29.223 \log T. \qquad (13)$$

The mean deviation of the observed log K_2 from the calculated value is 0.0011 for eq 12 and 0.0018 for eq 13. The first is the form suggested by Harned and Robinson [37]; the second has been used especially by Everett and Wynne-Jones [38]. If eq 12 and 13 were used solely for the interpolation of K_2 at various temperatures, either would serve the purpose. Likewise, $\Delta F°$, the standard free energy of dissociation, is readily obtained from the dissociation constant at each temperature. However, some expression of the variation of log K_2 with temperature is necessary in order to calculate, over the entire range, the quantities $\Delta H°$, $\Delta S°$, and $\Delta C_p°$, which are

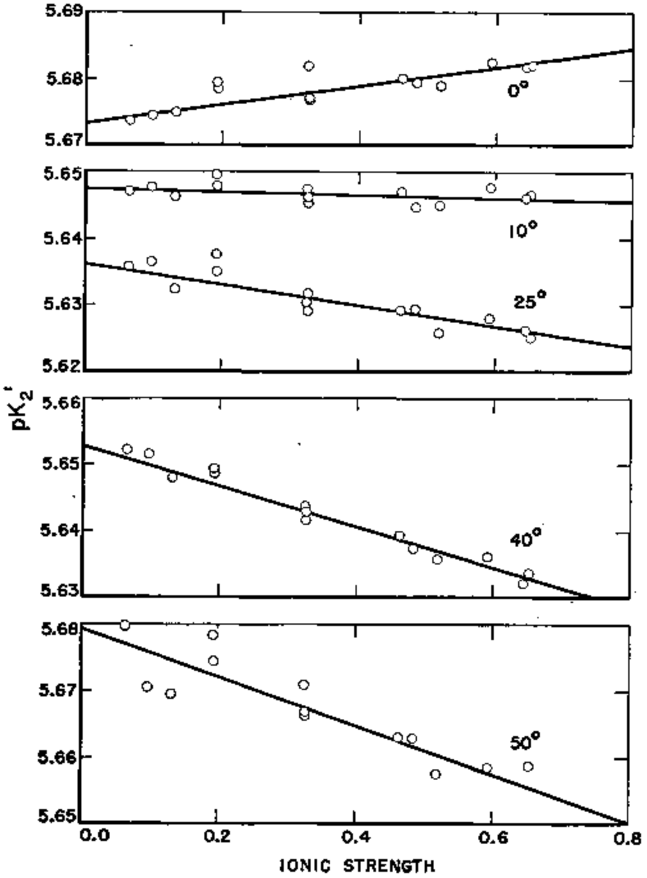

FIGURE 3. *Extrapolation lines from which $-\log K_2$ (pK_2) was obtained at 0°, 10°, 25°, 40°, and 50° C.*

respectively the changes of heat content, entropy, and heat capacity for the dissociation of 1 mole of acid succinate ion in the standard state. By differentiation of eq 12 and 13 with respect to temperature, the following expressions for $d \log K_2/dT$ are obtained:

$$d \log K_2/dT = 1679.13/T^2 - 0.019153 \qquad (12a)$$

and

$$d \log K_2/dT = 3756.1/T^2 - 12.6913/T. \qquad (13a)$$

Since the two equations yield somewhat different temperature coefficients, they will also furnish different values for these three thermodynamic functions. The difference is not large near the middle of the temperature range but is appreciable at the ends, as can be seen from the following comparison of $\Delta H°$ computed from the two equations:

Temperature	Eq 12	Eq 13
° C	*j mole^{-1}*	*j mole^{-1}*
0	4, 787	5, 541
25	−450	−533
50	−6, 146	−6, 607

Equation 12 rests upon the observation that the electromotive force of cells of the type used here (and hence $\Delta F°$) is closely a quadratic function of temperature. It implies that $\Delta C_p°$ is a linear function of temperature. Equation 13 is based upon a presumed linear variation of $\Delta H°$ with T, and hence a value of $\Delta C_p°$ that is constant over the entire temperature range. For this reason, eq 12 is sometimes considered theoretically less acceptable than eq 13. Nevertheless, the authors are of the opinion that the fit of the observed data provides the most valid justification for choice of one empirical or semiempirical equation over another. Equation 12 is usually found to represent the observed dissociation constants for weak acids and bases more closely than eq 13. Hence, the former was used to compute the thermodynamic functions given in table 5 by application of the usual formulas.

TABLE 5. *Thermodynamic quantities for the dissociation of acid succinate ion*

Temperature	$\Delta F°$	$\Delta H°$	$\Delta S°$	$\Delta C_p°$
°C	*abs j mole^{-1}*	*abs j mole^{-1}*	*abs j deg^{-1} mole^{-1}*	*abs j deg^{-1} mole^{-1}*
0	29, 675	4, 787	−91. 1	−200
5	30, 140	3, 776	−94. 8	−204
10	30, 623	2, 747	−98. 4	−208
15	31, 125	1, 690	−102. 1	−211
20	31, 645	633	−105. 8	−215
25	32, 182	−450	−109. 4	−219
30	32, 739	−1, 553	−113. 1	−222
35	33, 314	−2, 674	−116. 8	−226
40	33, 907	−3, 813	−120. 4	−230
45	34, 519	−4, 971	−124. 1	−233
50	35, 148	−6, 146	−127. 8	−237

The estimated uncertainty of 0.003 in $\log K_2$ implies a corresponding uncertainty of about 18 j mole^{-1} in $\Delta F°$. If the values of $\log K_2$ at 0° and 50° C were each in error by 0.003 unit and the errors were of opposite sign, $\Delta H°$ at 25° would be altered by about 300 j mole^{-1} and $\Delta S°$ by about 1 j deg^{-1} mole^{-1}. Similarly $\Delta C_p°$ at 25° C can be assigned an uncertainty of about 12 j deg^{-1} mole^{-1}.

Cottrell and Wolfenden [39] have reported a calorimetric determination of the heats of dissociation of the two steps of succinic acid from 5° to 30° C. By combination of their data with $\Delta F°$ taken from the work of Jones and Soper [33], they computed the entropy of dissociation, $\Delta S°$. The change of heat capacity, $\Delta C_p°$, was obtained from the temperature variation of $\Delta H°$. The value of Cottrell and Wolfenden for the entropy change has been adjusted to correspond with the $\Delta F°$ of this investigation, which seems more certain than the earlier result. The values at 25° C are:

	Cottrell and Wolfenden	Pinching and Bates
$\Delta H°$	176 j mole^{-1}	−450 j mole^{-1}
$\Delta S°$	−107.4 j deg^{-1} mole^{-1}	−109.4 j deg^{-1} mole^{-1}
$\Delta C_p°$	−218 j deg^{-1} mole^{-1}	−219 j deg^{-1} mole^{-1}

The two values for the heat of dissociation differ by the rather large amount of 626 j. Cottrell and Wolfenden state that their result is subject to considerable uncertainty, for it represents a difference between two experimental quantities and also rests upon a rather arbitrary extrapolation. Differences of extrapolation often do not affect the temperature coefficient, and it is perhaps significant that practically identical values of ΔC_p°, that is $d(\Delta H^\circ)/dT$, were obtained by the two methods. Cottrell and Wolfenden found ΔH° to pass through zero at 26° C, in reasonably good agreement with 23° C at which the value of $-\log K_2$ given in table 3 reaches a minimum.

V. References

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Methods of Sieve Analysis With Particular Reference to Bone Char[1]

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The procedure for separating particle sizes of solid adsorbents by sieving has been studied in detail because of the influence of the particle size on adsorbent properties. The investigation was conducted chiefly with sieve openings in the range between U. S. Standard Sieves No. 8 and No. 80. The largest source of error is in the testing sieves themselves. This is due to the tolerances permitted by the present specifications. It is feasible to calibrate testing sieves by the use of a calibrated sample of spherical glass beads and thus obtain the opening that is effective in sieving. The calibration of testing sieves in this manner can lead to reproducible sieve analyses by different laboratories. A simple procedure is proposed to determine the uniformity of sieve openings and, thereby, to furnish a criterion for the discard of distorted sieves. An analysis with seven Ro-Tap machines indicated that, in general, best results are obtained when the Ro-Tap is operated at 115 taps/min of the knocker mechanism. The other variables concerned with shaking that were examined are of minor importance and need not be rigidly controlled. As first choice, the weight of the sample should be between 100 and 150 g. The shaking time should be adjusted to the weight and the particle size distribution of the sample according to relationships developed.

I. Introduction

The adsorbent properties of bone char and other materials are greatly influenced by particle size. Sieve analysis is one of the basic tests for measuring the particle size of all powdered and granular materials. In sugar refining and many other industries great importance is ascribed to sieve analyses in spite of the fact that their reproducibility may be extremely poor, in comparison with other measurements such as volume, mass, or chemical composition. Differences in the results of sieve analyses of

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