Journal of Research of the National Bureau of Standards Vol. 62, No. 4, April 1959 Research Paper 2947

Resolution of the Dissociation Constants of *d,l*-Malic Acid From 0° to 50° C[1]

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A method for the precise determination of the dissociation constants for the two overlapping dissociation steps of a weak dibasic acid from the same set of experimental data is described. The procedure, based on an earlier suggestion of Speakman (J. Chem. Soc. **1940,** 855), is applied to the resolution of the thermodynamic dissociation constants of *d,l*-malic acid at intervals of five degrees from 0° to 50° C. The constants were derived from measurements of the electromotive force of cells of the type

$$\text{Pt; H}_2\text{(g), malate buffer solution, KCl}(m=0.008)\text{, AgCl; Ag.}$$

The 39 buffer solutions were prepared from potassium hydrogen malate and from mixtures of potassium hydrogen malate with perchloric acid or potassium hydroxide, and each contained potassium chloride. The first dissociation constant, K_1, is 3.48×10^{-4} at 25° C. It is given as a function of absolute temperature (T) by

$$-\log K_1=\frac{1358.85}{T}-5.1382+0.013550\,T.$$

The second constant, K_2, is 7.99×10^{-6} at 25° C. It is given by

$$-\log K_2=\frac{1658.53}{T}-6.2364+0.019353\,T.$$

The thermodynamic quantities ΔG°, ΔH°, ΔS°, and ΔC_p° related to each dissociation step were computed and compared with the corresponding constants for other acids closely related structurally to malic acid.

1. Introduction

The evaluation of the dissociation constants of a polybasic weak acid or polyacidic base is particularly difficult when the ratio of the constants for two successive dissociation steps is 100 or less. Even when the ratio of the first dissociation constant to the second is as high as 500, one of the constants cannot be evaluated without correcting for the effect of the other, inasmuch as some simultaneous dissociation occurs.

In view of these difficulties, the dissociation constants of only a few dibasic or polybasic acids with "overlapping" dissociation steps have been resolved in a precise way. Indeed, accurate values may be unobtainable by the usual experimental procedures. Consequently, little is known about the thermodynamic quantities associated with the separate overlapping ionization steps of acids of this type.

When the hydrogen ion concentration of a buffer solution is fixed by the interaction of a single acid or base with water, the dissociation constant can often be obtained with high accuracy from emf measurements by the method described by Roberts [1][3] and by Harned and Ehlers [2]. This procedure has been so successful and has been used so widely that it may justifiably be termed the "conventional" emf method. Difficulties are usually encountered, however, when the dissociation constant of the acid or base exceeds 0.002 [3].

The cell most commonly used is a cell without transference, composed of a hydrogen electrode and a silver-silver chloride electrode. The same cell was utilized in the present study. It is represented by the following scheme

$$\text{Pt; H}_2\text{(g), malate solution, KCl}(m=0.008)\text{, AgCl; Ag.} \tag{1}$$

The reaction taking place when current is drawn from this cell is

$$\tfrac{1}{2}\,\text{H}_2+\text{AgCl}=\text{Ag}+\text{H}^++\text{Cl}^-.$$

Consequently, the emf E (corrected to 1 atm partial pressure of hydrogen) is related to the composition of the solution in the cell by

$$\frac{E-E^\circ}{2.3026RT/F}+\log m_{\text{Cl}}=-\log\,(f_{\text{H}}f_{\text{Cl}}m_{\text{H}}). \tag{2}$$

In this equation, m represents molality (moles per kilogram of water), f is the activity coefficient on the molal scale, and E° is the standard potential (standard emf) of the cell. The values for the latter were derived from the work of Harned and

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[1] Based on a dissertation presented by Murray Eden in partial fulfillment of the requirements for the Doctor of Philosophy degree at the University of Maryland, 1951. Presented before the Division of Physical Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 1958.

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

Ehlers [2, 4]. They have been tabulated in absolute volts in an earlier publication [5], together with values of the function 2.3026 RT/F for temperatures from 0° to 60° C (absolute temperatures, T, from 273.16° to 333.16° K).

The expression relating the emf to the equilibrium constant, K, for the dissociation process,

$$HA^n + H_2O = H_3O^+ + A^{n-1}, \qquad (3)$$

where n represents the charge of the acid species HA, is derived by combining eq (2) with the mass-law expression for eq (3). The concentration of protons in dilute aqueous solutions is unknown, although it must be exceedingly small. However, as long as the activity of water remains substantially unity, the activity of protons will be proportional to the activity of the hydrates formed in reactions such as eq (3). Indeed, the hypothetical standard state of unit proton activity (to which $E°$ relates) corresponds by definition to an actual state in which hydrated protons or hydrogen ions are present at unit activity. Hence, m_H in eq (2) can be identified with m_{H3O^+} in the mass-law formulation of eq (3). These considerations are valid only as long as the activity of water remains substantially unity.

The indicated substitution gives

$$-\log K = -\log (f_H f_{Cl} m_H) - \log \frac{m_A}{m_{HA}} + \log \frac{f_{HA} f_{Cl}}{f_A} \qquad (4)$$

The activity-coefficient term at finite ionic strengths can be estimated by various means in order to facilitate the extrapolation of "apparent" values of $-\log K$ to infinite dilution, where the last term becomes zero and the true value of K is obtained. This method is quite elegant and completely satisfactory when the buffer pH is controlled by a single dissociation step of moderate strength and when the buffer solutions are stable in contact with the hydrogen and silver-silver chloride electrodes. It applies to polybasic acids and polyacidic bases if the ratios of the constants for successive dissociation steps are 10^3 or greater. The concentrations of the acid and its conjugate base are derived by correcting the stoichiometric molalities of these substances for hydrolysis and dissociation, that is, for reaction with the amphiprotic solvent.

The existence of a second acidic or basic group of a strength comparable with that under study complicates the determination considerably, for the concentration term of eq (4) can no longer be computed simply and accurately from stoichiometric concentrations [6, 7, 8, 9]. The quantity m_H in eq (2) is now a function simultaneously of more than one dissociation equilibrium, and the resolution of the individual constants may be a problem of considerable magnitude.

Nevertheless, it is sometimes possible to apply the "conventional" method successfully by choosing buffer ratios so that the hydrogen ion concentration is controlled almost exclusively by the dissociation step under study, a relatively small correction being made for the effect of the other. The procedure is an involved and laborious one. The dissociation constants of a number of weak dibasic acids have nonetheless been determined through variations of this general procedure [6, 10, 11, 12, 13]. In this way the dissociation constants of o-phthalic acid ($K_1/K_2=288$) have been resolved [12, 13] and the second dissociation constants of succinic acid ($K_1/K_2=27$) [14] and d-tartaric acid ($K_1/K_2=21$) [15] and the third dissociation constant of citric acid ($K_2/K_3=43$) [16] have been determined. In the last three instances a buffer ratio, m (neutral salt)/m (acid salt), of 3 was effective in keeping the hydrogen ion concentration low and in reducing the magnitude of the corrections for dissociation equilibria other than the one of primary concern.

Various attempts have been made to determine the overlapping dissociation constants simultaneously. In the method suggested by Speakman [17], the first and second dissociation constants for a weak dibasic acid are derived from a single set of observations. The experimental data are plotted in such a way that a straight line is obtained. The intercept is K_1K_2 and the slope determines the value of K_1. However, Speakman's method utilizes values of "hydrogen ion activity" ($\mathbf{a}_H$) from pH measurements and consequently does not furnish exact values of thermodynamic dissociation constants.

A method for determining the product of the overlapping ionization constants of a dibasic acid was proposed by Bates [18]. The complete resolution depends on an independent determination of one constant. The cell solutions contained known molalities of the acid salt of the weak dibasic acid and an alkali chloride. An apparent K_1K_2 was plotted as a function of ionic strength and extrapolated to infinite dilution to eliminate activity coefficient corrections and to obtain the true value of K_1K_2. The value of this method lies in the fact that the molality term is insensitive to relatively large uncertainties in the hydrolysis correction. In applying this procedure to a resolution of the dissociation constants of tartaric acid, Bates and Canham [15] evaluated the second constant with the aid of approximate values for the first. The product K_1K_2 was then evaluated and a new, more precise, value of K_1 was computed.

2. Method

It seemed worthwhile to explore the possibility of modifying the Speakman method to permit the simultaneous determination of the dissociation constants of a dibasic acid with a precision comparable with that obtainable by the "conventional" method for a single isolated dissociation step. To this end, the equations were formulated in terms of $f_H f_{Cl} m_H$ (that is, $\mathbf{a}_H \mathrm{f}_{Cl}$) instead of $\mathbf{a}_H$, since the former can be derived unambiguously from measurements of the emf of cell (1) by means of eq (2). This quantity will be termed P:

$$P \equiv \mathbf{a}_H \mathrm{f}_{Cl} = f_H f_{Cl} m_H \qquad (5)$$

2.1. Overlapping Dissociation

The malate buffer solutions were all prepared from potassium hydrogen malate with the addition of perchloric acid or potassium hydroxide as desired. It was convenient to define two new quantities as follows:

α=the amount of potassium hydrogen malate used, in moles per kg of water.

β=the amount of strong acid used, in moles per kg of water. If strong base is added instead of strong acid, the sign of β is negative.

The potassium chloride present in all solutions at a molality of 0.008 must, of course, enter into the computation of the ionic strength. It does not, however, participate in the dissociation equilibria of malic acid, and it is therefore omitted in the following derivation of the relationships among P, α, β, K_1, and K_2.

From the requirement of electroneutrality, we have the following condition:

$$[K^+]+[H^+]=[ClO_4^-]+[OH^-]+[HMal^-]+2[Mal^=], \tag{6}$$

where $HMal^-$ and $Mal^=$ are written for the hydrogen malate and malate ions, respectively, and where the quantity in brackets represents the molality of the particular species of ion. It is convenient to define a quantity B as follows:

$$B\equiv\beta-[H^+]+[OH^-]. \tag{7}$$

It will be noted that for all the malate buffer solutions

$$[K^+]-[ClO_4^-]=\alpha-\beta. \tag{8}$$

From eq (6), (7), and (8), therefore,

$$\alpha-B=[HMal^-]+2[Mal^=]. \tag{9}$$

It can also be shown that

$$\alpha+B=2[H_2Mal]+[HMal^-]. \tag{10}$$

These relationships can now be combined with the equations for the two thermodynamic constants, K_1 and K_2, of malic acid. In this way, an equation analogous to that of Speakman [17] is derived.

2.2. Resolution of K_1 and K_2

Unfortunately, Speakman's equation cannot be applied in an exact way to the determination of overlapping dissociation constants, inasmuch as there is no known experimental means of measuring hydrogen ion activities. The closely related function P, however, possesses the thermodynamic validity that $\mathbf{a}_H$ lacks. With the further substitution of $\mathbf{a}_H=P/f_{Cl}$, one obtains

$$P^2\frac{\alpha-B}{\alpha+B}\cdot\frac{f_{A^=}}{f_{H_2A}f_{Cl}^2}=P\,\frac{B}{\alpha+B}\cdot\frac{f_{A^=}}{f_{HA^-}f_{Cl^-}}K_1+K_1K_2, \tag{11}$$

which may be written

$$Y=X\sigma K_1+(K_1K_2)/\rho \tag{12}$$

where

$$X\equiv\frac{PB}{\alpha+B}, \tag{13}$$

and

$$Y\equiv\frac{P^2(\alpha-B)}{\alpha+B}, \tag{14}$$

and in which the activity coefficient terms are

$$\sigma\equiv\frac{f_{H_2A}f_{Cl^-}}{f_{HA^-}} \tag{15}$$

and

$$\rho\equiv\frac{f_{A^=}}{f_{H_2A}f_{Cl^-}^2}. \tag{16}$$

Apart from the correction for the concentration of free hydrogen or hydroxyl ions in the buffer solutions in the computation of B by eq (7) (see below), the quantities X and Y can be derived without difficulty from the stoichiometric molalities and the measured emf of cells of type (1). This correction is usually small, for the experimental conditions can often be so arranged that α and β are large compared with m_H and m_{OH}.

It can be seen that eq (12) will be linear in X and Y if certain conditions can be met, namely: if the different values of the independent variables do not appreciably effect the constancy of σ and $1/\rho$. Studies of salt effects indicate that the activity coefficient terms are often largely dependent on the ionic strength (μ) and not on the nature of the added salt [19, 20]. Therefore, it should be justifiable to consider σ and ρ constant, within the error of the determination, when comparing values of X and Y derived from the measurement of solutions containing different ratios of acid salt to strong acid (or strong base) at constant ionic strength. This treatment of salt effects appears to be adequate in malate buffers, because a straight line was obtained for each value of the ionic strength when Y was plotted as a function of X. The slope of each line is σK_1 and the intercept is (K_1K_2/ρ).

Fortunately, activity-coefficient terms of the same type as σ are often close to unity in the regions of low and intermediate ionic strength ($\mu<0.1$).[4] At $\mu=0.06$, σ was found to be 0.96. Furthermore, log σ shows the expected linear variation with ionic strength, and consequently the curves obtained by plotting log (σK_1) against ionic strength were easily extrapolated to zero ionic strength. Since σ approaches unity at infinite dilution, the intercept for $\mu=0$ is log K_1.

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[4] In buffer solutions composed of equimolal amounts of acetic acid, sodium acetate, and sodium chloride, log ($f_{HAc}\,f_{Cl}/f_{Ac}$) is given by $-0.06\,\mu$; in acetate buffers containing potassium iodide, log ($f_{HAc}\,f_I/f_{Ac}$) is $-0.14\,\mu$ [21].

Similarly, log K_2 is obtained by extrapolating log (K_2/ρ) to zero ionic strength. An activity-coefficient term of the charge type of ρ, however, cannot be expected to be very near unity at moderate ionic strengths (ρ was found to be about 0.6 at the highest ionic strengths included in this study), nor can log ρ be expected to vary linearly with ionic strength. In order to correct the curvature of the lines and to facilitate the extrapolation, estimated values of ρ (designated ρ^*) were computed from the Debye-Hückel formula

$$\log \rho^* = \frac{-2A\sqrt{\mu}}{1+6.25B\sqrt{\mu}}, \tag{17}$$

where A and B are constants of the Debye-Hückel theory [22]. The quantity log $\rho^*(K_2/\rho)$, instead of log K_2/ρ, was then plotted as a function of μ. Several values for the coefficient of the $B\sqrt{\mu}$ term in the denominator of eq (17) were tried, and 6.25 was found to furnish the best linear plot of log $\rho^*(K_2/\rho)$ as a function of μ. The lines obtained were readily extended to zero ionic strength, where $\rho^*(K_2/\rho)$ becomes equal to K_2.

2.3. Computation of B

In order to utilize eq (11) or (12) to resolve K_1 and K_2 as described in the preceding section, two other quantities, B and μ, must be known. The former can be obtained readily from β, the stoichiometric molality of strong acid or base, by eq (7), together with $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$. Inasmuch as the pH range of malate buffers extends from about 2.5 to 6.0, the concentration of hydroxyl ion is always less than 1 percent of m_H and can be neglected. Hence,

$$B \approx \beta - [\mathrm{H}^+]. \tag{7a}$$

2.4. Hydrogen Ion Concentration

Values of the molality of hydrogen ion, $[\mathrm{H}^+] = m_\mathrm{H}$, were derived directly from the emf by eq (2); $f_\mathrm{H} f_\mathrm{Cl}$ is (by definition) equal to f^2_HCl, the square of the mean ionic molal activity coefficient of hydrocloric acid in the malate-chloride buffer solution. Values of f_HCl in pure aqueous solutions of hydrochloric acid of the same ionic strength as the malate-chloride buffer solutions were used in the computation of $[\mathrm{H}^+]$. They were taken from Harned and Ehlers [4, 23].

2.5. The Ionic Strength

With the aid of eq (9) it can be shown that the ionic strength of the solutions containing acid salt (KHMal) and potassium chloride ($m=0.008$), or these components with added strong acid, is given by

$$\mu = 0.008 + \alpha + m_\mathrm{H} + m_{\mathrm{Mal}^=}, \tag{18}$$

inasmuch as the hydroxyl ion concentration is negligibly small.

When the solutions contain potassium chloride (0.008 m), potassium hydrogen malate, and potassium hydroxide (stoichiometric molality of $-\beta$), the ionic strength is

$$\mu = 0.008 + \alpha - 2\beta + 2m_\mathrm{H} + m\mathrm{H_2Mal} \tag{19}$$

In order to calculate the ionic strength by these two equations, it was necessary to evaluate the molalities of malic acid and bivalent malate ion as well as that of hydrogen ion. These quantities can only be obtained through successive approximations, as values of the ionic strength and also of the approximate dissociation constants must be used in their computation. However, all were small relative to α, and usually to β also, so that the approximations converged rapidly.

The molality of malate ion, needed to calculate the ionic strength by eq (18), can be expressed by

$$m_{\mathrm{Mal}^=} = \frac{K_1 K_2}{\rho P^2}\,(\beta - m_\mathrm{H} + m_{\mathrm{Mal}^=}) \tag{20}$$

with the aid of eq (5), (7a), and (16). In the solutions of acid salt, to which no strong acid or strong base has been added, β is zero and consequently

$$m_{\mathrm{Mal}^=} = \frac{-K_1 K_2 m_\mathrm{H}}{\rho P^2 - K_1 K_2}. \tag{21}$$

In the solutions to which perchloric acid had been added, β was large compared with m_H and $m_{\mathrm{Mal}^=}$; hence,

$$m_{\mathrm{Mal}^=} \approx \frac{K_1 K_2 \beta}{\rho P^2}. \tag{21a}$$

When the solutions contained added strong alkali, it was necessary to estimate the molality of free malic acid in order to compute the ionic strength by eq (19). From eq (5), (7a), (10), and (15),

$$m_{\mathrm{H_2Mal}} = \frac{[P/(\sigma K_1)](\alpha + \beta - m_\mathrm{H})}{1 + [2P/(\sigma K_1)]}. \tag{22}$$

When strong alkali had been added to the solution of acid salt, $2P/\sigma K_1$ was much less than unity. Furthermore, σ is nearly unity at low and intermediate ionic strengths; hence,

$$m_{\mathrm{H_2A}} \approx \frac{P}{K_1}\,(\alpha + \beta - m_\mathrm{H}). \tag{22a}$$

The accurate evaluation of $m_{\mathrm{H_2Mal}}$ and $m_{\mathrm{Mal}^=}$ as described above is quite evidently a laborious procedure. However, neither of these quantities makes a large contribution to the ionic strength obtained by eq (18) and (19), and therefore accurate values are unnecessary. Consequently, the following procedure was followed: A preliminary value of the ionic strength was derived with the omission of the last two terms of eq (18) and (19), and a first approximation to m_H was made, which led to a more accurate value of μ by eq (18) and (19), the last term of each of these equations being omitted.

The first approximation to $m_{\mathrm{Mal}^=}$ and $m_{\mathrm{H_2Mal}}$ was then made by eq (21), (21a), or (22a), the choice being dependent on the composition of the buffer solution. For this purpose, the values of K_1 and K_2 could be obtained with sufficient accuracy from the literature, from titration curves, or from a preliminary plot of Y as a function of X. The ionic strength was now recalculated, a new value of m_{H} obtained, and the process repeated until a consistent set of values resulted.

3. Experimental Procedures

Potassium hydrogen malate was prepared from reagent-grade *d,l*-malic acid and potassium bicarbonate. A solution of the salt was decolorized at 60° C with activated charcoal. The filtrate was cooled in a water-ice bath and the crude salt precipitated by the addition of ethanol. This precipitate was recrystallized five times from ethanol-water mixtures. The salt collected after the fifth crystallization was dried overnight at 130° C in air.

The potassium hydrogen malate was assayed by titration with the standard solution of potassium hydroxide described below. After the first recrystallization, the dried salt was found to assay 99.69 percent potassium hydrogen malate. After the third recrystallization, the assay was 99.99 percent.

Potassium chloride was prepared according to the procedure outlined by Pinching and Bates [24].

The standard carbonate-free solution of potassium hydroxide (0.1 molal) was standardized against potassium hydrogen phthalate (NBS Standard Sample 84b) in a carbon dioxide-free atmosphere. Weight burettes were used. This alkali solution was used both for titrations and for the preparation of the cell solutions.

Reagent-grade perchloric acid, 70 percent by weight, was diluted with conductivity water to make a solution of molality about 0.1. The acid solution was standardized against the potassium hydroxide solution. It was tested for the presence of chloride with silver nitrate solution according to the procedure described by Rosin [25] and was found to contain less than 0.001 percent.

Eight stock solutions of malate buffers were prepared. Additional cell solutions were prepared by diluting these with an 0.008-*m* solution of potassium chloride. The compositions of the solutions appear in the second and third columns of table 1.

TABLE 1. *Values of log $(-f_{\mathrm{H}}f_{\mathrm{Cl}}m_{\mathrm{H}})$ derived from emf measurements of cell (1)*

Series	α	β	$-\log(f_{\mathrm{H}}f_{\mathrm{Cl}}m_{\mathrm{H}})$ at temperature of—										
			0° C	5° C	10° C	15° C	20° C	25° C	30° C	35° C	40° C	45° C	50° C
	moles/kg H_2O	(±)*moles/kg* H_2O											
1	0.06240	0.04365	3.1749	3.1556	3.1392	3.1265	3.1150	3.1061	3.0987	3.0942	3.0923	3.0940	3.0951
	.04153	.02905	3.1881	3.1704	3.1554	3.1431	3.1315	3.1226	3.1153	3.1117	3.1096	3.1111	3.1127
	.02105	.014724	3.2229	3.2057	3.1918	3.1793	3.1685	3.1600	3.1536	3.1496	3.1477	3.1499	3.1499
	.013431	.009395	3.2608	3.2423	3.2299	3.2212	3.2148	3.2035	3.1970	3.1916	3.1859	3.1870	3.1886
	.005893	.004122	3.3355	3.3325	3.3121	3.3016	3.2944	3.2878	3.2811	3.2774	3.2761	3.2784	3.2806
2	.05398	.03402	3.2720	3.2515	3.2353	3.2225	3.2115	3.2044	3.1968	3.1933	3.1913	3.1928	3.1958
	.03572	.02251	3.2800	3.2597	3.2440	3.2314	3.2208	3.2126	3.2059	3.2024	3.2001	3.2020	3.2039
	.02025	.012764	3.3086	3.2878	3.2739	3.2617	3.2513	3.2436	3.2370	3.2337	3.2320	3.2332	3.2353
	.011394	.007182	3.3424	3.3245	3.3094	3.2985	3.2892	3.2822	3.2771	3.2743	3.2738	3.2746	3.2757
3	.05403	.019861	------	3.6709	3.6545	3.6418	3.6313	3.6231	3.6174	3.6143	3.6118	3.6150	3.6171
	.03560	.013087	------	3.6808	3.6642	3.6519	3.6412	3.6327	3.6262	3.6236	3.6208	3.6226	3.6241
	.018463	.006787	------	3.6931	3.6774	3.6655	3.6549	3.6467	3.6403	3.6383	3.6359	3.6392	3.6428
	.012235	.004498	------	3.7069	3.6916	3.6802	3.6697	3.6611	3.6552	3.6530	3.6507	3.6537	3.6563
	.005282	.0019417	------	3.7445	3.7304	3.7204	3.7109	3.7070	3.6991	3.6973	3.6955	3.6990	3.7024
4	.05444	0	4.2450	4.2284	4.2143	4.2054	4.1978	4.1939	4.1882	4.1878	4.1909	4.1977	4.2056
	.05314	0	4.2454	4.2288	4.2141	4.2038	4.1964	4.1921	4.1895	4.1912	4.1945	4.2012	4.2090
	.03563	0	4.2576	4.2411	4.2278	4.2184	4.2107	4.2040	4.2013	4.2009	4.2030	4.2088	4.2166
	.03469	0	4.2543	4.2384	4.2241	4.2141	4.2065	4.2021	4.1995	4.2005	4.2041	4.2118	4.2198
	.02244	0	4.2651	4.2491	4.2363	4.2278	4.2209	4.2170	4.2141	4.2148	4.2178	4.2249	4.2332
	.02069	0	4.2653	4.2482	4.2346	4.2249	4.2177	4.2146	4.2131	------	------	------	------
	.012406	0	4.2792	4.2630	4.2500	4.2415	4.2353	4.2319	4.2293	4.2302	4.2334	4.2406	4.2485
	.011267	0	4.2805	4.2641	4.2499	4.2403	4.2330	4.2280	4.2246	4.2249	4.2286	4.2355	4.2436
	.005193	0	4.2995	4.2830	4.2712	4.2627	4.2562	4.2535	4.2505	4.2519	4.2564	4.2648	4.2759
	.004721	0	4.2984	4.2826	4.2704	4.2625	4.2566	4.2530	4.2505	4.2511	4.2537	4.2595	4.2700
5	.03027	−0.012114	4.8546	4.8442	4.8331	4.8279	4.8231	4.8220	4.8221	4.8275	4.8346	4.8459	4.8583
	.02003	−.008016	4.8740	4.8616	4.8523	4.8479	4.8430	4.8411	4.8429	4.8482	4.8555	4.8670	4.8800
	.010129	−.004054	4.8939	4.8813	4.8719	4.8674	4.8632	4.8577	4.8624	4.8682	4.8761	4.8877	4.8996
	.006440	−.002577	4.9064	4.8942	4.8858	4.8807	4.8759	4.8758	4.8778	4.8836	4.8917	4.9033	4.9146
	.002819	−.0011282	4.9385	4.9111	4.9030	4.8984	4.8936	4.8945	4.8975	4.9032	4.9107	4.9224	4.9364
6	.03034	−.012624	4.8880	4.8741	4.8632	4.8566	4.8524	4.8522	4.8529	4.8578	4.8653	4.8767	4.8875
	.019568	−.008142	4.8921	4.8781	4.8678	4.8627	4.8721	4.8608	4.8602	4.8640	4.8721	4.8837	4.8964
	.011054	−.004600	4.9238	4.9107	4.9004	4.8946	4.8921	4.8912	4.8928	4.8991	4.9073	4.9195	4.9316
	.006819	−.002837	4.9284	4.9151	4.9052	4.9000	4.8973	4.8966	4.8988	4.9055	4.9139	4.9266	4.9385
	.002983	−.0012412	4.9613	4.9488	4.9390	4.9332	4.9299	4.9294	4.9314	4.9382	4.9463	4.9592	4.9715
7	.02319	−.015322	5.2845	5.2695	5.2591	5.2529	5.2493	5.2489	5.2509	5.2570	5.2652	5.2775	5.2909
	.017223	−.011379	5.3055	5.2902	5.2781	5.2747	5.2713	5.2716	5.2741	5.2808	5.2897	5.3019	5.3150
	.009695	−.006405	5.3200	5.3041	5.2936	5.2887	5.2862	5.2868	5.2894	5.2958	5.3043	5.3170	5.3297
	.007129	−.004710	5.3322	5.3183	5.3086	5.3029	5.2983	5.2983	5.3001	5.3049	5.3139	5.3264	5.3404
	.004592	−.003034	5.3435	5.3312	5.3225	5.3168	5.3141	5.3141	5.3174	5.3252	5.3343	5.3472	5.3608

The apparatus and the experimental procedures employed in this work were essentially as described by Bates and Acree [26]. The temperature of the bath containing the cells was maintained within ±0.02° C of the nominal temperatures. The temperature sequence used, with a few exceptions, was 25°, 15°, 5°, 0°, 10°, 20°, 30°, 40°, 50°, 45°, 35°, and 25° C. Individual emf readings were discarded if the cell potential varied by more than 0.2 mv from the smooth curve obtained by plotting emf against temperature. All measured values for a given solution were discarded if the final value of 25° C differed from the initial value by more than 0.3 mv.

The cells usually attained their equilibrium values in about 30 min after each change in temperature. Equilibrium was judged to have been reached when readings of the same set of electrodes taken 10 min apart differed by 0.03 mv or less.

4. Results and Calculations

The values of $-\log (f_{\mathrm{H}} f_{\mathrm{Cl}} m_{\mathrm{H}})$ for each solution from 0° to 50° C are assembled in table 1. The solutions were composed of potassium hydrogen malate (molality α) and potassium chloride (molality 0.008), and some of them also contained perchloric acid or potassium hydroxide (molality $\pm\beta$). A positive value of β signifies the presence of perchloric acid, whereas a negative value indicates that potassium hydroxide had been added. Each figure for $-\log (f_{\mathrm{H}} f_{\mathrm{Cl}} m_{\mathrm{H}})$ represents the mean value derived from the two pairs of electrodes in the same cell.

4.1. Calculation of K_1

The quantities X and Y, computed by means of eq (13) and (14), were plotted as a function of ionic strength. Different curves were obtained for each series of solutions and for the same series at different temperatures. Two representative plots are shown in figures 1 and 2. The values of X and Y corresponding to ionic strengths of 0.06, 0.05, 0.04, 0.03, 0.025, 0.02, and 0.014 were obtained by interpolation on each curve.

A second series of graphs was prepared, in which Y was plotted as a function of X at each of the seven values of the ionic strength and at each of the 11 temperatures. These plots consisted of straight lines, as shown in figure 3. The position of each line was determined by the method of least squares. The logarithm of the *slope* (σK_1) of these lines was next plotted as a function of ionic strength at each temperature (compare fig. 4). The least-squares straight line drawn through the points was extended to $\mu=0$, where $\log \sigma K_1 = \log K_1$. The mean deviation of the individual values of $\log \sigma K_1$ from the line was ±0.0010 unit. The values of $\log K_1$ obtained in this way are summarized in table 2.

4.2. Calculation of K_2

The second dissociation constant was derived from the *intercepts* ($K_1 K_2/\rho$) of the plots of Y with respect to X. If the experimental errors for all of the meas-

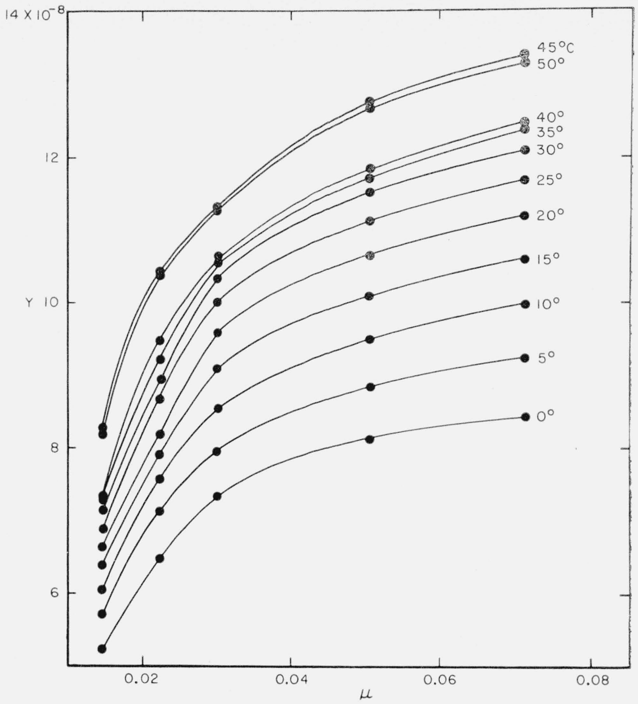

FIGURE 1. *Values of X from 0° to 50° C plotted as a function of ionic strength.*

Series 1.

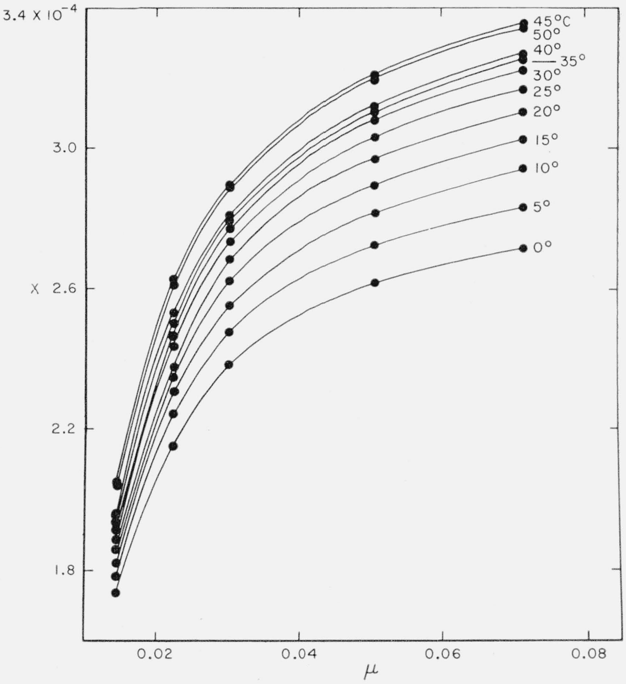

FIGURE 2. *Values of Y from 0° to 50° C plotted as a function of ionic strength.*

Series 1.

ured points were about equal in magnitude, it is to be expected that the best values of the intercept would be obtained by the shortest extrapolations. For this reason, only the data derived from the four series (4 through 7) composed of the least acidic solutions ($\beta \leq 0$) with the smallest values of X and Y were used to derive K_2. The value of K_1K_2/ρ corresponding to each of these experimental points was computed from the individual values of X and Y, together with the slope of the appropriate X, Y plot determined by the method of least squares.

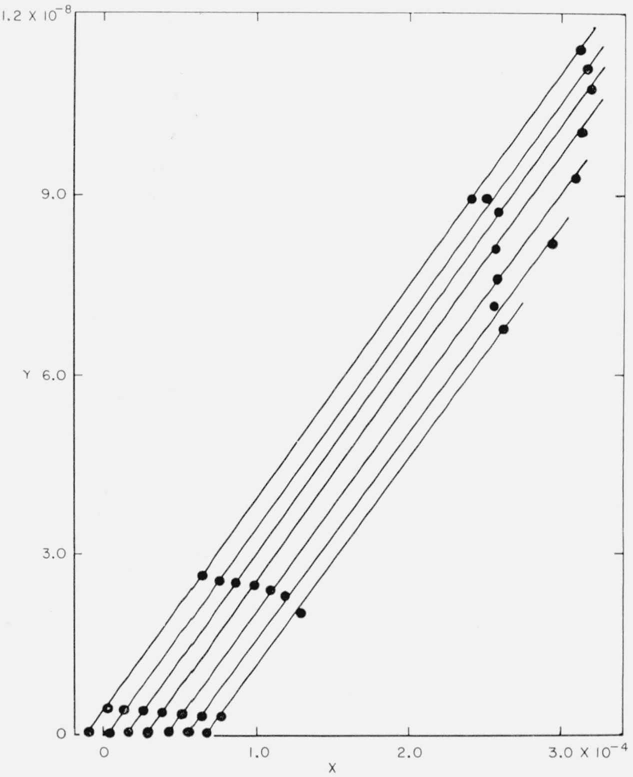

FIGURE 3. *Plots of Y versus X at 25° C.*

From left to right, the lines correspond to ionic strengths of 0.06, 0.05, 0.04, 0.03, 0.025, 0.020, and 0.014. The axis of ordinates has been transposed to the right by 0.125 unit for each successive member.

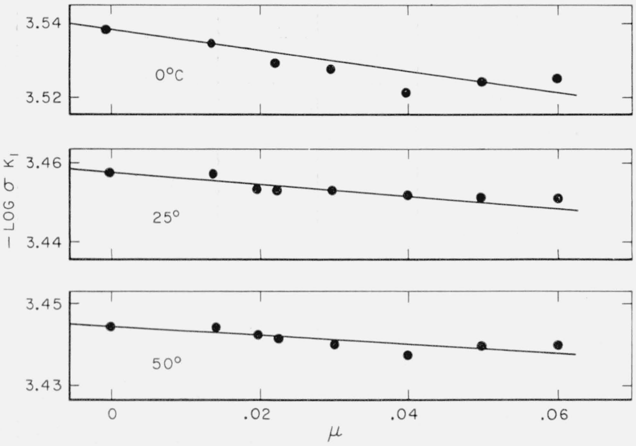

FIGURE 4. *Plots of –log σK_1 at 0°, 25°, and 50° C as a function of ionic strength.*

TABLE 2. *Summary of log K_1 and K_1 from 0° to 50° C*

Temperature	$-\log K_1$	$K_1 \times 10^4$
° C		
0	3. 537$_7$	2. 90
5	3. 520$_2$	3. 02
10	3. 494$_5$	3. 20
15	3. 482$_5$	3. 29
20	3. 472$_5$	3. 37
25	3. 458$_6$	3. 48
30	3. 452$_0$	3. 53
35	3. 446$_9$	3. 57
40	3 444$_0$	3. 60
45	3. 446$_3$	3. 58
50	3. 445$_2$	3. 59

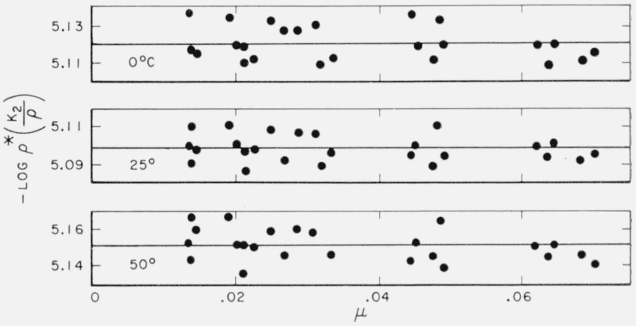

FIGURE 5. *Plots of –log $\rho^*(K_2/\rho)$ at 0°, 25°, and 50° C as a function of ionic strength.*

The values of log $\rho^*(K_2/\rho)$ were independent of ionic strength, within experimental error, as can be seen in figure 5. It appears, therefore, that ρ^* calculated by eq (17) is a very good representation of ρ at these ionic strengths, and it follows that $\rho^*(K_2/\rho)$ is equal to K_2. The mean values of log K_2 at each temperature are summarized in table 3. An arbitrary weight of 2 was assigned to those values computed from the 10 solutions (series 4) which contained neither strong acid nor strong base. For these solutions, β was 0. The values of X were consequently small, and errors in establishing the slope of the X, Y line had only a slight influence on the intercepts obtained.

TABLE 3. *Summary of log K_2 and K_2 from 0° to 50° C*

Temperature	Number of solutions	$-\log K_2$	Standard deviation of mean	$K_2 \times 10^6$
° *C*				
0	25	5. 119$_4$	0. 0014	7. 60
5	25	5. 108$_5$	. 0014	7. 79
10	25	5. 098$_8$	. 0013	7. 97
15	25	5. 096$_0$	. 0013	8. 02
20	25	5. 096$_2$	. 0012	8. 01
25	25	5. 097$_4$	. 0012	7. 99
30	25	5. 099$_5$	. 0012	7. 95
35	24	5. 104$_5$	. 0015	7. 86
40	24	5. 117$_9$	. 0014	7. 62
45	24	5. 133$_0$	. 0014	7. 36
50	24	5. 149$_4$	. 0015	7. 09

4.3. Dissociation Constants and Temperature

The values of $\log K_1$ and $\log K_2$ can be expressed by the equation suggested by Harned and Robinson [27], namely

$$-\log K=\frac{A}{T}+B+CT \qquad (23)$$

The parameters A, B, and C were determined by the method of least squares, and the following results were obtained:

$$-\log K_1=\frac{1358.85}{T}-5.1382+0.013550\, T \qquad (24)$$

and

$$-\log K_2=\frac{1658.53}{T}-6.2364+0.019353\, T, \qquad (25)$$

where T is the temperature on the Kelvin scale. The average differences between the "observed" values of $\log K_1$ and $\log K_2$ at the 11 temperatures and the corresponding values calculated by eq (24) and (25) were 0.0013 unit and 0.0011 unit, respectively.

4.4. Comparison With Earlier Work

A considerable number of determinations of the dissociation constants of malic acid has been made in the last half century. The values obtained by these earlier workers have been assembled in table 4. The columns headed K_1' and K_2' list values of the "concentration constants", uncorrected for activity coefficients. The columns headed K_1 and K_2 give values for the thermodynamic constants. Unless the author made a definite statement that activity coefficients had been used to correct the equilibrium equations, it was assumed that the dissociation constants had been calculated on a concentration basis. The values of the "concentration" dissociation constants K_1' and K_2' listed in table 4 are uniformly higher than the thermodynamic dissociation constants. This is to be expected, since the activity-coefficient correction would decrease the value of the dissociation constant in dilute solutions.

It is clear from table 4 that agreement between the results of various workers is much better for the first constant than for the second constant. All of the earlier values of K_2 are somewhat lower than those found in this investigation. Only the electrometric determination of K_2 by Larsson [28] agrees well with the value reported here. No statement can be made about the relative accuracy of these earlier determinations of K_2.

5. Thermodynamics of the Dissociation Processes

The thermodynamic quantities associated with the two dissociation steps were computed by the following equations:

$$\Delta G^\circ=2.3026\, R(A+BT+CT^2) \qquad (26)$$
$$\Delta H^\circ=2.3026\, R(A-CT^2) \qquad (27)$$
$$\Delta S^\circ=-2.3026\, R(B+2CT) \qquad (28)$$
$$\Delta C_p^\circ=-2.3026\, R(2CT) \qquad (29)$$

where R is the gas constant, 8.31439 j deg^{-1}mole^{-1}. The thermodynamic constants are summarized in table 5.

TABLE 4. *Summary of reported values of the first and second dissociation constants of malic acid*

Author	Year	Method	Temperature	$K_1'\times10^4$	$K_1\times10^4$	$K_2'\times10^6$	$K_2\times10^6$	Reference
			°*C*					
Ostwald	1889	Conductance	25	3.95	--------	--------	--------	[29]
Ostwald	1889	do	25	3.99	--------	--------	--------	[29]
Berthelot	1891	do	17	3.83	--------	--------	--------	[30]
Walden	1896	do	25	4.0	--------	--------	--------	[31]
Smith	1898	Inversion of sucrose	100	[a] 3.99	--------	8.3	--------	[32]
Wegscheider	1902	Conductance	17	[a] 4.0	--------	7.5	--------	[33]
Dhar and Datta	1913	Solubility	--------	--------	--------	9.0	--------	[34]
Larsson	1922	emf	18	[a] 4.0	--------	--------	7.8	[35]
Auerbach and Smolczyk	1924	do	20	3.86	--------	13.9	--------	[6]
Bjerrum	1924	do	15	4.0	--------	--------	--------	[36]
Coops	1924	Conductance	25	3.76	--------	--------	--------	[37]
Larsson	1924	do	15	--------	3.32	--------	--------	[38]
Larsson	1924	do	18	[a] 4.0	--------	--------	6.9	[28]
Roth and Wilms	------	do	25	3.93	--------	--------	--------	[39]
Mizutani	1925	emf	18	4.7	--------	13.5	--------	[40]
Larsson	1926	Solubility	25	[a] 4.0	--------	--------	7.3	[41]
Duboux and Frommelt	1927	Rate of decomposition of diazoacetic ester.	25	[a] 3.95	--------	--------	7.4	[42]
This investigation	------	emf without liquid junction	15	--------	3.29	--------	8.02	--------
			20	--------	3.37	--------	8.01	--------
			25	--------	3.48	--------	7.99	--------

[a] The value of K_1 was obtained from the data of Ostwald [29] and used to calculate K_2.

TABLE 5. *Thermodynamic quantities for the dissociation of malic acid and hydrogen malate ion from 0° to 50° C*

Temperature	$\Delta G°$	$\Delta H°$	$\Delta S°$	$\Delta C_p°$
Process: $H_2Mal \leftrightarrows H^+ + HMal^-$				
° *C*	*j mole*$^{-1}$	*j mole*$^{-1}$	*j deg*$^{-1}$ *mole*$^{-1}$	*j deg*$^{-1}$ *mole*$^{-1}$
0	18, 510	6, 662	−43. 4	−142
5	18, 730	5, 946	−46. 0	−144
10	18, 970	5, 219	−48. 6	−147
15	19, 220	4, 477	−51. 2	−150
20	19, 480	3, 723	−53. 7	−152
25	19, 750	2, 955	−56. 3	−155
30	20, 040	2, 176	−58. 9	−157
35	20, 340	1, 381	−61. 5	−160.
40	20, 680	576	−64. 1	−163
45	20, 980	−243	−66. 7	−165
50	21, 330	−1, 076	−69. 3	−168
Process: $HMal^- \leftrightarrows H^+ + Mal^=$				
0	26, 780	4, 112	−82. 9	−203
5	27. 210	3, 089	−86. 6	−206
10	27, 650	2, 049	−90. 3	−210
15	28, 120	990	−94. 0	−214
20	28, 590	−276	−97. 7	−217
25	29, 090	−1, 181	−101. 4	−221
30	29, 610	−2, 296	−105. 1	−225
35	30, 120	−3, 428	−108. 8	−228
40	30, 680	−4, 579	−112. 6	−232
45	31, 250	−5, 751	−116. 2	−236
50	31, 840	−6, 940	−120. 0	−240

6. Discussion

It is of interest to compare the dissociation constants and associated thermodynamic quantities for the three structurally related acids, succinic, malic and tartaric. The constants *A*, *B*, and *C* of eq (23) for the dissociation constants of these three acids are as follows:

		A	*B*	*C*
K_1	Succinic acid	1206. 25	−3. 3266	0. 011697
	Malic acid	1358. 85	−5. 1382	. 013550
	Tartaric acid	1525. 59	−6. 6558	. 015336
K_2	Succinic acid	1679. 13	−5. 7043	. 019153
	Malic acid	1658. 53	−6. 2364	. 019353
	Tartaric acid	1765. 35	−7. 3015	. 019276

A comparison of the thermodynamic data derived from these constants is presented in table 6.

It is noted first of all that progressive substitution of hydroxy groups on the two middle carbons enhances the strength of both acidic groups. This effect is the expected one. Thus, the value of $-\log K$ for glycolic acid [43] is 0.9 unit lower than that for acetic acid [2, 44], and that for lactic acid [45] is lower by 1.0 unit than that for propionic acid [46]. The decreases are somewhat smaller for both steps in the dissociation of the dibasic acids.

The interpretation of the changes of entropy and heat capacity associated with the dissociation of weak dibasic acids is not simple. Statistical, electrostatic, and structural factors have been discussed by Everett and his coworkers [47, 48]. It is likely that orientation of solvent molecules in the electrostatic field adjacent to the ions plays an important role in determining the sign and to some extent the magnitude of the changes of entropy and heat capacity when an acid dissociates.[5] Structural features leading to "screening" or solvent exclusion have an opposite effect. When the dissociation produces an increase of charge, as it does with uncharged acids and with acid anions, the increased solvent orientation and attendant immobilization of solvent molecules should bring about a decrease in both heat capacity and entropy. Indeed, $\Delta S°$ and $\Delta C_p°$ for acids of these types are almost invariably negative.

Although solvent orientation is recognized as a factor of primary importance, other factors often outweigh its effect, as shown by the contrary variation of $\Delta S°$ and $\Delta C_p°$ with chain length in a series of acids of the same charge type [47], and by the fact that the values of $\Delta S°$ for the dissociation of some cationic acids are negative while $\Delta C_p°$ is positive [51, 52]. At the present time, even qualitative predictions are often of little value.

It is nevertheless worthwhile to compare the observed values of these thermodynamic quantities for acids of like structure, to note the similarities, and to attempt to explain the differences. The constancy of $\Delta C_p°$ for the second dissociation steps is perhaps the most striking feature of the comparison given in table 6. The regular increase of $\Delta S°$ from succinic acid to tartaric acid suggests that progressive substitution of the two carbon atoms lying between the carboxyl groups is accompanied by an increased exclusion of solvent molecules. The concomitant decrease of $\Delta C_p°$ for the first dissociation step is also regular, but the reason for a change in this direction is not readily apparent.

TABLE 6. *Comparison of the thermodynamic constants for the two dissociation steps of succinic, malic, and tartaric acids at 25° C*

Acid	First step				Second step			
	$-\log K_1$	$\Delta H°$	$\Delta S°$	$\Delta C_p°$	$-\log K_2$	$\Delta H°$	$\Delta S°$	$\Delta C_p°$
		j mole^{-1}	*j deg*$^{-1}$ *mole*$^{-1}$	*j deg*$^{-1}$ *mole*$^{-1}$		*j mole*$^{-1}$	*j deg*$^{-1}$ *mole*$^{-1}$	*j deg*$^{-1}$ *mole*$^{-1}$
[a] Succinic $COOH\text{-}CH_2\text{-}CH_2\text{-}COOH$	4. 207	3, 186	−70	−134	5. 636	−450	−109	−219
Malic $COOH\text{-}CHOH\text{-}CH_2\text{-}COOH$	3. 459	2, 955	−56	−155	5. 097	−1181	−101	−221
[b] Tartaric $COOH\text{-}CHOH\text{-}CHOH\text{-}COOH$	3. 036	3, 100	−48	−170	4. 366	990	−80	−220

[a] Pinching and Bates [14, 53].
[b] Bates and Canham [15].

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[5] See, for example, references [49] and [50].

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WASHINGTON, December 9, 1958.
