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THE DISSOCIATION CONSTANT OF ACETIC  
ACID AT 25°C

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BY  
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TABLE OF CONTENTS

Introduction . . . . .	1
Theory . . . . .	2- 4
Experimental . . . . .	5- 11
Data and Results . . . . .	12- 17
Discussion of Results . . . . .	18
Summary . . . . .	19
Bibliography . . . . .	21

## INTRODUCTION

The dissociation constants of weak acids can be determined from thermodynamic data obtained from cells without liquid junction. The method was developed by Harned and his students.<sup>4</sup>

In applying the method to acetic acid, Harned and Ehlers<sup>3</sup> used a cell of the type:

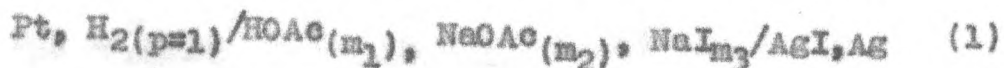


Consideration of the ionization reactions occurring in the cell electrolyte shows that the electrolyte acts as though it is a dilute solution of hydrochloric acid in a sodium acetate--acetic acid buffer mixture. The value derived for the dissociation constant of acetic acid at 25° from the potential of the cell was  $1.754 \times 10^{-5}$ .

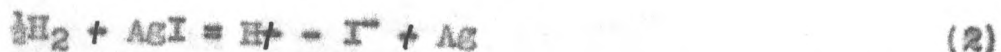
The purpose of this study is to examine the silver-silver iodide electrode in a similarly buffered acetic acid solution, and to test the reliability of the electrode by comparison of the values of the dissociation constant calculated from the observed potentials with that obtained from the highly reproducible measurements made by Harned.

## THEORY

According to the method of Harned<sup>3</sup> and his associates, the dissociation constant for acetic acid can be calculated from purely thermodynamic measurements using a cell without liquid junction of the type.



The reaction for this cell is:



If the pressure of the hydrogen is one atmosphere, the following equation expresses the potential of the cell:

$$E = E^0 - \frac{RT}{F} \ln (m_{\text{H}^+} \delta_{\text{H}^+} - m_{\text{I}^-} \delta_{\text{I}^-}) \quad (3)$$

Where  $E$  is the observed e.m.f.,  $E^0$  the standard reduction potential,  $R$  the molar gas constant,  $T$  the absolute temperature,  $F$  the faraday constant,  $m$  the respective molality, and  $\delta$  of the indicated ion, the activity coefficient in molality units. The ionization of acetic acid may be expressed:



and the ionization constant may be expressed by the following equation:

$$K_{\text{HOAc}} = \frac{[\text{H}_3\text{O}^+][\text{OAc}^-]}{[\text{HOAc}]} \quad (5)$$

Where  $[\text{H}_3\text{O}^+]$ ,  $[\text{OAc}^-]$ , and  $[\text{HOAc}]$  represent the activities of the hydronium, acetate ion, and the acetic acid

respectively, the thermodynamic equation for the dissociation of acetic acid is

$$K_{\text{HOAc}} = \frac{m_{\text{H}^+} m_{\text{OAc}^-}}{m_{\text{HOAc}}} \cdot \frac{\gamma_{\text{H}^+} \gamma_{\text{OAc}^-}}{\gamma_{\text{HOAc}}} \quad (6)$$

Where  $K$  is the dissociation constant of the acid, or, rearranging:

$$m_{\text{H}^+} = \frac{m_{\text{HOAc}}}{m_{\text{OAc}^-}} \cdot \frac{\gamma_{\text{HOAc}}}{\gamma_{\text{H}^+} \gamma_{\text{OAc}^-}} K \quad (7)$$

Substituting this value for  $m_{\text{H}^+}$  in equation (3)

$$E - E^0 - \frac{RT}{F} \ln \left( \frac{m_{\text{HOAc}} m_{\text{I}^-}}{m_{\text{OAc}^-}} \cdot \frac{\gamma_{\text{H}^+} \gamma_{\text{I}^-} \gamma_{\text{HOAc}}}{\gamma_{\text{H}^+} \gamma_{\text{OAc}^-}} \right) K \quad (8)$$

This may be rearranged to give the following:

$$\begin{aligned} E - E^0 - \frac{RT}{F} \ln \left( \frac{m_{\text{HOAc}} m_{\text{I}^-}}{m_{\text{OAc}^-}} \right) &= \\ - \frac{RT}{F} \ln \frac{\gamma_{\text{H}^+} \gamma_{\text{I}^-} \gamma_{\text{HOAc}}}{\gamma_{\text{H}^+} \gamma_{\text{OAc}^-}} - \frac{RT}{F} \ln K & \quad (9) \end{aligned}$$

The values of  $E$  are measured at various values of  $m_{\text{HOAc}}$ ,  $m_{\text{I}^-}$ , and  $m_{\text{OAc}^-}$ . In dilute solutions, the total concentration of the acetate ion,  $m_{\text{OAc}^-}$ , is the sum of the acetate ion formed by the dissociation of acetic acid, and that from the sodium acetate. The value  $m_{\text{HOAc}}$  is obtained by subtracting from the analytically determined molality of the acetic acid,  $m^{\text{a}}_{\text{HOAc}}$ , the molality of the hydronium ion,  $m_{\text{H}^+}$ . This is obtained by the use of the equation

$$m_{\text{H}^+} = \sqrt{(m^{\text{a}}_{\text{HOAc}}) (1.78 \times 10^{-5})} \quad (10)$$

where  $(1.78 \times 10^{-5})$  represents an assumed value for the

dissociation constant of acetic acid. These corrections remain small in the presence of excess sodium acetate. The value of  $m_{I^-}$  is known from the concentration of the sodium iodide, assuming complete dissociation and no hydrolysis.

The values of the quantities in the left side of equation (9) are all known; and so the value of this side of the equation is plotted against the ionic strength,  $\mu$ .

The ratio of the activity coefficients,  $\frac{\gamma_{H^+} \gamma_{I^-}}{\gamma_{H^+} \gamma_{OAc^-}}$ ,

is equal to unity when  $\mu = 0$ . The same is true for  $\gamma_{HOAc}$ . Since the first term on the right side of equation (9),  $-\frac{RT}{F} \ln \frac{\gamma_{H^+} \gamma_{I^-} \gamma_{HOAc}}{\gamma_{H^+} \gamma_{OAc^-}}$ , varies with ionic strength while the second,  $-\frac{RT}{F} \ln K$ , is constant, the equation is of the straight line form, and so a nearly straight line should result from the plot of the left side of the equation against  $\mu$ . Extrapolation of the left side to zero ionic strength eliminates the term involving the activity coefficients, and the intercept will be the value of  $-\frac{RT}{F} \ln K$ . Thus, measurement of the e.m.f. of the cell indicated leads to a direct evaluation of the thermodynamic dissociation constant.

## EXPERIMENTAL

### MATERIALS

Mallinkrodt's 99.5% Analytical Reagent acetic acid was used without further purification. The sodium iodide was Coleman & Bell's C.P. Analyzed product, and the sodium acetate was Coleman and Bell's C.P. Analytical Reagent grade. Neither was further purified.

**SILVER OXIDE:** Silver oxide was prepared by adding a hot solution of Mallinkrodt's Analytical Reagent sodium hydroxide to a hot solution containing an excess of Merck's C.P. silver nitrate. The precipitated oxide was washed twenty-six times by decantation, dried in a vacuum dessicator, and stored in a brown bottle.

**SILVER IODATE:** To a hot solution of Coleman and Bell's C.P. sodium iodate was added a solution of Merck's C.P. silver nitrate. The white precipitate was washed by decantation twenty-five times, dried for eight days in an oven at 60°C, and stored in a brown bottle.

**HYDROGEN:** Commercial tank hydrogen was passed over copper shavings at about 450°C and then through a chain of four gas saturating bulbs

containing successively sodium hydroxide, potassium permanganate (2), and redistilled water. The gas was then lead through a Bichowsky and Storch<sup>1</sup> gas saturating bulb and finally through the cell, these being immersed in a constant water bath. Connections consisted mainly of Corning's standard taper glass joints. Openings through which the various solutions were poured into their respective vessels were covered with paper and sealed with wax. Cork surfaces were entirely paraffined.

#### SOLUTIONS

**ACETIC ACID:** The stock solution of acid was standardized by titration against a sodium hydroxide solution, the strength of which was determined by titration against a carefully prepared potassium acid phthalate solution. Calibrated buretts were used in all titrations. The molality of the solution represents the average of several determinations which agreed to 0.1% of the total acetic acid.

**SODIUM ACETATE:** A sample of this salt was carefully weighed and added to the original acetic acid solution.

SODIUM IODIDE: An accurately weighed sample of sodium iodide was dissolved into the acetic acid solution.

CELL SOLUTIONS: The stock solution consisted of the standardized acetic acid solution containing the weighed amounts of sodium iodide and sodium acetate. The density of this solution and also of successive solutions was determined by weighing at 25° a pycnometer filled with the solution; the exact volume of the pycnometer had been determined previously at the same temperature.

The equation used for the determination of the density was:

$$d_l = \frac{G'a - Gg}{V} \left[ 0.99986 + \frac{0.0012}{d_l} \right] \quad (11)$$

Where  $d_l$  is the density of the liquid,  $G'a$  the apparent total weight,  $Gg$  the apparent weight of the pycnometer, and  $V$  the volume of the pycnometer.

Other factors in the equation correct for the buoyancy effect of air. The equation used to determine the volume of the pycnometer was:

$$V = \frac{(G_a - G_g) \left( 0.99986 + \frac{0.0012}{d_w} \right)}{d_w} \quad (12)$$

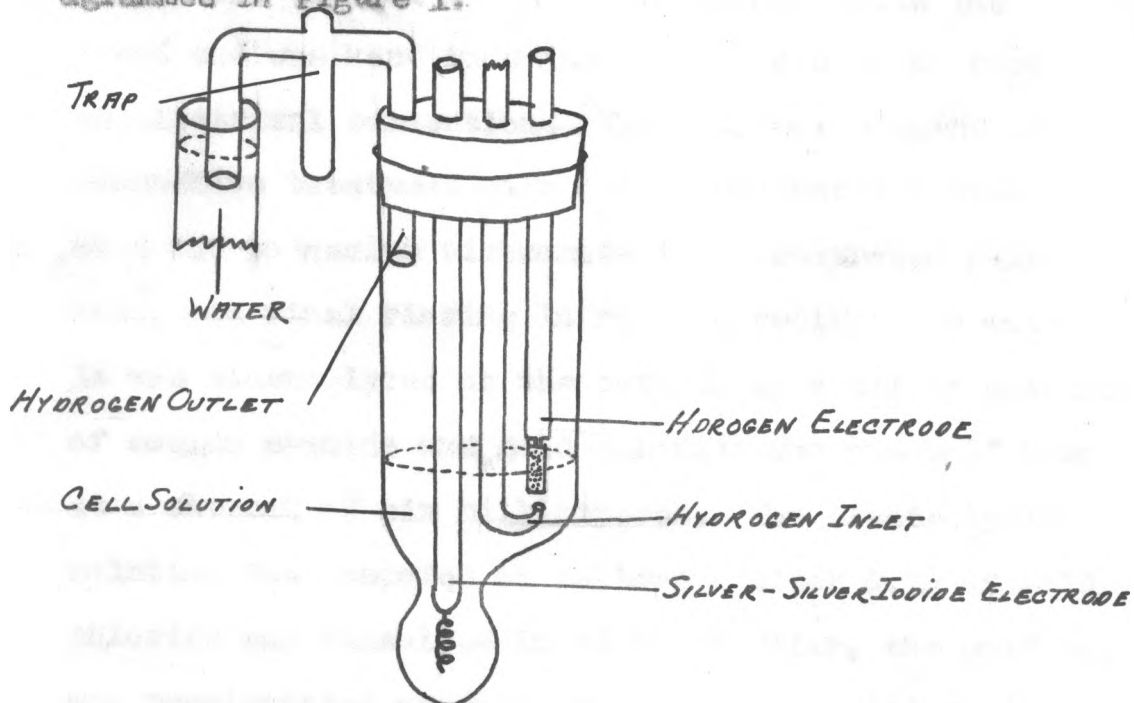
Where  $G_a$  is the apparent total weight,  $G_g$  the apparent weight of the pycnometer, and  $d_w$  the density of water at the temperature of the experiment. Other

factors correct for the buoyancy of air. Successive solutions of lesser molality were prepared by progressive dilution of the original solution. Auxiliary solutions were made for each of the various cell solutions.

### APPARATUS

A Leeds and Northrup Type "K" potentiometer reading to 0.01 millivolt was used. The galvanometer was a Leeds and Northrup "Type R" moving-coil instrument. The circuit was standardized with a standard Weston cell.

CELL VESSEL: The cell vessel used is diagrammed in Figure I.



All parts of the cell were made from Pyrex brand glassware. In each experiment, the gas saturating bulb was filled with the auxiliary solution. Both the cell and the gas saturating bulb were brought to constant temperature in a Sergeant constant temperature bath at  $25 \pm 0.02^\circ\text{C}$ .

**HYDROGEN ELECTRODE:** The hydrogen electrode was prepared according to the method of Popoff, Kunz, and Snow<sup>3</sup> modified according to the following procedure suggested by Kanning and Schmelzle<sup>5</sup>. The hydrogen electrode was made by sealing a piece of perforated platinum foil into the end of a soft glass tube. The exposed end measured  $8 \times 3 \text{ mm}$ , while the fused end was kept in contact with mercury to form an electrical connection. The foil was cleaned by successive treatment with hot concentrated nitric acid and potassium bichromate in concentrated sulfuric acid, and final rinsing in running redistilled water. It was electrolyzed as the cathode in a dilute solution of sodium cyanide and gold chloride for one-half hour at a current of six milliamperes. The electrolysis solution was prepared as follows: After 0.7g of gold chloride was dissolved in 50 ml of water, the gold was precipitated as gold hydroxide by addition of

sufficient ammonium hydroxide; an excess was avoided. The precipitate was washed by decantation and dissolved immediately in a solution of 1.5g of sodium cyanide in 100 ml of water. The ammonia was driven off by boiling. After gold plating the electrode, it was electrolyzed as the cathode in the following solutions; a chloroplatinic acid solution for five minutes at 20 milliamperes (then rinsed), a dilute solution of sodium hydroxide for five seconds at 10 milliamperes, and finally in a dilute solution of sulfuric acid for one minute at 10 milliamperes. The platinized electrode was kept in redistilled water until ready for use.

**SILVER-SILVER IODIDE ELECTRODE:** The silver-silver iodide electrode was of the type described by Owen<sup>6</sup>. A platinum wire 3cm long was coiled and sealed into the end of a soft glass tube; the fused end contacted mercury to afford an electrical connection. The coil was cleaned with concentrated nitric acid, heated to redness in a non-luminous flame, and immersed in a hot solution of potassium bichromate dissolved in concentrated sulfuric acid. The electrode was rinsed with running redistilled water, and dipped into a paste made by the addition of water to a mixture of nine parts of silver oxide

and one part silver iodate ground in anagate mortar. The electrode was heated in a Barkmeyer Electric Furnace at  $600^{\circ}\text{C}$  for ten minutes, cooled, and kept dry until ready for use.

All solutions were stored in glass-stoppered Pyrex bottles, and transferred by means of vacuum technique. At least fifteen minutes were allowed for the cell vessels to reach constant temperature; the thermometer used in the constant temperature bath was calibrated against a standard thermometer. The hydrogen electrode was so immersed that half of it was below the surface of the liquid--the electrode was placed one-fourth inch above the hydrogen inlet. Two silver-silver iodide electrodes were used throughout the experiment, each for one half of the readings. After purified hydrogen was passed through the cell for five minutes, the first reading was taken; further readings were taken at three minute intervals. The length of each run varied from three to thirty hours depending upon how quickly the electrode reached constancy. The tip of the outlet tube was kept just under water so that the gas within the cell was at atmospheric pressure.

## DATA AND RESULTS

The value of the standard potential of the silver-silver iodide electrode,  $E^{\circ}$ , used in the calculations was  $-0.1522$  volts; this was obtained from Owen's<sup>6</sup> equation which expresses the normal potential of this electrode over a range of temperature:

$$E_0 = -0.15219 - 328 \times 10^{-6} (t-25) - 3.6 \times 10^{-6} (t-25)^2 \quad (13)$$

A correction was made for the standard Weston cell by use of the following equation:

$$E_{25}^{\circ} = 1.0183 - 4.06 \times 10^{-5} (t-20) - 9.5 \times 10^{-7} (t-20)^2 + 10^{-8} (t-20)^3 \quad (14)$$

In Table I are listed the experimental data. The concentration is expressed in moles /1000 grams of water. The ionic strength,  $\mu$ , is based upon the 100% dissociation of salts, and the 1.34% dissociation of acetic acid. The percentage dissociation of acetic acid is determined by use of the following equation:

$$\% \alpha = \sqrt{100 \frac{K.M}{K.M}} \quad (15)$$

Where  $\alpha$  represents the ionized part of the acetic acid,  $K$  the dissociation constant for acetic acid, and  $M$  the concentration in moles /liter. The molality of acetic acid was determined by use of the equation:

$$m_{\text{HOAc}} = m'_{\text{HOAc}} - \sqrt{(m'_{\text{HOAc}})^2 (1.78 \times 10^{-5})} \quad (16)$$

Where  $m'_{\text{HOAc}}$  is the analytically determined molality of

TABLE I

Experimental Data Used in Determining the  
Dissociation Constant of Acetic Acid at 25°C

Sol'n.	$m_{\text{HOAc}}$	$m_{\text{OAc}^-}$	$m_{\text{I}^-}$	$E_{\text{OBS}}$	$\mu$
1	0.110466	0.1108544	0.110858	0.17590	0.110407
2	0.099	0.09752	0.099525	0.19095	0.099193
3	0.087886	0.086767	0.08845	0.19401	0.08826
4	0.079066	0.075724	0.07951	0.19799	0.077973
5	0.069809	0.066856	0.070266	0.20823	0.068623
6	0.059367	0.056864	0.059307	0.20679	0.058603
7	0.04937	0.047284	0.049849	0.21072	0.04909
8	0.036399	0.036484	0.037191	0.22149	0.037245
9	0.026775	0.026758	0.027426	0.22576	0.027402
10	0.0157	0.016096	0.016227	0.24065	0.016432
11	0.00785	0.008287	0.008236	0.25916	0.008458

acetic acid,  $m_{\text{HOAc}}$  the final molality of the acetic acid, ( $1.78 \times 10^{-5}$ ) the assumed dissociation constant for acetic acid, and  $(m'_{\text{HOAc}})$  ( $1.75 \times 10^{-5}$ ) the part of the original acetic acid that dissociated. The equations used for determining the molality of the acetate ion were; for dilute solutions,

$$m_{\text{OAc}^-} = m_{\text{NaOAc}} + \sqrt{(m'_{\text{HOAc}}) (1.78 \times 10^{-5})}, \quad (17)$$

and for very dilute solutions,

$$m_{\text{OAc}^-} = m_{\text{NaOAc}} + m'_{\text{HOAc}} \quad (18)$$

$$\left( \frac{1.78 \times 10^{-5}}{m'_{\text{HOAc}}} - \sqrt{\frac{3.17 \times 10^{-10}}{(m'_{\text{HOAc}})^2} + 7.12 \times 10^{-5} \times m'_{\text{HOAc}}} \right)$$

where  $m_{\text{OAc}^-}$  is the total molality of the acetate ion, and  $m_{\text{NaOAc}}$  the molality of the sodium acetate. Other terms are defined in equation (16).

The molality of the iodide ion is expressed by the following equation:

$$m_{\text{I}^-} = m_{\text{NaI}} \quad (19)$$

where  $m_{\text{I}^-}$  is the molality of the iodide ion, and  $m_{\text{NaI}}$  the molality of the sodium iodide.

The values for the electromotive force represent the maximum values for each experiment; these values were reached within a half hour. In all experiments a drift of potential was encountered; this drift was not thought to be due to the loss of acetic acid in the hydrogen stream

because of the low vapor pressure at the concentration employed.

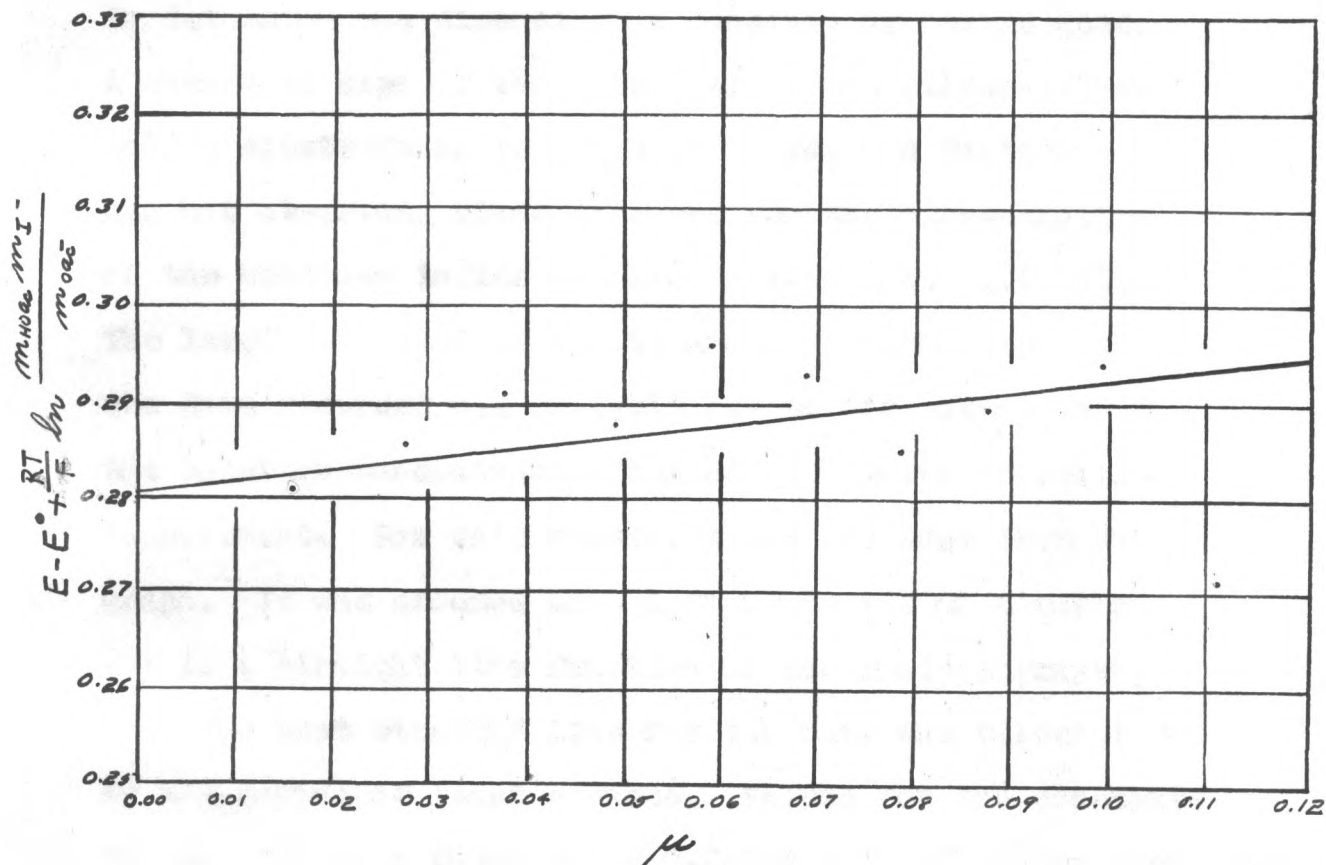


Figure II

Plot of  $E - E^0 + \frac{RT}{F} \ln \frac{m_{HOAc}^m I^-}{m_{OAc^-}}$  Against  $\mu$  in the  
Determination of the K of Acetic Acid at 25°

In Figure II, the values obtained for the left side of equation (9) are plotted against the ionic strength  $\mu$ . The extrapolated value to  $\mu = 0$  was used to determine the dissociation constant of acetic acid. A change in sign of the potential of the silver-silver iodide electrode as reported by Pearce and Fortsch<sup>7</sup> was not observed, since in every run the concentration of the hydrogen iodide was always less than 0.05 molal. The large deviation of solution #11 from the rest of the data recorded was probably due to the extension of the solution concentration beyond the limits of reliable measurement. For this reason it was excluded from the graph. It was assumed that left hand side of equation (9) is a straight line function of the ionic strength,  $\mu$ . The best straight line for the data was calculated by the method of least squares. Values for the constants "a" and "b" were found to be 0.28075 and 0.11039 respectively; the equation employed took the form:

$$y = 0.28075 + 0.11039 x \quad (20)$$

where x represents the ionic strength,  $\mu$ . At  $\mu = 0$ , the extrapolated value is 0.2809.

Table II lists the values for the left side of equation (9) and the corresponding ionic strength. These values are used in Figure I.

TABLE II

Values for  $E - E^{\circ} + \frac{RT}{F} \ln \frac{m_{\text{HOAc}} m_{\text{I}^-}}{m_{\text{OAc}^-}}$  and Corresponding Values of the Ionic Strength,  $\mu$ , for Various Concentrations

Solution	$E - E^{\circ} + \frac{RT}{F} \ln \frac{m_{\text{HOAc}} m_{\text{I}^-}}{m_{\text{OAc}^-}}$	$\mu$
1	0.2715	0.110407
2	0.29427	0.099193
3	0.28976	0.08826
4	0.28567	0.077973
5	0.29333	0.068623
6	0.29672	0.058603
7	0.28701	0.04909
8	0.29139	0.037245
9	0.28561	0.027402
10	0.28045	0.016432
11	0.28668	0.008458

## DISCUSSION OF RESULTS

The value of  $K_a$  computed from the data is  $1.779 \times 10^{-5}$  at  $25^\circ$ , is in good agreement with the value of  $1.754 \times 10^{-5}$  obtained by Harned and Owen<sup>4</sup> from thermodynamic data employing cells without liquid junction but using the silver-silver chloride electrode. According to Vosburgh<sup>9</sup> and his associates, no single electrolyte has been found which did not affect the silver-silver iodide electrode.

As a general conclusion, the silver-silver chloride does not seem to be as reliable as the silver-silver chloride electrode in the determination of the dissociation constants of weak acids. Since, however, the value of the dissociation constant of acetic acid obtained by use of the silver-silver iodide electrode is very close to that obtained for the same solution by use of the silver-silver chloride electrode, the silver-silver iodide electrode undoubtedly has some use in determinations of this kind.

### SUMMARY

The dissociation constant of acetic acid has been determined from electromotive force measurements of cells of the type:



The thermodynamic dissociation constant of this weak acid was found to be  $1.779 \times 10^{-5}$  at  $25^\circ\text{C}$ .

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