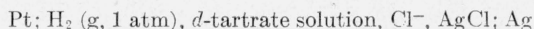


Resolution of the Dissociation Constants of *d*-Tartaric Acid from 0° to 50° C*

Roger G. Bates and Richard G. Canham

The ratio of the first thermodynamic dissociation constant, K_1 , of tartaric acid to the second, K_2 , is only 20 to 23 at temperatures between 0° and 50° C. The two dissociative steps therefore overlap to a considerable extent. The greater the amount of overlapping, the more difficult it is to resolve the two equilibria and to determine each individual dissociation constant.

Electromotive-force measurements of the cell



were made at intervals of five degrees from 0° to 50° C. Thirty-two tartrate solutions were studied. All but 5 of the 22 solutions of series 1 were composed of sodium hydrogen tartrate, sodium tartrate, and sodium chloride in the molar proportions 1:3:1. The other 17 contained sodium hydrogen tartrate, sodium tartrate, and potassium chloride in the molar proportions 1:1.3411:0.5853. The 10 solutions of series 2 were 1:1 mixtures of sodium hydrogen tartrate and sodium chloride.

The calculation of the second dissociation constant by the conventional method requires not only a knowledge of the concentration of hydrogen ion but also that of the free tartaric acid formed as a result of the overlapping. Neither can ordinarily be evaluated exactly from the emf. However, the 1:3 buffer ratio of series 1 reduced the hydrogen-ion concentration and at the same time lowered the ratio of the concentrations of tartaric acid and hydrogen tartrate ion to about 0.03. Hence, an adequate correction for the amount of acid could be made with an approximate value of the first dissociation constant. However, it is impossible to lower the K_2 correction for the determination of K_1 without increasing the hydrogen-ion concentration. Accordingly, a method developed earlier, utilizing emf data for solutions of the acid salt (series 2), was employed. Thus the hydrogen-ion concentration was kept relatively low, and the emf became a function of the product of K_1 and K_2 rather than substantially independent of K_2 .

The two dissociation constants of tartaric acid from 0° to 50° C are given by the equations

$$-\log K_1 = 1525.59/T - 6.6558 + 0.015336 T$$

and

$$-\log K_2 = 1765.35/T - 7.3015 + 0.019276 T,$$

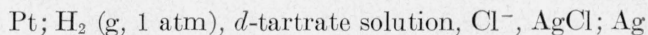
where T is the temperature in degrees K. The standard thermodynamic quantities for the two dissociation steps were calculated.

1. Introduction

Although tartaric acid and its salts have been widely used as constituents of buffer solutions for the regulation of acidity [1, 2],¹ little accurate information on the strengths of the two acidic groups as a function of temperature is available. This neglect is due, in part at least, to the complex composition of solutions containing these substances. The ratio of the first thermodynamic dissociation constant, K_1 , of tartaric acid to the second, K_2 , is only 20 to 23 at temperatures between 0° and 50° C. Hence, the two dissociative steps "overlap" to such an extent that appreciable amounts of molecular tartaric acid and both the primary and secondary tartrate ions exist simultaneously in tartrate buffer solutions. The concentrations of all three tartrate species must be established in order to calculate accurate values of either constant.

The second dissociation constant was calculated

from data for the electromotive force of cells of the type



by what can be termed the conventional method [3, 4, 5]. All but five of the 22 solutions of series 1 were composed of sodium hydrogen *d*-tartrate, sodium *d*-tartrate, and sodium chloride in the molar proportions 1:3:1. The rest of the solutions of series 1 contained sodium hydrogen *d*-tartrate, sodium *d*-tartrate, and potassium chloride in the proportions 1:1.3411:0.5853. The computation of $\log K_2$ from the data for these 22 buffer solutions requires, in addition to the stoichiometric molalities of the three components, a knowledge of the concentration of hydrogen ion and also that of the molecular tartaric acid formed as a result of overlapping of the dissociative steps. Neither of these quantities can ordinarily be evaluated exactly from the emf. However, the 1:3 buffer ratio of most of the solutions of series 1 kept the hydrogen-ion concentration reasonably low and at the same time reduced the ratio of the concentrations of tartaric

* Presented before the Twelfth International Congress of Pure and Applied Chemistry at New York City (Sept. 11, 1951).

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

acid and hydrogen tartrate ion to about 0.03. Hence, an adequate correction for the amount of tartaric acid present could be made with an approximate value of the first dissociation constant.

Unfortunately, a similar application of the conventional method to the determination of the first dissociation constant is not as successful. Any attempt to minimize the concentration of bivalent tartrate ion inevitably increases the concentration of hydrogen ion. Thus the advantage gained on the one hand is offset by a parallel disadvantage on the other. In order to facilitate the separation of the constants for overlapping equilibria, the senior author suggested in 1948 [6] the use of emf data for cells containing aqueous mixtures of the acid salt, in this case sodium hydrogen tartrate, with a soluble chloride. The relationship between the electromotive force of the cell and the product of the two overlapping constants was developed. Together with the data of experiments such as series 1 designed for the determination of K_2 , it is possible to obtain consistent values of K_1K_2 by a short series of approximations. Thus, no attempt is made to minimize both the K_2 correction and the hydrogen-ion concentration. Instead, the latter is kept fairly low in all of the solutions, and the emf of the cells from which K_1 is determined becomes a function of the product of K_1 and K_2 rather than substantially independent of K_2 , a condition the conventional method

seeks to achieve. On the other hand, experimental errors in the measurement of the emf have twice as large an effect upon the final value of K_1 determined in this way as upon that determined by the conventional method. Nevertheless, this new approach is of particular advantage when the primary object is to determine K_2 and when economy of time and effort is a factor. Further measurements by the conventional method serve to establish K_1 accurately once the value of K_2 has been fixed.

The 10 solutions of series 2 were 1:1 mixtures of sodium hydrogen tartrate and sodium chloride. By analysis of the data for series 1 and 2, apparent values of $\log K_2$ and $1/2 \log K_1K_2$ at intervals of 5 deg from 0° to 50° C were calculated. The true thermodynamic dissociation constants were obtained by extrapolation of the apparent values to infinite dilution. The second dissociation constant and its temperature coefficient were used to compute the changes of free energy, heat content, entropy, and heat capacity for the dissociation of hydrogen tartrate ion in the standard state from 10° to 40° C. These quantities were also computed for the first dissociation step at 25° C.

2. Experimental Procedures and Results

Each cell contained two hydrogen electrodes and two silver-silver-chloride electrodes. At least two values of the emf, E , were therefore obtained for each

TABLE 1. pH of tartrate-chloride solutions from 0° to 50° C

m_{NaHTar}	Temperature, °C										
	0	5	10	15	20	25	30	35	40	45	50
Series 1a. NaHTar:Na ₂ Tar:NaCl=1:3:1											
0.05200	4.6184	4.5961	4.5765	4.5621	4.5513	4.5416	4.5367	4.5343	4.5375	4.5403	4.5464
.04983	4.6218	4.5991	4.5795	4.5649	4.5528	4.5461	4.5403	4.5392	4.5397	4.5449	4.5503
.04502	4.6277	4.6000	4.5812	4.5676	4.5591	4.5514	4.5436	4.5408	4.5456	4.5520	4.5588
.04161	4.6327	4.6101	4.5915	4.5771	4.5662	4.5581	4.5533	4.5527	4.5537	4.5585	4.5640
.03976	4.6367	4.6144	4.5955	4.5809	4.5695	4.5637	4.5561	4.5564	4.5569	4.5619	4.5664
.03605	4.6417	4.6195	4.6013	4.5874	4.5763	4.5671	4.5642	4.5629	4.5641	4.5683	4.5740
.03105	4.6491	4.6294	4.6120	4.5983	4.5875	4.5762	4.5746	4.5739	4.5735	4.5792	4.5879
.03010	4.6546	4.6331	4.6143	4.6004	4.5895	4.5834	4.5776	4.5773	4.5787	4.5844	4.5910
.02986	4.6548	4.6323	4.6138	4.5997	4.5878	4.5819	4.5758	4.5735	4.5751	4.5822	4.5888
.02700	4.6620	4.6397	4.6221	4.6084	4.5974	4.5899	4.5846	4.5828	4.5855	4.5910	4.5975
.02058	4.6768	4.6555	4.6381	4.6254	4.6166	4.6086	4.6034	4.6016	4.6017	4.6087	4.6165
.02012	4.6796	4.6585	4.6404	4.6277	4.6165	4.6102	4.6048	4.6021	4.6065	4.6103	4.6178
.019977	4.6821	4.6607	4.6427	4.6295	4.6192	4.6127	4.6078	4.6075	4.6092	4.6152	4.6233
.011993	4.7116	4.6924	4.6753	4.6629	4.6524	4.6448	4.6408	4.6393	4.6418	4.6474	4.6566
.010218	4.7228	4.7031	4.6858	4.6728	4.6628	4.6547	4.6523	4.6516	4.6534	4.6596	4.6701
.010183	4.7263	4.7059	4.6880	4.6753	4.6653	4.6576	4.6533	4.6531	4.6550	4.6631	4.6721
.009016	4.7319	4.7113	4.6944	4.6817	4.6712	4.6638	4.6604	4.6602	4.6625	4.6699	4.6773
Series 1b. NaHTar:Na ₂ Tar:KCl=1:1.3411:0.5853											
0.03276	4.3773	4.3587	4.3406	4.3287	4.3136	4.3075	4.3022	4.3020	4.3039	4.3093	4.3162
.02732	4.3866	4.3664	4.3478	4.3362	4.3253	4.3195	4.3144	4.3144	4.3160	4.3208	4.3287
.02175	4.4022	4.3799	4.3617	4.3495	4.3381	4.3338	4.3267	4.3258	4.3276	4.3327	4.3396
.016300	4.4191	4.3985	4.3799	4.3683	4.3575	4.3515	4.3478	4.3476	4.3492	4.3541	4.3620
.010582	4.4448	4.4229	4.4052	4.3938	4.3835	4.3769	4.3724	4.3739	4.3755	4.3809	4.3897
Series 2. NaHTar:NaCl=1:1											
0.06000	3.6517	3.6311	3.6134	3.6002	3.5889	3.5794	3.5739	3.5724	3.5717	3.5751	3.5804
.05000	3.6517	3.6311	3.6134	3.6002	3.5889	3.5794	3.5739	3.5724	3.5717	3.5751	3.5804
.04488	3.6654	3.6452	3.6277	3.6149	3.6038	3.5976	3.5908	3.5829	3.5815	3.5854	3.5896
.04000	3.6710	3.6505	3.6324	3.6198	3.6066	3.5955	3.5901	3.5878	3.5872	3.5909	3.5953
.03485	3.6816	3.6600	3.6428	3.6290	3.6168	3.6014	3.5955	3.5928	3.5927	3.5975	3.6022
.03026	3.6856	3.6650	3.6475	3.6341	3.6222	3.6153	3.6078	3.6063	3.6066	3.6106	3.6155
.02543	3.6923	3.6742	3.6570	3.6434	3.6323	3.6241	3.6181	3.6161	3.6155	3.6191	3.6239
.02011	3.7079	3.6867	3.6698	3.6561	3.6447	3.6369	3.6303	3.6287	3.6285	3.6332	3.6376
.015041	3.7205	3.6996	3.6823	3.6694	3.6586	3.6520	3.6475	3.6464	3.6465	3.6506	3.6564
.010043	3.7447	3.7244	3.7074	3.6948	3.6840	3.6749	3.6714	3.6700	3.6706	3.6753	3.6802

cell solution. These were averaged, and the corresponding values of the quantity pwH were computed by the equation²

$$\text{pwH} \equiv -\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}}) = (E - E^\circ) F / (2.3026 RT) + \log m_{\text{Cl}}, \quad (1)$$

where m is molality; f is the activity coefficient on the scale of molality; E° is the standard potential³ of the cell; F is the faraday, 96,496 abs coulombs equiv⁻¹ [9]; R is the gas constant, 8.3144 abs j deg⁻¹ mole⁻¹ [9]; and T is the absolute temperature, $T = t$ (°C) + 273.16. The values of pwH are summarized in table 1. As eq 1 shows, pwH is a physically defined property of each buffered chloride solution.

Fifteen of the aqueous tartrate-chloride mixtures that made up series 1a and 1b were prepared by the addition of the appropriate weights of sodium hydrogen tartrate and bromide-free sodium chloride (or potassium chloride) to a carbonate-free solution of sodium hydroxide. The remaining seven were prepared from sodium chloride and the anhydrous primary and secondary sodium tartrates. These two tartrate salts were purified by two crystallizations from water. The sodium hydrogen tartrate was dried at 50° in a vacuum oven and was found to assay 99.98 percent by titration with standard alkali to the endpoint of phenolphthalein. The same solution of alkali was used for the titration and for the preparation of the cell solutions. The secondary sodium tartrate was dried to the anhydrous condition in air at 150°. Three samples of the dry salt were ashed in platinum in a muffle furnace at temperatures near 800°. The weight of residue, assumed to be sodium carbonate, was 99.94 percent of the theoretical.

Solutions of the purified sodium hydrogen tartrate and sodium tartrate were strongly dextrorotatory. The dissociation constants of the dextro, levo, and dl forms of tartaric acid appear to be identical, but the meso acid is somewhat weaker than the other three forms [10].

The solutions were freed of dissolved air by passage of nitrogen. Details of the procedure followed in making the hydrogen electrodes, in filling the cells, and in measuring the emf have been set forth in an earlier article [11]. The design of the cells [5] and the method of preparing the silver-silver-chloride electrodes [12] have also been described elsewhere.

3. Calculation of the Dissociation Constants

As indicated in an earlier section, neither dissociation constant of an overlapping pair can be obtained independently of the other. However, to resolve the two constants it is sufficient that equations for $K_1 K_2$ and for K_2 in terms of the same unknowns be set up and solved simultaneously or by successive approximations. This approach has been used to determine the second dissociation constant of succinic acid

accurately and the first constant approximately [11]. Its application was described in some detail and will not be repeated in its entirety for tartaric acid.

3.1. Calculation of K_2 from pwH (series 1)

If m_1 represents the stoichiometric molality of sodium hydrogen tartrate and m_2 that of sodium tartrate, the formal expression for the relation between the pwH of the mixtures of series 1 and the second dissociation constant, K_2 , of tartaric acid is

$$-\log K_2' \equiv -\log K_2 - \beta \mu = \text{pwH} - \log \frac{m_2 + m_{\text{H}} + m_{\text{H}_2 \text{Tar}}}{m_1 - m_{\text{H}} - 2m_{\text{H}_2 \text{Tar}}} + \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}}, \quad (2)$$

where K_2' is the "apparent" value of K_2 , μ is the ionic strength, β and a^* are adjustable parameters, A and B are constants of the Debye-Hückel theory [13], and $\text{H}_2 \text{Tar}$ is written for tartaric acid ($\text{COOH-CHOH-CHOH-COOH}$). If $f_{\text{H}} f_{\text{H Tar}^-} m_{\text{H}} / f_{\text{H}_2 \text{Tar}}$ is taken equal to $f_{\text{H}} f_{\text{Cl}} m_{\text{H}}$, that is, to $1/(\text{antilog pwH})$, a reasonable assumption for dilute solutions, the concentration of free (molecular) tartaric acid is given by

$$-m_{\text{H}_2 \text{Tar}} = (m_1 - m_{\text{H}}) / (2 + K_1 \text{antilog pwH}) \quad (3)$$

and the ionic strength by

$$\mu = m_1 + 3m_2 + m_{\text{Cl}} + 2m_{\text{H}} + m_{\text{H}_2 \text{Tar}}. \quad (4)$$

Unfortunately, the hydrogen-ion concentration, m_{H} , can only be established approximately, as the activity coefficients needed to compute it from pwH (compare eq 1) are not known. The apparent or inexact concentration of hydrogen ion, m_{H}' , is obtained by use of the Debye-Hückel equation with a reasonable value of the ion-size parameter, a^* :⁴

$$-\log m_{\text{H}}' = \text{pwH} - 2A\sqrt{\mu} / (1 + Ba^*\sqrt{\mu}). \quad (5)$$

The uncertainty in a^* (and hence in m_{H}') is of little importance when the hydrogen-ion concentration is much smaller than m_1 or m_2 but limits the accuracy with which the dissociation constant of moderately strong acids such as the first step of phosphoric acid can be obtained [14]. Evidently m_{H}' approaches the true m_{H} at low values of the ionic strength. Inasmuch as the thermodynamic dissociation constants are obtained by an extrapolation procedure, m_{H}' can be used for m_{H} when the dissociation constant is 10^{-3} or smaller without perceptible effect on the result.

3.2. $K_1 K_2$ from pwH (series 2)

The formal relationship between $(K_1 K_2)'$, the apparent value of $K_1 K_2$ calculated with estimated

² In the equations of the following sections, the charges of the hydrogen and chloride ions will not be indicated. Furthermore, the term "hydrogen ion" will be understood to embrace all forms of this ion, hydrated or unhydrated.

³ E° is obtained from the experimental data of Harned and Ehlers [7]. Values of E° and $2.3026 RT/F$ in absolute volts are listed in reference [8].

⁴ As m_{H} is so small, the choice of a^* has little influence on the result. Values of 5.5 and 6 were chosen, for these furnished the best straight-line plots of $\log K_2'$ with respect to ionic strength when used in eq 2.

activity coefficients, and pH for the solutions of series 2 is written [6]

$$-1/2 \log (K_1 K_2)' = \text{pH} - 1/2 \log \frac{m_{\text{H}_2\text{Tar}} + m_{\text{H}}}{m_{\text{H}_2\text{Tar}}} + \frac{A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (6)$$

If m_1 is the molality of sodium hydrogen tartrate and also that of sodium chloride, the ionic strength of the solutions of series 2 is

$$\mu = 2m_1 + 2m_{\text{H}} + m_{\text{H}_2\text{Tar}} \quad (7)$$

The concentration of molecular tartaric acid, $m_{\text{H}_2\text{Tar}}$, is given by eq 3. The apparent hydrogen-ion concentration, m_{H} , was computed by eq 5 with $a^*=4$ and used for m_{H} in eq 6 and 7. A value of 4 was also used for a^* in eq 6. A choice of 6 instead of 4 for a^* (eq 5) altered the second term on the right of eq 6 by only 0.0003.

3.3. Resolution of K_1' and K_2

The two constants were resolved as follows: The ionic strength of the solutions of series 1 was first estimated, m_{H}' computed (eq 5), and $-\log K_2'$ obtained (eq 2) neglecting $m_{\text{H}_2\text{Tar}}$. Extrapolation of the results to zero ionic strength then furnished a first approximation to K_2 . Next, an estimated value of K_1 was employed in eq 3 to compute the approximate $m_{\text{H}_2\text{Tar}}$ and, from this, the approximate ionic strength and m_{H}' in the solutions of series 2. A value of $K_1 K_2$ was obtained by use of eq 6 and subsequent extrapolation to zero ionic strength, and $K_1 K_2$ was divided by the first value of K_2 to obtain a first measure of K_1 . The latter was then used in eq 3 to obtain $m_{\text{H}_2\text{Tar}}$ and, hence, the ionic strength of series 1 solutions needed for the second approximation. After the dissociation constants at 0°, 25°, and 50° had been established, interpolation furnished reasonably accurate estimates of the various quantities at the intermediate temperatures and simplified the computations considerably.

The extrapolation of $\log K_2'$ for the 22 solutions of series 1 to zero ionic strength at 0°, 25°, and 50° is shown in figure 1. The circles represent data for series 1a and the dots for series 1b. Figure 2 shows the determination of $\log K_1 K_2$ at the same temperatures. In both cases, the lines were drawn by inspection. The final values of $\log K_1$, $\log K_2$, and $1/2 \log K_1 K_2$ are summarized in tables 2 and 3. The accuracy of $\log K_2$ is thought to be about ± 0.003 and that of $\log K_1$ about ± 0.006 .

TABLE 2. $\log K_2$ and K_2 from 0° to 50° C

Temperature (°C)	$-\log K_2$	$K_2 \times 10^5$	Temperature (°C)	$-\log K_2$	$K_2 \times 10^5$
0	4.426	3.75	25	4.366	4.31
5	4.407	3.92	30	4.365	4.32
10	4.391	4.06	35	4.367	4.30
15	4.381	4.16	40	4.372	4.25
20	4.372	4.25	45	4.380	4.17
			50	4.391	4.06

TABLE 3. $\log K_1 K_2$ and $\log K_1$ from 0° to 50° C

Temperature (°C)	$-1/2 \log K_1 K_2$	$-\log K_1$	Temperature (°C)	$-1/2 \log K_1 K_2$	$-\log K_1$
0	3.772	3.118	25	3.701	3.036
5	3.751	3.095	30	3.695	3.025
10	3.733	3.075	35	3.693	3.019
15	3.719	3.057	40	3.695	3.018
20	3.708	3.044	45	3.700	3.020
			50	3.706	3.021

Some of the more recent determinations of the dissociation constants of *d*-tartaric acid are summarized in table 4. As a result, no doubt, of the difficulty of resolving equilibria that overlap so extensively, these values show very little uniformity. Several of the emf determinations were based upon the analysis of pH-titration curves plotted from data for cells with the hydrogen or quinhydrone electrode and the calomel reference electrode. Jones and Soper [10] used the same cell as was used in this investigation. They computed m_{H} by an equation similar to eq 5 and used the values thus

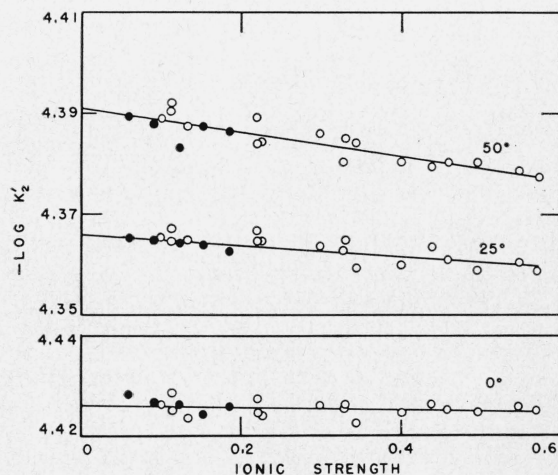


FIGURE 1. Extrapolation of $\log K_2'$ to zero ionic strength at 0°, 25°, and 50°.

Circles represent data of series 1a; dots represent those of series 1b.

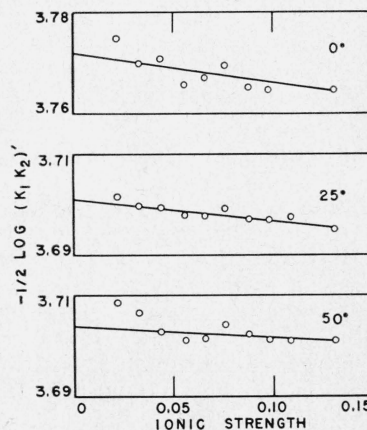


FIGURE 2. Extrapolation of $-1/2 \log (K_1 K_2)'$ to zero ionic strength at 0°, 25°, and 50°.

Data of series 2.

TABLE 4. Summary of determinations of $\log K_1$ and $\log K_2$ for *d*-tartaric acid

Reference	Temperature (°C)	$-\log K_1$	$-\log K_2$	Method
[15].....	20	3.05	4.13	emf Conductance, sucrose inversion.
[16].....	18	3.01	4.55	
[17].....	18	2.90	4.02	emf Solubility.
[18].....	25	-----	4.29	
[19].....	25	-----	4.40	Rate of decomposition of diazoacetic ester.
[20].....	{ 16.8	2.93	-----	}emf, KCl added.
	{ 17.6		4.23	
[21].....	18	3.02	4.55	}emf
[22].....	20	3.04	4.40	
[10].....	{ 25	2.98	4.34	}Do.
	{ 50		4.39	
	{ 74	3.01	4.51	}Do.
[23].....	{ 20		2.98	
This investigation	{ 0	3.12	4.426	}Do.
	{ 25		3.04	
	{ 50	3.02	4.391	

obtained to calculate the dissociation constants in much the same manner as pH measurements had been used by earlier investigators.

The values of $\log K_1$ and $\log K_2$ at the 11 temperatures were fitted to the following equation by the method of least squares:

$$-\log K = A/T + B + CT, \quad (8)$$

where T is the temperature in degrees K. The constants of eq 8 for the first and second steps are

	A	B	C
First dissociation.....	1525.59	-6.6558	0.015336
Second dissociation.....	1765.35	-7.3015	.019276

The average difference between the "observed" $\log K$ and that calculated by eq 8 is 0.0008 for $\log K_1$ and 0.0005 for $\log K_2$.

In figure 3, $-\log K_1$, $-\log K_2$, and $-\frac{1}{2} \log K_1 K_2$ are plotted as a function of temperature, and each of these quantities is seen to pass through a minimum in the experimental temperature range. It was shown in an earlier paper [24] that the absolute temperature, T_{\min} , at which the minimum is reached can be readily calculated from the constants of eq 8:⁵

$$T_{\min} = \sqrt{A/C}.$$

Hence, T_{\min} is found to be 42.2° C for $-\log K_1$ and 29.5° C for $-\log K_2$.

4. Thermodynamic Quantities

By application of familiar thermodynamic formulas, the dissociation constants and their changes with temperature yield values of the changes of free energy, heat content, entropy, and heat capacity that would take place if 1 mole of tartaric acid or hydrogen tartrate ion were to dissociate completely

⁵ The square-root sign has been omitted from the right side of eq 20, reference [24].

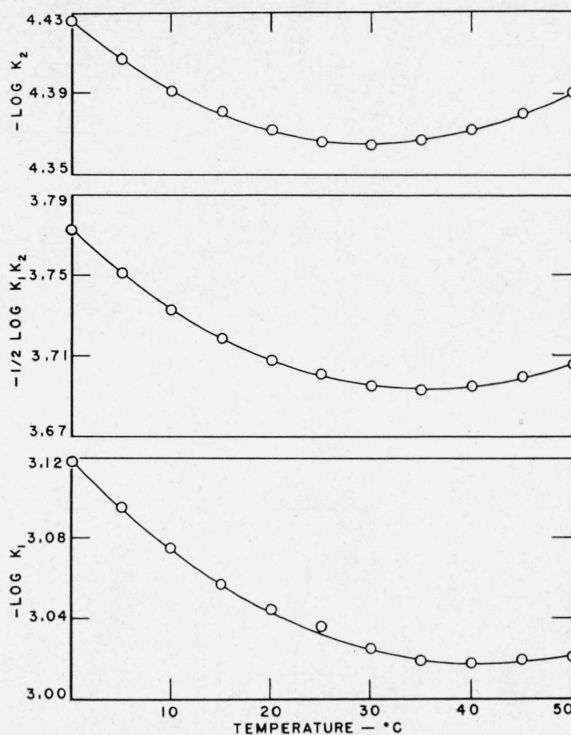
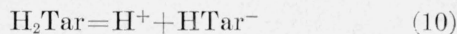
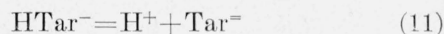


FIGURE 3. $\log K_1$, $\log K_2$, and $\frac{1}{2} \log K_1 K_2$ plotted as a function of temperature.

under conditions obtaining in the standard state for aqueous solutions. These quantities, which are designated ΔF° , ΔH° , ΔS° , and ΔC_p° , respectively, correspond to the processes



and



when unit activity of both reactants and products is maintained at all times. Inasmuch as overlapping of the two steps prevents either process from achieving completion without involvement of the other, these thermodynamic functions can only be used in practice when a detailed analysis of the solution has been made. They are, nevertheless, of some theoretical interest.

In terms of the constants A , B , and C of eq 8, the formulas for the four thermodynamic quantities are

$$\Delta F^\circ = -2.3026 RT \log K, \quad (12)$$

$$\Delta H^\circ = 2.3026 R(A - CT^2), \quad (13)$$

$$\Delta S^\circ = 2.3026 R(-B - 2CT), \quad (14)$$

$$\Delta C_p^\circ = 2.3026 R(-2CT). \quad (15)$$

With the use of $R = 8.3144 \text{ j deg}^{-1} \text{ mole}^{-1}$, these quantities were obtained in joules. The accuracy of the quantities derived from the first or second derivatives of $\log K$ with respect to temperature is greater near

the middle of the experimental temperature range than at the ends. Hence, ΔH° , ΔS° , and ΔC_p° were computed only for the range 10° to 40° C. In view of the lower accuracy of $\log K_1$, the thermodynamic quantities were computed for the first dissociation step only at 25° C. The results are summarized in table 5.

TABLE 5. Thermodynamic quantities for the dissociation of tartaric acid and hydrogen tartrate ion

Temperature	ΔF°	ΔH°	ΔS°	ΔC_p°
Tartaric acid (eq 10)				
$^\circ\text{C}$	$j \text{ mole}^{-1}$	$j \text{ mole}^{-1}$	$j \text{ deg}^{-1} \text{ mole}^{-1}$	$j \text{ deg}^{-1} \text{ mol}^{-1}$
25	17,330	3,100	-47.7	-170
Hydrogen tartrate ion (eq 11)				
0	23,150	-----	-----	-----
5	23,470	-----	-----	-----
10	23,800	4,210	-69.2	-209
15	24,170	3,150	-72.9	-213
20	24,540	2,080	-76.6	-216
25	24,920	990	-80.3	-220
30	25,330	-120	-84.0	-224
35	25,760	-1,250	-87.7	-227
40	26,210	-2,390	-91.4	-231
45	26,680	-----	-----	-----
50	27,170	-----	-----	-----

5. References

- [1] D. I. Hitchcock and A. C. Taylor, *J. Am. Chem. Soc.* **59**, 1812 (1937).
 [2] J. J. Lingane, *Anal. Chem.* **19**, 810 (1947).

- [3] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.* **54**, 1350 (1932).
 [4] W. J. Hamer, J. O. Burton, and S. F. Acree, *J. Research NBS* **24**, 269 (1940) RP1284.
 [5] R. G. Bates and S. F. Acree, *J. Research NBS* **30**, 129 (1943) RP1524.
 [6] R. G. Bates, *J. Am. Chem. Soc.* **70**, 1579 (1948).
 [7] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.* **55**, 2179 (1933).
 [8] R. G. Bates and G. D. Pinching, *J. Research NBS* **42**, 419 (1949) RP1982.
 [9] J. W. DuMond and E. R. Cohen, *Rev. Modern Phys.* **20**, 82 (1948).
 [10] I. Jones and F. G. Soper, *J. Chem. Soc.* 1836 (1934).
 [11] G. D. Pinching and R. G. Bates, *J. Research NBS* **45**, 322 (1950) RP2142.
 [12] R. G. Bates, G. D. Pinching, and E. R. Smith, *J. Research NBS* **45**, 418 (1950) RP2153.
 [13] G. G. Manov, R. G. Bates, W. J. Hamer, and S. F. Acree, *J. Am. Chem. Soc.* **65**, 1765 (1943).
 [14] R. G. Bates, *J. Research NBS* **47**, 127 (1951) RP2236.
 [15] F. Auerbach and E. Smolczyk, *Z. physik. Chem.* **110**, 65 (1924).
 [16] T. Paul, *Z. physik. Chem.* **110**, 417 (1924).
 [17] H. T. S. Britton, *J. Chem. Soc.* **127**, 1896 (1925).
 [18] E. Larsson, *Z. anorg. allgem. Chem.* **155**, 247 (1926).
 [19] M. Duboux and J. Frommelt, *J. chim. phys.* **24**, 245 (1927).
 [20] R. Kuhn and T. Wagner-Jauregg, *Ber.* **61**, 483 (1928).
 [21] I. M. Kolthoff and W. Bosch, *Rec. trav. chim.* **47**, 861 (1928).
 [22] F. L. Hahn and R. Klockmann, *Z. physik. Chem.* **A571**, 206 (1931).
 [23] H. Bode and K. Peterson, *Ber.* **71B**, 871 (1938).
 [24] G. D. Pinching and R. G. Bates, *J. Research NBS* **45**, 444 (1950) RP2156.

WASHINGTON April 27, 1951