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The Secondary Ionization Constant of Malonic Acid

From 0 to 60° C and the Heat of Ionization

of the Acid Malonate Ion.

By

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I. INTRODUCTION

The determination of the second ionization constant of dibasic organic acids has long been a matter of uncertainty and values reported in the literature vary over a wide range. Illustrative of this, values of the second ionization constant, K_2 , of malonic acid (at 25° C) varying from 1.0×10^{-6} to 10.0×10^{-6} have been reported. (See table 14). This divergence may be ascribed partially to the use of classical solution laws and neglect of the interionic attraction theories developed by Milner [1]* and by Debye and Hückel [2], partially to erroneous assumptions made in interpreting the data, and partially to errors inherent in the method employed.

Several methods have been developed for determining the second ionization constant of dibasic organic acids. Two which have received the most attention are the electrical conductivity and the electrometric titration methods. The first of these, used by Chandler [3], Wegscheider [4] and others, involves the measurement of the electrical conductance of solutions of the acid salt of known concentrations,

*The numbers in brackets here and throughout the text refer to the numbered references at the end of this paper.

from which the degree of dissociation and ionization constant can be calculated. The degree of dissociation must be corrected for the effects of interionic attraction. The chief disadvantage of the method is that the acid salt forms some free acid and dibasic salt, whose individual conductances must be known and the measurement of which is difficult. The electrometric titration method is based upon the measurement of the hydrogen ion concentration in a solution of the acid titrated to give desired fractions of acid salt and dibasic salt of known concentration. This method has been developed and used by a number of workers [5-12]. Here, also, the concentrations must be corrected for the effects of interionic attraction. This method has the inherent weakness of involving a liquid junction, the potential of which cannot be eliminated or calculated with certainty and which is included in the potential from which the hydrogen ion concentration is calculated. Moreover, most measurements made with the electrometric titration method have been in solutions of relatively high salt concentrations so that the value of K_2 obtained is not the true ionization constant but is the dissociation constant in a solution of that salt concentration. Other methods which have been used for the determination of the second ionization constant of dibasic organic acids are the partition method [13] in which the

concentration of dibasic acid arising from the solution of the acid salt in water is measured by partitioning with an immiscible solvent, the carbon dioxide absorption method [14] in which the amount of carbon dioxide absorbed by a solution of the dibasic salt is used as a measure of the acidic strength, and the sucrose inversion method [15] in which the rate of inversion of sucrose by a solution of the acid salt is used as a measure of the hydrogen ion concentration. None of the latter methods have been sufficiently developed for work of high precision.

Recently Harned and his associates [16, 17, 18] have developed an accurate electromotive force method for determining the true thermodynamic ionization constants of weak electrolytes. This method is based entirely on purely thermodynamical considerations and involves no liquid junction. Relatively simple apparatus is required, the measurements can be made rapidly and the method is capable of a high degree of precision. The method also has the advantage of being well adapted to measurements over a wide temperature range. This method has been used for the determination of the ionization constants of several monobasic acids [18, 19], and of the second ionization constants of two inorganic polybasic acids, sulphuric [20] and phosphoric [21]. It has also been used in a modified form for the measurement of the two ionization constants of carbonic acid [22]. The present work is

an application of the method to the measurement of the second ionization constant of a dibasic organic acid, malonic acid. To extend the knowledge of the ionization constants over a wide temperature range and to enable the calculation of various thermodynamical properties of the acid malonate ion, the measurements have been made from 0° to 60° C at 5° temperature intervals.

II. DISCUSSION OF THE METHOD.

In the following discussion and throughout the dissertation the symbols HAN and AN will be used to designate the monovalent and divalent anions respectively of malonic acid. Thus, H₂AN is malonic acid itself, NaHAN is its sodium acid salt and Na₂AN is its disodium salt. Malonic acid, like other dibasic acids, dissociates in two steps, thus:



Application of the mass action law to the second step gives

$$K_2 = \frac{m_{\text{H}^+} m_{\text{AN}^{2-}} \gamma_{\text{H}^+} \gamma_{\text{AN}^{2-}}}{m_{\text{HAN}^-} \gamma_{\text{HAN}^-}} \quad (1)$$

where K_2 is the equilibrium constant, in this case the second ionization constant of malonic acid, and the "m's" and "γ's" are the concentrations and activity coefficients respectively of the ionic species denoted by subscripts. m and γ are defined in terms of mols of solute per 1000 g of solvent.

Inspection of the reaction expressing the second step of the dissociation reveals that if the concentration of the hydrogen ions, m_H , arising from the dissociation of HAN^- is known, the concentrations of the other two ions can be calculated. The problem, therefore, is to measure m_H in a solution containing HAN^- and AN^- ions and to obtain an expression for the activity coefficient ratio. The value of m_H , however, must depend solely upon the hydrogen ions formed by the dissociation of HAN^- . For this reason the measurements cannot be made in solutions of malonic acid for then m_H would include the hydrogen ions arising from the primary dissociation. Instead they are made in solutions of the sodium salts of malonic acid, NaHAN and Na_2AN , which solutions contain Na^+ , H^+ , HAN^- and AN^- ions.* The optimum value of the salt ratio is 1:1 for under these conditions the hydrolysis of the salts is minimized and $\text{pH} = \text{pK}_2$ (approx.)**, a relation which is

*The possible ionization step $\text{NaHAN} \rightleftharpoons \text{H}^+ + \text{NaAN}^-$ in concentrated solutions was discussed in a dissertation for the M.S. degree by J. O. Burton (University of Maryland, 1933) but has been neglected for the very dilute solutions considered in this dissertation.

**This relationship can be arrived at from a consideration of equation (3). Neglecting the activity coefficients and changing to the logarithmic form yields

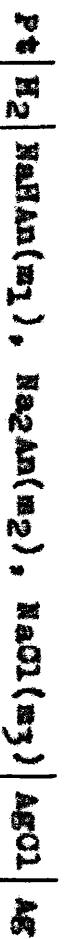
$$-\log m_H = -\log K_2 - \log \frac{m_{\text{HAN}}}{m_{\text{AN}}}$$

or
$$\text{pH} = \text{pK}_2 - \log \frac{m_{\text{HAN}}}{m_{\text{AN}}}$$

Hence, if $m_{\text{HAN}} = m_{\text{AN}}$, which will be approximately true if the stoichiometrical concentrations of NaHAN and Na_2AN are equal, then $\text{pH} = \text{pK}_2$ (approx.).

desirable as under these conditions the curves used for determining the ionization constants have less slope and lead to more certain extrapolations.

The most accurate method of measuring m_{H} is the electromotive force method employing the hydrogen electrode and another suitable electrode to complete the cell. In the present work the silver-silver chloride electrode was used. When properly prepared this electrode has been found to be highly reproducible [23] and has the very desirable feature of requiring no liquid junction. Since the electrode is reversible to the chloride ion, this ion was used in the solution in the form of sodium chloride. The cell employed then was



where m_1 , m_2 and m_3 are the stoichiometrical concentrations of KOHAN, Na_2AN and NaCl respectively expressed in moles of solute per 1000 g of solvent. The cell reaction is



and the electromotive force of the cell is given by the equation

$$E = E_0 - \frac{RT}{nF} \ln m_{\text{H}} m_{\text{Cl}}^{\gamma_{\text{H}^+ \text{Cl}^-}} \quad (2)$$

since the activities of H_2 (gas, 1 atm.), AgCl (solid) and Ag (solid) are unity by definition. In this equation E_0 is the standard potential of the silver-silver chloride electrode, R is the gas constant, T the absolute temperature, n the number of faradays and F the value of the

faraday. Solving equation (1) for m_H gives

$$m_H = K_2 \frac{m_{HAN}^2}{m_{AN}} \cdot \frac{\gamma_{HAN}}{\gamma_H \gamma_{AN}} \quad (3)$$

Upon elimination of m_H between equations (2) and (3) there is obtained

$$E = E_0 - \frac{RT}{nF} \ln K_2 - \frac{RT}{nF} \ln \frac{m_{HAN}^2 m_{Cl}}{m_{AN}} - \frac{RT}{nF} \ln \frac{\gamma_{HAN} \gamma_{Cl}}{\gamma_{AN}} \quad (4)$$

Rearrangement of equation (4) so that all terms known or capable of being measured are on the left hand side gives

$$E - E_0 + \frac{RT}{nF} \ln \frac{m_{HAN}^2 m_{Cl}}{m_{AN}} = - \frac{RT}{nF} \ln K_2 - \frac{RT}{nF} \ln \frac{\gamma_{HAN} \gamma_{Cl}}{\gamma_{AN}}$$

$$\text{or } \frac{(E-E_0)nF}{2.3026RT} + \log \frac{m_{HAN}^2 m_{Cl}}{m_{AN}} = - \log K_2 - \log \frac{\gamma_{HAN} \gamma_{Cl}}{\gamma_{AN}} \quad (5)$$

Each individual ionic activity coefficient in dilute solutions is given by the equation

$$\log \gamma = - A z^2 \sqrt{\mu} + \beta \mu \quad (6)$$

which is the Debye-Hückel equation for activity coefficients with the addition of the linear term $\beta \mu$. In this equation z is the valence of the ion, μ is the ionic strength of the solution, β is an empirical constant proportional to the ionic diameter and A is the universal constant of the Debye-Hückel theory and is given by the equation

$$A = \frac{1.414 \times 2.954 \times 10^6}{D^{3/2} T^{3/2}} \quad (6a)$$

where D is the dielectric constant of the solvent and T is the absolute temperature. The addition of the linear

term, $\beta\mu$, is made to express the deviations of the activity coefficients from those predicted by the limiting law of Debye and Hückel. These deviations are due to salt effects arising from repulsive forces between ions in moderately concentrated solutions [24], and the $\beta\mu$ term is sometimes called the "salt coefficient." This procedure for individual ions has been justified by Brönsted and LaMer [25] and by LaMer and Mason [26]. Application of equation (6) to the three ionic activity coefficients in equation (5) gives

$$\log \gamma_{\text{HAN}} = -A\sqrt{\mu} + \beta'\mu$$

$$\log \gamma_{\text{Cl}} = -A\sqrt{\mu} + \beta''\mu$$

$$\log \gamma_{\text{An}} = -4A\sqrt{\mu} + \beta'''\mu$$

Hence
$$\log \frac{\gamma_{\text{HAN}}\gamma_{\text{Cl}}}{\gamma_{\text{An}}} = 2A\sqrt{\mu} + (\beta' + \beta'' - \beta''')\mu$$

and since β' , β'' and β''' are constants they may be combined into one constant β . Making these substitutions in equation (5) and rearranging to put the measurable term $2A\sqrt{\mu}$ on the left side yields

$$\frac{(E - E_0)nF}{2.3026 RT} + \log \frac{m_{\text{HAN}}m_{\text{Cl}}}{m_{\text{An}}} + 2A\sqrt{\mu} = -\log K_2 - \beta\mu \quad (7)$$

This equation is suitable for the evaluation of K_2 since all terms on the left side can be obtained and the $\beta\mu$ term vanishes at zero ionic strength. E is the measured electromotive force and the values of E_0 are known [27].

As a first approximation the values of m_{HAN} , m_{AN} and m_{Cl} can be taken as equal to the stoichiometrical concentrations m_1 , m_2 and m_3 respectively if it is assumed that the dissociation of the sodium salts is complete, which is undoubtedly true in sufficiently dilute solutions.

This also assumes, however, that the dissociation of HAN^- into H^+ and AN^- ions is negligible, an assumption which is not valid except for very weak acids. Instead, m_{HAN} and m_{AN} are equal to $(m_1 - m_H)$ and $(m_2 + m_H)$ respectively. Moreover, the ionic strength, μ , is not simply $(m_1 + 3m_2 + m_3)$ as would be the case if HAN^- did not dissociate, but is $(m_1 + 3m_2 + m_3 + 2m_H)$. It is therefore necessary to evaluate m_H before equation (7) can be used to calculate K_2 . Harned and Ehlers [18] accomplished this by a series of successive approximations. In their method an approximate value of K_2 is assumed and substituted in equation (1) which is then solved for m_H after the evaluation of the activity coefficient ratio by the limiting law of Debye and Hückel. The value of m_H obtained in this manner is used to correct m_{HAN} , m_{AN} and μ and the corrected values substituted in equation (7). The left side of the equation is solved, plotted against μ and extrapolated to zero ionic strength to obtain a value of K_2 . This value of K_2 is used to re-estimate m_H and μ by means of equation (1) and the process repeated until the extrapolated and assumed values are the same.

Hamer [20] employed a somewhat more direct derivation of equation (7). In his method an apparent value of m_H is obtained from equation (2). Substitution of the Debye-Hückel expressions as given in equation (6) for the activity coefficients in equation (2), rearranging and changing to Briggsian logarithms gives

$$-\log m_H = \frac{(E - E_0)nF}{2.3026 RT} + \log m_{01} - 2A\sqrt{\mu} + 2B\mu \quad (8)$$

The term $2B\mu$ has been neglected here, a procedure which is justified because its effect on the value of m_H is small in dilute solutions and m_H itself is small by comparison with m_1 and m_2 . This equation also must be solved by successive approximations since μ is a function of m_H . The ionic strength is first calculated on the basis of the stoichiometrical concentrations and equation (8) solved for the "apparent" value of m_H . With this value of m_H , μ is recalculated and equation (8) again solved for m_H . This process is repeated until successive values of m_H are the same. Equation (1) is then put in its logarithmic form,

$$\log K_2 = \log \frac{m_H m_{AN}}{m_{HAN}} + \log \frac{\gamma_H \gamma_{AN}}{\gamma_{HAN}}$$

and the activity coefficients replaced by their equivalents according to the Debye-Hückel theory (Equation (6))

to give

$$\log K_2 = \log \frac{m_H^m m_{AH}}{m_{HAN}} - 4A\sqrt{\mu} + \beta\mu$$

Upon rearrangement to put all terms known or capable of being measured on the left side, there is obtained

$$-\log \frac{m_H^m m_{AH}}{m_{HAN}} + 4A\sqrt{\mu} = -\log K_2 + \beta\mu \quad (9)$$

In this equation m_H and μ are calculated by successive approximations of equation (8) as described above, $m_{AH} = m_2 + m_H$ and $m_{HAN} = m_1 - m_H$. Therefore, by plotting the left side of the equation against μ and extrapolating to zero ionic strength, the $\beta\mu$ term vanishes and the intercept is $-\log K_2$. Equations (7) and (9) are identical as can be shown by replacing $-\log m_H$ in equation (9) with its value given in equation (8). Furthermore, Hamer showed that the two methods gave identical results upon extrapolation, thus justifying neglect of the $\beta\mu$ term in the calculation of m_H by his method. The derivation of equation (9), however, is more direct and the evaluation of m_H requires fewer successive approximations and avoids the laborious extrapolations of the method of Harned and Ehlers. For these reasons, in the present work m_H was calculated by the method of Hamer and K_2 determined by means of equation (9). It must be emphasized that the values of m_H and μ calculated by either method are apparent,

due to the assumption that the solutions obey the Debye-Hückel limiting law, but that they approach the true values as the solutions become more dilute, thus leading to a correct thermodynamic constant.

III. EXPERIMENTAL PROCEDURE

1. Apparatus

(a) Cells and bubble tubes.

The cells for the electromotive force measurements were of the usual H-type. Six Pyrex glass cells constructed as shown in figure 1 were used. In the diagram A is the silver chloride electrode compartment and B that for the hydrogen electrodes. The solutions were prepared in the flask J which was connected to the cells with pure gum rubber tubing when they were ready to be filled. Each cell had an individual bubble tube D sealed directly to it for saturating the hydrogen with water vapor previous to its entrance into the cell. The bubble tubes were sealed to the manifold F which supplied the hydrogen. The rate of bubbling of hydrogen was controlled at about 2 bubbles per second by the stopcock G. The insertion of a 5 cm length of 0.2 mm bore capillary tubing between this stopcock and the manifold aided in the regulation of the rate of bubbling. The hydrogen, after passage through the solution and over the electrodes, escaped as shown.

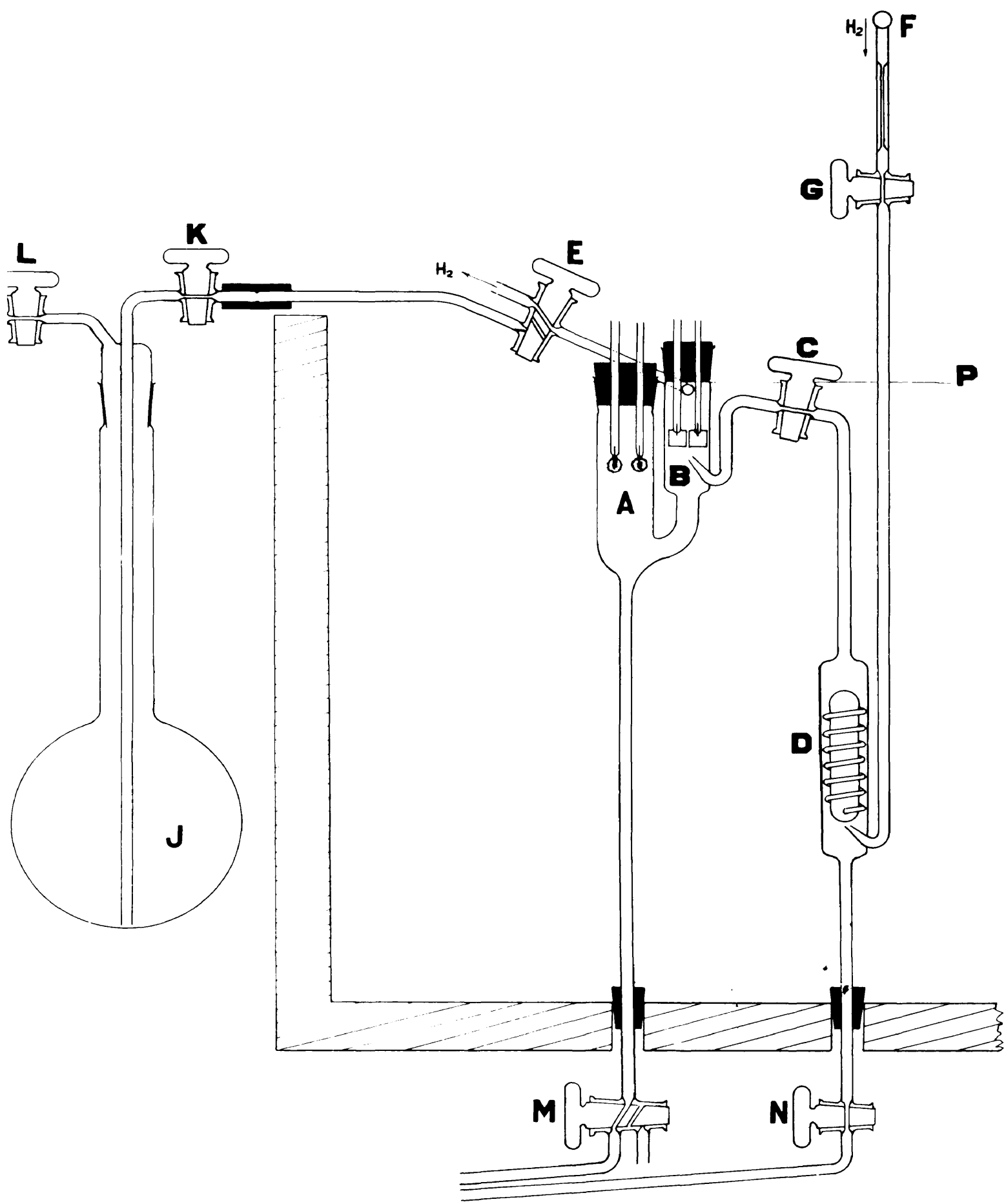


Diagram of apparatus for the study of the reaction of hydrogen with oxygen.

The cells and bubble tubes were evacuated and drained through stopcocks M and N. The level of the water in the thermostat, P, was maintained so that no part of the cells below the rubber stoppers was exposed. The rubber stoppers were thoroughly cleaned by removing the "bloom" with a wire brush and soaking in water.

(b) Thermostat and thermometer.

The thermostat was especially constructed to accommodate the cells, as shown in figure 1. The volume of water was approximately nine cubic feet. Cooling was provided by ten turns of one-half inch copper tubing around the inside edge of the thermostat which served as the expansion coil of a refrigerator. One gallon of ethylene glycol was added to the water to decrease the amount of ice formed on the coil. Heating was provided by a 1500-watt American Instrument Co. "Lolag" immersion heater encircling the bottom of the bath. This was augmented by two 1000-watt "Hotpoint" heaters which were used only while changing the temperature. The water was stirred with a 10-inch, 6-blade propeller making 108 revolutions per minute. The thermostat was explored with a Beckman thermometer and the temperature found to be uniform to within $\pm 0.002^{\circ}$ C throughout the bath. An enclosed glass scale thermometer 19 inches long and graduated from -10° to 102° C in tenths of a degree was used. This thermometer had been

calibrated by the National Bureau of Standards. In addition to this, the ice-point was redetermined immediately prior to this series of measurements so that any changes in the volume of the bulb could be included in the corrections. Since the temperature of the thermostat had to be changed frequently it was found more convenient to use hand regulation. This was not particularly difficult as the volume of the bath was large enough to make temperature variations slow. From 20° to 50° the temperature was held constant to $\pm 0.01^\circ \text{C}$. Below 20° it was constant to within $\pm 0.05^\circ \text{C}$ and above 50° it was constant to within $\pm 0.02^\circ \text{C}$. The temperature within the cells varied probably much less.

(c) Potentiometer, galvanometer and wiring.

The electromotive force measurements were made with a Leeds and Northrup type "K" potentiometer which was calibrated by the Bureau of Standards immediately before this series of measurements was started. The standard cell was an "unsaturated" Eppley type. This had also been recently checked by the Bureau of Standards and found to be in good condition. It was protected from rapid temperature changes which might occur within the room by wrapping in cotton and enclosure in a box. The working battery for the potentiometer was an air cell which was also wrapped in

cotton. This possesses the advantage over the usual lead storage battery of having a very constant voltage over long periods of time. A Leeds and Northrup type "R" galvanometer with lamp and scale was used. This galvanometer had an "F" suspension (sensitivity 0.0001 m.a.). The copper wire leads from the potentiometer to the cells were insulated with rubber covering inside heavily paraffined cotton and shielded by passing them through well grounded copper tubes. The potentiometer, galvanometer, standard cell and other leads were also well shielded. To make contact with the electrodes, mercury was placed in the electrode tubes and copper wires inserted in the mercury. The leads from the potentiometer were then connected to these copper wires by means of spring clips.

(d) Other apparatus.

The balance used in the analyses made in conjunction with this investigation was the usual analytical "Chainomatic" type. The heavy duty balance used for the standardization of the hydrochloric acid solution, the preparation of the stock solution and the dilution of the stock solution was sensitive to 0.5 mg under a 2000 g load. The weights for both balances were calibrated by the Bureau of Standards and conformed to the specifications for class S weights. All weighings were made in a constant temperature

room at 25° C and tares used wherever possible. Vacuum corrections were applied wherever necessary. A mercurial barometer of the Fortin type calibrated by the Bureau of Standards was used in correcting the hydrogen electrode potentials to standard pressure.

2. Materials

The solutions for the electromotive force measurements were prepared from malonic acid and solutions of sodium hydroxide and hydrochloric acid in a manner to be described later. An absolute purity of 99.9 percent or better was sought in the preparation of all materials. It is believed that this has been achieved in all instances with the exception of malonic acid. Its purity is very close to the desired value (99.88 percent) and may be even better as will be discussed later. Reagents of the highest purity obtainable were used throughout and were subjected to further purification where necessary as described below.

(a) Sodium hydroxide solution.

Analytical reagent quality sodium hydroxide sticks were dissolved in an equal weight of water and allowed to stand several weeks to permit the sodium carbonate to settle out. The clear solution was carefully poured from the precipitated carbonate on to a Büchner funnel containing

a well washed heavy mat of asbestos and filtered under reduced pressure. The concentrated solution was diluted by transferring to a 4-liter Pyrex bottle containing distilled water. This bottle had been used over a period of four years for the storage of sodium hydroxide solutions. The water had been boiled several hours and cooled in the absence of CO_2 . Both the water and concentrated sodium hydroxide solution were transferred to the bottle in such a manner as to avoid contamination with CO_2 . After preparation the solution was protected at all times with soda-lime guard tubes. The concentration of a solution prepared in this way changed only 0.05 percent during a period of 6 months.

The concentration of the solution was determined by titration of benzoic acid, Bureau of Standards standard sample 39e, and acid potassium phthalate, Bureau of Standards standard sample 84, using 5 drops of 1 percent phenolphthalein as the indicator. All titrations were made with weighing burettes in a constant temperature room at 25°C . When using benzoic acid, 2.5 g were dissolved in 25 ml of 95 percent alcohol. When using acid potassium phthalate, 4 g were dissolved in 100 ml of CO_2 -free distilled water. These concentrations are greater than those recommended for the titration by the Bureau of Standards in the

certificate of analysis accompanying the standard samples. These changes were required because the concentration of the sodium hydroxide solution was approximately 0.6 M whereas the recommended procedures were based upon 0.1 M solutions. During the titrations, CO₂-free air was passed through the solutions. The titrations were carried to the faintest discernible pink color, the last portion of solution being removed from the burette tip with a stirring rod. The end point was sensitive to about 0.005 g of solution which is the smallest amount that could be removed from the burette tip. Corrections were made for the weight of sodium hydroxide solution required to produce the same color in another flask containing a volume of CO₂-free water, or of water and 25 ml of alcohol, equal to the final volume of the titrated solution. The results of duplicate titrations seldom varied more than 0.02 percent. However, the values obtained by the titration of the two standards differed consistently by 0.08-0.10 percent, the acid potassium phthalate giving the higher value for the concentration of the sodium hydroxide solution. That this difference was apparently caused by a difference in the effect of the salts upon the indicator, was shown by accurately diluting the solution by weight to an approximately 0.1 M concentration and then titrating the benzoic

acid and acid potassium phthalate exactly as recommended by the Bureau of Standards. Under these conditions the two standards gave values for the concentration which agreed within the experimental error. Using this value and the known degree of dilution, the concentration of the solution before dilution was calculated. This calculated concentration agreed with that obtained by the direct titration of benzoic acid, showing that sodium benzoate has a constant affect on phenolphthalein throughout this concentration range whereas the salts of phthalic acid do not. Inasmuch as the purity of the standard samples was based upon their titration with 0.1 M sodium hydroxide solution, and the benzoic acid has the same neutralizing power when titrated with 0.1 M or 0.6 M solutions whereas the acid potassium phthalate does not, the benzoic acid value for the concentration of the 0.6 M solution was considered the more reliable and later calculations were based upon it.

(b) Hydrochloric acid solution.

The hydrochloric acid solution was prepared by passing pure, dry hydrogen chloride into distilled water. The hydrogen chloride was prepared by the action of concentrated C.P. sulphuric acid upon fused C.P. ammonium chloride in a Kipp generator. After leaving the generator the

hydrogen chloride passed through a wash bottle containing concentrated sulphuric acid and thence into the distilled water. The distilled water was contained in a flask similar to the solution flask J shown in figure 1, except that the inlet tube was drawn out to a fine capillary to promote a more rapid absorption of the hydrogen chloride by the water. The rate at which the hydrogen chloride was generated was maintained at about two bubbles per second in the sulphuric acid wash bottle. It is believed this rate is low enough to prevent sulphuric acid spray from being carried into the solution. No sulphates could be detected with barium chloride in the hydrochloric acid solution. The stopcock L was kept closed at all times to prevent loss of water vapor. A known weight of water was used and the solution was weighed after its preparation. From the weight of water and the weight of hydrogen chloride absorbed the concentration of the solution was calculated. The value obtained in this manner agreed within 0.04 per cent with that determined by titration with sodium hydroxide solution, the concentration of the latter being based upon the benzoic acid titration.

(c) Malonic acid.

All values reported here for the purity of malonic acid are based upon its titration with standard sodium hydroxide. This appears to be the best method available,

a conclusion also arrived at by Norris and Tucker [28]. The melting point cannot be relied upon as a criterion of purity, for malonic acid decomposes at temperatures considerably below its melting point [28, 29]. The titrations were made with the 0.6 M sodium hydroxide solution, using approximately 1 g of malonic acid dissolved in 100 ml of CO₂-free water and the same procedure as described under the preparation of the sodium hydroxide solution. The results of duplicate titrations seldom differed more than 0.04 percent.

The malonic acid used in this work was obtained from the Eastman Kodak Co. When received the acid appeared to be wet and had a pronounced ester-like odor. Ignition in a platinum crucible at a dull red heat left 0.11 percent residue, which when extracted with water and filtered gave a distinct reaction for sulphates. Titration showed the acid to be 98.92 percent pure. The impurities were probably diethyl malonate and potassium sulphate, both of which are formed during the preparation of the acid. To remove the ester the acid was triturated and washed in small portions six times with redistilled C.P. carbon tetrachloride. After this treatment the acid was dried at 60° C. Drying at 105° C was tried at first but it was

impossible to get a constant weight, indicating slow decomposition at that temperature. There was no evidence of decomposition at 60° C. The acid had no ester odor after washing with carbon tetrachloride. Its purity at this stage was 99.67 percent. The acid was next placed in an extraction thimble and extracted with ether in a Soxhlet extractor. The ether had previously been distilled over sodium. The extraction was continued until all soluble material had been removed from the thimble. A fine grey powder remained. The acid crystallized from the ether in large well-formed crystals. These were crushed coarsely in an agate mortar and dried 48 hours at 60° C. However, this treatment did not serve to remove the ether; when some of the crystals were ground to a fine powder there was a distinct odor of ether. Consequently the entire lot of acid was reduced to a fine powder and dried again 48 hours at 60° C. The ether extraction increased the purity to 99.81 percent and reduced the residue remaining after ignition to less than 0.01 percent. A very faint odor of ester could be detected after the ether extraction. Whether this had been retained within the crystals and not removed by the carbon tetrachloride treatment or whether the ester had been formed by the action of the ether on the acid during the extraction is problematical. The acid

was given another treatment with carbon tetrachloride similar to the first which increased its purity to 99.88 percent. Further treatment of the acid failed to improve it. Another ether extraction and carbon tetrachloride washing, followed by drying 48 hours in vacuo at 60° C, produced no change. Other solvents were tried for the recrystallization. Vogel [30] used a mixture of benzene and ether containing 5 percent petroleum ether. Three recrystallizations from this solvent failed to improve our product. Recrystallization from hot (50° C) methyl alcohol was tried but was unsuccessful. Methyl alcohol apparently promotes the decomposition of malonic acid at this temperature as there was a strong odor of acetic acid after the removal of the alcohol.

A part of the impurity which remained in the malonic acid may be only apparent. The purity is based upon the benzoic acid value for the concentration of the sodium hydroxide solution. If it is based upon the acid potassium phthalate value it is 99.94 percent. As was mentioned in the discussion of the preparation of the sodium hydroxide solution, benzoic acid and acid potassium phthalate gave different values for the concentration of the sodium hydroxide solution apparently because of the effect of the phthalate salts on the indicator at the concentration

used. If the malonate salts have the same effect on the indicator as the phthalate salts have, it would be legitimate to base the calculation of the purity on the acid potassium phthalate value, since the malonic acid was titrated at approximately the same molar concentration as was the acid potassium phthalate. However, no information was obtained on the effect of malonate salts on phenolphthalein, and in the absence of such information it was considered best to base all calculations on the benzoic acid value.

(d) Hydrogen.

Tank hydrogen was used. It was passed first through a soda-lime scrubber to remove any traces of CO_2 , then through a Chamberlin filter to remove dust particles, and finally through a tube 30 cm in length and 1 cm in diameter packed with palladinized asbestos heated to 220°C to remove the oxygen. The removal of the oxygen is very important as shown by MacInnes and Cowperthwaite [31], who found that the presence of oxygen may cause errors in the potential of the hydrogen electrode of as much as 50 millivolts. Palladinized asbestos has been recommended by Loomis and Acree [32] and by Bodenstein and Unger [33] as a very efficient catalyst for the removal of oxygen. After passage through this tube the hydrogen was conducted

through copper tubing to the manifold supplying the cells. All connections were made with solder or de Khotinsky cement, no rubber being used.

(e) Hydrogen electrodes.

Strips of platinum foil approximately one square centimeter in area were fused to a platinum wire and sealed into a glass tube. The electrodes were cleaned by placing in 50 percent aqua regia solution for two hours and then thoroughly washed in distilled water before plating with platinum black. The platinum black was deposited by electrolyzing in a solution of chlorplatinic acid for three to four minutes at a current density of 400 milliamperes per square centimeter. The chlorplatinic acid solution contained 30 g of platinum per liter and was 0.25 N in excess hydrochloric acid. No lead acetate was used. After the deposition of the platinum black the electrodes were washed with a strong stream of distilled water from a wash bottle and immediately placed in the cells. Freshly prepared electrodes were used for each cell.

(f) Silver chloride electrodes

The silver chloride electrodes were prepared as described by Harned [34], using his method for type 2. This form of electrode is easily prepared and has been found to be very satisfactory in other investigations. Furthermore,

it is the only form of silver chloride electrode whose E_0 values are known over the desired temperature range. Silver oxide, precipitated from silver nitrate solution by the addition of sodium hydroxide, was washed repeatedly by decantation with distilled water. The electrodes, consisting of a helix of platinum wire sealed into a glass tube, were coated with the silver oxide, after which they were heated in a furnace at 400°C to reduce the oxide to metallic silver. Four or five such treatments served to build up a globule of silver approximately 0.5 cm in diameter. After cooling, the electrodes were coated with silver chloride by electrolyzing as anode in 1 M hydrochloric acid solution for two hours at a current density of 8 milliamperes per square centimeter of apparent electrode surface. The electrodes were thoroughly washed with distilled water, soaked over night in distilled water and washed again before use. They were protected from the action of light as much as possible after the silver chloride plating. Freshly prepared electrodes were used for each cell.

3. Method

(a) Preparation of solutions for electromotive force measurements.

To a known weight of accurately analyzed sodium hydroxide solution in a flask protected by soda-lime guard tubes there was added its exact equivalent of purified

malonic acid. A portion of the di-sodium malonate solution thus prepared was withdrawn and phenolphthalein solution added. The resulting color of the solution was a very good match for the color used as the end-point in the analysis of the sodium hydroxide solution and malonic acid. Sufficient hydrochloric acid solution was then weighed into the sodium malonate solution to convert one-half of the disodium malonate to sodium acid malonate and sodium chloride. Thus, the solution contained equimolar quantities of NaHA , Na_2A and NaCl . CO_2 -free water was added by weight so that the concentration of each constituent was approximately 0.1 M. This solution was used as a stock from which the more dilute ones for the electromotive force measurements were prepared by addition of known weights of water. Since oxygen is known to have a deleterious effect on the silver chloride and hydrogen electrodes it was necessary that the solutions contain no dissolved air. A known weight of the stock solution was placed in the solution flask J of figure 1 and the flask evacuated. Purified hydrogen was then slowly admitted to the flask and bubbled through the solution until the pressure was again normal. This process of evacuation and flushing with hydrogen was repeated twice more. The flask was again evacuated and connected to a large flask containing distilled water which had been boiled three hours

and cooled while a stream of purified hydrogen passed through it. By opening the stopcock on the solution flask the distilled water was drawn over until the total weight of water was approximately 1000 g. The pressure was again restored to normal by admitting hydrogen, and hydrogen was then passed through the solution for 30 minutes. Finally the solution was thoroughly mixed by inverting the flask several times and the flask weighed. Knowing the weight of salts in the stock solution added and the weight of the diluted solution, the concentration was calculated in terms of mols of salts per 1000 g of water. In the prep- of all solutions having a concentration of 0.01 M or less the stock solution was weighed in a weighing burette and added to the flask. For solutions of concentration greater than 0.01 M the stock solution was added directly to the flask and the weight determined by difference. A flask similar to the solution flasks was filled with water and used as a tare in making the weighings, the solutions thus being weighed by displacement so as to eliminate errors caused by any difference in the length of the balance arms. The empty flasks were weighed while filled with air whereas the solutions were weighed with the space above them containing hydrogen. Hence, a small correction had to be made, in addition to the usual vacuum correction, for the difference in density of air and hydrogen. This amounted to about 0.03 percent in all cases.

(b) Filling the cells and measurements of the electromotive force.

Immediately before filling the cells two hydrogen and two silver chloride electrodes were placed in their respective compartments as shown in figure 1. With stopcocks Q and K closed and stopcock E open to the solution flask, the cells and bubble tubes were evacuated through stopcocks M and N. The latter were then closed and hydrogen admitted to the system through stopcock G. This process of evacuation and flushing with hydrogen was repeated twice more. Next stopcock Q was closed and the system evacuated again, after which stopcock K was opened and the cells and bubble tubes completely filled with solution. During the removal of the solution from the flask hydrogen was passed through stopcock L so that the pressure would remain normal and evaporation of the solution would be avoided. With the cells and bubble tubes filled stopcock Q was closed and the solution pumped out of the bubble tube through stopcock N. Then stopcock Q was opened and the solution in the cell drawn into the bubble tube. Stopcock Q was again closed and a part of the solution in the bubble tube forced through N by admitting hydrogen. The solution which remained in the bubble tube served to presaturate the hydrogen with water vapor before entering the cell. The remainder of the solution in the cell was

drained out, the cell evacuated and again filled with solution. Hydrogen was then admitted to the cell and the solution forced through M until its level in compartment B was low enough to permit the hydrogen to escape through the side tube. Finally stopcock E was opened and the amount of hydrogen passing over the electrodes was regulated by adjusting stopcock G.

The cells were filled while the thermostat was at room temperature to facilitate the manipulation of the stopcocks. As soon as they were filled the refrigerator was started, the bath cooled to 0°C and maintained there until the electromotive force readings between each pair of AgCl and hydrogen electrodes were constant to within 0.03 millivolt. Usually about four hours were required. The temperature was difficult to maintain at exactly 0°C due to the ethylene glycol in the thermostat water, but was nearly self-regulatory at about -0.2°C . For this reason the electromotive force measurements were made at the latter temperature and corrected to 0°C as will be described later. As soon as constant potentials were obtained at -0.2° the temperature of the thermostat was raised during a period of about 30 minutes to 5°C and electromotive force measurements again made. Readings were taken at about 10 minute intervals until successive values were constant to within 0.03 millivolt. Usually

the first and second readings so taken had the required constancy and it was seldom necessary to take more than three readings. Equilibrium, once attained at 0°, apparently shifted nearly as rapidly as did the temperature thereafter. This procedure was repeated at 5° C temperature intervals, the final measurements being made at 60° C. The barometric pressure was recorded immediately after the measurements had been completed at each temperature.

The electromotive forces reported are the averages of two cells, each containing two hydrogen and two silver chloride electrodes. The average deviation between electrode pairs in the same cell was ± 0.01 millivolt. Somewhat larger deviations were found between the two cells containing the same solution. Here the average agreement was ± 0.03 millivolt except in the most dilute solutions and at the higher temperatures where deviations of as much as 0.2 millivolt were encountered at times. After application of the temperature and scale corrections to the observed barometric pressures the partial pressure of hydrogen over each solution at each temperature was calculated by subtracting from the corrected barometric pressure the partial pressure of water vapor. The latter was assumed to be the same as the partial pressure of water vapor over pure water at the same temperature, an assumption which causes a negligible error when the solutions are as dilute

as those used in this work. The observed electromotive forces were then corrected to a partial hydrogen pressure of one atmosphere by means of the equation [35]

$$E = E' + \frac{RT}{2F} \ln \frac{P}{P'}$$

where E' is the observed electromotive force at the partial hydrogen pressure P' and E is the corrected electromotive force at the standard pressure P (1 atmosphere). The calibration and stem exposure corrections were applied to the observed thermometer readings and the electromotive forces calculated to even temperatures. The change of electromotive force with temperature was very nearly 1.0 millivolt per degree for all concentrations so that the calculations to even temperatures could be made on the basis of 0.01 millivolt for each 0.01 degree between the observed and even temperature. This procedure is justifiable for the small temperature differences encountered (0.03-0.07°).

IV. RESULTS

1. The second ionization constant of malonic acid from 0° to 60° C. The results of the electromotive force measurements are given in tables 1 to 13 inclusive. The first column contains the molal concentrations of MAHAN, MAZAN and NaCl, all of which were equal in each solution. In the

second column μ' is the ionic strength calculated from these stoichiometrical concentrations. The values of E in the third column are the observed electromotive forces corrected to one atmosphere hydrogen pressure and to the even temperature stated in the table. The fourth column contains the values calculated from the left side of equation (7), which is a function of E , using the stoichiometrical concentrations. They are designated as E_f' to signify that they do not contain the corrections for the hydrogen ion concentration. The "apparent" hydrogen ion concentrations and ionic strengths calculated from equation (8), neglecting the 8μ term, are given in the fifth and sixth columns respectively. One approximation was found to be sufficient for their calculation. The final column contains the values of the left side of equation (9), designated as E_f . The values of E_0 , A and $2.3026RT/F$

used in these calculations are given at the top of each table. Those of E_0 are the observed values of Harned and Ehlers [27]. Equation (6a) was used for the evaluation of A , using Wyman's equation [36]

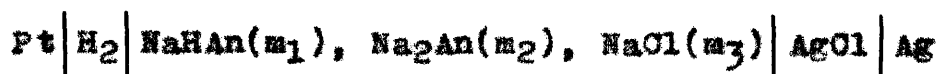
$$D = 78.54[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2]$$

for the dielectric constant of water at any temperature t and

$$T = 273.16 + t$$

Table 1.

Results obtained from the electromotive forces of the cell



at 0° C.

$$E_0 = 0.23634$$

$$A = 0.4869$$

$$2.3026RT/F = 0.05419$$

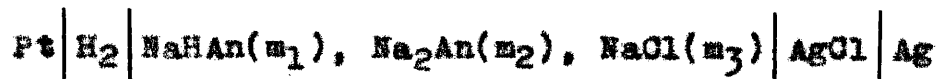
$m_1=m_2=m_3$	μ'	E	E_f'	$m_H \times 10^5$	μ	E_f
.0009867	.0049334	.70313	5.6765	.2886	.0049406	5.6741
.0010619	.0053095	.70156	5.6820	.2883	.0053168	5.6797
.0011095	.0055475	.70041	5.6814	.2908	.0055540	5.6793
.0019114	.0095570	.68695	5.6919	.3145	.0095648	5.6906
.0019420	.0097100	.68605	5.6830	.3228	.0097185	5.6816
.0024182	.012091	.68042	5.6854	.3378	.012099	5.6843
.0029128	.014564	.67580	5.6913	.3489	.014573	5.6906
.0030385	.015193	.67454	5.6891	.3557	.015201	5.6885
.0040020	.020010	.66761	5.6985	.3776	.020019	5.6978
.0047561	.023781	.66326	5.7057	.3932	.023790	5.7051
.0050248	.025124	.66145	5.7003	.4059	.025134	5.6996
.0068161	.034081	.65384	5.7177	.4384	.034091	5.7172
.0068596	.034298	.65339	5.7127	.4446	.034309	5.7122
.0094543	.047272	.64506	5.7297	.4940	.047284	5.7293
.0095398	.047699	.64478	5.7294	.4965	.047711	5.7290
.018622	.093110	.62664	5.7696	.6679	.093127	5.7693
.029535	.14768	.61393	5.8125	.8630	.14770	5.8123
.044566	.22283	.60230	5.8620	1.1413	.22286	5.8618

$$-\log K_2 \text{ (extrapolated)} = 5.6696$$

$$K_2 = 2.140 \times 10^{-6}$$

Table 2.

Results obtained from the electromotive forces of the cell



at 5° C.

$$E_0 = 0.23392$$

$$A = 0.4899$$

$$2.3026RT/F = 0.05519$$

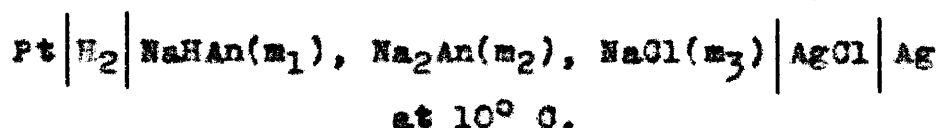
$m_1=m_2=m_3$	μ^0	E	E_f	$m_H \times 10^5$	μ	E_f
.0009867	.0049334	.70874	5.6664	.2960	.0049408	5.6639
.0010619	.0053095	.70714	5.6719	.2958	.0053168	5.6696
.0011095	.0055475	.70622	5.6758	.2952	.0055550	5.6736
.0019114	.0095570	.69230	5.6826	.3228	.0095652	5.6812
.0019420	.0097100	.69157	5.6771	.3281	.0097188	5.6757
.0024182	.012091	.68598	5.6822	.3414	.012100	5.6812
.0029128	.014564	.68115	5.6859	.3551	.014573	5.6852
.0030385	.015193	.67993	5.6848	.3604	.015202	5.6838
.0040020	.020010	.67285	5.6939	.3831	.020020	5.6932
.0047561	.023781	.66841	5.7010	.3992	.023790	5.7003
.0050248	.025124	.66654	5.6952	.4125	.025134	5.6945
.0068161	.034081	.65887	5.7142	.4440	.034092	5.7136
.0068596	.034298	.65829	5.7070	.4528	.034309	5.7065
.0094543	.047272	.64992	5.7263	.5010	.047284	5.7259
.0095398	.047699	.64942	5.7221	.5081	.047712	5.7217
.018622	.093110	.63114	5.7663	.6786	.093127	5.7660
.029535	.14768	.61816	5.8090	.8792	.14770	5.8088
.044566	.22283	.60629	5.8586	1.1654	.22286	5.8584

$$- \log K_2 \text{ (extrapolated)} = 5.6653$$

$$K_2 = 2.161 \times 10^{-6}$$

Table 3.

Results obtained from the electromotive forces of the cell.



$$E_0 = 0.23126$$

$$\Delta = 0.4937$$

$$2.3026RT/F = 0.05618$$

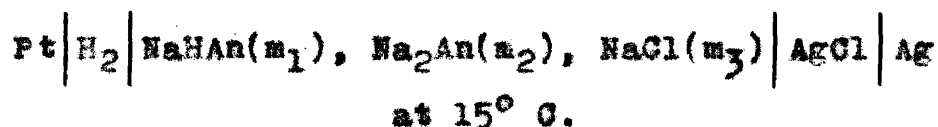
$m_1=m_2=m_3$	μ'	E	E_f'	$m_H \times 10^5$	μ	E_f
.0009867	.0049334	.71461	5.6671	.2962	.0049407	5.6646
.0010619	.0053095	.71304	5.6737	.2953	.0053168	5.6714
.0011095	.0055475	.71211	5.6778	.2947	.0055548	5.6756
.0019114	.0095570	.69790	5.6840	.3229	.0095650	5.6827
.0019420	.0097100	.69724	5.6800	.3271	.0097185	5.6786
.0024182	.012091	.69148	5.6839	.3414	.012099	5.6828
.0029128	.014564	.68665	5.6892	.3538	.014573	5.6885
.0030385	.015193	.68538	5.6877	.3596	.015202	5.6867
.0040020	.020010	.67819	5.6973	.3820	.020020	5.6965
.0047561	.023781	.67362	5.7035	.3991	.023790	5.7028
.0050248	.025124	.67172	5.6978	.4123	.025134	5.6971
.0068161	.034081	.66400	5.7185	.4425	.034092	5.7181
.0068596	.034298	.66334	5.7102	.4525	.034309	5.7096
.0094543	.047272	.65482	5.7296	.5009	.047284	5.7292
.0095398	.047699	.65439	5.7269	.5063	.047712	5.7265
.018622	.093110	.63562	5.7689	.6819	.093127	5.7686
.029535	.14768	.62246	5.8131	.8827	.14770	5.8129
.044566	.22283	.61037	5.8632	1.1722	.22286	5.8630

$$-\log K_2 \text{ (extrapolated)} = 5.6667$$

$$K_2 = 2.154 \times 10^{-6}$$

Table 4.

Results obtained from the electromotive forces of the cell.



$$E_0 = 0.22847$$

$$A = 0.4975$$

$$2.3026RT/F = 0.05717$$

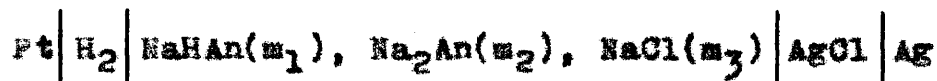
$m_1 = m_2 = m_3$	μ'	E	E_f'	$m_H \times 10^5$	μ	E_f
.0009867	.0049334	.72076	5.6751	.2916	.0049406	5.6726
.0010619	.0053095	.71930	5.6777	.2891	.0053168	5.6818
.0011095	.0055475	.71808	5.6834	.2917	.0055548	5.6812
.0019114	.0095570	.70358	5.6891	.3202	.0095650	5.6877
.0019420	.0097100	.70276	5.6824	.3263	.0097185	5.6810
.0024182	.012091	.69706	5.6893	.3384	.012099	5.6882
.0029128	.014564	.69217	5.6952	.3505	.014573	5.6945
.0030385	.015193	.69076	5.6915	.3579	.015201	5.6906
.0040020	.020010	.68356	5.7033	.3786	.020019	5.7026
.0047561	.023781	.67886	5.7088	.3964	.023790	5.7080
.0050248	.025124	.67698	5.7040	.4087	.025134	5.7034
.0068161	.034081	.66901	5.7230	.4409	.034092	5.7225
.0068596	.034298	.66845	5.7166	.4487	.034309	5.7161
.0094543	.047272	.65970	5.7349	.4986	.047284	5.7345
.0095398	.047699	.65916	5.7303	.5135	.047712	5.7300
.018622	.093110	.64023	5.7760	.6780	.093127	5.7758
.029535	.14768	.62674	5.8191	.8823	.14770	5.8189
.044566	.22283	.61442	5.8696	1.1743	.22286	5.8694

$$- \log K_2 \text{ (extrapolated)} = 5.6726$$

$$K_2 = 2.125 \times 10^{-6}$$

Table 5.

Results obtained from the electromotive forces of the cell.



at 20° C.

$$E_0 = 0.22551$$

$$A = 0.5018$$

$$2.3026RT/F = 0.05816$$

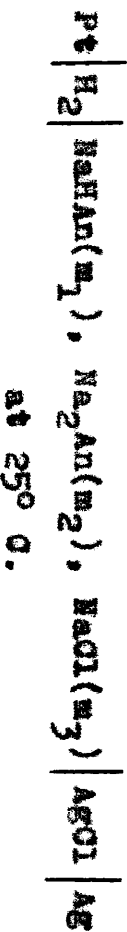
$m_1=m_2=m_3$	μ	E	E_f'	$m_H \times 10^5$	μ	E_f
.0009867	.0049334	.72709	5.6888	.2833	.0049405	5.6864
.0010619	.0053095	.72549	5.6958	.2821	.0053165	5.6937
.0011095	.0055475	.72414	5.6933	.2859	.0055547	5.6911
.0019114	.0095570	.70933	5.6982	.3148	.0095648	5.6969
.0019420	.0097100	.70868	5.6947	.3185	.0097183	5.6935
.0024182	.012091	.70277	5.6998	.3318	.012099	5.6987
.0029128	.014564	.69771	5.7042	.3449	.014573	5.7032
.0030385	.015193	.69631	5.7013	.3517	.015201	5.7003
.0040020	.020010	.68903	5.7140	.3715	.020019	5.7132
.0047561	.023781	.68416	5.7180	.3904	.023790	5.7173
.0070248	.025124	.68233	5.7147	.4013	.025134	5.7141
.0068161	.034081	.67405	5.7310	.4361	.034091	5.7305
.0068596	.034298	.67357	5.7261	.4423	.034309	5.7256
.0094543	.047272	.66460	5.7435	.4931	.047284	5.7431
.0095398	.047699	.66426	5.7426	.4964	.047711	5.7421
.018622	.093110	.64478	5.7852	.6719	.093127	5.7849
.029535	.14768	.63101	5.8281	.8774	.14770	5.8280
.044566	.22283	.61848	5.8795	1.1697	.22286	5.8793

$$-\log K_2 \text{ (extrapolated)} = 5.6835$$

$$K_2 = 2.073 \times 10^{-6}$$

Table 6.

Results obtained from the electromotive forces of the cell.



$E_0 = 0.22239$ $A = 0.5063$ $2.3026RT/F = 0.05915$

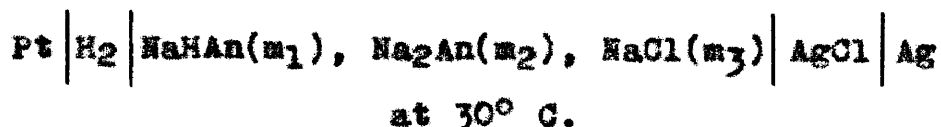
$m_1 = m_2 = m_3$	μ'	E	E_f'	$m_3 \times 10^5$	μ	E_f
.0009867	.0049334	.73350	5.7062	.2729	.0049402	5.7039
.0010619	.0053095	.73140	5.7053	.2769	.0053165	5.7031
.0011095	.0055475	.73023	5.7062	.2784	.0055445	5.7041
.0019114	.0095570	.71508	5.7099	.3077	.0095647	5.7085
.0019420	.0097100	.71444	5.7067	.3110	.0097180	5.7054
.0024182	.012091	.70853	5.7136	.3229	.012099	5.7125
.0029126	.014564	.70329	5.7166	.3369	.014572	5.7189
.0030385	.015193	.70195	5.7150	.3425	.015201	5.7141
.0040020	.020010	.69442	5.7258	.3637	.020019	5.7250
.0047561	.023781	.68945	5.7296	.3826	.023790	5.7290
.0050248	.025124	.68767	5.7278	.3920	.025134	5.7271
.0068161	.034081	.67921	5.7436	.4269	.034091	5.7431
.0068596	.034298	.67877	5.7395	.4321	.034309	5.7390
.0094543	.047272	.66957	5.7559	.4835	.047284	5.7555
.0095398	.047699	.66923	5.7551	.4867	.047711	5.7547
.0186622	.093110	.64939	5.7980	.6607	.093127	5.7977
.0295335	.14768	.63540	5.8419	.8637	.147770	5.8417
.044566	.22283	.62263	5.8936	1.1547	.22286	5.8934

- log K₂ (extrapolated) = 5.6964

K₂ = 2.012x10⁻⁶

Table 7.

Results obtained from the electromotive forces of the cell.



$E_0 = 0.21912$

$A = 0.5112$

$2.3026RT/F = 0.06015$

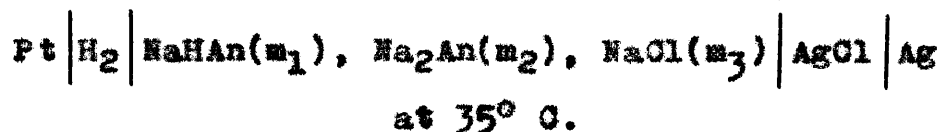
$m_1 = m_2 = m_3$	μ^0	E	E_f^1	$m_H \times 10^5$	μ	E_f
.0009867	.0049334	.73986	5.7233	.2632	.0049400	5.7211
.0010619	.0053095	.73743	5.7175	.2702	.0053163	5.7154
.0011095	.0055475	.73637	5.7206	.2702	.0055543	5.7186
.0019114	.0095570	.72095	5.7243	.2990	.0095645	5.7230
.0019420	.0097100	.72033	5.7217	.3019	.0097180	5.7204
.0024182	.012091	.71430	5.7283	.3137	.012099	5.7273
.0029128	.014564	.70895	5.7310	.3277	.014572	5.7304
.0030385	.015193	.70744	5.7271	.3350	.015201	5.7262
.0040020	.020010	.69993	5.7404	.3539	.020018	5.7397
.0047561	.023781	.69484	5.7438	.3728	.023790	5.7432
.0050248	.025124	.69310	5.7431	.3810	.025134	5.7425
.0068161	.034081	.68435	5.7568	.4176	.034091	5.7563
.0068596	.034298	.68398	5.7540	.4214	.034309	5.7535
.0094543	.047272	.67456	5.7697	.4731	.047283	5.7693
.0095398	.047699	.67430	5.7702	.4746	.047711	5.7699
.018622	.093110	.65400	5.8119	.6487	.093125	5.8117
.029535	.14768	.63971	5.8556	.8510	.14770	5.8557
.044566	.22283	.62674	5.9084	1.1400	.22286	5.9082

$-\log K_2 \text{ (extrapolated)} = 5.7106$

$K_2 = 1.947 \times 10^{-6}$

Table 8.

Results obtained from the electromotive forces of the cell.



$$E_0 = 0.21563$$

$$A = 0.5164$$

$$2.3026RT/F = 0.06114$$

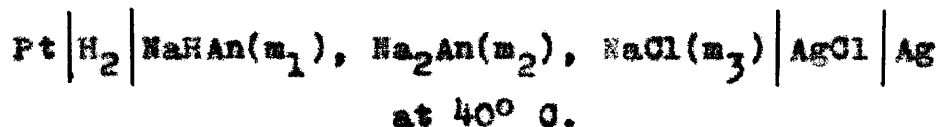
$m_1=m_2=m_3$	μ'	E	E_f'	$m_H \times 10^5$	μ	E_f
.0009867	.0049334	.74580	5.7381	.2552	.0049395	5.7361
.0010619	.0053095	.74366	5.7378	.2587	.0053160	5.7357
.0011095	.0055475	.74251	5.7397	.2595	.0055540	5.7377
.0019114	.0095570	.72686	5.7440	.2871	.0095642	5.7427
.0019420	.0097100	.72613	5.7397	.2910	.0097179	5.7385
.0024182	.012091	.72009	5.7480	.3014	.012098	5.7469
.0029128	.014564	.71467	5.7511	.3147	.014572	5.7505
.0030385	.015193	.71309	5.7464	.3224	.015201	5.7455
.0040020	.020010	.70532	5.7577	.3424	.020018	5.7570
.0047561	.023781	.70020	5.7621	.3601	.023790	5.7615
.0050248	.025124	.69855	5.7634	.3664	.025133	5.7628
.0068161	.034081	.68954	5.7754	.4036	.034091	5.7750
.0068596	.034298	.68919	5.7731	.4069	.034308	5.7726
.0094543	.047272	.67959	5.7887	.4576	.047283	5.7883
.0095398	.047699	.67936	5.7898	.4585	.047710	5.7895
.018622	.093110	.65864	5.8310	.6299	.093125	5.8308
.029535	.14768	.64411	5.8754	.8286	.14770	5.8753
.044566	.22283	.63085	5.9278	1.1149	.22286	5.9277

$$-\log K_2 \text{ (extrapolated)} = 5.7300$$

$$K_2 = 1.863 \times 10^{-6}$$

Table 9.

Results obtained from the electromotive forces of the cell.



$E_0 = 0.21200$

$A = 0.5219$

$2.3026RT/F = 0.06213$

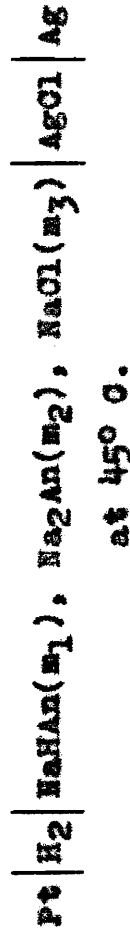
$m_1=m_2=m_3$	μ'	E	E_f'	$m_H \times 10^5$	μ	E_f
.0009867	.0049334	.75178	5.7554	.2462	.0049393	5.7533
.0010619	.0053095	.75008	5.7627	.2451	.0053158	5.7605
.0011095	.0055475	.74878	5.7625	.2472	.0055537	5.7605
.0019114	.0095570	.73284	5.7665	.2739	.0095638	5.7653
.0019420	.0097100	.73208	5.7620	.2778	.0097178	5.7608
.0024182	.012091	.72588	5.7693	.2886	.012098	5.7683
.0029128	.014564	.72045	5.7735	.3007	.014571	5.7730
.0030385	.015193	.71884	5.7691	.3078	.015200	5.7682
.0040020	.020010	.71079	5.7781	.3290	.020018	5.7774
.0047561	.023781	.70565	5.7837	.3454	.023789	5.7831
.0050248	.025124	.70416	5.7880	.3490	.025133	5.7875
.0068161	.034081	.69476	5.7964	.3886	.034090	5.7954
.0068596	.034298	.69452	5.7959	.3897	.034308	5.7955
.0094543	.047272	.68467	5.8103	.4401	.047282	5.8100
.0095398	.047699	.68443	5.8114	.4411	.047710	5.8111
.018622	.093110	.66336	5.8533	.6077	.093125	5.8531
.029535	.14768	.64850	5.8971	.8039	.14770	5.8969
.044566	.22283	.63501	5.9502	1.0846	.22286	5.9500

$-\log K_2 \text{ (extrapolated)} = 5.7515$

$K_2 = 1.772 \times 10^{-6}$

Table 10.

Results obtained from the electromotive forces of the cell.



$m_1 = m_2 = m_3$	μ	E	E'	$m_{\text{HCl}} \times 10^5$	μ	E''
.0011095	.0055475	.75514	5.7887	.2335	.0055533	5.7870
.0019114	.0095570	.73890	5.7922	.2596	.0095635	5.7911
.0019420	.0097100	.73837	5.7915	.2609	.0097168	5.7904
.0024182	.012091	.73147	5.7895	.2708	.012098	5.7886
.0030385	.015193	.72460	5.7938	.2927	.015200	5.7931
.0040020	.020010	.71654	5.8050	.3117	.020018	5.8043
.0047561	.023781	.71104	5.8064	.3283	.023789	5.8064
.0068161	.034081	.70000	5.8197	.3715	.034090	5.8193
.0068596	.034298	.69982	5.8203	.3722	.034307	5.8199
.0094543	.047272	.68981	5.8350	.4207	.047282	5.8347
.0095398	.047699	.68942	5.8338	.4239	.047709	5.8335
.018622	.093110	.66800	5.8765	.5858	.093125	5.8763
.029535	.14768	.65284	5.9202	.7783	.14769	5.9200
.044566	.22283	.63919	5.9752	1.0505	.22286	5.9751

$E_0 = 0.20821$

$A = 0.5278$

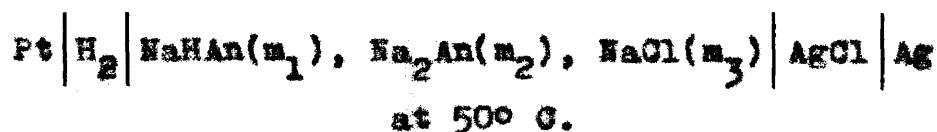
$2.3026RT/F = 0.06312$

$-\log K_2 \text{ (extrapolated)} = 5.7769$

$K_2 = 1.672 \times 10^{-6}$

Table 11.

Results obtained from the electromotive forces of the cell.



$E_0 = 0.20437$

$A = 0.5340$

$2.3026RT/F = 0.06412$

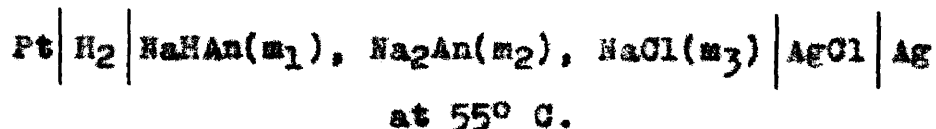
$m_1=m_2=m_3$	μ'	K	E_f'	$m_H \times 10^5$	μ	E_f
.0011095	.0055475	.76156	5.8145	.2211	.0055530	5.8129
.0019114	.0095570	.74566	5.8120	.2494	.0095632	5.8109
.0019420	.0097100	.74444	5.8163	.2478	.0097163	5.8153
.0024182	.012091	.73763	5.8176	.2614	.012098	5.8167
.0030385	.015193	.73054	5.8203	.2773	.015199	5.8196
.0040020	.020010	.72212	5.8281	.2979	.020017	5.8275
.0047561	.023781	.71653	5.8295	.3136	.023788	5.8295
.0068161	.034081	.70516	5.8409	.3576	.034089	5.8405
.0068596	.034298	.70525	5.8457	.3547	.034307	5.8453
.0094543	.047272	.69497	5.8591	.4033	.047282	5.8588
.0095398	.047699	.69487	5.8625	.4018	.047709	5.8622
.018622	.093110	.67274	5.9005	.5640	.093125	5.9003
.029535	.14768	.65725	5.9438	.7534	.14769	5.9415
.044566	.22283	.64340	6.0002	1.0189	.22286	6.0000

$-\log K_2 \text{ (extrapolated)} = 5.8028$

$K_2 = 1.575 \times 10^{-6}$

Table 12.

Results of obtained from the electromotive forces of the cell.



$$E_0 = 0.20035$$

$$A = 0.5405$$

$$2.3026RT/F = 0.06511$$

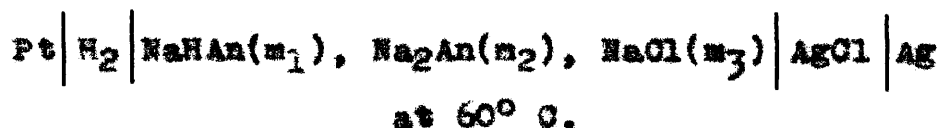
$m_1=m_2=m_3$	μ'	E	E_f'	$m_H \times 10^5$	μ	E_f
.0011095	.0055475	.76798	5.8437	.2077	.0055527	5.8421
.0019114	.0095570	.75115	5.8466	.2317	.0095629	5.8456
.0019420	.0097100	.75063	5.8463	.2327	.0097160	5.8453
.0024182	.012091	.74368	5.8472	.2458	.012097	5.8463
.0030385	.015193	.73644	5.8495	.2612	.015199	5.8488
.0040020	.020010	.72768	5.8543	.2829	.020017	5.8537
.0047561	.023781	.72232	5.8607	.2970	.023788	5.8602
.0068161	.034081	.71075	5.8721	.3365	.034089	5.8718
.0068596	.034298	.71082	5.8766	.3340	.034306	5.8762
.0094543	.047272	.70019	5.8875	.3828	.047281	5.8872
.0098398	.047699	.69999	5.8894	.3826	.047708	5.8891
.018622	.093110	.67742	5.9270	.5404	.093123	5.9268
.029535	.14768	.66172	5.9718	.7219	.14769	5.9698
.044566	.22283	.64760	6.0284	.9821	.22285	6.0283

$$-\log K_2 \text{ (extrapolated)} = 5.8327$$

$$K_2 = 1.470 \times 10^{-6}$$

Table 13.

Results obtained from the electromotive forces of the cell.



$$E_0 = 0.19620$$

$$\Lambda = 0.5472$$

$$2.3026RT/F = 0.06610$$

$m_1=m_2=m_3$	μ'	E	E_f'	$m_H \times 10^5$	μ	E_f
.0011095	.0055475	.77466	5.8779	.1928	.0055523	5.8765
.0019114	.0095570	.75739	5.8784	.2166	.0095625	5.8774
.0019420	.0097100	.75683	5.8776	.2178	.0097155	5.8768
.0024182	.012091	.74968	5.8772	.2309	.012097	5.8765
.0030385	.015193	.74254	5.8829	.2437	.015199	5.8823
.0040020	.020010	.73334	5.8833	.2669	.020017	5.8827
.0047561	.023781	.72794	5.8905	.2799	.023787	5.8900
.0068161	.034081	.71617	5.9020	.3177	.034088	5.9026
.0068596	.034298	.71670	5.9134	.3106	.034306	5.9128
.0094543	.047272	.70538	5.9168	.3624	.047281	5.9165
.0095398	.047699	.70509	5.9174	.3637	.047708	5.9171
.018622	.093110	.68217	5.9560	.5151	.093123	5.9558
.029535	.14768	.66624	6.0020	.6905	.14769	6.0018
.044566	.22283	.65187	6.0593	.9418	.22285	6.0591

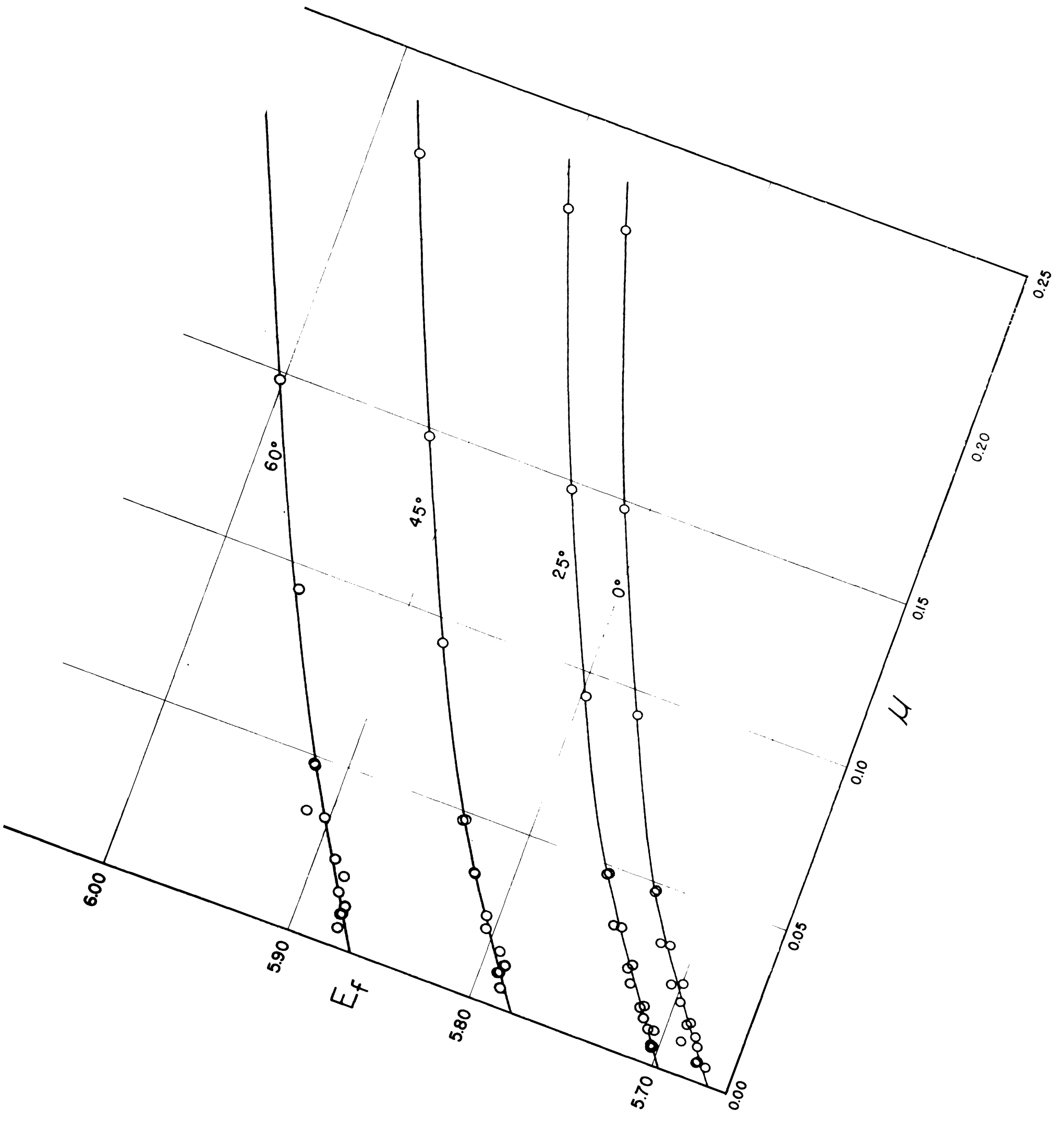
$$-\log K_2 \text{ (extrapolated)} = 5.8655$$

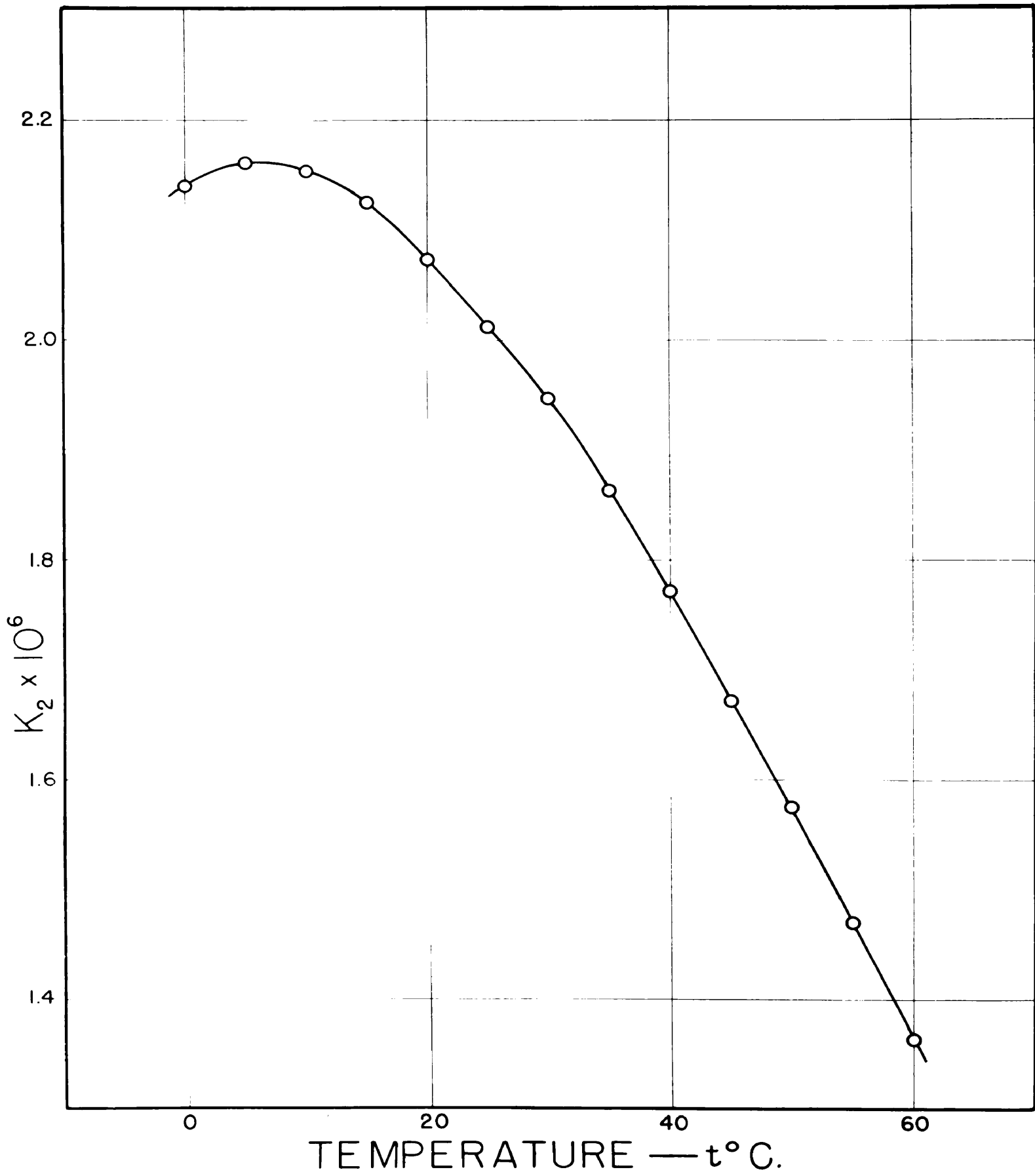
$$K_2 = 1.363 \times 10^{-6}$$

for the absolute temperature. The values of R and F used in the calculation of $2.3026RT/F$ are those recommended by Lewis and Randall [37].

For the determination of the ionization constants E_f was plotted against the ionic strength μ and the curves extrapolated to zero ionic strength. For purposes of illustration the curves at 0° , 25° , 45° and 60° are given in figure 2. This shows the form and slope of the curves, all of which were very similar. The actual extrapolations were made from plots on a much larger scale. The extrapolated values of E_f are equal to $-\log K_2$, or pK_2 . The values of $-\log K_2$ and of K_2 derived therefrom are given at the bottom of each table. The change of the ionization constant with temperature is shown graphically in figure 3.

The precision with which the constants were determined can be estimated from a consideration of the curves in figure 2. The sensitivity of this method of plotting is seen to be very great when it is considered that 0.1 millivolt causes a change of 0.002 in the value of $-\log K_2$. With few exceptions, most of which are in the low concentration range or at the higher temperatures, the deviations of the observed points from the smooth curves are less than this. The extrapolations, however, are made more certain by the facts that theory dictates



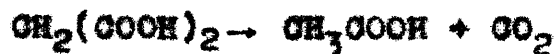


and previous experimental evidence has shown that the curves must approach straight lines as the concentration decreases, that they must be parallel or their slopes change uniformly with temperature, and that the ionization constant must change uniformly with temperature. With these aids in the extrapolations it is believed that pK_2 has been estimated with a precision of ± 0.001 , which corresponds to a precision of ± 0.3 percent in the value of K_2 .

The deviations from the smooth curves occurring in the more dilute solutions may have been caused by incomplete removal of the air or the diffusion of air into the cells during the measurements. The effects of air are increasingly pronounced as the concentration is decreased. Furthermore, all solutions having an ionic strength of less than 0.01 had a lower chloride-ion concentration than has been used in any previous work with the silver chloride electrode. Inasmuch as the potential of this electrode is dependent only upon the concentration of chloride ion, uncertainties may be expected at the very low concentrations. For this reason in making the extrapolations less weight was given to the points below an ionic strength of 0.01.

The deviations at the higher temperatures may have been caused by a slight decomposition of the malonic acid salts. Malonic acid is known to decompose in solution

according to the reaction



Bernoulli and Wege [38] determined the velocity constant for this reaction through the temperature interval 75°-110° C and by extrapolation found 66° C to be the lowest temperature at which measurable decomposition takes place. Later Bernoulli and Jakubowicz [39] measured the decomposition at 66° and found it to be 0.1 percent in 4 hours. No data are available on the decomposition of malonic acid salts, but inasmuch as they form a slight amount of free malonic acid by hydrolysis and the temperature at which its decomposition is known to take place was approached, there is a possibility that some decomposition occurred at the higher temperatures. Decomposition would probably be more readily detected by an electrometric method such as was used here than by the titration method of Bernoulli and Jakubowicz.

MacInnes and Belcher [22] found in their work on the second ionization constant of carbonic acid that the stoichiometrical concentrations were appreciably altered by the hydrolysis of the dibasic salt. For malonic acid this hydrolysis is expressed by the reaction



The concentration of NaOH produced by this reaction is

given by the equation

$$\frac{X(m_1 + X)}{m_2 - X} = \frac{K'_W}{K'_2}$$

where X , m_1 and m_2 are the stoichiometrical concentrations of NaOH, NaHAN and Na₂AN respectively and K'_W and K'_2 are the stoichiometrical ionization constants of water and of the acid malonate ion. Using the approximate values $K'_W = 10^{-14}$ and $K'_2 = 2 \times 10^{-6}$ at 25° C, X was calculated to be of the order of 10^{-8} mols per liter in the most dilute solutions where the hydrolysis would be the greatest. This concentration of NaOH is negligible in comparison with those of NaHAN and Na₂AN. Hence, no corrections were made for the hydrolysis in this work.

Previous work on the determination of the second ionization constant of malonic acid has been limited to the two temperatures 18° and 25° C. Hence, the results of this work are comparable with those obtained by others only at those temperatures. Table 14 contains the previous values and the methods by which they were obtained. The marked divergence is due both to experimental differences and to the assumptions involved in the methods employed. The earlier work of Wegscheider, Smith, Chandler and Datta and Dhar embodied the classical solution laws and neglected the effects of interionic attraction. Furthermore, their work was handicapped by the lack of refined pH and conductance methods at that time. The values

Table 14.
 Values of the Second Ionization Constant of Malonic Acid Obtained
 by Various Workers

Observer	Method	Ref.	$K_2 \times 10^6$
Wegecheider	Conductivity, classical treatment.	[4]	10.0
Smith	Conductivity and sucrose inversion, classical treatment.	[15]	1.0
Chandler	Conductivity, classical treatment.	[3]	2.1
Chandler	Partition, classical treatment	[3]	2.03
Datta and Dhar	Carbon dioxide absorption, classical treatment	[14]	1.36
Britton	Electrometric titration, classical treatment. No correction for liquid junction potential.	[6]	4.45
Larsson	Electrometric titration with corrections for effects of interionic attraction by the empirical Bjerrum [43] equation. Liquid junction calculated by the Bjerrum equation [44].	[7]	2.0
Gane and Ingold	Electrometric titration, classical treatment. No corrections for liquid junction potential.	[9]	4.37
Gane and Ingold	Electrometric titration at various concentrations and empirical extrapolation to zero concentration. No corrections for liquid junction potential.	[9]	2.03

Simms	Electrometric titration at 0.1 M concentration [8] and correction for effects of interionic attraction by Debye-Hückel equation. No corrections for liquid junction potential.		1.8
Burton	Electrometric titration at 0.1 M concentration, [10] classical treatment. No corrections for liquid junction potential.		3.89
German and Vogel	Electrometric titration with corrections for [12] effects of interionic attraction. No corrections for liquid junction potential.		2.20
Burton, Hamer and Acree	Application of Debye-Hückel theory and [11] Henderson's equation for liquid junction potentials to Burton's data.		2.94
Hamer and Acree	Correction of the above for the liquid [41] junction potential of the reference electrode.		2.51
The author	Electromotive force method employing cells without liquid junctions. Debye-Hückel equation used in the calculation for interionic attraction effects.	2.102 *	2.012

*Calculated from equation (13).

obtained by Chandler agree quite well with those obtained in this work but this can hardly be considered as anything but coincidence. Chandler found that the constant, as determined by his methods, changed with concentration and reported the value he obtained at 0.001M as the ionization constant. The divergence of the constants obtained by the electrometric titration method is due to several factors. Those of Britton and Burton and the earlier value of Gane and Ingold are high because the measurements were made in solutions of relatively high salt concentrations, no corrections were made for the effects of interionic attractions, and the liquid junction potentials were disregarded. Gane and Ingold later extended their measurements over a series of concentrations and extrapolated their data to zero concentration by an empirical method. Larson, Simms and German and Vogel corrected for the effects of interionic attraction but they employed cells with liquid junctions and the precision of their work was not better than 5 percent. Burton, Hamer and Acree recalculated Burton's results on the basis of the Debye-Hückel theory and made corrections for the liquid junction potential by means of the Henderson [40] equation. A further correction was later applied by Hamer and Acree for the liquid junction potential included in the standard potential of the reference electrode. They found

a direct comparison of the value obtained in this manner cannot be made with that found in the present work since the former value includes salt errors while the latter value is at infinite dilution where salt errors have been eliminated.

2. The determination of the "salt coefficient", β .

It has been explained previously that the term β was introduced in equations (7) and (9) to express the deviations of the observed values of the left side of the equations from those predicted by theory, and that these deviations were caused by the presence of the salts. Thus β may be called a "salt coefficient" and is expressed by

$$E_f = -\log K_2 + \beta\mu = pK_2 + \beta\mu \quad (10)$$

which is the same as equation (9) since E_f has been employed to represent the left side of that equation. In order to evaluate β and at the same time obtain a check on the extrapolated values of K_2 this equation has been solved for pK_2 and β at each temperature by the method of least squares. Only values of E_f for concentrations below 0.007 M were employed since the plots showed that the slopes of the curves were changing rapidly at higher concentrations. Values of pK_2 and β found in this manner are given in the second and third columns of table 15.

Table 15.

Comparison of Extrapolated and Least Square Equation Values of pK_2 , X_2 and β for Malonic Acid from 0° to 60° C.

$t^\circ C$	pK_2 Eq.(10)	β Eq.(10)	pK_2 Eq.(11)	pK_2 (Calc.)	pK_2 (Obs.)	δpK_2	$X_2 \times 10^{-6}$ (Calc.)	$X_2 \times 10^{-6}$ (Obs.)	$\delta X_2 \times 10^{-6}$
0	5.6716	1.258	1.344	5.6699	5.6696	+0.003	2.139	2.140	-0.001
5	5.6634	1.390	1.356	5.6641	5.6653	-0.0012	2.167	2.161	+0.006
10	5.6651	1.448	1.362	5.6667	5.6667	.0000	2.154	2.154	.000
15	5.6712	1.419	1.363	5.6723	5.6726	-0.0003	2.127	2.125	+0.002
20	5.6831	1.327	1.357	5.6825	5.6835	-0.0010	2.077	2.073	+0.004
25	5.6960	1.317	1.346	5.6959	5.6764	-0.0005	2.014	2.012	+0.002
30	5.7107	1.298	1.329	5.7101	5.7106	-0.0005	1.949	1.947	+0.002
35	5.7293	1.312	1.307	5.7294	5.7300	-0.0006	1.865	1.863	+0.002
40	5.7511	1.326	1.276	5.7521	5.7515	+0.0006	1.770	1.772	-0.002
45	5.7780	1.205	1.244	5.7772	5.7769	+0.0003	1.670	1.672	-0.002
50	5.8034	1.114	1.204	5.8021	5.8028	-0.0007	1.577	1.575	+0.002
55	5.8334	1.144	1.159	5.8333	5.8327	+0.0006	1.468	1.470	-0.002
60	5.8650	1.172	1.107	5.8664	5.8655	+0.0009	1.360	1.363	-0.003

The values of β show marked fluctuations, a large part of which may be ascribed to the least square method of giving equal weight to all points. However, it is reasonable to expect that β should bear some relation to the temperature and on this basis it was assumed that it was expressed by the equation

$$\beta = a + bt + ct^2$$

Using the values of β in the third column of table 15, the constants a , b and c were determined by the method of least squares and the equation was found to be

$$\beta = 1.344 + 0.002953t - 0.0001766t^2 \quad (11)$$

This equation was solved for β at each temperature, the results of which are given in the fourth column of table 15. Equation (10) was then solved for pK_2 at each temperature using these values of β . The results are designated as pK_2 (calc.) in the fifth column of the same table. For purposes of comparison the values of pK_2 obtained by extrapolation, pK_2 (obs.), are also included in the table. The two agree very well, thus confirming the accuracy of the extrapolations. The deviations, designated as δpK_2 , are due partly to the use of a linear expression for E_f and would undoubtedly have been smaller if an equation of the type

$$E_f = pK_2 + 8\mu + \omega\mu^2$$

had been employed, where ω may be considered a coefficient

similar to Brönsted's coefficient for specific interaction of ions [42].

3. The heat of ionization and other thermodynamical properties of the acid malonate ion.

The knowledge of the ionization constant over a temperature range makes possible the calculation of the heat of ionization by means of the van't Hoff equation. This equation is

$$\frac{d \ln K_2}{dT} = \frac{\Delta H_1}{RT^2} \quad (12)$$

Expressing ΔH_1 by the equation

$$\Delta H_1 = A + BT + CT^2 + DT^3$$

and substituting in equation (12) yields upon integration

$$\log K_2 = - \frac{A}{2.3026RT} + \frac{B}{R} \log T + \frac{C}{2.3026R} T + \frac{D}{4.6052R} T^2 + I$$

where I is the constant of integration. By substituting the experimental values of K_2 and T in this equation, thirteen equations were obtained from which the constants A , B , C , D and I were determined by the method of least squares. The equation for K_2 was found to be

$$\log K_2 = - \frac{1053.08}{T} + 20.3223 \log T - 0.058379 T + 0.000023597 T^2 - 37.1402 \quad (13)$$

and that for ΔH_1 was

$$\Delta H_1 = 4821.8 + 40.4109T - 0.2673T^2 + 0.00021608T^3 \quad (14)$$

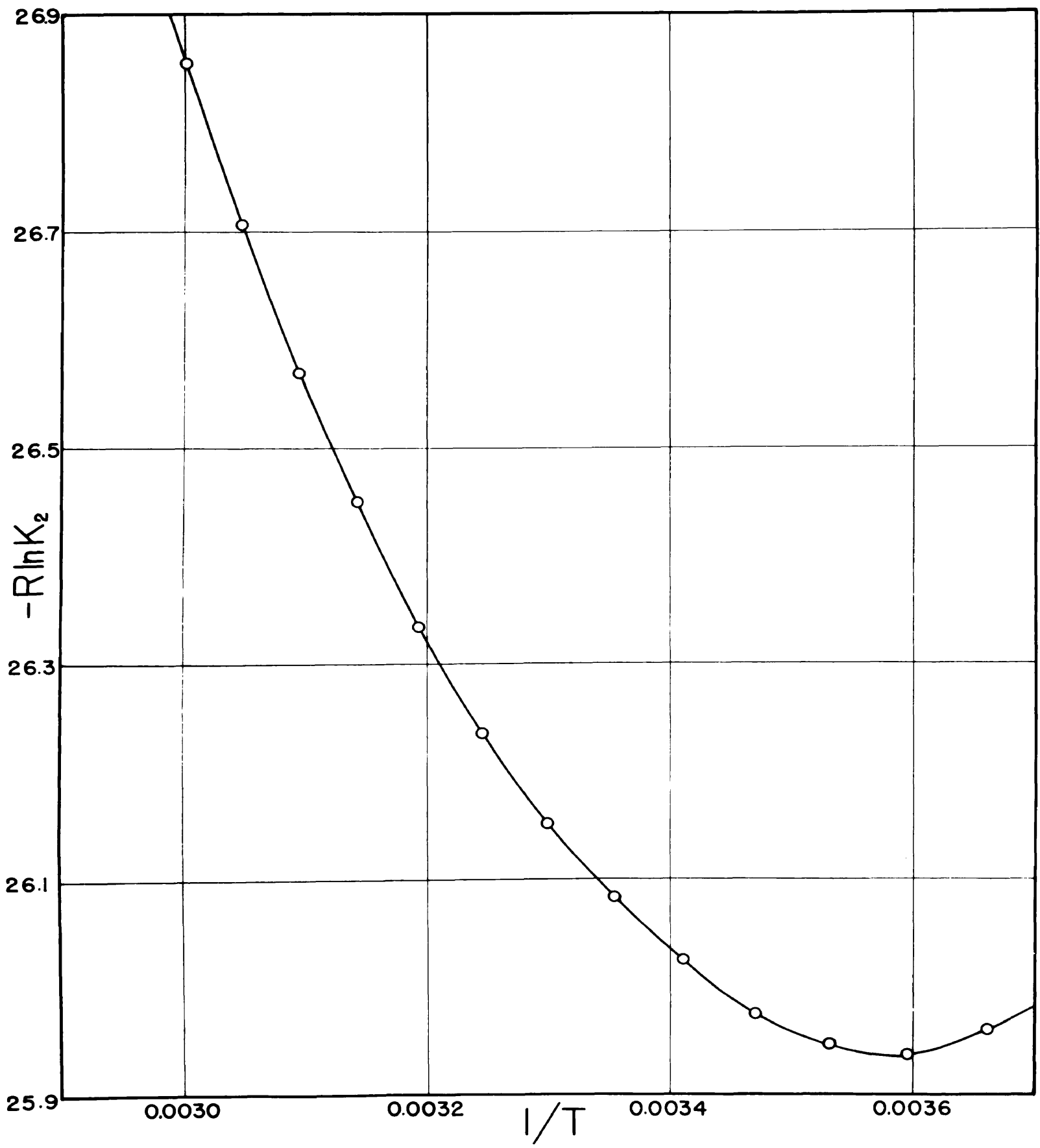
The values of K_2 calculated by means of equation (13) are given in the third column of table 16. The observed values are included for comparison. The deviations between the two

Table 16.

The Ionization Constant, Heat of Ionization and Related Thermodynamic

Properties of the Acid Malonate Ion from 0° to 60° C.

t° C	$K_2 \times 10^6$ (Obs.)	$K_2 \times 10^6$ Eq. (13)	$\delta K_2 \times 10^6$	ΔH_1 -Cals. Eq. (14)	ΔH_1 -Cals. (graph)	ΔO_f Cals./deg.	ΔF_f Cals.	ΔS_f Cals./deg.
0	2.140	2.144	+0.004	+ 320	+ 430	-56.3	7091	-24.8
5	2.161	2.157	-0.004	+ 31	+ 74	-58.1	7215	-25.8
10	2.154	2.149	-0.005	- 262	- 313	-59.0	7347	-26.5
15	2.125	2.122	-0.003	- 659	- 640	-59.8	7484	-27.9
20	2.073	2.078	+0.005	- 860	- 926	-60.6	7629	-29.0
25	2.012	2.018	+0.006	-1165	-1143	-61.5	7777	-30.0
30	1.947	1.946	-0.001	-1473	-1431	-62.1	7927	-31.0
35	1.863	1.863	.000	-1785	-1741	-62.8	8085	-32.0
40	1.772	1.771	-0.001	-2101	-2108	-63.4	8247	-33.0
45	1.672	1.673	+0.001	-2420	-2389	-64.1	8416	-34.1
50	1.575	1.570	-0.005	-2741	-2703	-64.7	8586	-35.1
55	1.470	1.466	-0.004	-3066	-3084	-65.2	8764	-36.1
60	1.363	1.361	-0.002	-3394	-3398	-65.7	8948	-37.1



are for the most part within the experimental error. The values of ΔH_1 calculated from equation (14) are given in the fifth column of table 16. Although they are recorded to four significant figures their precision is estimated to be of the order of ± 50 cal.

The heat of ionization can also be determined by a graphical method. Upon rearrangement of equation (12) there is obtained

$$\frac{d(-R \ln K_2)}{d(1/T)} = \Delta H_1$$

from which it is seen that ΔH_1 is the slope of the curve obtained by plotting $-R \ln K_2$ against $1/T$. This plot is given in figure 4 and the values of ΔH_1 determined from the slope of the curve recorded in the sixth column of table 16. They agree with those calculated from equation (14) within the precision of the measurements except at the lower temperatures where the slope was changing so rapidly as to be difficult to measure.

Other thermodynamical properties of the acid malonate ion can be calculated from the data. Thus the difference in specific heat of the HAN^- ions and the H^+ and AN^- ions produced by its dissociation is obtained by differentiating equation (14). That is

$$\Delta C_{p_1} = 40.4109 - 0.5346T + 0.00064824T^2$$

The change of free energy produced by the dissociation of

HAN^- ion when in its standard state is given by the equation

$$\Delta F_1^{\circ} = - 2.3026RT \log K_2$$

and the corresponding entropy change by the equation

$$\Delta S_1^{\circ} = - \frac{\Delta F_1^{\circ} - \Delta H_1}{T}$$

The values of ΔG_{P_1} , ΔF_1° and ΔS_1° calculated from these equations are given in the seventh, eighth and ninth columns of table 16.

V. SUMMARY.

1. It has been shown that the method of determining the ionization constants of weak electrolytes by means of cells without liquid junctions is applicable to the measurement of the second ionization constant of a representative dibasic organic acid, malonic acid, with an accuracy greater than heretofore possible by other methods.

2. Malonic acid has been refined to a purity of 99.88 percent as indicated by weight titration with a standard sodium hydroxide solution.

3. From measurements of the electromotive forces of the cell



over the concentration range 0.001-0.05 M, the thermodynamic ionization constant of the acid malonate ion has

been determined from 0° to 60° C at 5° temperature intervals.

4. The "salt coefficient" of malonic acid, expressing the deviations of the observed results at finite concentrations from those predicted by the Debye-Hückel theory of electrolytic dissociation, has been evaluated over the concentration range 0 - 0.007 M and from 0° to 60° C.

5. Equations have been obtained from which the ionization constant and heat of ionization of the acid malonate ion can be calculated at any temperature between 0° and 60° C. From these equations the changes of specific heat, free energy and entropy for the dissociation of the acid malonate ion have been determined.

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