THE THERMODYNAMIC DISSOCIATION CONSTANTS
OF OXALIC ACID IN WATER

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R.C. Gibbons
Codeword: R.C. Gibbons
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The values given in literature for the first and second dissociation constants of oxalic acid at 25°C. vary considerably. For the first dissociation constant some of the values given are: .068 (Chandler, by conductivity)\(^1\); .17 (Britton, by electrometric titration)\(^2\); .057 (Dawson and Smith, by catalysis)\(^3\); .057 (Drucker)\(^4\); .059 (Cane and Ingold, by electrometric titration)\(^5\), and .02 (Glassstone)\(^6\), which do not show good agreement. For the second dissociation constant, values are: \(4.9 \times 10^{-5}\) (Chandler)\(^1\); \(6.9 \times 10^{-5}\) (Drucker)\(^4\); \(15.8 \times 10^{-5}\) (Britton)\(^2\); \(6.2 \times 10^{-5}\) (Cane and Ingold)\(^5\); \(3 \times 10^{-5}\) (Glassstone)\(^6\) and \(5 \times 10^{-5}\) (Hilbrick)\(^7\) which also show poor agreement.

In the present work an endeavor is made to determine by an accurate thermodynamic method the true second dissociation constant of oxalic acid at 25°, 30°, and 35°C. and the true first dissociation constant at 25°C.

The early work of Ostwald, Walden, Voormann, Smith, Bethmann and others during 1899 - 1904 on the classical dissociation "constants" of dibasic acids is now regarded as of very little quantitative value. According to Jeffery and
Vogel, "In spite of numerous determinations of the dissociation constants of dibasic acids by conductivity methods, during the last 47 years," by these methods "neither the primary nor secondary dissociation constant of any such acid was known with accuracy as judged by modern physico-chemical standards" .... until Jeffery and Vogel in 1935 measured the true or thermodynamic primary dissociation constants of malonic, succinic, and glutamic acids.

"Oxalic acid has been found to be too strong an acid in its first dissociation to give satisfactory results by a conductivity method" (Gane and Ingold) and "... as it has not yet been found possible to calculate satisfactorily the second dissociation constants from conductivity data alone, attention is directed to potentiometric methods for the simultaneous evaluation of both $K'$s" (German and Vogel).

By measurement on cells of the type

$$H_2 | Hg_2Cl_2 | HgCl (Sstd.) | \text{solution, } H_2 | Pt$$

which involve the use of a bridge solution of saturated potassium chloride containing 1.5% agar, Gane and Ingold have calculated the first and second thermodynamic dissociation constants of the acids of the oxalic, malonic, succinic acid series.

Among investigators using the potentiometric
titration method there exist large differences between the results for succinic acid which cannot be attributed solely to the various concentrations and temperatures at which the titrations were performed. A particularly large discrepancy is that for succinic acid obtained by Cane and Ingold\textsuperscript{5} with the hydrogen electrode, and Ashton and Partington\textsuperscript{10} with the quinhydrone electrode. Cane and Ingold remark in connection with the correction of their data for interionic effects that "the application of the Debye and Hückel equation for activities of electrolytes ... involves practical difficulties", and they have accordingly employed an empirical method involving the determination of the dissociation constant at a series of concentrations and extrapolating to zero concentration. German and Vogel\textsuperscript{7} employed cells of the type,

\begin{align*}
\text{U} &\mid \text{U}_2\text{G} \text{L}_2 \text{KCl (saturated solution)} \mid \text{quinhydrone} \mid \text{Pt},
\end{align*}

in which the boundary potential was assumed to be negligible, to measure the first and second dissociation constants of malonic, succinic, and glutaric acids. Although the determinations were made with the finest experimental technique the accuracy of the readings was \(0.2 - 0.3\) m.v. and consequently the dissociation constants could be known to only \(2 \times 10^{-5}\).

The following table gives a comparison of the results for malonic succinic and glutaric acids, by the
methods of Jeffery and Vogel, German and Vogel, and Cane and Ingold. The values of Jeffery and Vogel for the first dissociation constants are the mean of several which differ from the value given by ± .01 for malonic acid and ± .02 for succinic acid.

<table>
<thead>
<tr>
<th></th>
<th>$k_1 \times 10^5$</th>
<th>$k_2 \times 10^6$</th>
<th>$k_1 \times 10^5$</th>
<th>$k_2 \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>malonic</td>
<td>1.32</td>
<td>1.73</td>
<td>2.29</td>
<td>2.03</td>
</tr>
<tr>
<td>succinic</td>
<td>6.626</td>
<td>6.37</td>
<td>2.54</td>
<td>3.33</td>
</tr>
<tr>
<td>glutamic</td>
<td>4.555</td>
<td>4.46</td>
<td>3.77</td>
<td>3.80</td>
</tr>
</tbody>
</table>

In 1936 Nager and Acres\(^{11}\) made determinations of the errors in $p\text{H}$, dissociation constants, ionic strength, and hydrogen ion activity coefficients arising from neglect of corrections or from application of partial corrections for the potential of the liquid junction between saturated KCl (4.1 N KCl HgCl$_2$ electrode) and sodium malonate buffer solutions, and showed that partial corrections produce a larger error in these quantities than no corrections at all. An error as small as .3% in $p\text{H}$ may produce a change as large as 25% in dissociation constants.

In 1950 Warned and Owen\(^{12}\) showed that it was possible to determine the dissociation constants of weak acids from cells without liquid junction of the type
This type of cell was in 1932 modified by Hermel and Kihara who used cells of the type

\[
\begin{array}{c|c|c|c}
\text{H}_2 & \text{HAc} (m_1), \text{NaAc} (m_2), \text{NaCl} (m_3) & \text{AgCl} & \text{Ag}
\end{array}
\]

containing an acetic acid sodium acetate buffer mixture to measure the dissociation constant of acetic acid. In this cell one electrode is reversible to the hydrogen ion and the other to the chloride ion. Hence the electromotive force is given by the equation

\[
E = E_0 - \frac{RT}{F} \ln \frac{m_{H^+}m_{Na^+}}{m_{HAc}m_{NaAc}} \quad (1)
\]

where \(E\) is the measured electromotive force in volts, and \(E_0\) the normal electrode potential of the cell

\[
\begin{array}{c|c|c|c}
\text{H}_2 & \text{HCl} & \text{AgCl} & \text{Ag}
\end{array}
\]

and the "m's" and "f's" represent the molar concentrations and the activity coefficients of the ionic species denoted by the subscripts.

The thermodynamic dissociation constant \(K_1\) of acetic acid is given by the equation

\[
K_1 = \frac{m_{H^+}m_{Ac^-}}{m_{HAc}} \quad (2)
\]

Upon eliminating \(m_{H^+}\) from equations (1) and (2) and rearranging terms the formula becomes
\[ E - E_0 + \frac{RT}{F} \ln \frac{m_{\text{HAc}}}{m_{\text{Ac}}} = \frac{RT}{F} \ln \frac{\text{pH} \text{Ac}}{\text{pH}_{\text{HAc}}} - \frac{RT}{F} \ln K_1 \quad (3) \]

and by dividing through by \(2.3026 \frac{RT}{F}\)

\[ (E - E_0) \frac{F}{2.3026 \cdot RT} + \log \frac{m_{\text{HAc}}}{m_{\text{Ac}}} = - \log \frac{\text{pH} \text{Ac}}{\text{pH}_{\text{HAc}}} - \log K_1 \quad (4) \]

This equation is easy to use if the \(E_0\) values are known at the desired temperatures. The first term on the right contains the logarithm of the ratio of two ionic activity coefficient products. This ratio equals unity at infinite dilution and varies little from unity at low ionic strength. This is also true for \(\text{pH}_{\text{HAc}}\). Further the logarithm of such a quantity as this ratio has been shown by E. M. Arnold and Robinson \(^{30}\) and by E. M. Arnold and Owen \(^{12}\) to vary linearly with the ionic strength. If therefore the quantity on the left side of the equation be plotted against, \(\mu\), the ionic strength of the solution, a curve which is very nearly straight should be obtained. The intercept at \(\mu = 0\) will be \(- \log K_1,\) or \(\text{pK}\), by analogy with \(- \log \frac{M}{\mu}\) and \(\text{pH}\). In the second term on the left side of the equation \(m_{\text{HAc}}\) and \(m_{\text{Ac}}\) represent the true molalities of the undissociated acetic acid and acetate ion in the solution. The true molality of the undissociated acetic acid \(m_{\text{HAc}}\) will be \(m_1\), the stoichiometrical molality, less the molality of the dissociated acid which is equal to \(m_4\) as

\[ m_4 = m_{\text{HAc}} + m_{\text{H}} + m_{\text{Ac}} \]

where \(m_{\text{H}} = m_{\text{Ac}} - m_{\text{HAc}}\)
Hence \( m_{\text{HAc}} = m_1 - m_\text{H} \)

Similarly the true molality of the acetate ion \( m_{\text{Ac}} \) will be equal to the stoichiometrical molality of the sodium acetate, which is assumed to be completely dissociated, plus the molality of the acetate ion formed by the dissociation of the acetic acid, or,

\[
m_{\text{Ac}} = m_2 + m_\text{H}
\]

Thus the second term on the left becomes

\[
\log \left( \frac{m_1 - m_\text{H}}{(m_2 + m_\text{H})} \right)
\]

In this term \( m_1 \), \( m_2 \) and \( m_3 \) are known, assuming complete dissociation of the salts, and \( m_\text{H} \) must be evaluated arithmetically. This is done by a method of successive approximations. To determine a preliminary value of the dissociation constant, \( K_1^\text{p} \), the stoichiometrical molalities of acetic acid, sodium acetate and sodium chloride, \( m_1 \), \( m_2 \) and \( m_3 \) respectively are substituted in the second term on the left of equation (4), for the true molalities \( m_{\text{HAc}} \), \( m_{\text{Ac}} \) and \( m_\text{Cl} \). The curve obtained by plotting the left side against the ionic strength, \( \mu \), is extrapolated to zero \( \mu \) so determining \(- \log K_1^\text{p}\) or \( \frac{\mu K_1^\text{p}}{1} \) from which \( K_1^\text{p} \) is determined. The preliminary value of \( K_1 \), i.e. \( K_1^\text{p} \), so obtained is substituted in the equation for the thermodynamic dissociation constant.
\[ K_4 = \frac{m_H}{m_H \cdot m_F} \cdot \frac{F^+ \cdot Fa^-}{Fa^-} \]

which may be written

\[ K_4 = \frac{m_H (m_2 + m_H)}{(m_1 - m_H)} \cdot \frac{F^+ \cdot Fa^-}{Fa^-} \]

Following the method of Warned and Embree\textsuperscript{14}, the activity coefficient ratio in this equation is replaced as an approximation by the values of $F^+ \cdot Cl^-$. In sodium chloride solutions determined by Warned\textsuperscript{15}.

The equation then becomes

\[ K_4 = \frac{m_H (m_2 + m_H)}{(m_1 - m_H)} \cdot \frac{F^+ \cdot Cl^-}{Fa^-} \] \hspace{1cm} (5)

All the terms in this equation, except $m_H$, are then known and the equation may be solved for $m_H$. The value of $m_H$ so obtained is substituted in the equation

\[ \frac{(F - Fa)}{2.5026 RT} \cdot \log \left( \frac{m_1 - m_H}{m_2 + m_H} \right) \cdot Cl^- = - \log \frac{F^+ \cdot Cl^-}{F^+ \cdot Fa^-} \]

\[ - \log K_4 \] \hspace{1cm} (6)

and another extrapolation carried out to determine a second value of $K_4$, $K_4'$. This method of successive approximations is continued until $K_4$ and $m_H$ values are obtained which fulfill the requirements of both equations (5) and (6), the value of $K_4$ so obtained being recorded as the thermodynamic dissociation constant at the temperature employed.
In 1933 Rimu used the cell

\[ H_2 | NaH_2PO_4 (m_1), Na_2HPO_4 (m_2), NaCl (m_3) | AgCl | Ag. \]

to measure the second dissociation constant of phosphoric acid. The essence of the method employed is that the dissociation constant is obtained from electromotive force measurements upon cells without liquid junction, containing appropriate buffer mixtures. No extrathermodynamical methods are employed other than the use of the Debye-Hückel limiting function for the activity coefficients of the ions involved.

The electromotive force of the cell is given by

the equation

\[ \mathcal{E} = \mathcal{E}_0 - \frac{RT}{F} \ln \frac{m_{HCl} m_{H}}{m_{Cl} m_{Cl}} \]  \hspace{1cm} (7)

The equation for the second dissociation constant of phosphoric acid is

\[ K = \frac{m_{H} m_{H}PO_4}{m_{H_2}PO_4 \cdot m_{H} m_{H}PO_4} \]  \hspace{1cm} (8)

By eliminating \( m_H \) from equations (7) and (8) equation (9) is obtained

\[ - \log \mathcal{E}_2 = \frac{(E - E_0) F}{2.3026 RT} - \log \frac{m_{H_2}PO_4 m_{Cl}}{m_{H_2}PO_4} - \log \frac{m_{H_2}PO_4 m_{Cl}}{m_{H_2}PO_4} \]  \hspace{1cm} (9)

by applying the Debye-Hückel formula expressed after von Staudt.
\[-\log f_+ = Z_+ Z_- \frac{N}{\mu} - B \mu\]

where \(Z_+\), \(Z_-\) are the valences of the ions and \(A\) and \(B\) are constants for the solvent, and solvent and solute respectively, which approximation is accurate enough for the present work, the last term of the equation (9) is seen to be given by

\[
\log \frac{f_{\text{Cl} f_{\text{H}_2\text{PO}_4}}}{f_{\text{HPO}_4}} = 2A \sqrt{\mu} - B \mu
\]

By substituting this result in equation (9) there is finally obtained

\[
-\log k_2 + B \mu = \frac{(E - E_0) F}{2 \cdot 3026 RT} + \log \frac{m_{\text{Cl}} m_{\text{H}_2\text{PO}_4}}{m_{\text{HPO}_4}} + 2A \sqrt{\mu} \quad (10)
\]

\(E\) represents the measured electromotive force of the cell, \(E_0\) the normal electrode potential of the cell

\[H_2 \text{HCl} \text{AgCl} \text{ Ag}^+ \]

\(m\) the molal concentrations of the respective subscript ions, \(A\) the theoretical constant of the Debye-Hückel equation, \(\mu\) the ionic strength of the solution, \(k_2\) the second dissociation constant of phosphoric acid, and \(B\), a complicated function of the concentration which, while essentially constant over the concentration range employed, need not be evaluated. It is important to note that any slight error involved in using equation (10) becomes progressively less as the concentration decreases and that \(m_{\text{H}_2\text{PO}_4}\) and \(m_{\text{HPO}_4}\) are essentially equal to the molalities of the
salts making up the solutions since the salts are regarded as fully dissociated, and since the dissociation constant of $H_2PO_4^1$ is small compared with the concentrations employed.

The right hand side of equation (10) whose terms are known, or may be evaluated, is plotted against the ionic strength. The curve obtained is extrapolated to zero ionic strength and the intercept gives the true thermodynamic value of $-log K_2$ or $pK_2$. This extrapolation is very easy to carry out as the plot both by theory and in practice is nearly a straight line.

The cell used in the present work for determining the first dissociation constant of oxalic acid is

$$\text{Pt} \mid \text{quinhydnone, } H_2C_2O_4(m_1), \text{KCl, } H_2C_2O_4(m_2), \text{KCl (m_3)} \mid \text{AgCl} \mid \text{Ag}.$$ 

In using this cell the salt effect of the quinhydnone electrode, which according to Wright$^{17}$ becomes negligible in the extrapolation to infinite dilution, or zero $\mu$, is neglected. This cell differs from the cell used by Neined and Ehlers$^{15}$ for acetic acid, only in that a quinhydnone electrode is used in place of a hydrogen electrode and an oxalic acid - potassium hydrogen oxalate buffer solution instead of an acetic acid - sodium acetate buffer solution. Since the same considerations apply as in
the case of the dissociation of acetic acid, the
electromotive force of this cell is related to the first
dissociation constant, $K_1$, of oxalic acid as follows

$$\frac{(E - E_0) F}{2.3026 RT} + \log \frac{m_1 \text{H}_2\text{C}_2\text{O}_4}{m_2 \text{H}_2\text{O}} = - \log \frac{f_{\text{HCl}} f_{\text{H}_2\text{C}_2\text{O}_4}}{f_{\text{H}_2\text{O}} f_{\text{H}_2\text{C}_2\text{O}_4}} - \log K_1$$

or

$$\frac{(E - E_0) F}{2.3026 RT} + \log \left(\frac{m_1 - m_2}{m_2 + m_H}\right) m_H = - \log \frac{f_{\text{HCl}} f_{\text{H}_2\text{C}_2\text{O}_4}}{f_{\text{H}_2\text{O}} f_{\text{H}_2\text{C}_2\text{O}_4}} - \log K_1$$

where $E$ is the measured electromotive force of the cell; $E_0$
the normal electrode potential of the cell.

| Pt      | quinhydrone | HCl | AgCl | Ag. |

$m_1$, $m_2$, $m_H$ the stoichiometrical molalities of oxalic acid,
potassium hydrogen oxalate and potassium chloride, in the
cell solution and the "f's" the activity coefficients of
the ionic species denoted by the subscripts. The molality
of the hydrogen ion $m_H$ must be evaluated by arithmetical
approximation, and the true dissociation constant $K$
evaluated by a series of successive approximations.

The cell used for the determination of the second
dissociation constant of oxalic acid is analogous with that
used by Nims for the second dissociation of phosphoric
acid, and is
Pt | quinhydrone, \( \text{K}_2\text{C}_2\text{O}_4 \) \((m_1)\), \( \text{K}_2\text{C}_2\text{O}_4 \) \((m_2)\), \( \text{HCl} \) \((m_3)\) | \( \text{AgCl} \) | \( \text{Ag} \).

and since the same considerations apply in both cases the formula relating the electromotive force of the cell and the second dissociation constant, \( k_2 \), of oxalic acid is

\[
- \log k + B \mu = \frac{(E - E_0) F}{2.3026 RT} + \log \frac{\text{H}_2\text{O} \cdot \text{HCl}}{\text{H}_2\text{O}_4 \cdot \text{HCl}} + 2A \sqrt{\mu}.
\]

where \( E \) is the measured electromotive force of the cell; \( E_0 \) the normal electrode potential of the cell.

Pt | quinhydrone | HCl | AgCl | Ag.

and the "m's" the molalities of the ionic species denoted by the subscripts. \( A \) is the theoretical constant of the Debye-Hückel equation, the ionic strength of the solution, and \( B \) a complicated function of the concentration, which while essentially constant over the concentration range employed need not be evaluated.
**EXPERIMENTAL**

**The Quinhydrone Electrode.**

The normal electrode potentials $0^\circ - 40^\circ C.$ of the quinhydrone electrode have been determined by Harned and Wright from the measurements of the electromotive force of the cell

\[
\text{Pt} \mid \text{quinhydrone, HCl (0.01)} \mid \text{AgCl} \mid \text{Ag} \quad (1)
\]

The values obtained were combined with data from the cell

\[
(1 \text{ atm.}) \text{H}_2 \mid \text{HCl (0.01)} \mid \text{AgCl} \mid \text{Ag} \quad (2)
\]

which was investigated under similar conditions by Harned and Shlars. This procedure gave the normal electrode potential of cell (1) and new values for the cell

\[
\text{Pt} \mid \text{quinhydrone, HCl} \mid \text{H}_2 (1 \text{ atm.}) \quad (3)
\]

The values obtained at $25^\circ, 30^\circ,$ and $35^\circ C.$ were

<table>
<thead>
<tr>
<th>Temp. $^\circ C.$</th>
<th>Cell (1)</th>
<th>Cell (2)</th>
<th>Cell (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$25^\circ$</td>
<td>-1.774</td>
<td>2.223</td>
<td>-2.9969</td>
</tr>
<tr>
<td>$30^\circ$</td>
<td>-1.7707</td>
<td>2.1984</td>
<td>-2.9600</td>
</tr>
<tr>
<td>$35^\circ$</td>
<td>-1.7634</td>
<td>2.1544</td>
<td>-2.9230</td>
</tr>
</tbody>
</table>
These values are in agreement with the values calculated from data of Bulmann and Jensen\textsuperscript{19} and Bulmann and Krarup\textsuperscript{20} which are given in the fifth column of the table.

The $E_0$ values for the cell

Pt quinhydrone; HCl AgCl Ag.

used in the present work are

\begin{align*}
25^\circ & \quad .4774 \text{ volts.} \\
30^\circ & \quad .4770 \quad " \\
35^\circ & \quad .4768 \quad "
\end{align*}

The electrodes used were of heavy platinum foil of area 2.5 x 3 cm., welded to platinum wire sealed into glass tubes and making contact with mercury. These electrodes were cleaned after the method of Morgan Emmart and Campbell\textsuperscript{21}, by immersion in a cold sulphuric acid dichromate cleaning mixture, prepared from c.p. chemicals, which is then heated to 125\textdegree C. and allowed to cool to room temperature. The electrodes were thoroughly rinsed with distilled water, then heated in a beaker of distilled water. Before insertion in the cells the electrodes were rinsed with a little of the cell solution. The cleaning process was repeated between runs and the electrodes allowed to stand in the cleaning mixture over-night as a matter of convenience.
The quinhydrone used in the cell was Hopkins and Williams' "Analar" which was used untreated.

**Silver Chloride Electrodes.**

These were of the "Jahn" type as used by MacInnes and Beattie, Allmand and Hunter and others. They consisted of approximately 75 cm. squares of platinum gauze, welded to platinum wire which in turn made contact with mercury through glass tubes. They were plated sight at a time with silver, by deposition from cyanide solution (7 grams AgNO₃ + 10 grams KCN in 200 c.c. of distilled water), 2 milliamps per electrode being passed for 16 hours. They were then chloridised anodically in 0.1M HCl solution with a current density of six milliamps per electrode for half an hour as recommended by Allmand and Hunter. Electrodes so prepared were placed in solutions similar to those being measured, and allowed to come to equilibrium. They agreed to within 1 m.v. except on a few occasions when cracks appeared in the seal.

**Materials**

Oxalic acid was purified by two recrystallisations of Hopkins and Williams' "Analar" from distilled water. The crystals were drained on a suction pump, and dried in a desiccator.
Potassium Hydrogen Oxalate was prepared by crystallising from a hot aqueous solution of A.R. oxalic acid and A.R. potassium hydroxide, the potassium hydroxide being just sufficiently in excess to prevent the precipitation of the tetraoxalate. The crystals were drained on a suction pump, washed with a small quantity of ice cold distilled water, and dried in a vacuum desiccator. The sample obtained in this way was found on analysis with a standard potassium permanganate solution to be 100 ± 1% pure.

Potassium oxalate was purified by three recrystallisations of Hopkins and Williams' "Analal" from distilled water.

Potassium Chloride. Hopkins and Williams' "Analal" was used untreated.

Water. The solutions were made up with distilled water.

Nitrogen. Nitrogen was prepared by pumping air saturated with ammonia vapour over red hot copper gauze in a Fletcher furnace. The issuing gas was thoroughly washed by bubbling through concentrated potassium hydroxide solution, sulphuric acid solution, distilled water, and finally through some of the cell solution.

Solutions. The solution for the determination of the second dissociation constant was made up as follows:— A solution of oxalic acid was made up approximately .05 molar and weighed
samples analysed by titration with standard potassium permanganate solution. The molality was found to be 0.05145 m. To a weighed quantity of this solution a calculated weight of potassium oxalate was added such that the resultant solution contained 3 mol. of $H_2C_2O_4$ to 1 mol. of $H_2C_2O_4$ or was equimolar in both $K_2C_2O_4$ and $K_2C_2O_4$. Due to the water of crystallisation of the potassium oxalate the molality of each the $K_2C_2O_4$ and $H_2C_2O_4$ was reduced from 2x0.05145 m. to 0.10265 molal. Weighed samples of this solution were analysed to determine the total oxalate present and the analytical result agreed to within 0.1% of the calculated result. To a weighed quantity of this solution dry potassium chloride was added such that the resulting solution was equimolar (0.10265 m.) in $K_2C_2O_4$, $H_2C_2O_4$, and KCl.

The solution for the determination of the first dissociation constant was made up by adding weighed quantities of potassium hydrogen oxalate and potassium chloride to a standardised solution of oxalic acid. The weight of potassium hydrogen oxalate determined by analysis agreed to within 0.1% of the weight added. The resulting solution was 0.49595 molal in each.

The solutions used in the cells were made by dilution of weighed amounts of the stock solutions with weighed amounts of distilled water.
Cells.

The cells used were of the N type of Harned and Wright modified so that they could be swept out with a stream of nitrogen (fig. 1). The quinhydrone electrode is represented by A and the silver—silver chloride electrode by B. Measurements by Harned and Wright 18 showed that because of diffusion of quinhydrone to the silver—silver chloride electrode no equilibrium could be obtained without complete separation of the two electrode compartments D and E. A 3 mm. stopcock, C, and 7–8 cm. of 3 mm. capillary tubing are therefore interposed between the electrode compartments. Cell compartment E is connected with a filling tube G bearing a stopcock H, and compartment D is fitted with a mercury trap P.

In compartment E a silver—silver chloride electrode attached to a rubber stopper, was inserted and forced down to form a cup, which was then filled with mercury. Solid quinhydrone more than sufficient to saturate the solution of compartment D was placed in the bottom of D, and a platinum electrode fitted with a rubber stopper forced in and the cup formed filled with mercury. The arm G of the cell was connected through the stopcock H to a modified Hempel flask which contained the cell solution. The Hempel flask was so constructed that the nitrogen stream
could be reversed without changing the leads. Nitrogen which, by bubbling through some of the cell solution, had attained the same vapour pressure as the solution, was bubbled through the solution in the Hempel flask and then passed through the cell. This was continued for one hour, then the nitrogen flow in the Hempel flask was reversed, and the solution forced over into the cell, which by tilting during the filling operation could be filled almost to the rubber stoppers ($S'$, $S''$). As the solution flowed into compartment D it stirred up the solid quinhydrone. On completion of the filling operation, the stopcocks $H$ and $C$ were closed and the cell clamped in position in the thermostat. The stopcock $G$ was kept closed except at the moment of reading the electromotive force.

The second dissociation constant was measured at 25°, 30°, and 35°C., the first dissociation constant at 25°C. only. All cells attained equilibrium within 50 to 45 minutes and remained constant for at least 5 hours at 25°C. and at least 4 hours at 35°C. In isolated cases when equilibrium was not reached within 45 minutes the cells were discarded.

The cells were measured together in duplicate or triplicate and the results given are the mean with deviations of less than 2.1 m.v.
The cell described above was modified by replacing the stopcock C and capillary tubing by a single piece of 2 m.m. capillary tubing 7 - 8 cm. in length so that the two compartments were always directly united with cell solution. This cell was easier to handle. When used in conjunction with duplicates of the first type of cell at 25° and 35°C. no difference was observed in the time required to come to equilibrium, the equilibrium value, or the length of time the cells remained at equilibrium. At 30°C. all measurements were made with cells of the modified type.

Other Apparatus.

A gas heated thermostat was used controlled by a two bulb mercury - chloroform regulator to the required temperatures: 25°± .005; 30°± .005; 35°± .01, recorded by a thermometer calibrated against the laboratory standards. The fluctuations were recorded by a Beckmann thermometer.

A Cambridge Instrument Co. potentiometer with a range of 0 - 1.8 volts. and an accuracy of .05 m.v. was used.

The Weston Normal cell used was made by the Cambridge Instrument Co.
Tables.

Table I records the values of the electromotive force at 25°C. of the cell used to determine the second dissociation constant of oxalic acid. In the first column are recorded the molalities of the salts making up the cell solution. The second column records the corresponding observed values of the electromotive force in volts, the third column the calculated ionic strength, and the fourth column the calculated values of

$$\frac{(E - E_o) F}{2.3026 RT} + \log \frac{[H_2O] [H^+]}{[H_2O]} + 26 \mu - \log K^2.$$ 

Tables II and III record similar values at 30°C. and 35°C.

The last line of each Table I, II, III, shows the extrapolated value of $-\log K_2$ or $pK$ the true value of the second dissociation constant at zero ionic strength.

Table IV records the values of the electromotive force at 25°C. of the cell used to determine the first dissociation constant of oxalic acid. In the first column are recorded the molalities of the cell solution, in the second column the calculated molalities of the hydrogen ion which in the first approximation are neglected. The third column records the measured electromotive force, the fifth the calculated values of
\[
\frac{(E - E_0) F}{2.3026 R T} + \log \frac{b_{H_2}C_2O_4 \cdot H_2O}{b_{H_2}C_2O_4} \quad \text{or} \quad \log \alpha_1,
\]

and the fourth the calculated ionic strength. Tables V and VI record similar values for the fifth and eighth (final) approximations. The values in the second column, \( b_H \), are those determined from the fourth and seventh approximations respectively.
### TABLE I.

**Temp. = 25° C.**

<table>
<thead>
<tr>
<th>n = m₁ = m₂ = m₃</th>
<th>E</th>
<th>μ = 5 m</th>
<th>- log K₂'</th>
</tr>
</thead>
<tbody>
<tr>
<td>.051325</td>
<td>.1663 volts</td>
<td>.2566</td>
<td>4.5022</td>
</tr>
<tr>
<td>.034216</td>
<td>.1533   &quot;</td>
<td>.1711</td>
<td>4.4350</td>
</tr>
<tr>
<td>.02566</td>
<td>.1445   &quot;</td>
<td>.1283</td>
<td>4.4027</td>
</tr>
<tr>
<td>.017108</td>
<td>.1322   &quot;</td>
<td>.0855</td>
<td>4.3685</td>
</tr>
<tr>
<td>.01283</td>
<td>.1236   &quot;</td>
<td>.0642</td>
<td>4.3491</td>
</tr>
<tr>
<td>.008344</td>
<td>.1115   &quot;</td>
<td>.0427</td>
<td>4.3290</td>
</tr>
<tr>
<td>.006415</td>
<td>.1032   &quot;</td>
<td>.0321</td>
<td>4.3179</td>
</tr>
<tr>
<td>.003208</td>
<td>.0624   &quot;</td>
<td>.0160</td>
<td>4.3158</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>0</td>
<td></td>
<td>4.300</td>
</tr>
</tbody>
</table>

### TABLE II.

**Temp. = 50° C.**

<table>
<thead>
<tr>
<th>n = m₁ = m₂ = m₃</th>
<th>E</th>
<th>μ = 5 m</th>
<th>- log K₂'</th>
</tr>
</thead>
<tbody>
<tr>
<td>.05131</td>
<td>.1584 volts</td>
<td>.2565</td>
<td>4.5269</td>
</tr>
<tr>
<td>.03421</td>
<td>.1459   &quot;</td>
<td>.1710</td>
<td>4.4603</td>
</tr>
<tr>
<td>.02565</td>
<td>.1375   &quot;</td>
<td>.1283</td>
<td>4.4224</td>
</tr>
<tr>
<td>.01710</td>
<td>.1249   &quot;</td>
<td>.0855</td>
<td>4.3886</td>
</tr>
<tr>
<td>.01283</td>
<td>.1161   &quot;</td>
<td>.0644</td>
<td>4.3703</td>
</tr>
<tr>
<td>.008344</td>
<td>.1035   &quot;</td>
<td>.0427</td>
<td>4.3560</td>
</tr>
<tr>
<td>.006413</td>
<td>.0949   &quot;</td>
<td>.0321</td>
<td>4.3463</td>
</tr>
<tr>
<td>.003208</td>
<td>.0741   &quot;</td>
<td>.0160</td>
<td>4.3377</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>0</td>
<td></td>
<td>4.320</td>
</tr>
</tbody>
</table>
### TABLE III.

Temp. = 35° C.

<table>
<thead>
<tr>
<th>m = m₁ = m₂ = m₃</th>
<th>H</th>
<th>μ = 5 m</th>
<th>- log K₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>.05132</td>
<td>-1518 volts</td>
<td>.2566</td>
<td>4.5530</td>
</tr>
<tr>
<td>.03421</td>
<td>-1592</td>
<td>.1711</td>
<td>4.4070</td>
</tr>
<tr>
<td>.02662</td>
<td>-1300</td>
<td>.1283</td>
<td>4.4520</td>
</tr>
<tr>
<td>.01710</td>
<td>-1175</td>
<td>.0855</td>
<td>4.4156</td>
</tr>
<tr>
<td>.01283</td>
<td>-1034</td>
<td>.0642</td>
<td>4.3993</td>
</tr>
<tr>
<td>.008544</td>
<td>-962</td>
<td>.0427</td>
<td>4.3775</td>
</tr>
<tr>
<td>.006415</td>
<td>-874</td>
<td>.0321</td>
<td>4.3654</td>
</tr>
<tr>
<td>.005208</td>
<td>-654</td>
<td>.0160</td>
<td>4.3699</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>0</td>
<td>4.348</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE IV.

First Approximation

<table>
<thead>
<tr>
<th>m = m₁ = m₂ = m₃</th>
<th>m₁H</th>
<th>H = m₁ + m₂ + m₃</th>
<th>μ</th>
<th>- log K₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>.02959</td>
<td>Assumed to be zero in the first approximation</td>
<td>-2944 volts</td>
<td>.0992</td>
<td>1.7909</td>
</tr>
<tr>
<td>.03506</td>
<td></td>
<td>-2734</td>
<td>.0661</td>
<td>1.8854</td>
</tr>
<tr>
<td>.02430</td>
<td></td>
<td>-2664</td>
<td>.0496</td>
<td>1.9634</td>
</tr>
<tr>
<td>.01934</td>
<td></td>
<td>-2575</td>
<td>.0396</td>
<td>2.0171</td>
</tr>
<tr>
<td>.01655</td>
<td></td>
<td>-2500</td>
<td>.0330</td>
<td>2.0648</td>
</tr>
<tr>
<td>.009919</td>
<td></td>
<td>-2274</td>
<td>.0198</td>
<td>2.2251</td>
</tr>
<tr>
<td>.006959</td>
<td></td>
<td>-1863</td>
<td>.0099</td>
<td>2.4502</td>
</tr>
<tr>
<td>.002479</td>
<td></td>
<td>-1643</td>
<td>.0049</td>
<td>2.6904</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>0</td>
<td>2.070</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table V.
Fifth Approximation - assuming $K = .0157$ or $kK = 1.304$

<table>
<thead>
<tr>
<th>$m$</th>
<th>$m_H$</th>
<th>$E$</th>
<th>$\mu$</th>
<th>$\log$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.04959</td>
<td>.00951</td>
<td>-2944 volts</td>
<td>.1067</td>
<td>1.6222</td>
</tr>
<tr>
<td>.03306</td>
<td>.00826</td>
<td>-2784 &quot;</td>
<td>.0744</td>
<td>1.6636</td>
</tr>
<tr>
<td>.02430</td>
<td>.00735</td>
<td>-2664 &quot;</td>
<td>.0569</td>
<td>1.6979</td>
</tr>
<tr>
<td>.01984</td>
<td>.00655</td>
<td>-2575 &quot;</td>
<td>.0463</td>
<td>1.7140</td>
</tr>
<tr>
<td>.01653</td>
<td>.00610</td>
<td>-2500 &quot;</td>
<td>.0392</td>
<td>1.7263</td>
</tr>
<tr>
<td>.009919</td>
<td>.00465</td>
<td>-2274 &quot;</td>
<td>.02443</td>
<td>1.7835</td>
</tr>
<tr>
<td>.004959</td>
<td>.00302</td>
<td>-1963 &quot;</td>
<td>.0129</td>
<td>1.8374</td>
</tr>
<tr>
<td>.002479</td>
<td>.00180</td>
<td>-1643 &quot;</td>
<td>.0067</td>
<td>1.8887</td>
</tr>
</tbody>
</table>

Extrapolated: 0 1.780

### Table VI.
Sixth Approximation - assuming $K = .01715$ or $kK = 1.766$

<table>
<thead>
<tr>
<th>$m$</th>
<th>$m_H$</th>
<th>$E$</th>
<th>$\mu$</th>
<th>$\log$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.04959</td>
<td>.01007</td>
<td>-2944 volts</td>
<td>.1092</td>
<td>1.6120</td>
</tr>
<tr>
<td>.03306</td>
<td>.00869</td>
<td>-2784 &quot;</td>
<td>.0743</td>
<td>1.6515</td>
</tr>
<tr>
<td>.02430</td>
<td>.00770</td>
<td>-2664 &quot;</td>
<td>.0573</td>
<td>1.6834</td>
</tr>
<tr>
<td>.01984</td>
<td>.00695</td>
<td>-2575 &quot;</td>
<td>.0466</td>
<td>1.6992</td>
</tr>
<tr>
<td>.01653</td>
<td>.00635</td>
<td>-2500 &quot;</td>
<td>.0394</td>
<td>1.7150</td>
</tr>
<tr>
<td>.009919</td>
<td>.00481</td>
<td>-2274 &quot;</td>
<td>.0246</td>
<td>1.7656</td>
</tr>
<tr>
<td>.004959</td>
<td>.00308</td>
<td>-1963 &quot;</td>
<td>.0130</td>
<td>1.8182</td>
</tr>
<tr>
<td>.002479</td>
<td>.00184</td>
<td>-1643 &quot;</td>
<td>.0068</td>
<td>1.8625</td>
</tr>
</tbody>
</table>

Extrapolated: 0 1.765
CALCULATION OF RESULTS

The Second Dissociation Constant.

The formula used in the calculation of the second dissociation constant is

\[ -\log K_2 + \beta \nu = \frac{(E - E_0) F}{2.3026 RT} + \log \frac{m_{H_2C_2O_4}}{m_{K_2C_2O_4}} + \log \frac{m_{KCl}}{m_{K_2C_2O_4}} + 2A \sqrt{\mu} \]

The right hand side of this equation is plotted against the ionic strength and the curve obtained extrapolated to zero ionic strength; the intercept is \(-\log K_2\) or \(pK_2\). The first term on the right contains \(E_0\) which is known from the work of Warned and Wright\(^{16}\) and \(E\), the electro motive force of the cell, which is measured. The second term contains the ratio of the molalities of the hydrogen oxalate ion and oxalate ion. These two molalities are assumed to be equal to the respective stoichiometrical molalities of the potassium hydrogen oxalate and potassium oxalate in the solution, since as salts of strong bases they are completely dissociated, and the dissociation constant of the hydrogen oxalate ion is small compared with the concentrations employed. The potassium chloride in the solution is also regarded as being completely dissociated. The molality of the potassium hydrogen oxalate in the solution is equal to
the molality of the potassium oxalate and equal to the
molality of the potassium chloride to within .1%.

Hence the second term becomes

\[ \log m \]

where \( m_1 = m_2 = m_3 = \ldots = m \)

\[ = nK_2C_2O_4 = nC_2O_4^- = nCl^- \]

The third term on the right contains the product of
the theoretical constant of the Debye-Hückel equation, and,
the ionic strength. The ionic strength of a solution is
defined by Lewis and Randall by the formula

\[ \mu = \frac{1}{2} \sum m^2 \]

where \( \mu \) = ionic strength

\( m \) = the molality of each ion

\( z \) = the valence of each ion

the summation being carried out for all ions present. In
this instance there are present potassium hydrogen oxalate
\( (m_1) \) potassium oxalate \( (m_2) \), and potassium chloride \( (m_3) \),
which ionize as follows:

\[ KHC_2O_4 (m_1) \rightarrow K^+ (m_1) + HC_2O_4^- (m_1) \]

\[ K_2C_2O_4 (m_2) \rightarrow K^+ (m_2) + K^+ (m_2) + C_2O_4^- (m_2) \]

\[ KCl (m_3) \rightarrow K^+ (m_3) + Cl^- (m_3) \]
and since \( m_1 = m_2 = m_3 = m \) by summing

\[
\text{K}_2\text{SO}_4(m_1) + \text{K}_2\text{SO}_4(m_2) + \text{KCl}(m_3) = \text{K}^+(4m) + \text{K}_2\text{SO}_4(m) + \text{Cl}^-(m) + \text{SO}_4^{2-}(m)
\]

and

\[
\frac{4m \times 1^2}{2} + \frac{m \times 1^2}{2} + \frac{m \times 1^2}{2} + \frac{m \times 2^2}{2}
\]

\[
= 5m
\]

The values of the constant \( A \) used were calculated from data in Clark's "Determination of Hydrogen Ions" and were

- 25°C. \( A = .506 \)
- 30°C. \( " = .510 \)
- 35°C. \( " = .517 \)

As an example of the calculation of a point, take the measurement of the cell

Pt quinhydrone, \( \text{K}_2\text{SO}_4(m_1), \text{K}_2\text{SO}_4(m_2), \text{KCl}(m_3) \) AgCl Ag

at 25°C., where

\[
m_1 = m_2 = m_3 = .051325
\]

\[
E_0 = -.4774 \text{ volts}
\]

\[
A = .506
\]

\[
\mu = 5m = .2566
\]

\[
E = -.1653 \text{ volts}
\]

\[
\frac{1}{(2.5026) R_T} = .05392 \text{ (Clark, "Determination of Hydrogen Ions")}
\]
On substituting these values in the equation

\[- \log K_2 + B = \frac{E - E_0}{2.3026RT} + \log \frac{\text{HCl} M \text{H}_2\text{O}_2}{\text{K}_2 \text{O}_4} + 2a \sqrt{\mu}\]

the equation becomes

\[- \log K_2 + B \rightarrow \frac{-1.655 - (-0.4774)}{0.05912} + \log \cdot 051325 + 1.012 \sqrt{0.2566}\]

\[= 4.5072\]

which value is tabulated in the fourth column of Table I, headed \(- \log K_2^4\). The ionic strength 0.2566 is tabulated in the third column. Similarly a series of values for \(- \log K_2\) are worked out from cell measurements and plotted against the ionic strengths. The plot so obtained is found to be a straight line and is easily extrapolated to zero ionic strength where the intercept is \(- \log K_2\) or \(pK_2\).

The plots for 25\(^\circ\), 30\(^\circ\), and 35\(^\circ\)C. and the extrapolations are shown by graph I. The values of \(pK_2\) and \(K_2\) so obtained are:

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(pK_2)</th>
<th>(K_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4.300</td>
<td>5.012 (\times 10^{-5})</td>
</tr>
<tr>
<td>30</td>
<td>4.320</td>
<td>4.787 &quot;</td>
</tr>
<tr>
<td>35</td>
<td>4.348</td>
<td>4.488 &quot;</td>
</tr>
</tbody>
</table>

These results are reproducible to ± 0.002 \(pK\).

**The First Dissociation Constant.**

The formula used in calculating the first dissociation constant is
\[ \frac{(R - E_0) F}{(2.3025)RT} + \log \frac{m_{H_2C_2O_4}m_{Cl}}{m_{H_2C_2O_4}} = - \log \frac{m_{H_2C_2O_4}m_{Cl}}{m_{H_2C_2O_4}} - \log K_1 \]

The first term on the left contains \( K_0 \) which is known, and \( R \) which is measured. In the second term, the true molalities of the undissociated oxalic acid and the hydrogen oxalate ion \( m_{H_2C_2O_4} \) and \( m_{H_2C_2O_4} \) respectively, must be evaluated by arithmetical approximation. As has been pointed out by Harned and Ehlers \(^{13} \) in the case of acetic acid, by Harned and Embree \(^{14} \) in the case of formic acid, and by Wright \(^{17} \) in the case of chloracetic acid, this is necessary, and since oxalic acid in its first dissociation is a stronger acid than either acetic, formic and chloracetic acid, the second term on the left of this equation must be evaluated with care. Since the first term on the right has been shown to vary linearly with the ionic strength the left side of the equation may be plotted against the ionic strength and if the curve is extrapolated to zero ionic strength the intercept will be \( \log K_1 \) or \( - \log K_1 \).

The method discussed in terms of acetic acid, for calculating the first dissociation constant, was applied in this case. The plot obtained by substituting the stoichiometrical molalities \( m_1, m_2, m_3 \) of oxalic acid, potassium hydrogen oxalate and potassium chloride respectively, which are equal to each other to within \( 0.1% \), for the true molalities of the undissociated oxalic acid, hydrogen oxalate
ion, and chloride ion \( \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \) and \( \text{HCl} \) (\( m_3 = m_1 \) as \( \text{KCl} \) is regarded as fully dissociated) is shown by plot I in graph II. The flat part of this curve, corresponding to the stronger solutions, is extrapolated as shown, and the value of \( -\log K_1 \) so determined used to calculate \( K_1 \) which is substituted in the equation for the thermodynamic first dissociation constant of oxalic acid

\[
K_1 = \frac{(m_2 + m_3)}{(m_4 - m_7)} \quad \text{fH fCl.}
\]

The required values for fH fCl are obtained from the paper of Marnad and Ramesh.\(^{24}\)

This equation is solved for \( m_7 \) which is then used to re-determine values for \( m_2\text{C}_2\text{O}_4 \) and \( m_3\text{C}_2\text{O}_4 \) by using the relations

\[
\begin{align*}
m_2\text{C}_2\text{O}_4 &= m_4 - m_1 \\
m_3\text{C}_2\text{O}_4 &= m_2 + m_7
\end{align*}
\]

In this way a second value of \( K_1 \) is determined which in turn is used to calculate new values of \( m_7 \). Successive approximations of this type are used till values of \( K_1 \) and \( m_7 \) are found which satisfy both equations.

Plot II, Graph II, shows the eighth and final plot. The final values of pH or \(-\log K_1\) were found to be at 25\(^\circ\)C.
\[ pK_1 = 1.765 \]
\[ K_1 = 0.01718 \]

In plot 1 in Graph II, the curve rises sharply as the ionic strength decreases. This is due to the first approximation that \( n_{H_2C_2O_4} = n_1 \) and \( n_{H_2C_2O_4^-} = n_2 \). In the more concentrated solutions this is roughly true since \( n_1 \) will be relatively small due to the repression of the dissociation of the oxalic acid by the fully dissociated potassium hydrogen oxalate, and the curve will be fairly flat. As the molality of the solution decreases \( n_1 \) will relatively increase, that is the ratio of the molality of the hydrogen ion to the molality of the undissociated acid will increase, and the error introduced by substituting \( \log \frac{n_1 n_3}{n_2} \) for \( \log \frac{(n_1 - n_2) n_3}{(n_2 + n_3)} \) will progressively increase and the plotted value of \( pK_1^4 \) or \(-\log K_1^4\) will be greater than the true value. This will cause the curve to become steeper in the dilute solutions. As successive approximations are made, the values of \( n_1 \) and \( K_1^4 \) obtained, gradually approach the true values, until with the eight approximation a value of \( n_1 \) and a value \( K_1^4 \) which satisfy both equations are obtained. These values are the true values of \( n_1 \) and \( K_1^4 \). This curve approximates to a straight line, and the straight line which connects five of the total eight points is extrapolated to zero ionic strength to give the
intercept of \( -\log K_4 \) or the true \( pK_4 \) value.

The value obtained was

\[
\begin{align*}
pK_4 & = 1.765 \\
K_4 & = 0.01718
\end{align*}
\]

the temperature being 25\(^{\circ}\)C.
COMPARISON

The agreement between results obtained by the method used in determining the first dissociation constant and other methods of determining dissociation constants is shown by the agreement between the value of Warned and Ehlers\textsuperscript{25} for the dissociation constant of acetic acid, and the value of MacInnes and Shadovsky\textsuperscript{26} determined by conductivity. Warned and Ehlers determined the value $1.754 \times 10^{-5}$ while MacInnes and Shadovsky determined the value $1.753 \times 10^{-5}$. These values are in excellent agreement.

Nims\textsuperscript{16}, using the same method as used in the present work for the second dissociation constant of oxalic acid, determined the second dissociation constant of phosphoric acid at $18^\circ$ and $25^\circ$C. His values are in good agreement with values determined by Bjerrum and Unmack\textsuperscript{27}, using an electrometric titration method with a calomel electrode.

The value determined in the present work for the first dissociation constant of oxalic acid, 0.01748, is in fair agreement with the value 0.02 quoted by Glasstone.

The values of the second dissociation constants
of oxalic acid at $25^\circ$, $30^\circ$, and $35^\circ$C are plotted against
the temperature in Graph III. The point $\square$ represents
the value obtained at $20^\circ$C. by Swarzenbach\textsuperscript{23} from an
electrometric titration method, and is seen to be of the same
order as the other values plotted. This value $\square$ appears
from the Graph to be too low. The value obtained at $25^\circ$,
$5.042 \times 10^{-5}$, agrees fairly well with Chandler's value
$4.9 \times 10^{-5}$ and very well with the value $50 \times 10^{-5}$, quoted
by Philbrick. No values at $30^\circ$ or $35^\circ$C. were available for
comparison.
DISCUSSION

In calculating the dissociation constant of acetic acid Harned and Ehlers\textsuperscript{13} found that an approximation of $K_1$ of $1.75 \times 10^{-5} - 1.76 \times 10^{-5}$ was sufficiently accurate to give the true value of $K_1$ when used to calculate values of $m_H$. Harned and Embree\textsuperscript{14} found that three approximations were always sufficient when calculating the dissociation constant of formic acid. In calculating the first dissociation constant of oxalic acid eight successive approximations were found to be necessary, and a closer approximation than .0173 for $K_1$ was necessary if the true value of $K_1$, .01718 was to be given by the resulting extrapolation. Thus it appears that for stronger acids than acetic acid the method employed is more sensitive to changes in the $m_H$ of the solution, than in the case of acetic acid.

It has been found by Britton\textsuperscript{29} that the relation

$$pH_m = \frac{PK_1 + PK_2}{2}$$

holds for dibasic acids in which both stages of ionisation are similar to those of weak monobasic acids. $pH_m$ is the pH at half neutralisation of the dibasic acid and the "PK's" have their usual meaning. Britton gives the $pH_m$ value 2.88.
for oxalic acid at 25°C. and the value 2.32 for

\[
\frac{\text{pK}_1 + \text{pK}_2}{2}
\]

and remarks that "with the exception of oxalic acid, in which case the first association is that of a fairly strong acid, \(\text{pK}_\text{m}\) and \(\frac{\text{pK}_1 + \text{pK}_2}{2}\) are in fair accord."

The value \(\frac{\text{pK}_1 + \text{pK}_2}{2}\) for oxalic acid at 25°C. calculated from the results of Gane and Ingold is 3.21, while the value obtained from the present work is 3.01 which is fairly close to the value 2.88 for \(\text{pK}_\text{m}\) given by Britton.

The mean heat of ionisation of the second dissociation of oxalic acid has been calculated between 25°C. and between 30°C. - 35°C. by means of the integrated form of the "Isochore"

\[
\log \frac{K_2}{K_1} = \frac{\Delta H}{2.3026RT_2} \frac{T_2 - T_1}{T_2T_1}
\]

or

\[
\text{pK}_1 - \text{pK}_2 = \frac{\Delta H}{2.3026RT_2} \frac{T_2 - T_1}{T_2T_1}
\]

This equation may be used if \(\Delta H\) is assumed to be constant over the temperature range employed. Let \(T_2 = 30°C.\), \(T_1 = 25°C.\) and let \(\text{pK}_1\) and \(\text{pK}_2\) be the values of \(\text{pK}\) (the - log of the second dissociation constant) corresponding to \(T_2\) and \(T_1\) respectively, and assume \(\Delta H\) the mean heat of ionisation to be constant between 25°C and
and 30°C.

Then

\[ 4.300 - 4.320 = \frac{\Delta H}{2.3026 \times 1.988} \frac{5}{298 \times 303} \]

and \[ H = -1653 \text{ cals}. \]

That is, the mean heat of ionisation of the second dissociation of oxalic acid between 25°C and 30°C. is -1653 cals. Similarly by using the same formula between 30°C and 35°C.

\[ 4.250 - 4.348 = \frac{\Delta H}{2.3026 \times 1.988} \frac{5}{303 \times 208} \]

and \[ H = -2392 \text{ cals}. \]

Thus the mean heat of ionisation between 30°C and 35°C is -2392 cals. An error of ±.001 in pH is sufficient to produce an error as large as 83 in \( \Delta H \).
SUMMARY.

1. The second dissociation constant of oxalic acid has been determined from electromotive force measurements of cells without liquid junction at 25°C, 30°C and 35°C.

2. The first dissociation constant of oxalic acid has been determined from electromotive force measurements of cells without liquid junction at 25°C.

3. The mean heat of ionisation of the second dissociation of oxalic acid has been calculated between 25°C - 30°C and between 30°C - 35°C.
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