# SECOND IONIZATION CONSTANT AND RELATED THERMODYNAMIC QUANTITIES FOR MALONIC ACID FROM 0° TO 60°C [1]

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### ABSTRACT

The second ionization constant of malonic acid in aqueous solution was determined at 0° to 60° C from measurements of the electromotive force of galvanic cells without liquid junction. Solutions containing sodium acid malonate, sodium malonate, and sodium chloride were employed for these determinations. From the values of the ionization constants, the closest distance of approach, or the so-called diameters, of the ions in the solution was calculated for the different temperatures. These ionic diameters, the electromotive force, and the known molalities were then employed to calculate pH values of the solutions. The ionization constant at the different temperatures was determined from the experimental data by three different methods, using a least-square calculation in each. The values are different for the various temperatures, and may be computed for temperatures from 0° to 60° C, inclusive, by the equation

$$\log K_2 = -\frac{1053.08}{T} + 20.3223 \log T - 0.05838\ T + 0.0000236\ T^2 - 37.1402.$$

Equations were formulated to express the variation of pH as a function of the ionic strength of the solution, to give the heat of ionization of the acid malonate ion, and to give the difference in the specific heats of the ions and the undissociated acid malonate ion at each temperature. The change in free energy and entropy for the ionization of the acid malonate ion were also calculated for each temperature. All of these quantities are of importance in arriving at explanations for the variation of hydrogen-ion activity with temperature.

It has been found that solutions containing equal concentrations of sodium acid malonate, sodium malonate, and sodium chloride, each varying from 0.001 to 0.044 molal, have pH values ranging from 5.272 to 5.761 at 0° to 60° C. These solutions are suitable for use as pH standards.

## CONTENTS

[1] This paper includes data presented in a dissertation submitted by John O. Burton to the Faculty of the Graduate School of the University of Maryland, represented by M. M. Haring, of the Department of Chemistry, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1937.

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# I. INTRODUCTION

Solutions of most dibasic acids and their salts resist a change in hydrogen-ion activity on dilution or on the addition of a small amount of acid or alkali. This ability to resist a change in hydrogen-ion activity is called buffer capacity. Hence, such solutions are called buffer solutions, and they are well suited for use as solutions of a definite and known hydrogen-ion activity, or as pH standards. Only qualitative data are available on the buffer capacity, the pH values, and the thermodynamics of solutions of malonic acid and its salts, especially for a wide range of temperature. These quantities are expressed in terms of the equilibrium values for the dissociation of malonic acid. The equilibria for the two steps in the dissociation of malonic acid into its ions are represented by definite numerical quantities, called ionization constants. It is the purpose of this report to present (a) quantitative data for determinations of the second ionization constant of malonic acid, (b) pH values for some solutions of malonate salts, and (c) related thermodynamic data.

In previous reports [1, 2] [2] "apparent" [3] values of the first and second ionization constants for malonic acid at 25° C were given. These values were termed "apparent" in that only partial corrections were made for the presence of salts in the solutions which were employed for their determinations. Furthermore, these values were obtained from measurements of galvanic cells with liquid junctions. The values of the potentials of liquid junctions can only be estimated and cannot be obtained on a thermodynamic basis [3]. Hence, the values reported previously also included uncertainties arising from liquid-junction potentials. In order to determine the real or thermodynamic values of the constants and eliminate the uncertainties due to liquid junctions, measurements were made of the hydrogen-ion activities of solutions of malonate salts of different known molalities by means of galvanic cells without liquid junctions, as described in a previous Research Paper [4].

This paper will be confined to determinations of the second constant and related quantities. Values [1, 2, 5] previously reported in the literature for this constant are for temperatures of 18° and 25° C only. In practice, dibasic acids and materials containing them are frequently studied or used at other temperatures. It is, therefore, important that a knowledge of the equilibrium values for their dissociation at various temperatures be made available. With this in view, measurements were made at 5° intervals from 0° to 60° C. From measurements of the effect of temperature upon the equilibrium value, it is possible to determine the increase in the free energy, entropy, and the heat of ionization for the ionic dissociation. These thermodynamic quantities are of importance in general studies of ionic dissociation, of the effect of temperature on the hydrogen-ion activity of solutions, and for additional information about the properties and structure of organic materials in aqueous solutions.

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[2] Figures in brackets indicate the literature references at the end of this paper.
[3] The term "apparent" has also been used to designate the ionization constants of indicators and other tautomers. The ionization constant of an indicator is a complex one, involving both the ratios of the tautomeric molecules or ions and their separate ionization constants, and is, therefore, termed "apparent." See Acree, Am. Chem. J. **38**, 1 (1907); White and Acree, J. Am. Chem. Soc. **40**, 1092 (1918); and Birge and Acree, J. Am. Chem. Soc. **41**, 1031 (1919). The use here of the term "apparent" should be distinguished from its use in reference to tautomeric indicators.

## II. DISSOCIATION OF MALONIC ACID

Malonic acid, $H_4C_3O_4$, dissociates in aqueous solutions in two steps represented by the equations

$$H_2An \rightleftharpoons H^+ + HAn^- \tag{1}$$

and

$$HAn^- \rightleftharpoons H^+ + An^=, \tag{2}$$

where $H_2An$, $H^+$, $HAn^-$, and $An^=$ are employed to denote malonic acid, hydrogen ion, acid malonate ion, and malonate ion, respectively. This paper is confined to the determination of the equilibrium value for the second step in the ionization of malonic acid, and therefore, only eq 2 need be considered here. The ions represented in eq 2 exist in solution in dynamic equilibrium, which is expressed by the law of mass action [6] given by the equation

$$K_2 = \frac{a_H a_{An}}{a_{HAn}} = \frac{m_H m_{An} \gamma_H \gamma_{An}}{m_{HAn} \gamma_{HAn}}, \tag{3}$$

in which $a$, $m$, and $\gamma$ represent, respectively, the activity; the concentration of the solution in moles per 1,000 g of water, or molality; and the activity coefficient of the species denoted by subscripts; and $K_2$ represents a definite numerical value for the equilibrium at a given temperature and pressure, and is conventionally termed the second ionization constant.[4]

For determinations of $K_2$, solutions are prepared which contain only the ions of malonic acid represented in eq 3, and measurements are made of the hydrogen-ion activity of these solutions. It was shown in a previous paper [1] that an aqueous solution containing one-third or more of a mole of sodium malonate to 1 mole of sodium acid malonate will satisfy this requirement. It may be shown from known facts about the hydrolysis of these salts and the ionic equilibria that besides the $Na^+$ ions, only $H^+$, $HAn^-$, and $An^=$ ions will be present in such solutions in significant and measurable amounts. For convenience in subsequent calculations of $K_2$, solutions were prepared containing equal molal quantities of sodium acid malonate $(m_1)$ and sodium malonate $(m_2)$. Complete dissociation of these salts[5] is assumed, and hence they may be considered to ionize according to the equations

$$Na_2An \rightarrow 2Na^+ + An^= \tag{4}$$

$$NaHAn \rightarrow Na^+ + HAn^-. \tag{5}$$
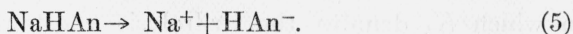
Therefore, upon substitution,

$$K_2 = \frac{m_H m_2 \gamma_H \gamma_{An}}{m_1 \gamma_{HAn}}. \tag{6}$$

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[4] If the ions in solution conformed to the law for ideal solutes, only the molalities would be used to define $K_2$. Actually, they do not; therefore, the activity coefficients are introduced to express their deviations from the laws of ideal solutes. The values of the activity coefficients are unity at infinite dilution, at which point the ions are considered to behave as ideal solutes. See Falkenhagen, Electrolytes, p. 6 [translation by Bell] (Clarendon Press, Oxford, London, 1934) for conceptions of infinite dilution.

[5] Salts of the alkaline metals are considered by most workers to be completely dissociated at all concentrations of the salt solutions. Ample justification of this assumption has been reported in the literature from results obtained from experiment and conclusions deduced from theory. See Falkenhagen, Electrolytes, p. 51 [translation by Bell] (Clarendon Press, Oxford, London, 1934); Glasstone, The Electrochemistry of Solutions, p. 134-162 (D. Van Nostrand Co., Inc., New York, N. Y., 1937); Lewis and Randall, Thermodynamics, p. 317 (McGraw-Hill Book Co., Inc., New York, N. Y., 1923).

However, the HAn⁻ion partially ionizes further in accordance with eq 2, or

$$\text{HAn}^- \text{ or } [m_1-m_\text{H}] \rightleftharpoons \text{H}^+ \text{ or } [m_\text{H}] + \text{An}^= \text{ or } [m_\text{H}] \qquad (7)$$
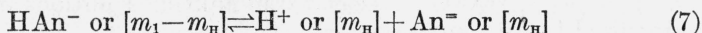
to give an additional amount of An⁼ion equal to the hydrogen-ion concentration. Therefore, the actual molality of the HAn⁻ and An⁼ ions in solution is not equal to the stoichiometrical molalities of the salts, but equal, respectively, to $[m_1-m_\text{H}]$ and $[m_2+m_\text{H}]$. Hence

$$K_2 = \frac{[m_\text{H}][m_2+m_\text{H}]\gamma_\text{H}\gamma_\text{An}}{[m_1-m_\text{H}]\gamma_\text{HAn}}. \qquad (8)$$

By measuring the hydrogen-ion activity of the solution and using the known values of $m_1$ and $m_2$, values of $K_2\gamma_\text{HAn}/\gamma_\text{H}\gamma_\text{An}$ may be obtained for a series of values of $[m_\text{H}]\,[m_2+m_\text{H}]/[m_1-m_\text{H}]$. To obtain $K_2$, values of $K_2\gamma_\text{HAn}/\gamma_\text{H}\gamma_\text{An}$ are plotted against the ionic strengths of the solutions, $\mu$, defined as half the sum of the molality of each ion multiplied by the square of its valence. Extrapolation is then made to infinite dilution, or zero ionic strength, at which point $\gamma_\text{HAn}/\gamma_\text{H}\gamma_\text{An}$ is equal to unity (see footnote 4).

Two other reactions occur between the ions in solution, both of which are insignificant in comparison with the experimental error. The ions of the dibasic salt hydrolyze according to the reaction

$$\text{An}^= + \text{H}_2\text{O} \rightarrow \text{HAn}^- + \text{OH}^-, \qquad (9)$$
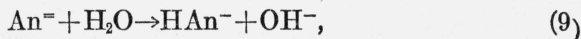
and an amount of malonic acid is formed in the reaction

$$2\text{HAn}^- \rightarrow \text{H}_2\text{An} + \text{An}^=. \qquad (10)$$

If $X$ is the molality of OH⁻ion formed in reaction 9, and $Y$ is the molality of $\text{H}_2\text{An}$ formed by reaction 10, and these reactions are assumed to occur independently, values of $X$ and $Y$ may be obtained by the mass action expressions for these reactions, or by

$$\frac{[X][\text{HAn}^- - \text{H}^+ + X]}{[\text{An}^= + \text{H}^+ - X]} = K_h = \frac{K_w}{K_2} \qquad (11)$$

and

$$\frac{[Y][\text{An}^= + \text{H}^+ + Y]}{[\text{HAn}^- - \text{H}^+ - Y]^2} = \frac{K_2}{K_1}, \qquad (12)$$

in which $K_h$ denotes the hydrolysis constant, $K_w$ the ionization constant of water, and $K_1$ the first ionization constant of malonic acid. Using 0.0009867 $M$ (the lowest molality employed in this investigation, and for which the effect of the above reactions would be greatest) for the molalities of HAn⁻ and An⁼; $1.67\times10^{-3}$ for $K_1$ [2]; $2.104\times10^{-6}$ (table 6) for $K_2$; and $1.008\times10^{-14}$ for $K_w$ [7] in the equations, $X$ and $Y$ are found to be $4.5\times10^{-9}$ $M$ and $1.23\times10^{-6}$ $M$, respectively, at 25° C. These amounts are so small that reactions 9 and 10 may be disregarded, and eq 8 may therefore be used for calculations of accurate values of $K_2$. Simultaneous occurrence of these reactions in solution, which is the case, would give even smaller values of $X$ and $Y$.

## III. EXPERIMENTAL

### 1. MATERIALS

Malonic acid obtained from the Eastman Kodak Co. was used for the preparation of the solutions. Its purity (98.92 percent) was determined by titration with a standardized solution of carbonate-free sodium hydroxide, using phenolphthalein as the indicator. This method (neutralization equivalent) of ascertaining the purity, although subject to the usual errors of titration, is the best one available. The melting point, when measured in the usual manner, is not sufficiently well defined to be used as a reliable test of purity [8], and the other accepted methods for the determination of molecular weights are not well adapted to malonic acid.

The malonic acid was purified as follows. It was triturated, washed six times with redistilled carbon tetrachloride to remove esters, and dried at 60° C. (higher temperatures cause decomposition) for 48 hours. It was then extracted with diethyl ether (previously dried over metallic sodium and redistilled) in a Soxhlet extractor, and then dried under reduced pressure at 60° C for 96 hours to remove the ether. It was finally rewashed with redistilled carbon tetrachloride and dried at 60° C for 96 hours. The purity of the acid was found by titration to be 99.88 percent by weight. A second and third repurification removed no more impurities. A small portion of the purified acid was then extracted and recrystallized from a mixture of benzene and ether containing 5 percent of petroleum ether, recommended as a solvent for purification of malonic acid by Vogel [9]. No more impurities were removed by this solvent. The purity of the malonic acid used in this work was 99.84 to 99.92 percent by weight, based on an estimated error of 0.04 percent in titration. The ash content determined by ignition of a portion to a dull red heat in a platinum crucible was 0.005 to 0.007 percent. In the preparation of the solutions, allowance was made for the percentage of inert impurities, which were considered to be due to the occlusion of the solvent used in the purification.

The sodium hydroxide solution was prepared from high-grade material which exceeded the ACS specifications for analytical reagents.[6] It was freed of carbonate by preparing a saturated solution, siphoning off the supernatant liquid above the insoluble sodium carbonate into a bottle, and diluting to 0.5 $N$ with deaerated conductivity water. In all manipulations with sodium hydroxide solutions, the apparatus was protected from the atmosphere by soda-lime tubes, or by passing a stream of $CO_2$-free air over the apparatus or solutions. The solution was standardized against benzoic acid, National Bureau of Standards Sample 39e, using phenolphthalein solution as the indicator. Results of four titrations agreed to 0.02 percent.
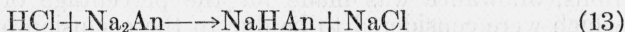
The hydrochloric acid solution was prepared by the method of Brunel and Acree [10]. Hydrogen chloride gas formed in a Kipp generator by the action of concentrated sulfuric acid on ammonium

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[6] Analysis was made by the Chemistry Division of this Bureau.

chloride was passed into conductivity water. After leaving the generator, the gas was passed at a rate of two bubbles per second through a wash bottle containing concentrated sulfuric acid. The hydrochloric acid was tested and found free of sulfate. The concentration of the acid was determined in two ways. One was by weighing the flask containing a known weight of conductivity water before and after the introduction of the gas, and subsequent calculation of the molality. The other was by weight titration with the standardized sodium hydroxide solution, using phenolphthalein as the indicator. The two analyses agreed to 0.04 percent.

## 2. SOLUTIONS

The solutions employed in this investigation were prepared from a stock solution, containing equal molal quantities ($0.09923\ M$) of sodium malonate, sodium acid malonate, and sodium chloride, by dilution with known weights of conductivity water freed of dissolved air and carbon dioxide. The specific conductance of the water was $1.0 \times 10^{-6}$ mho. The presence of chloride ion in the solutions is required for the emf method without liquid junctions (section IV) used in this investigation. Four liters of stock solution was prepared from purified materials as follows. A weighed amount of dry malonic acid in a 4-liter flask was completely neutralized by a calculated amount of standardized sodium hydroxide ($0.5\ N$ and carbonate-free) added from a weight burette. Completeness of the neutralization was tested by using phenolphthalein indicator with a small measured portion of the solution. To this solution of sodium malonate, purified and standardized hydrochloric acid ($0.5\ N$) was added from a weight burette, in an amount calculated to be sufficient to convert only half of the sodium malonate to sodium acid malonate and sodium chloride, according to the reaction

$$HCl + Na_2An \longrightarrow NaHAn + NaCl \tag{13}$$

The final solution, therefore, contained equal molal quantities of NaCl, NaHAn, and $Na_2An$. The molality of the stock solution was calculated from the known weights of malonic acid, sodium hydroxide, hydrochloric acid, and the final weight of the solution. The molality was known with an uncertainty of not more than 0.06 percent (titration error $\approx 0.04$ percent; dilution error $\approx 0.02$ percent). Weights calibrated by the Mass Section of the National Bureau of Standards were used. Weighings were made in a constant temperature room at $25°\ C \pm 0.2°\ C$ and at about 50-percent relative humidity. All weights were corrected to the "vacuum" basis.

The dissolved gases in the solutions were removed by bubbling hydrogen gas through them for 2 hours. The solutions were not boiled, because it is known that malonic acid decomposes in aqueous

solutions heated above 66° C [11]. Corrections for loss of water from the solutions during this operation were made by determining their weights before and after the deaeration.

### 3. APPARATUS

The apparatus employed in this investigation, including the cells, bubble tubes, electrodes, thermostat, and the emf recording instruments, were described in detail in a previous paper [4]. Suffice it to say that the cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled to about 0.01° C, and the emf was measured by means of a calibrated potentiometer with galvanometer and standard cell. The emf values were corrected to 1 atmosphere of hydrogen pressure in the usual manner [12].

### IV. ELECTROMOTIVE-FORCE MEASUREMENTS

The galvanic cell employed may be represented by

$$Pt|H_2(g)|NaHAn(m_1),\ Na_2An(m_2),\ NaCl(m_3)|AgCl)(s)|Ag(s),\ (14)$$
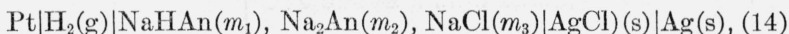
in which g=gas, s=solid, the vertical lines indicate the junction of two phases, and the commas indicate different components within one phase. This cell has no liquid junction; the two electrodes dip into the same solution. In this work, molality was chosen as the concentration unit (see reference [4] for other concentration units which may be used), since the value of molality is the same at all temperatures. The emf of this galvanic cell at 1 atmosphere of hydrogen pressure is given by

$$E=E°-\frac{RT}{F}\ln m_H m_{CL}\gamma_H\gamma_{CL},\qquad (15)$$

in which $E$ is the measured emf, $E°$ the potential of the silver-silver chloride electrode measured relative to the "normal hydrogen electrode", $R$, $T$, and $F$ have their usual meaning, and $m$ and $\gamma$ have the significance given previously in this paper.

The values of the various molalities of malonate solutions used in the galvanic cells are given in column 1 of table 1. In the other columns of this table, the emf obtained when these solutions were used in the galvanic cells are given at the designated temperatures. These values of the emf are averages of four emf measurements on the same solution, obtained as described in a previous paper [4]. The average and maximum deviations (deviations of the average emf from the four are the same within 0.01 mv at all temperatures) of individual readings of the emf from the average are listed in columns 2 and 3 of table 1. It will be noted that in all cases the maximum deviation is ±0.11 mv or less, which is equivalent to 0.0037 or less in pH units or in $pK_2$ values, pH being defined as the negative of the common logarithm of the hydrogen-ion activity and $pK_2$ as the negative of the common logarithm of the second ionization constant.

TABLE 1.—*Average emf of four measurements of the galvanic cell* Pt | $H_2$(g) | NaHAn($m_1$), $Na_2$An($m_2$), NaCl($m_3$) | AgCl(s) | Ag(s), *from 0° to 60°C*

| Concentrations of solutions | Deviation of emf from average | | Temperature in degrees centigrade | | | | | | | | | | | | |
| | Average | Maximum | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of each solute per 1,000 g of water* | mv | mv | mv | mv | mv | mv | mv | mv | mv | mv | mv | mv | mv | mv | mv |
| 0.0009867 | 0.06 | 0.11 | 703.13 | 708.74 | 714.61 | 720.76 | 727.09 | 733.50 | 739.86 | 745.80 | 751.78 | | | | |
| .0010619 | .05 | .06 | 701.56 | 707.14 | 713.04 | 719.30 | 725.49 | 731.40 | 737.43 | 743.66 | 750.08 | | | | |
| .0011095 | .01 | .02 | 700.41 | 706.22 | 712.11 | 718.08 | 724.14 | 730.23 | 736.37 | 742.51 | 748.78 | 755.14 | 761.56 | 767.98 | 774.66 |
| .0019114 | .02 | .03 | 686.95 | 692.30 | 697.90 | 703.58 | 709.33 | 715.08 | 720.95 | 726.86 | 732.84 | 738.90 | 745.66 | 751.15 | 757.39 |
| .0019420 | .04 | .06 | 686.05 | 691.57 | 697.24 | 702.76 | 708.68 | 714.44 | 720.33 | 726.13 | 732.08 | 738.37 | 744.44 | 750.63 | 756.83 |
| .0024182 | .01 | .02 | 680.42 | 685.98 | 691.48 | 697.06 | 702.77 | 708.53 | 714.30 | 720.09 | 725.88 | 731.47 | 737.63 | 743.68 | 749.68 |
| .0029128 | .01 | .02 | 675.80 | 681.15 | 686.65 | 692.17 | 697.71 | 703.29 | 708.95 | 714.67 | 720.45 | | | | |
| .0030385 | .02 | .03 | 674.54 | 679.93 | 685.38 | 690.76 | 696.31 | 701.95 | 707.44 | 713.09 | 718.84 | 724.60 | 730.54 | 736.44 | 742.54 |
| .0040020 | .01 | .02 | 667.61 | 672.85 | 678.19 | 683.56 | 689.03 | 694.42 | 699.93 | 705.32 | 710.79 | 716.54 | 722.12 | 727.68 | 733.34 |
| .0047561 | .03 | .04 | 663.26 | 668.41 | 673.62 | 678.86 | 684.16 | 689.45 | 694.84 | 700.20 | 705.65 | 711.04 | 716.53 | 722.32 | 727.94 |
| .0050248 | .01 | .02 | 661.45 | 666.54 | 671.72 | 676.98 | 682.33 | 687.67 | 693.10 | 698.55 | 704.16 | | | | |
| .0068161 | .03 | .05 | 653.84 | 658.87 | 664.00 | 669.01 | 674.05 | 679.21 | 684.35 | 689.54 | 694.76 | 700.00 | 705.16 | 710.75 | 716.17 |
| .0068596 | .01 | .02 | 653.39 | 658.29 | 663.34 | 668.45 | 673.57 | 678.77 | 683.98 | 689.19 | 694.52 | 699.82 | 705.25 | 710.82 | 716.70 |
| .0094543 | .02 | .02 | 645.06 | 649.92 | 654.82 | 659.70 | 664.60 | 669.57 | 674.56 | 679.59 | 684.67 | 689.81 | 694.97 | 700.19 | 705.38 |
| .0095398 | .01 | .02 | 644.78 | 649.42 | 654.39 | 659.16 | 664.26 | 669.23 | 674.30 | 679.36 | 684.43 | 689.42 | 694.87 | 699.99 | 705.09 |
| .018622 | .01 | .02 | 626.64 | 631.14 | 635.62 | 640.23 | 644.78 | 649.30 | 654.00 | 658.64 | 663.36 | 668.00 | 672.74 | 677.42 | 682.17 |
| .029535 | .01 | .02 | 613.93 | 618.16 | 622.46 | 626.74 | 631.01 | 635.40 | 639.71 | 644.11 | 648.50 | 652.84 | 657.25 | 661.72 | 666.24 |
| .044566 | .01 | .02 | 602.30 | 606.29 | 610.37 | 614.42 | 618.48 | 622.63 | 626.74 | 630.85 | 635.01 | 639.19 | 643.40 | 647.60 | 651.87 |

## V. CALCULATION OF THE SECOND IONIZATION CONSTANT OF MALONIC ACID

The second ionization constant of malonic acid is calculated for each temperature by means of eq 6,[7] which defines the constant in terms of the ionic activities, and by eq 15, which gives the hydrogen-ion activity in terms of the measured emf. Upon solving for the hydrogen-ion molality in these two equations, converting to common logarithms, and rearranging, the equations

$$-\log m_H = -\log K_2 - \log \frac{m_{HAn}}{m_{An}} - \log \frac{\gamma_{HAn}}{\gamma_H \gamma_{An}} \qquad (16)$$

and

$$-\log m_H = \frac{(E-E^0)F}{2.3026RT} + \log m_{Cl} + \log \gamma_H \gamma_{Cl} \qquad (17)$$

result. Elimination of $-\log m_H$ from these equations and rearrangement, keeping all the measured quantities on the left side, gives

$$\frac{(E-E^0)F}{2.3026RT} + \log m_{Cl} + \log \frac{m_{HAn}}{m_{An}} = -\log K_2 - \log \frac{\gamma_{Cl}\gamma_{HAn}}{\gamma_{An}}. \qquad (18)$$

All terms on the left side of this equation are known from experiment, hence values of $-\log K_2 - \log \gamma_{Cl}\gamma_{HAn}/\gamma_{An}$ may be obtained for various molalities of malonate solutions. The logarithm of the ratio containing the activity coefficients becomes zero at infinite dilution or at zero ionic strength (see footnote 4). Hence, if values of the left side of eq 18 for various molalities are plotted against the ionic strength, extrapolation gives the value of $-\log K_2$ at the intercept at zero ionic strength. Extrapolation can be made with more certainty by using the equations of Debye and Hückel [13].

Debye and Hückel, from theoretical considerations of the electrostatic forces between positive and negative ions and assuming that the ions are point charges, obtained the equation [8]

$$\log \gamma_i = -Az^2_i \sqrt{\mu} \qquad (19)$$

for the activity coefficient of an ion in terms of the ionic strength of the solution, $\mu$, its valence, $z_i$, and a general constant, $A$.[9] Experi-

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[7] To illustrate the method of calculating the constant, eq 6 is used here instead of eq 8. For accurate results, the latter is used. The H+ corrections in eq 8 are obtained by successive approximations in the following manner. After $K_2$ has been obtained by eq 18, and neglecting these corrections, it is used in eq 8 and calculations made of H+. These values of H+ are then used in eq 18 to correct $m_{HAn}$ and $m_{An}$, and new values of $K_2$ are then calculated. This arithmetical procedure is repeated until values of $K_2$ and H+ are consistent. Since H+ values are so low for the solutions investigated here, only one approximation of this type is required.

[8] In the original derivation, Debye and Hückel used concentrations in terms of moles of solute per liter of solution. In this work, because of investigations at different temperatures, concentrations in terms of moles of solute per 1,000 g of water, or molality, were employed because the values of molality do not change with a change in temperature. For dilute solutions, these terms become very nearly the same. It is of interest to note that Scatchard, Chem. Rev. **19,** 309 (1936) states that molality should be used in the Debye-Hückel equation instead of concentration as originally done by Debye and Hückel.

[9] The general constants, $A$ and $B$, used in eq 19, 20, 21, 22, 23, 24, 25, 26, and 28 are defined by

$$A = \frac{\sqrt{2\pi}}{2.3026}\left(\frac{\epsilon^2}{\sqrt{Dk(t+T_0)}}\right)^3\left(\frac{N}{1000}\right)^{1/2}$$

and

$$B = \frac{4.6052Dk(t+T_0)}{\epsilon^2} A,$$

where $\epsilon$ is the electronic charge, $N$ the Avogadro number, $D$ the dielectric constant of water, $k$ the Boltzmann constant, $t$ the temperature of the solutions in degrees centigrade, and $T_0$ the temperature of the ice point in degrees Kelvin.

mental evidence [14] has shown that this equation is valid only for very dilute solutions, 0.01 $M$ or less, and to extend its range of application it is necessary to add a term $\lambda\mu$ to the right side of eq 19. $\lambda$ is an empirical constant, the value of which must be determined from experiments, and is the slope of the straight-line portion of curve $A$, figure 1. Making this correction in eq 19 and substituting eq 19 for each activity coefficient term in eq 18 and transposing all known values to the left gives

$$\frac{(E-E^0)F}{2.3026RT}+\log m_{\mathrm{Cl}}+\log \frac{m_{\mathrm{HAn}}}{m_{\mathrm{An}}}+2A\sqrt{\mu}=-\log K_2-\lambda\mu. \tag{20}$$

Later, Debye and Hückel modified their equation to take into account the closest distance of approach of the ions, $a_i$, and obtained

$$\log \gamma_i=-\frac{Az_i'\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} \tag{21}$$

where $B$ is a general constant. Experimental evidence [14] and theoretical considerations by Hückel [13] have shown that this form of equation is valid for solutions about 0.05 $M$ or less, provided the proper value of $a_i$ is used. If an approximate value of $a_i$ is employed, it is necessary to add a term $\beta\mu$ to the right side of eq 21. $\beta$ is an empirical constant, the value of which must be determined from experiments, and is the slope of the straight-line portion of curve $B$, figure 1. Guggenheim [15] suggested using 3 angstrom units for $a_i$. $Ba_i$ is then approximately equal to unity. Using this approximate value for $a_i$ and also using $\beta\mu$, eq 21 becomes

$$\log \gamma_i=-\frac{Az_i'\sqrt{\mu}}{1+\sqrt{\mu}}+\beta\mu \tag{22}$$

Substituting this equation for each activity coefficient term in eq 18 and transposing all known terms to the left gives

$$\frac{(E-E^0)F}{2.3026RT}+\log m_{\mathrm{Cl}}+\log \frac{m_{\mathrm{HAn}}}{m_{\mathrm{An}}}+\frac{2A\sqrt{\mu}}{1+\sqrt{\mu}}=-\log K_2-\beta\mu. \tag{23}$$

There are, therefore, three expressions (eq 18, 20, and 23) which are functions of $-\log K_2$, all of which become equal to $-\log K_2$ at zero ionic strength. Using the molalities and the emf given in table 1, values of the ionic strength given by $(m_1+3m_2+m_3+2m_{\mathrm{H}})$, and the general constants given in table 2, values of the left sides of eq 18, 20, and 23 were calculated for each molality of the malonate solutions at 25° C and are given in table 3.

TABLE 2.—*Numerical values of constants at temperatures from 0° to 60° C used for calculations of the second ionization constant of malonic acid and the pH values of malonate solutions*

| Temperature, t | $\frac{2.3026RT}{F}$ | $E^0$, the normal potential of the silver-silver chloride electrode [1] | $D$, the dielectric constant of water [2] | $A$, the Debye-Hückel constant [3] | $B$, a constant in the Debye-Hückel equation | $a_i$, the average distance of approach of the ions | $B \times a_i$ |
|---|---|---|---|---|---|---|---|
| °C | v | v | | | Reciprocal A | A | |
| 0 | 0.05420 | 0.23644 | 88.15 | 0.4890 | 0.3253 | 4.99 | 1.62 |
| 5 | .05519 | .23396 | 86.12 | .4928 | .3261 | 4.98 | 1.62 |
| 10 | .05618 | .23132 | 84.15 | .4967 | .3270 | 4.96 | 1.62 |
| 15 | .05717 | .22846 | 82.23 | .5009 | .3279 | 4.89 | 1.60 |
| 20 | .05816 | .22550 | 80.36 | .5053 | .3289 | 4.81 | 1.58 |
| 25 | .05916 | .22238 | 78.54 | .5098 | .3298 | 4.75 | 1.57 |
| 30 | .06015 | .21911 | 76.76 | .5147 | .3309 | 4.64 | 1.54 |
| 35 | .06114 | .21564 | 75.03 | .5197 | .3320 | 4.53 | 1.50 |
| 40 | .06213 | .21207 | 73.35 | .5250 | .3330 | 4.42 | 1.47 |
| 45 | .06313 | .20822 | 71.70 | .5303 | .3342 | 4.29 | 1.43 |
| 50 | .06412 | .20432 | 70.10 | .5358 | .3353 | 4.12 | 1.38 |
| 55 | .06511 | .20033 | 68.53 | .5417 | .3366 | 3.96 | 1.33 |
| 60 | .06610 | .19619 | 67.00 | .5478 | .3378 | 3.76 | 1.27 |

[1] These values were calculated from the emf data obtained by Harned and Ehlers, J. Am. Chem. Soc. **54**, 1350 (1932); **55**, 652, 2179 (1933), using the numerical values of $R$, $T_0$, $F$, $k$, and $\epsilon$ given by Wensel, the numerical values of $D$ given by the equation of Wyman and Ingalls, and the densities of HCl solutions given in the Int. Crit. Tables, **3**, 54 (1928). Values of $E^0$ were obtained by the method of Harned and Ehlers, except that the method of least squares was used instead of a graphical method (data below 0.03 M HCl were employed). These values agree with the values reported by Harned and Ehlers within 0.1 mv.

[2] Values of $D$ were calculated from the equation of Wyman and Ingalls, J. Am. Chem. Soc. **60**, 1182 (1938). This equation is $D=78.54[1-4.579\times10^{-3}(t-25)+1.19\times10^{-5}(t-25)^2-2.8\times10^{-8}(t-25)^3]$.

[3] Values of $A$ were calculated, using $R=8.3142$ absolute joules deg⁻¹ mole⁻¹, $F=96,490$ absolute coulomb mole⁻¹; $\epsilon=4.800\times10^{-10}$ esu; $k=1.380\times10^{-16}$ erg deg⁻¹; and $T_0=273.16°$ K, given by Wensel, J. Research NBS **22**, 375 (1939) RP1189. The value of $N=6.026\times10^{23}$ was obtained by the relation $N=Fc/\epsilon$, where $c=2.99776 \times10^{10}$ cm sec⁻¹, the velocity of light or the conversion factor between electrostatic and electromagnetic units. $E$ and $E^0$ were measured in international volt and were converted to absolute units for subsequent calculations.

TABLE 3.—*Values of the left sides of eq 18, 20, 23, and 25 at 25° C for different molalities of sodium malonate solutions*

| Concentration of solutions | Values of the left side of eq 18 | Values of the left side of eq 20 | Values of the left side of eq 23 | Values of the left side of eq 25 | Estimated uncertainties in these values corresponding to the maximum deviations in the emf [1] |
|---|---|---|---|---|---|
| Moles of each solute per 1,000 g of water | | | | | |
| 0.0009867 | 5.6328 | 5.7039 | 5.6993 | 5.6969 | 0.0037 |
| .0010619 | 5.6293 | 5.7031 | 5.6982 | 5.6956 | .0020 |
| .0011095 | 5.6287 | 5.7041 | 5.6989 | 5.6984 | .0004 |
| .0019114 | 5.6096 | 5.7085 | 5.6998 | 5.6955 | .0009 |
| .0019420 | 5.6057 | 5.7054 | 5.6966 | 5.6922 | .0022 |
| .0024182 | 5.6012 | 5.7125 | 5.7016 | 5.6963 | .0007 |
| .0029128 | 5.5935 | 5.7159 | 5.7028 | 5.6964 | .0005 |
| .0030385 | 5.5893 | 5.7141 | 5.7006 | 5.6940 | .0011 |
| .0040020 | 5.5818 | 5.7250 | 5.7075 | 5.6993 | .0007 |
| .0047561 | 5.5729 | 5.7290 | 5.7083 | 5.6987 | .0015 |
| .0050248 | 5.5666 | 5.7271 | 5.7054 | 5.6953 | .0007 |
| .0068161 | 5.5561 | 5.7431 | 5.7143 | 5.6914 | .0018 |
| .0068596 | 5.5515 | 5.7390 | 5.7100 | 5.6970 | .0006 |
| .0094543 | 5.5353 | 5.7555 | 5.7167 | 5.6985 | .0005 |
| .0095398 | 5.5335 | 5.7547 | 5.7155 | 5.6981 | .0005 |
| .018622 | 5.4887 | 5.7977 | 5.7261 | 5.6959 | .0005 |
| .029535 | 5.4525 | 5.8417 | 5.7348 | 5.6906 | .0005 |
| .044566 | 5.4154 | 5.8934 | 5.7426 | 5.6961 | .0007 |

[1] These uncertainties are the same for all temperatures from 0° to 60° C.

It will be seen that the values calculated in molality terms alone by eq 18 (column 2, table 3) are different for the various values of the molality; hence a conversion to activity units must be made. In column 3, values obtained by using the Debye-Hückel equation, in which ions are assumed to be point charges, are given. These likewise vary with molality, but in opposite direction from those obtained in molality units, indicating that the Debye-Hückel equation gives too large a correction. In column 4 are given the values obtained by eq 23, assuming the closest distance of approach of the ions to be 3 Å. These values show a variation with molality which is smaller than the one obtained by assuming that the ions are point charges. In figure 1 these three sets of values are shown plotted against the ionic
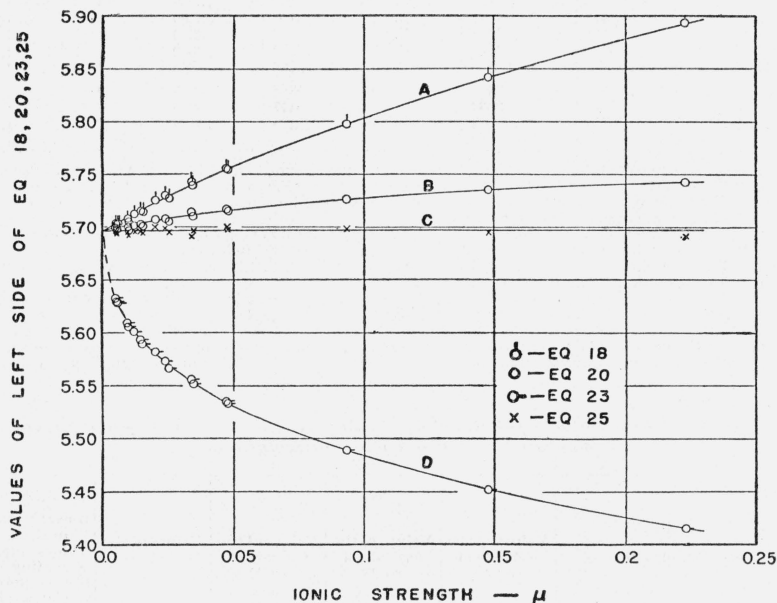


FIGURE 1.—*Plots of the values of the left sides of equations 18, 20, 23, and 25 for different molalities of solutions of sodium malonate salts against the ionic strength, at 25° C.*

strength. It will be noted that all three sets converge to the same point at zero ionic strength, at which point the value of $-\log K_2$ is obtained. Extrapolation of the lower curve, D, is difficult, but extrapolation of the upper two curves, A and B, to zero ionic strength may be made with certainty. To insure better extrapolation, the method of least squares was employed.[10] By this method, a value of 5.6959

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[10] Values for the three most concentrated solutions were not used. The others are all on a straight line within the experimental error, and the method of least squares was used with a linear equation through these points.

was obtained for $-\log K_2$ from the top curve, $A$, and a value of 5.6960 was obtained for $-\log K_2$ from the second curve, $B$. Since these two curves give identical values of $-\log K_2$, it is of interest to see if a value may be obtained for $a_i$ which, when used to calculate $-\log K_2$, will give the same value at all the molalities of malonate solutions. Substituting eq 21 for each activity coefficient term in eq 18 and solving for $a_i$, we have

$$a_i = -\frac{1}{B\sqrt{\mu}} - \frac{2A}{B[\log m_{Cl} + \log K_2 + \log (m_{HAn}/m_{An}) + (E - E^0)F/2.3026RT]}. \quad (24)$$

By using the values of $B$ given in column 6 of table 2, the value of $-\log K_2$ given above, the molalities of the solutions, and the emf, values of $a_i$ were calculated for 25° C for each value of $\mu$ and averaged, the average value being 4.75 A. This value of $a_i$ is an average value for the distance of approach of the ions, the $H^+$ ion being excepted. Using this value of $a_i$ in eq 21 and substituting this equation for each activity coefficient term in eq 18, we have

$$\frac{(E - E^0)F}{2.3026RT} + \log m_{Cl} + \log \frac{m_{HAn}}{m_{An}} + \frac{2A\sqrt{\mu}}{1 + 4.75B\sqrt{\mu}} = -\log K_2. \quad (25)$$

Values of $-\log K_2$ were then calculated for each molality of the malonate solutions by this equation. The values are given in column 5 of table 3 and are shown plotted against the ionic strength in figure 1, curve $C$. These values are the same, within the experimental error, at all molalities, and eq 25, therefore, gives the same values of $-\log K_2$ at all ionic strengths from 0 to 0.22 for 25° C. In the last column of table 3, the uncertainties in all four sets of values which arise from the maximum deviations in the emf are given.

Similar calculations were made for the other temperatures. In table 4, values of the left side of eq 20 are given for all the temperatures, and are shown plotted against the ionic strength in figure 2 for 0°, 25°, 45°, and 60° C. In table 5, values of the left side of eq 23 are given for all the temperatures, and are shown plotted against the ionic strength in figure 3. Values of $-\log K_2$ were obtained at each temperature from these two sets of values by the method of least squares, as described above for 25° C. Values thus obtained are given in columns 2 and 3 of table 6. It will be seen that the two sets of values of $-\log K_2$ are in close agreement. In column 4, the average of these values with the limits of uncertainty is given for each temperature. In column 5, values of $K_2$, or the second ionization constant of malonic acid, are listed. Columns 6 and 7 give the limits of uncertainty in $K_2$; the sixth gives the uncertainty due to extrapolation and the seventh gives the total uncertainty arising from the errors in the molality, the ionic strength, extrapolation, and the emf.

TABLE 4.—*Values of the left side of eq 20 from 0° to 60° C for different molalities of sodium malonate solutions*

[Ions are assumed to be point charges—Debye and Hückel]

| Concentration of solutions | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of each solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.0009867___ | 5.6741 | 5.6639 | 5.6646 | 5.6726 | 5 6864 | 5 7039 | 5.7211 | 5.7361 | 5.7533 | | | | |
| .0010619____ | 5.6797 | 5.6696 | 5.6714 | 5.6818 | 5.6937 | 5.7031 | 5.7154 | 5.7357 | 5.7605 | | | | |
| .0011095____ | 5.6793 | 5.6736 | 5.6756 | 5.6812 | 5.6911 | 5.7041 | 5.7186 | 5.7377 | 5.7605 | 5.7870 | 5.8129 | 5.8421 | 5.8765 |
| .0019114____ | 5.6906 | 5.6812 | 5.6827 | 5.6877 | 5.6969 | 5.7085 | 5.7230 | 5.7427 | 5.7653 | 5.7911 | 5.8109 | 5.8456 | 5.8774 |
| .0019420____ | 5.6816 | 5.6757 | 5.6786 | 5.6810 | 5.6935 | 5.7054 | 5.7204 | 5.7385 | 5.7608 | 5.7904 | 5.8153 | 5.8453 | 5.8768 |
| .0024182____ | 5.6843 | 5.6812 | 5.6828 | 5.6882 | 5.6987 | 5.7125 | 5.7273 | 5.7469 | 5.7683 | 5.7886 | 5.8167 | 5.8463 | 5.8765 |
| .0029128____ | 5.6906 | 5.6852 | 5.6885 | 5.6945 | 5.7032 | 5.7159 | 5.7304 | 5.7505 | 5.7730 | | | | |
| .0030385____ | 5.6885 | 5.6838 | 5.6867 | 5.6906 | 5.7003 | 5.7141 | 5.7262 | 5.7455 | 5.7682 | 5.7931 | 5.8196 | 5.8488 | 5.8823 |
| .0040020____ | 5.6978 | 5.6932 | 5.6965 | 5.7026 | 5.7132 | 5.7250 | 5.7397 | 5.7570 | 5.7774 | 5.8043 | 5.8275 | 5.8537 | 5.8827 |
| .0047561____ | 5.7051 | 5.7003 | 5.7028 | 5.7080 | 5.7173 | 5.7290 | 5.7432 | 5.7615 | 5.7831 | 5.8064 | 5.8295 | 5.8602 | 5.8900 |
| .0050248____ | 5.6996 | 5.6945 | 5.6971 | 5.7034 | 5.7141 | 5.7271 | 5.7425 | 5.7628 | 5.7875 | | | | |
| .0068161____ | 5.7172 | 5.7136 | 5.7181 | 5.7225 | 5.7305 | 5.7431 | 5.7563 | 5.7750 | 5.7954 | 5.8193 | 5.8405 | 5.8718 | 5.9026 |
| .0068596____ | 5.7122 | 5.7065 | 5.7096 | 5.7161 | 5.7256 | 5.7390 | 5.7535 | 5.7726 | 5.7955 | 5.8199 | 5.8453 | 5.8762 | 5.9128 |
| .0094543____ | 5.7293 | 5.7259 | 5.7292 | 5.7345 | 5.7431 | 5.7555 | 5.7693 | 5.7883 | 5.8100 | 5.8347 | 5.8588 | 5.8872 | 5.9165 |
| .0095398____ | 5.7290 | 5.7217 | 5.7265 | 5.7300 | 5.7421 | 5.7547 | 5.7699 | 5.7895 | 5.8111 | 5.8335 | 5.8622 | 5.8891 | 5.9171 |
| .018622_____ | 5.7693 | 5.7660 | 5.7686 | 5.7758 | 5.7849 | 5.7977 | 5.8117 | 5.8308 | 5.8531 | 5.8763 | 5.9003 | 5.9268 | 5.9558 |
| .029535_____ | 5.8123 | 5.8088 | 5.8129 | 5.8189 | 5.8280 | 5.8417 | 5.8557 | 5.8753 | 5.8969 | 5.9200 | 5.9415 | 5.9698 | 6.0018 |
| .044566_____ | 5.8618 | 5.8584 | 5.8630 | 5.8694 | 5.8793 | 5.8934 | 5.9082 | 5.9277 | 5.9500 | 5.9751 | 6.0000 | 6.0283 | 6.0591 |

TABLE 5.—*Values of the left side of eq 23 from 0° to 60° C for different molalities of sodium malonate solutions* [1]

[Closest distance of approach of the ions is assumed to be 3 A—Guggenheim]

| Concentration of solutions | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of each solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.0009867____ | 5.6697 | 5.6598 | 5.6601 | 5.6681 | 5.6818 | 5.6993 | 5.7164 | 5.7312 | 5.7485 | | | | |
| .0010619____ | 5.6750 | 5.6648 | 5.6665 | 5.6759 | 5.6887 | 5.6982 | 5.7104 | 5.7306 | 5.7556 | | | | |
| .0011095____ | 5.6743 | 5.6686 | 5.6700 | 5.6758 | 5.6860 | 5.6989 | 5.7133 | 5.7334 | 5.7553 | 5.7814 | 5.8073 | 5.8365 | 5.8708 |
| .0019114____ | 5.6823 | 5.6729 | 5.6742 | 5.6792 | 5.6882 | 5.6998 | 5.7142 | 5.7343 | 5.7562 | 5.7818 | 5.8016 | 5.8361 | 5.8679 |
| .0019420____ | 5.6732 | 5.6662 | 5.6700 | 5.6724 | 5.6847 | 5.6966 | 5.7115 | 5.7294 | 5.7516 | 5.7810 | 5.8058 | 5.8357 | 5.8670 |
| 0024182____ | 5.6739 | 5.6706 | 5.6722 | 5.6775 | 5.6869 | 5.7016 | 5.7163 | 5.7358 | 5.7570 | 5.7770 | 5.8050 | 5.8345 | 5.8644 |
| .0029128____ | 5.6781 | 5.6716 | 5.6757 | 5.6816 | 5.6906 | 5.7028 | 5.7171 | 5.7370 | 5.7593 | | | | |
| .0030385____ | 5.6752 | 5.6708 | 5.6736 | 5.6774 | 5.6869 | 5.7006 | 5.7125 | 5.7316 | 5.7542 | 5.7788 | 5.8051 | 5.8341 | 5.8673 |
| .0040020____ | 5.6811 | 5.6763 | 5.6795 | 5.6854 | 5.6959 | 5.7075 | 5.7220 | 5.7390 | 5.7592 | 5.7858 | 5.8087 | 5.8346 | 5.8633 |
| .0047561____ | 5.6855 | 5.6805 | 5.6829 | 5.6880 | 5.6970 | 5.7083 | 5.7223 | 5.7403 | 5.7617 | 5.7840 | 5.8069 | 5.8378 | 5.8673 |
| .0050248____ | 5.6790 | 5.6737 | 5.6761 | 5.6822 | 5.6926 | 5.7054 | 5.7206 | 5.7406 | 5.7649 | | | | |
| .0068161____ | 5.6898 | 5.6860 | 5.6902 | 5.6944 | 5.7020 | 5.7143 | 5.7272 | 5.7453 | 5.7660 | 5.7889 | 5.8097 | 5.8405 | 5.8698 |
| .0068596____ | 5.6847 | 5.6787 | 5.6816 | 5.6778 | 5.6969 | 5.7100 | 5.7242 | 5.7429 | 5.7654 | 5.7893 | 5.8143 | 5.8448 | 5.8811 |
| .0094543____ | 5.6923 | 5.6886 | 5.6916 | 5.6965 | 5.7047 | 5.7167 | 5.7290 | 5.7483 | 5.7696 | 5.7927 | 5.8172 | 5.8451 | 5.8736 |
| .0095398____ | 5.6917 | 5.6841 | 5.6885 | 5.7036 | 5.7034 | 5.7155 | 5.7303 | 5.7493 | 5.7704 | 5.7922 | 5.8203 | 5.8466 | 5.8739 |
| .018622_____ | 5.7013 | 5.6975 | 5.6994 | 5.7059 | 5.7142 | 5.7261 | 5.7395 | 5.7575 | 5.7789 | 5.8010 | 5.8239 | 5.8493 | 5.8771 |
| .029535_____ | 5.7104 | 5.7061 | 5.7093 | 5.7143 | 5.7222 | 5.7348 | 5.7473 | 5.7656 | 5.7859 | 5.8074 | 5.8294 | 5.8557 | 5.8841 |
| .044566_____ | 5.7170 | 5.7125 | 5.7159 | 5.7209 | 5.7291 | 5.7426 | 5.7547 | 5.7721 | 5.7925 | 5.8153 | 5.8380 | 5.8639 | 5.8922 |

[1] Acknowledgment is made to J. H. Payne, Student Assistant, summers of 1937 and 1938, for aid in calculations of the data in this table.

TABLE 6.—*Negative of the common logarithm and the numerical values of the second ionization constant of malonic acid from 0° to 60° C, as obtained by two different functions (Debye-Hückel and Guggenheim)*

| Temperature, $t$ | Values of $-\log K_2$ obtained from the values of the left side of eq 20 | Values of $-\log K_2$ obtained from the values of the left side of eq 23 | Average values of $-\log K_2$ and limits of uncertainty | Values of the second ionization constant of malonic acid, $K_2$ | Uncertainty in $K_2$ arising from the two methods used to solve for $-\log K_2$ | Total estimated uncertainty in $K_2$ arising from known uncertainties in emf, concentration, ionic strength, and extrapolation |
|---|---|---|---|---|---|---|
| °C | | | | $K_2 \times 10^6$ | | |
| 0 | 5.6699 | 5.6693 | 5.6696 ±0.0003 | 2.140 | ±0.002 | ±0.006 |
| 5 | 5.6641 | 5.6651 | 5.6646 ± .0005 | 2.165 | .003 | .007 |
| 10 | 5.6667 | 5.6675 | 5.6671 ± .0004 | 2.152 | .002 | .006 |
| 15 | 5.6723 | 5,6734 | 5.6729 ± .0005 | 2.124 | .003 | .006 |
| 20 | 5.6825 | 5.6830 | 5.6828 ± .0003 | 2.076 | .002 | .006 |
| 25 | 5.6959 | 5.6960 | 5.6960 ± .0001 | 2.014 | .001 | .006 |
| 30 | 5.7101 | 5.7107 | 5.7104 ± .0003 | 1.948 | .001 | .006 |
| 35 | 5.7294 | 5.7299 | 5.7297 ± .0003 | 1.863 | .001 | .006 |
| 40 | 5.7521 | 5.7529 | 5.7525 ± .0004 | 1.768 | .002 | .005 |
| 45 | 5.7772 | 5.7771 | 5.7772 ± .0001 | 1.670 | .001 | .006 |
| 50 | 5.8021 | 5.8030 | 5.8026 ± .0005 | 1.575 | .001 | .005 |
| 55 | 5.8333 | 5.8329 | 5.8331 ± .0002 | 1.469 | .001 | .005 |
| 60 | 5.8664 | 5.8652 | 5.8658 ± .0006 | 1.362 | .002 | .005 |



FIGURE 2.—*Plots of the values of the left side of equation 20 for different molalities of solutions of sodium malonate salts against the ionic strength at 0, 25, 45, and 60° C.*

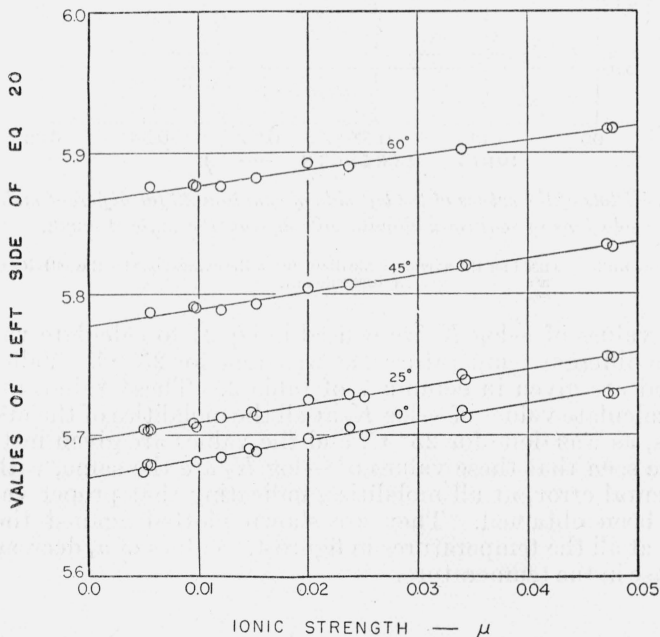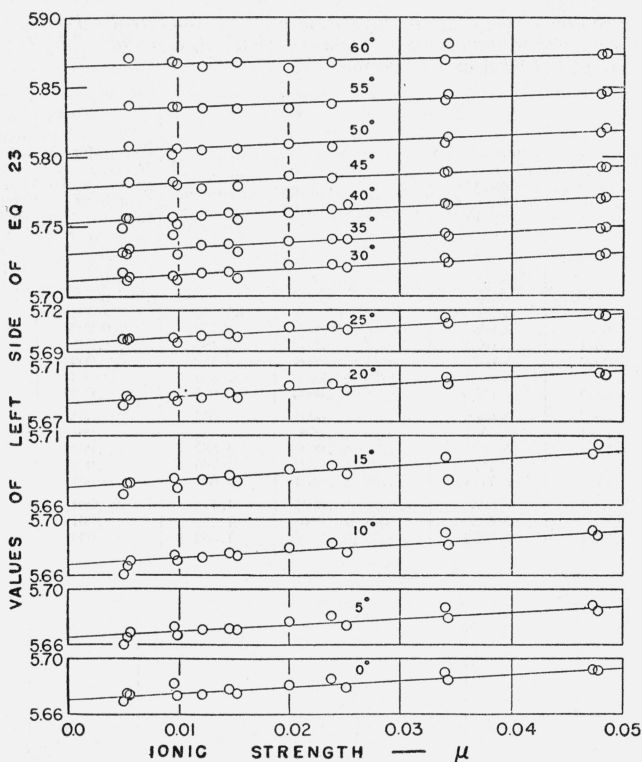Ions are assumed to be point charges (Debye-Hückel).

FIGURE 3.—*Plots of the values of the left side of equation 23 for different molalities of solutions of sodium malonate salts against the ionic strength.*

Three angstrom units was used for the average ionic diameter in the expressions for the activity coefficients (Guggenheim).

These values of $-\log K_2$ were used in eq 24 to calculate values of $a_i$ for the different temperatures, as was done for 25° C. Values thus calculated are given in column 7 of table 2. These values are then used to calculate values of $-\log K_2$ at all the molalities of the malonate solutions, as was done for 25° C, and the values are given in table 7. It will be seen that these values of $-\log K_2$ are the same, within the experimental error, at all molalities, indicating that proper values of $a_i$ have been obtained. They are shown plotted against the ionic strength at all the temperatures in figure 4. Values of $a_i$ decrease with an increase in the temperature.

TABLE 7.—*Negative of the common logarithm of the second ionization constant of malonic acid from 0° to 60° C and at various molalities of solutions of malonate salts, calculated with use of the values for the average ionic diameters given in column 7 of table 2 in expressions for activity coefficients*

| Concentration of solutions | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of each solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.0009867 | 5.6671 | 5.6572 | 5.6575 | 5.6655 | 5.6793 | 5.6969 | 5.7141 | 5.7291 | 5.7465 | | | | |
| .0010619 | 5.6722 | 5.6620 | 5.6637 | 5.6742 | 5.6860 | 5.6956 | 5.7079 | 5.7283 | 5.7534 | | | | |
| .0011095 | 5.6711 | 5.6657 | 5.6676 | 5.6729 | 5.6832 | 5.6984 | 5.7108 | 5.7300 | 5.7530 | 5.7793 | 5.8054 | 5.8348 | 5.8695 |
| .0019114 | 5.6775 | 5.6681 | 5.6694 | 5.6746 | 5.6837 | 5.6955 | 5.7100 | 5.7298 | 5.7515 | 5.7784 | 5.7985 | 5.8334 | 5.8665 |
| .0019420 | 5.6684 | 5.6624 | 5.6652 | 5.6677 | 5.6801 | 5.6922 | 5.7072 | 5.7254 | 5.7478 | 5.7776 | 5.8027 | 5.8330 | 5.8648 |
| .0024182 | 5.6681 | 5.6647 | 5.6663 | 5.6718 | 5.6824 | 5.6963 | 5.7111 | 5.7309 | 5.7524 | 5.7738 | 5.8012 | 5.8312 | 5.8617 |
| .0029128 | 5.6712 | 5.6656 | 5.6688 | 5.6749 | 5.6840 | 5.6964 | 5.7110 | 5.7312 | 5.7538 | | | | |
| .0030385 | 5.6681 | 5.6637 | 5.6664 | 5.6704 | 5.6801 | 5.6940 | 5.7062 | 5.7256 | 5.7485 | 5.7736 | 5.8005 | 5.8300 | 5.8640 |
| .0040020 | 5.6721 | 5.6673 | 5.6705 | 5.6766 | 5.6873 | 5.6993 | 5.7140 | 5.7314 | 5.7520 | 5.7792 | 5.8028 | 5.8295 | 5.8592 |
| .0047561 | 5.6750 | 5.6701 | 5.6724 | 5.6778 | 5.6870 | 5.6987 | 5.7131 | 5.7316 | 5.7533 | 5.7763 | 5.8000 | 5.8319 | 5.8624 |
| .0050248 | 5.6681 | 5.6628 | 5.6651 | 5.6715 | 5.6822 | 5.6953 | 5.7109 | 5.7314 | 5.7562 | | | | |
| .0068161 | 5.6758 | 5.6720 | 5.6761 | 5.6806 | 5.6886 | 5.6914 | 5.7147 | 5.7336 | 5.7548 | 5.7786 | 5.8005 | 5.8324 | 5.8633 |
| .0068596 | 5.6706 | 5.6646 | 5.6674 | 5.6739 | 5.6835 | 5.6970 | 5.7117 | 5.7310 | 5.7541 | 5.7789 | 5.8051 | 5.8367 | 5.8745 |
| .0094543 | 5.6732 | 5.6703 | 5.6733 | 5.6777 | 5.6873 | 5.6998 | 5.7138 | 5.7330 | 5.7550 | 5.7803 | 5.8052 | 5.8345 | 5.8651 |
| .0095398 | 5.6734 | 5.6657 | 5.6701 | 5.6737 | 5.6859 | 5.6985 | 5.7139 | 5.7338 | 5.7557 | 5.7786 | 5.8082 | 5.8360 | 5.8652 |
| .018622 | 5.6711 | 5.6672 | 5.6690 | 5.6762 | 5.6853 | 5.6981 | 5.7124 | 5.7318 | 5.7545 | 5.7785 | 5.8038 | 5.8317 | 5.8626 |
| .029535 | 5.6687 | 5.6643 | 5.6673 | 5.6733 | 5.6823 | 5.6959 | 5.7099 | 5.7301 | 5.7521 | 5.7762 | 5.8015 | 5.8312 | 5.8639 |
| .044566 | 5.6626 | 5.6580 | 5.6612 | 5.6674 | 5.6769 | 5.6906 | 5.7058 | 5.7260 | 5.7483 | 5.7743 | 5.8012 | 5.8316 | 5.8655 |
| Average | 5.6708 | 5.6651 | 5.6676 | 5.6733 | 5.6836 | 5.6961 | 5.7110 | 5.7302 | 5.7524 | 5.7774 | 5.8026 | 5.8327 | 5.8649 |
| Average deviation | 0.0027 | 0.0029 | 0.0027 | 0.0029 | 0.0025 | 0.0020 | 0.0022 | 0.0019 | 0.0022 | 0.0018 | 0.0021 | 0.0017 | 0.0025 |
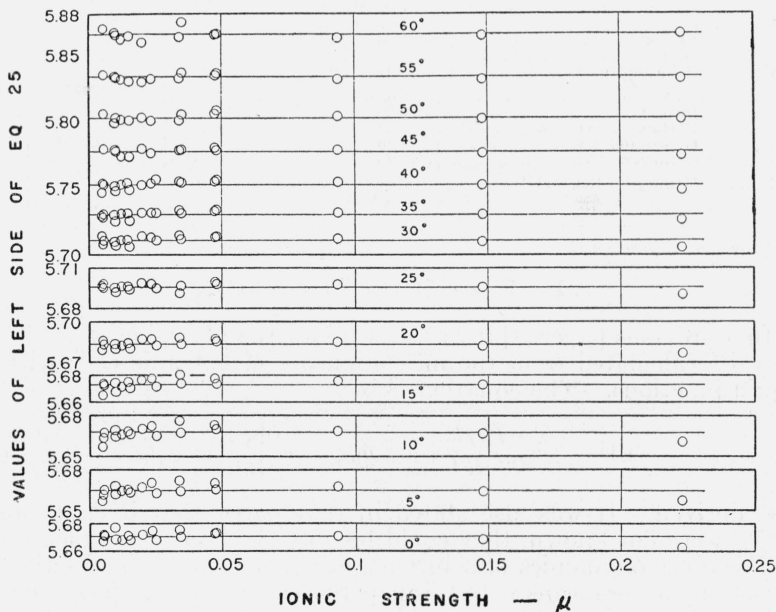


FIGURE 4.—*Plots of the values of* $-\log K_2$ *calculated by equation 25 for different molalities of solutions of sodium malonate salts against the ionic strength at temperatures from 0° to 60° C.*

Closest distance of approach of the ions at the different temperatures are given in column 7 of table 2.

The magnitude of the second ionization constant of malonic acid is different at the various temperatures. The maximum value is at a temperature of about 6° C. This variation is similar to that found for a number of other weak electrolytes [16]. Since $K_2$ expresses the ionization of the $HAn^-$ ion into $H^+$ and $An^=$ ions, the $HAn^-$ ionizes less at the higher temperatures, giving less $H^+$ ions and, therefore, decreased acidity.

In table 8 the previous values found at 18° and 25° C, as well as the corresponding ones obtained in this investigation, are listed. The table is self-explanatory.

TABLE 8.—*Values of the second ionization constant of malonic acid obtained by different workers at 18° and 25° C*

a, Estimated values.
b, Values include approximations.
c, Values include salt errors.
d, Values include values of liquid-junction potentials.

e, Empirical method used in calculation of the values.
f, Values include errors of quinhydrone electrode. (See Hovorka and Dearing, J. Am. Chem. Soc. **57**, 446 (1935), for a study of "salt errors" of the quinhydrone electrode.)

| Year | Observer | Method | $K_2 \times 10^6$ 18° C | $K_2 \times 10^6$ 25° C | Note on the values |
|---|---|---|---|---|---|
| 1898 | Smith | Sucrose inversion | | 1.0 | a |
| 1902-05 | Wegscheider | Conductivity | | 10.0 | a |
| 1908 | Chandler | Partition | | 2.03 | b |
| 1908 | do | Conductivity | | 2.1 | b |
| 1915 | Datta and Dhar | $CO_2$ absorption | | 1.36 | b |
| 1916 | Wegscheider | Conductivity | | 1.0 | a |
| 1924 | Larsson | Potentiometric titration | 2.0 | | c, e |
| 1925 | Britton | do | 4.45 | | c, d, e |
| 1928 | Simms | do | | 1.8 | d, e |
| 1928 | Gane and Ingold | do | | 4.37 | c, d |
| 1931 | do | do | | 2.03 | d |
| 1933 | Burton | do | | 3.89 | b, c, d |
| 1936 | Burton, Hamer, and Acree | do | | 2.94 | c, d |
| 1936 | Hamer and Acree | do | | 2.51 | c |
| 1936 | German and Vogel | do | | 2.20 | c, f |
| 1940 | Hamer, Burton, and Acree | Galvanic cells without liquid junctions. | ᵃ 2.102 | 2.014 | |

ᵃ Value calculated by eq 32.

## VI. pH AND pH EQUATIONS

In a previous paper [4] it was shown how the pH value of a solution may be calculated from the measurements of galvanic cells without liquid junctions. The equation

$$\text{pH} = \frac{(E-E^0)F}{2.3026RT} + \log m_{Cl} - \frac{A\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} + \beta\mu \qquad (26)$$

was derived. It was also stated in that paper that if values of $a_i$ and $\beta$ were not known, they could be obtained from a detailed study of the thermodynamics of solutions, considerations of interactions of ions, or by other means. In this paper it has been shown how accurate values of $a_i$ may be obtained from values of the ionization constant. It follows that with the use of these value of $a_i$, $\beta$ has a value of zero (see section V). Using the values of $a_i$ and $Ba_i$ given in table 2, the pH values of the malonate solutions here investigated were calculated by eq 26 and are given in table 9. The uncertainties in these pH values are the same as those given in the last column of table 3. The

pH of the malonate solutions is lower at the higher concentrations, mainly because of the increase in the salt concentration and interionic attraction given by the $-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$ term. These solutions are suitable as buffer solutions, because the change is small.

TABLE 9.—pH *values of malonate solutions from 0° to 60° C, calculated with use of the values for the closest distance of approach of the ions given in column 7 of table 2 in the expressions for activity coefficients* [1]

| Concentration of solutions | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of each solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.0009867 | 5.5774 | 5.5670 | 5.5666 | 5.5739 | 5.5866 | 5.6030 | 5.6191 | 5.6328 | 5.6588 | | | | |
| .0010619 | 5.5783 | 5.5685 | 5.5695 | 5.5782 | 5.5899 | 5.5969 | 5.6095 | 5.6286 | 5.6523 | | | | |
| .0011095 | 5.5765 | 5.5703 | 5.5714 | 5.5763 | 5.5851 | 5.5970 | 5.6103 | 5.6281 | 5.6497 | 5.6745 | 5.6989 | 5.7265 | 5.7592 |
| .0019114 | 5.5556 | 5.5455 | 5.5458 | 5.5500 | 5.5576 | 5.5679 | 5.5798 | 5.5989 | 5.6198 | 5.6437 | 5.6616 | 5.6941 | 5.7238 |
| .0019420 | 5.5456 | 5.5389 | 5.5407 | 5.5422 | 5.5530 | 5.5637 | 5.5771 | 5.5936 | 5.6152 | 5.6419 | 5.6647 | 5.6927 | 5.7219 |
| .0024182 | 5.5129 | 5.5287 | 5.5293 | 5.5336 | 5.5425 | 5.5547 | 5.5678 | 5.5856 | 5.6001 | 5.6232 | 5.6491 | 5.6764 | 5.7041 |
| .0029128 | 5.5248 | 5.5183 | 5.5203 | 5.5251 | 5.5323 | 5.5431 | 5.5557 | 5.5738 | 5.5942 | | | | |
| .0030385 | 5.5190 | 5.5137 | 5.5152 | 5.5179 | 5.5258 | 5.5379 | 5.5480 | 5.5653 | 5.5859 | 5.6084 | 5.6324 | 5.6590 | 5.6897 |
| .0040020 | 5.5047 | 5.4990 | 5.5008 | 5.5055 | 5.5140 | 5.5238 | 5.5363 | 5.5513 | 5.5693 | 5.5935 | 5.6138 | 5.6370 | 5.6628 |
| .0047461 | 5.4955 | 5.4894 | 5.4903 | 5.4941 | 5.5010 | 5.5105 | 5.5224 | 5.5382 | 5.5571 | 5.5768 | 5.5969 | 5.6248 | 5.6512 |
| .0050248 | 5.4845 | 5.4781 | 5.4790 | 5.4837 | 5.4910 | 5.5029 | 5.5159 | 5.5336 | 5.5555 | | | | |
| .0068161 | 5.4687 | 5.4637 | 5.4661 | 5.4688 | 5.4740 | 5.4841 | 5.4945 | 5.5101 | 5.5279 | 5.5478 | 5.5652 | 5.5925 | 5.6181 |
| .0068596 | 5.4630 | 5.4557 | 5.4569 | 5.4616 | 5.4683 | 5.4792 | 5.4909 | 5.5070 | 5.5266 | 5.5475 | 5.5692 | 5.5961 | 5.6287 |
| .0094543 | 5.4397 | 5.4345 | 5.4356 | 5.4387 | 5.4441 | 5.4535 | 5.4640 | 5.4794 | 5.4974 | 5.5180 | 5.5376 | 5.5613 | 5.5856 |
| .0095398 | 5.4382 | 5.4290 | 5.4316 | 5.4329 | 5.4419 | 5.4514 | 5.4633 | 5.4793 | 5.4972 | 5.5154 | 5.5397 | 5.5618 | 5.5848 |
| .018622 | 5.3731 | 5.3673 | 5.3668 | 5.3809 | 5.3756 | 5.3843 | 5.3936 | 5.4078 | 5.4249 | 5.4423 | 5.4600 | 5.4799 | 5.5017 |
| .029535 | 5.3229 | 5.3164 | 5.3167 | 5.3190 | 5.3225 | 5.3311 | 5.3390 | 5.3521 | 5.3678 | 5.3836 | 5.3993 | 5.4189 | 5.4401 |
| .044566 | 5.2720 | 5.2650 | 5.2651 | 5.2655 | 5.2700 | 5.2779 | 5.2856 | 5.2976 | 5.3120 | 5.3282 | 5.3434 | 5.3714 | 5.3811 |

[1] Uncertainties in these pH values corresponding to the maximum deviations in the emf are the same as those listed in the last column of table 3.

The pH values may also be calculated by eq 6 expressed in the form

$$pH = pK_2 - \log\frac{m_{HAn}}{m_{An}} + \log\frac{\gamma_{An}}{\gamma_{HAn}}. \qquad (27)$$

Log $\gamma_{An}/\gamma_{HAn}$ is given by $-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$. The solutions measured in this investigation were made from equal molal quantities of sodium malonate and sodium acid malonate, and therefore, the log $(m_{HAn}/m_{An})$ term is zero, except for the small $H^+$ correction (see eq 8 and footnote 7). It was found that the log $(m_{HAn}-m_{H})/(m_{An}+m_{H})$ term could be expressed by $-1.0\times10^{-4}/\mu$ at all the temperatures. With these modifications, the pH is given by

$$pH = pK_2 + 0.0001/\mu - 3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}). \qquad (28)$$

The values of $pK_2$ and $Ba_i$ have been determined and $A$ and $B$ are given in table 2. The pH values may be calculated by this equation for solutions containing equal molal quantities of sodium acid malonate and sodium malonate of any concentration between 0.001 and 0.044 $M$, and for temperatures from 0° to 60° C, inclusive, with an accuracy of $\pm0.003$ pH unit. For the convenience of the experimenter, the pH was calculated for different molalities of the malonate solutions by means of eq 28. This equation is more suitable for this purpose than eq 26. These values are given in table 10 and are shown plotted against the temperature, $t°$ C, in figure 5.

TABLE 10.—pH *values of malonate solutions from 0° to 60° C and for rounded concentration.*[1]

[pH values of pure water at the same temperatures are included for comparison]

| Rounded concentration of the solutions | $\mu$, the ionic strength | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of each solute per 1,000 g of water* | *Ionic strength per 1,000 g of water* | | | | | | | | | | | | | |
| 0.001 | 0.005 | 5.579 | 5.574 | 5.575 | 5.581 | 5.589 | 5.601 | 5.614 | 5.633 | 5.655 | 5.677 | 5.702 | 5.730 | 5.761 |
| .002 | .010 | 5.545 | 5.540 | 5.541 | 5.545 | 5.554 | 5.565 | 5.578 | 5.596 | 5.617 | 5.639 | 5.663 | 5.691 | 5.721 |
| .003 | .015 | 5.521 | 5.515 | 5 516 | 5.520 | 5.529 | 5.540 | 5.552 | 5.570 | 5.591 | 5.612 | 5.635 | 5.662 | 5.692 |
| .004 | .020 | 5.502 | 5.496 | 5.497 | 5.501 | 5.509 | 5.520 | 5.532 | 5.549 | 5.570 | 5.591 | 5.613 | 5.640 | 5.669 |
| .007 | .035 | 5.460 | 5.454 | 5.454 | 5.458 | 5.466 | 5.476 | 5.487 | 5.506 | 5.523 | 5.543 | 5.565 | 5.590 | 5.618 |
| .010 | .050 | 5.430 | 5.424 | 5.424 | 5.427 | 5.434 | 5.444 | 5.454 | 5.471 | 5.490 | 5.509 | 5.529 | 5.554 | 5.580 |
| .020 | .100 | 5.365 | 5.358 | 5.357 | 5.360 | 5.366 | 5.374 | 5.383 | 5.398 | 5.415 | 5.432 | 5.450 | 5.472 | 5.496 |
| .030 | .150 | 5.323 | 5.315 | 5.315 | 5.316 | 5.321 | 5.329 | 5.337 | 5.350 | 5.367 | 5.382 | 5.399 | 5.418 | 5.440 |
| .040 | .200 | 5.291 | 5.284 | 5.283 | 5.284 | 5.289 | 5.296 | 5.303 | 5.315 | 5.331 | 5.345 | 5.360 | 5.378 | 5.398 |
| .044 | .220 | 5.281 | 5.273 | 5.272 | 5.273 | 5.277 | 5.285 | 5.291 | 5.303 | 5.318 | 5.332 | 5.347 | 5.365 | 5.383 |
| Pure water, Harned and Hamer [7] | | 7.469 | 7.365 | 7.267 | 7.173 | 7.084 | 6.998 | 6.916 | 6.840 | 6.768 | 6.698 | 6.631 | 6.569 | 6.509 |

[1] pH is defined as the negative of the common logarithm of the hydrogen-ion activity. See reference [4] for discussion of this definition. The values in this table are accurate to ±0.003 pH unit.
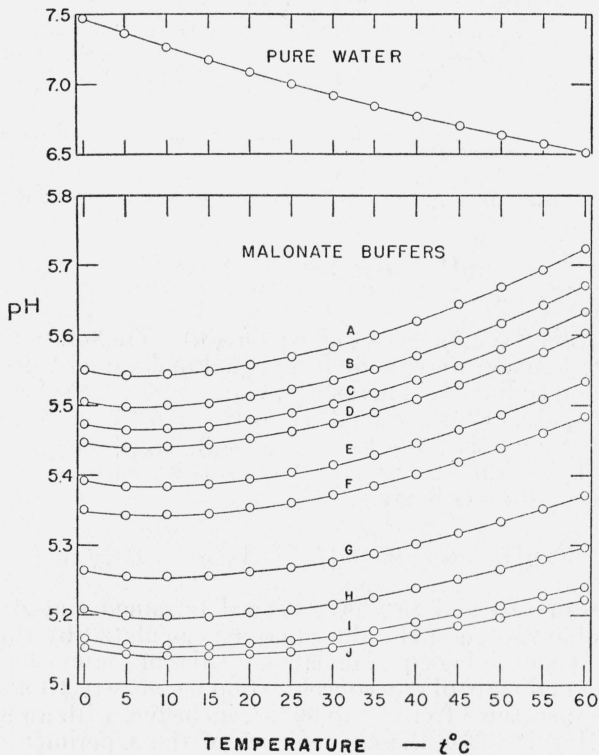


FIGURE 5.—*Plot of the* pH *values of different concentrations of malonate solutions and of pure water against the temperature*

| | | | |
|---|---|---|---|
| A=0.001 M. | C=0.003 M. | E=0.007 M. | G=0.025 M. | I=0.04 M. |
| B=0.002 M. | D=0.004 M. | F=0.01 M. | H=0.03 M. | J=0.044 M. |

The pH of a known molality of malonate solution may be conveniently obtained from the data of table 10 by interpolation. For comparison with the neutral point (pH of pure water) [7], values of the pH of pure water are given at the different temperatures in the bottom row of table 10 and are plotted in figure 5. It is to be noted that the ordinate scale for water is five times that for the solutions. Since the pH of water decreases with an increase in the temperature, the malonate solutions are very much more acidic at 0° C than at 60° C. At 0° C the pH of water minus the pH of a 0.001 $M$ malonate solution is 1.919, whereas at 60° C the same difference is 0.785. In other words, at 0° C the 0.001 $M$ malonate solution is 1.919 pH units on the acid side, and at 60° C it is only 0.785 pH unit on the acid side of the neutral point.

## VII. THERMODYNAMIC QUANTITIES

The second ionization constant of malonic acid was determined at 13 temperatures between 0° to 60° C. It is therefore possible to determine several thermodynamic quantities. The variation of an
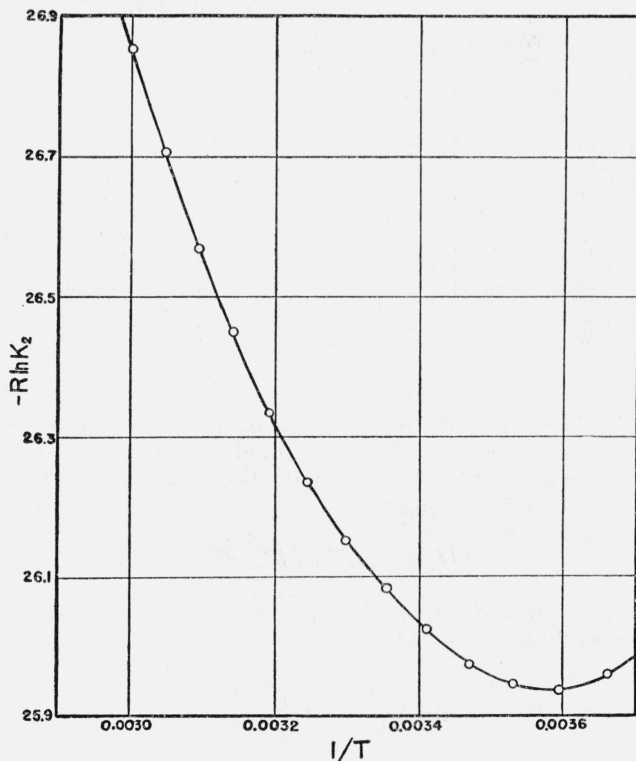


FIGURE 6.—*Plot of values of* $-R \ln K_2$ *against* $1/T$ *for a graphical evaluation of the heat of ionization of the acid malonate ion at various temperatures.*

ionization constant with temperature is given by the van't Hoff [17] isochor

$$\frac{d \ln K_2}{dT} = \frac{\Delta H_i}{RT^2},\tag{29}$$

where $\Delta H_i$ is the heat of ionization, in this case, of the $HAn^-$ ion, and the other terms have their usual significance. To integrate this equation, it is necessary to know the relation between $\Delta H_i$ and $T$. This may be ascertained graphically by plotting $-R \ln K_2$ against $1/T$, figure 6, since the above equation may be written $d\ (-R \ln K_2)/d\ (1/T) = \Delta H_i$.

TABLE 11.—*Thermodynamic data from 0° to 60° C*

| Temperature, t | $K_2 \times 10^6$ (observed) | $\Delta H_i$, the heat of ionization of the acid malonate ion (obtained by a graphical method) | $K_2 \times 10^6$ (obtained from the least square equation) | $\Delta H_i$, the heat of ionization of the acid malonate ion (obtained from the least square equation) | $\Delta C_p$, the difference between the sum of the specific heats of the hydrogen and malonate ions and the specific heat of acid malonate ion. | $\Delta F°$, the increase in free energy for the ionization of the acid malonate ion | $\Delta S°$, the increase in entropy for the ionization of the acid malonate ion |
|---|---|---|---|---|---|---|---|
| °C | | cal | | cal | cal degrees [1] | cal | cal |
| 0 | 2.140 | +436 | 2.144 | +322 | −57.2 | 7086 | −24.8 |
| 5 | 2.165 | +79 | 2.157 | +34 | −58.1 | 7209 | −25.8 |
| 10 | 2.152 | −307 | 2.149 | −259 | −58.9 | 7342 | −26.8 |
| 15 | 2.124 | −634 | 2.122 | −556 | −59.8 | 7480 | −27.9 |
| 20 | 2.076 | −920 | 2.078 | −856 | −60.5 | 7623 | −28.9 |
| 25 | 2.014 | −1137 | 2.018 | −1161 | −61.3 | 7771 | −30.0 |
| 30 | 1.948 | −1424 | 1.946 | −1469 | −62.0 | 7921 | −31.0 |
| 35 | 1.863 | −1734 | 1.863 | −1781 | −62.7 | 8079 | −32.0 |
| 40 | 1.768 | −2100 | 1.771 | −2096 | −63.4 | 8243 | −33.0 |
| 45 | 1.670 | −2381 | 1.673 | −2414 | −64.0 | 8410 | −34.0 |
| 50 | 1.575 | −2695 | 1.570 | −2736 | −64.6 | 8580 | −35.0 |
| 55 | 1.469 | −3076 | 1.466 | −3060 | −65.1 | 8758 | −36.0 |
| 60 | 1.362 | −3390 | 1.361 | −3387 | −65.7 | 8942 | −37.0 |

$\Delta H_i$ is obtained at each temperature by measuring the tangent to the curve. Values of $\Delta H_i$ thus obtained at each temperature are given in column 3 of table 11. The variation of $\Delta H_i$ with temperature can be expressed by the equation

$$\Delta H_i = a + bT + cT^2 + dT^3,\tag{30}$$

where $a$, $b$, $c$, and $d$ are unknown constants. Substituting this equation in eq 29 and integrating, we have

$$\log K_2 = -\frac{a}{2.3026RT} + \frac{b}{R} \log T + \frac{cT}{2.3026R} + \frac{dT^2}{4.6052R} + I,\tag{31}$$

where $I$ is the integration constant. The 13 determined values of $K_2$ and the corresponding temperatures were substituted in this equation. From the 13 equations, the constants were obtained by

the method of least squares. The equation for $K_2$ with numerical values [11] is

$$\log K_2 = -\frac{1053.08}{T} + 20.3223 \log T - 0.05838T$$
$$+ 0.0000236T^2 - 37.1402 \quad (32)$$

and the equation for $\Delta H_i$, in calories, with numerical values is

$$\Delta H_i = 4818.4 + 40.3824T - 0.2671T^2 + 0.0002160T^3 \text{ cal.} \quad (33)$$

To obtain the values in calories, $R = 1.9871$ cal deg$^{-1}$ mole$^{-1}$, derived by Rossini [18], was employed. This value is consistent with the constants given in table 2. Values of $K_2$ computed by eq 32 for the different temperatures, are given in column 4. Values of $\Delta H_i$ computed by eq 33 for the different temperatures are given in column 5. They agree fairly closely with the approximate values in column 3, obtained graphically, except at the lower temperatures, where it is difficult to read the tangent with accuracy. The sign of $\Delta H_i$ changes at about 6° C, corresponding to the maximum in the ionization constant-temperature curve.

Since $d(\Delta H_i)/dT$ equals $\Delta C_p$ [19] or $[C_p(H^+) + C_p(An^=)] - Cp$ (HAn$^-$), the difference between the sum of the specific heats of the H$^+$ and An$^=$ions and the specific heat of the HAn$^-$ion is given by

$$\Delta C_p = 40.3824 - 0.5342T + 0.0006480T^2 \text{ cal.} \quad (34)$$

Values of $\Delta C_p$ computed by this equation for the different temperatures are given in column 6 of table 11. They increase slightly with the temperature, as predicted by a semiempirical equation derived by Moelwyn-Hughes [20]. The value of $\Delta C_p$ is of the expected order of magnitude. For dissociations of molecules into ions, Pitzer [21] found from theoretical considerations that $\Delta C_p$ is about $-40$ cal/deg. For dissociations of ions into other ions, the value of $\Delta C_p$ should be somewhat higher owing to the increased electrostatic forces present in the latter type of dissociation.

The change in free energy, $\Delta F^0$, and entropy, $\Delta S^0$, for the ionization of the HAn$^-$ ion are given by the equations

$$\Delta F^0 = -2.3026RT \log K_2 \text{ cal.} \quad (35)$$

and

$$\Delta S^0 = \frac{\Delta H_i - \Delta F^0}{T} \text{ cal.} \quad (36)$$

Values of these quantities at the different temperatures computed by the equations are given in columns 7 and 8, respectively, of table 11. The former give a measure of the extent of dissociation of the HAn$^-$ ion. The latter are of importance in explanations of ionic dissociations [16, 20, 21], of the variation of equilibrium values and hydrogen-ion activities with temperature [22], and in interpretations of chemical reactions involving ions [23].

---

[11] Equations of simpler form have been proposed by Harned and Embree, J. Am. Chem. Soc. **56**, 1050 (1934) and Pitzer, J. Am. Chem. Soc. **59**, 2365 (1937) for the variation of the ionization constants of weak electrolytes with temperature. Using the forms of equations proposed by these authors and the data obtained for $K_2$ in this investigation, these equations are, respectively,

$$\log K_2 = -5.6675 - 0.000064(t - 4.1)^2$$

and

$$\log K_2 = 80.700 + 3626.4/T - 30 \log T.$$

Although these equations give values of $K_2$ at the different temperatures which agree fairly closely with the observed values, they do not reproduce the experimental data as well as eq 32. The first equation is based upon the supposition that the temperature function for ionization constants is a parabolic function. The second is based upon the assumption that $\Delta C_p$ for ionic dissociations does not vary with the temperature. Both of these assumptions represent limiting cases.

The values of $\Delta F^0$ are obtained directly from those for $K_2$. The uncertainties in $K_2$ introduce uncertainties in the values of $\Delta F^0$ of only 0.1 percent, or 7 to 9 calories. The values of $\Delta H_i$ and $\Delta C_p$ are subject to large error, estimated to be of the order of 100 calories in $\Delta H_i$ and 3 calories in $\Delta C_p$. An error in $\Delta S^0$ is determined by the errors in $\Delta H_i$ and $\Delta F^0$ and is approximately 0.3 calorie. These uncertainties are the same at all of the temperatures. Hence, the variation of these quantities with temperature is significant. According to Pitzer [21], there are uncertainties of about 3 to 15 percent in direct calorimetric measurements of heats of ionization. In general, the heats of ionization obtained calorimetrically agree with values calculated by differentiation of emf data within this limit. Although these thermodynamic quantities are less accurate than the ionization constants from which they are derived, they are important in elucidating the state of ions in solutions and the variation with temperature of the colligative properties of electrolytes.

## VIII. REFERENCES

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