Calculation of acid dissociation constants

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by

Wayne Woodson Dunning

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I. INTRODUCTION

The determination of the dissociation constants of acids\(^1\) -- though sometimes considered to be a very straightforward procedure -- entails in practice numerous experimental and theoretical difficulties. The variety of experimental methods that have been used, the corrections applied to the data, the numerous manners in which data for identical procedures have been treated, and the considerable disagreement in values of the dissociation constants obtained are all indicative of the difficulties. The research reported in this work was undertaken primarily for the purpose of developing computational methods that would furnish the best possible values of dissociation constants from the data of any of several different experimental procedures.

A. Experimental Background

Among the many experimental procedures used in the past, one of the most common was the measurement of the conductance of an aqueous solution of the acid. This method was used primarily on monobasic acids, since polybasic acids presented great mathematical difficulties. As late as 1959, Dippy et al. (1) expressed the opinion that there was still no wholly satisfactory method of calculating the second and higher thermo-

---

\(^1\)Although this work deals specifically with acids, the treatment of bases is quite analogous, and the necessary modifications to the theoretical equations and the computer program are included.
dynamic dissociation constants of polybasic acids from conductivity data. Conductance methods are now considered obsolete by some authorities (2).

Another common procedure, and one which still sees extensive use, is that of optical measurement. This may be either colorimetric or spectrophotometric. The colorimetric method enables one to obtain a pH titration curve while avoiding some of the problems arising in standard electrometric determinations. However, standards of known dissociation constant are necessary for calibration of the indicators, and this can give rise to other difficulties. Spectrophotometric methods are quite useful in many cases, though extensive computations, similar in principle to those employed in this work, are often required.

Among the other methods or measurements that have been employed at one time or another for the determination of dissociation constants are: a) the change in freezing point; b) hydrolysis of salts (3); c) catalytic effect on the rates of sugar inversion (4); d) solubility of slightly soluble acids in solutions of salts of other acids (5); and e) kinetic methods.

Perhaps the most common procedure, in both past and present use, for determining dissociation constants is that of electrometric measurement. It has long been recognized that the measurement of the change in pH during the neutralization
of a weak acid with a strong base can be employed to obtain an accurate value for the concentration of the acid and its dissociation constant(s). In an electrometric titration, the pH values are measured at successive steps in the titration by means of the changing potentials of suitable electrodes immersed in the solution. According to usual practice, successive portions of a solution of strong base are added to a sample of pure acid and the pH values of the several mixtures are determined. The titration is performed in a vessel that contains a hydrogen, glass, or quinhydrone electrode, and the cell system is completed by a reference half-cell (calomel, AgCl, etc.) whose electrolyte is brought into liquid-liquid contact with the acid solution in the titration vessel.

The pH values derived from the e.m.f. measurements of such a cell often involve considerable uncertainty, and in unfavorable cases they may be in error by more than 0.05 pH units (6). A principle reason for this difficulty is the neglect of the contribution of the potential of the liquid junction or in the application of improper or inadequate corrections. Such corrections are laborious and unsatisfactory, and require a knowledge, often unavailable, of the mobilities and activities of the ions of which the solutions are composed.

1Numerous variations are possible, and under certain conditions may be more practical. The computational methods developed in this work are designed to accommodate some of the variations.
It has been shown (7) that partial corrections may produce a larger error than no corrections at all. Therefore, for accurate work, liquid junctions are to be avoided whenever possible. For approximate work, however, cells with liquid junctions are often useful.

A second limitation to the accuracy of these titrations has its origin in the changing concentration of ionized solutes in the vessel during the titration. A solution of a weak acid has a low ionic strength, whereas its salt is a strong electrolyte. There is no unique titration curve for a weak acid; it is well known that the curve is affected by the ionic strength of the solution. Several procedures are available for resolving this difficulty. One can make 1) a series of pH measurements of buffered solutions at varying ionic strengths, with extrapolation to zero ionic strength; 2) a series of titrations at varying ionic strength, with extrapolation to zero, or 3) a titration with corrections for ionic strength at each point by means of the Debye-Hückel equation

\[
-\log f_i = \frac{A z_i^2 \sqrt{\mu}}{1 + B a_i \sqrt{\mu}} - \Theta \mu
\]

where \( f_i \) is the activity coefficient, \( z_i \) is the valence of the ion \( i \), \( a_i \) is the average effective diameter of the ion in Angstroms, \( \Theta \) is an empirical coefficient dependent upon the system under study, and \( A \) and \( B \) are coefficients whose values vary with the temperature and dielectric constant of the
solvent. The ionic strength, \( \mu \), is defined by Lewis and Randall (8) as

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

where \( m_i \) is the molal concentration of ion \( i \).

The lack of a completely standardized scale of pH may lead to further problems, particularly in the re-evaluation of older data. The simple hydrogen ion concentration

\[
\text{pH} = - \log c_H \quad \text{or} \quad \text{pH} = - \log m_H
\]

is used in much of the older literature, and great care must be taken when recalculating data from such work, if one wishes to obtain meaningful answers.

The Sorensen scale is a conventional one\(^2\), defined in terms of the potential of the cell Pt;\( H_2,\text{Soln. X/Salt bridge/} 0.1 \text{ N Calomel electrode,} \)

\[
\text{pSH} = \frac{E - 0.3376}{0.05916} \quad \text{at } 25^\circ \text{C.}
\]

It is a measure of neither concentration, nor activity of the

---

\(^1\)The standard state of unit activity coefficient at infinite dilution requires that activity on the scales of volume concentration (\( c \)) and molality (\( m \)) shall be related by \( a_c = a_m d^0 \), where \( d^0 \) is the density of water. At 25\(^\circ\) or less, this difference is negligible and will be ignored in this work.

\(^2\)A conventional scale is one in which the values of \( a_H \) although not truly hydrogen ion activities, will nonetheless be numbers which, inserted in equations involving \( a_H \), will furnish results consistent with those obtained by rigorous thermodynamic methods.
hydrogen ion. In spite of this fact that pSH bears no simple direct relationship to chemical equilibria, this scale has been widely used, and extensive tables of pSH values for buffer mixtures are available (9).

The recognition that the e.m.f. of galvanic cells reveals changes of activity rather than of concentration, brought about the proposal by Sorensen and Linderstrom-Lang (10) of a new pH unit

$$\text{paH} = - \log a_H = - \log (f_H c_H)$$  \hspace{1cm} (5)

where $a_H$ is the activity, and $f_H$ the activity coefficient corresponding to the scale of concentration. The fact that the activity of a single ionic species is a concept lacking unique physical definition does not preclude the establishment of a reasonable scale of paH, but this scale must be a conventional one.

Guggenheim (11) and Hitchcock (12) have called attention to the advantages of a unit of acidity defined as

$$\text{pWH} = - \log (f_H f_{Cl} m_H)$$  \hspace{1cm} (6)

Unlike paH, this quantity is physically defined at all ionic strengths, and can be determined exactly from measurements of cells without liquid junction comprising electrodes reversible to hydrogen and chloride ions.

Since pWH is therefore a quite useful concept, it is fortunate that conversion can be made between it and paH with sufficient accuracy for most purposes, provided that the
ionic strength is not too high.

The common "pH meter" employing a glass electrode enjoys widespread popularity, and it is worthwhile to note that the development of pH standards allows one, without the necessity of liquid junction corrections, to make determinations of what is essentially $p\text{H}$, but only under certain specific conditions. It is safe to say that no quantitative interpretation of measured pH values should be attempted unless the medium can be classified as a dilute aqueous solution of simple solutes. This requirement excludes all non-aqueous media, suspensions, colloids, and aqueous solutions of ionic strengths greater than 0.2. From this point of view, the "ideal" solutions are those which match the standards of reference, namely aqueous solutions of buffers and simple salts with ionic strengths between 0.01 and 0.1. Under these very restricted conditions, the measured pH may be expected to approach an experimental $-\log f_{H}^{mH}$, where $f_{H}$ is defined in a conventional manner consistent with the assignment of the pH values of the standards with which the instrument was adjusted. For all practical purposes, the value of $f_{H}$ in this dilute range is given by equation 1 with $a_{i}$ values of 4 to 6.

B. Computational Methods

The number of mathematical treatments that have been applied to electrometric or pH titration data may well be larger
than the number of experimental procedures devised for determining dissociation constants. A thorough analysis of them is not practicable in this work, but a brief discussion of some of the methods will be given.

A simple approximation — one that has been in use for more than fifty years (13) — is that \( K = [H^+] \) at the one-half neutralization point of a monobasic acid. This is, of course, not strictly true, and has the further disadvantage of making the value of the dissociation constant dependent upon only one pH determination.

Auerbach and Smolczyk (14) proposed a set of theoretical equations involving some assumptions which were shown by Britton (15) to be erroneous. Nonetheless, these equations have been widely used. The final values of dissociation constants obtained by this treatment are generally the averages of constants calculated from various combinations of the titration points.¹

A logarithmic equation was derived by Cohn et al. (16) but does not appear to have seen any further use. It is apparently limited to monobasic acids.

¹This method of "using all the data" is apparently still popular. It is generally applied in a rather random fashion, as there is no known formal procedure for its use. The process is essentially one of averaging, and is not generally considered to have the merit of the least-squares method.
Several workers have developed equations by means of which a polybasic acid is treated as a mixture of monobasic acids. The "titration constants" thus obtained are presumably convertible to the true dissociation constants by means of simple relationships. This approach has apparently not seen extensive use, despite its multiple development.

Speakman (17) devised an approach that appears to have considerable merit, although it is in general limited to dibasic acids. The data, modified by the appropriate equations, are recorded graphically, and an essentially linear plot is obtained. The slope of the line gives $K_1$, and the intercept gives $K_1K_2$. Drawing the "best" straight line is considered to give the best use of all the data. Speakman considers extrapolation to zero ionic strength to be inferior to making proper activity corrections at finite ionic strength.

The general treatment of polybasic acid titration curves has been a matter of much study and many suggestions. So far as is known, this work presents the first completely general treatment of such situations. Previously, it was common to develop specific data treatments for varying situations, depending largely upon the ratio(s) of the several dissociation constants. Where this ratio is over 500 to 1000, the acid was generally treated as a mixture of monobasic acids. As the ratio decreased, various approximations were necessary, graphical treatment might be required, etc. In at least one
study, equations were developed for five different cases, none of the treatments being exact. It is the intention of this work to present a treatment that is applicable to mono- or polybasic acids, or to mixtures of acids under certain conditions, which makes no simplifying assumptions for any case, and which utilizes all the data for any of several types of titrations. The method of least-squares is employed, and an estimate of the errors in the individual constants is obtained.
II. EXPERIMENTAL

A. Materials

1. Acids

Standard commercial reagents, in grades meeting A. C. S. specifications, were used without further purification.

2. Base

A stock solution of sodium hydroxide was prepared by the dilution of a filtered, concentrated solution of the reagent grade chemical. It was standardized against potassium biphthalate by potentiometric titration.

3. Buffer

Primary standard grade potassium biphthalate was used to standardize the pH meter for all titrations. A 0.05 M solution has a pH of 4.01 at 25°.

4. Water

Tap distilled water was redistilled from alkaline permanganate solution for use in all preparations and titrations.

B. Equipment

A Beckman model "G" pH meter was used in all pH determinations. Shielded electrodes, model 1190-80, permitted pH determinations outside the shielded cabinet. No electrode corrections were applied to any readings.
III. MATHEMATICAL THEORY

A. Titration of a Single Acid

The simplified chemical equation for the dissociation of an acid, represented by the formula $H_nA$, in water or other suitable solvent is

$$H_nA \rightleftharpoons H^+ + H_{n-1}A^-$$ \hspace{1cm} 7

or, for the $i^{th}$ step of the reaction, where $i$ varies from one to $n$,

$$H_{n+1-i}A^{-(i-1)} \rightleftharpoons H^+ + H_{n-i}A^{-i}.$$ \hspace{1cm} 8

The general equation for the thermodynamic dissociation constants of the acid is

$$K_i = \frac{[H_{n-1}A^{-i}] \gamma_i (H^+)}{[H_{n+1-i}A^{-(i-1)}] \gamma_{i-1}}$$ \hspace{1cm} 9

where the brackets represent ionic concentrations, and the parentheses represent ionic activities. The $\gamma_i$ are the activity coefficients for the ions of charge $-i$; since uncharged species are considered to be of unit activity, $\gamma_0 = 1$.

Equation 9 may be rearranged to

$$[H_{n-i}A^{-i}] = K_i \frac{\gamma_{i-1}}{\gamma_i} \frac{[H_{n+1-i}A^{-(i-1)}]}{(H^+)}$$ \hspace{1cm} 10

and proper substitution of successive terms will give

$$[H_{n-i}A^{-i}] = \frac{\gamma_0}{\gamma_i} \frac{[H_nA]}{(H^+)^i} \prod_{i=1}^{n} K_i.$$ \hspace{1cm} 11
Since the products of the dissociation constants will be encountered so frequently, it is useful to define

\[ k_i = \frac{i}{q=1} k_q \]

and

\[ k_0 = 1. \]

The total concentration of the acid, \( C_a \), is the sum of the concentrations of the unionized molecule and all the ionized species, and may be expressed as

\[ C_a = [H_nA] \left(1 + \sum_{i=1}^{n} \frac{k_i}{\gamma_i (H^+)^i}\right). \]

For ionic balance in solution, it is necessary that the following condition be met:

\[ [H^+] + [Na^+] = [OH^-] + [Cl^-] + \sum_{i=1}^{n} i[H_{n-i}A^{-i}] \]

where \([Na^+]\) is usually due to the base added, and \([Cl^-] = 0\).

If the salt of an acid is being titrated with a strong acid, then \([Na^+]\) is equal to the salt concentration, and \([Cl^-]\) is due to the acid added.

The equations may be simplified somewhat by making the convenient definition

\[ N = [H^+] + [Na^+] - [OH^-] - [Cl^-] \]

or, in terms including activities, activity coefficients, and the dissociation constant of water,

\[ N = \frac{[H^+]}{\gamma_H} + [Na^+] - \frac{K_w}{\gamma_{OH}} \gamma_{OH}^2 - [Cl^-]. \]
Combination of Equations 15 and 16 gives

\[ N = \sum_{i=1}^{n} i \left[ H_{n-i} A^{-i} \right] \]

and from Equations 11, 12 and 14, one finds that

\[ N = \left( \sum_{i=1}^{n} \frac{iki}{Y_i (H^+)^i} \right) \left( \frac{Ca}{1 + \sum_{i=1}^{n} \frac{k_i}{Y_i (H^+)^i}} \right) \]

Multiplication of this by \((H^+)^n/(H^+)^n\) gives

\[ N = \left( \sum_{i=1}^{n} \frac{iki (H^+)^{n-i}}{Y_i} \right) \left( \frac{Ca}{(H^+)^n + \sum_{i=1}^{n} \frac{k_i (H^+)^{n-i}}{Y_i}} \right) \]

Rearrangement of terms gives

\[ N \left( H^+ \right)^n + \sum_{i=1}^{n} \frac{k_i (H^+)^{n-i}}{Y_i} = \sum_{i=1}^{n} \frac{iki (H^+)^{n-i} Ca}{Y_i} \]

and the separation and recombination of terms gives

\[ N(H^+)^n = \sum_{i=1}^{n} k_i \left( \frac{i Ca - N}{Y_i} \right) (H^+)^{n-i} \]

There is one such equation for each data point, resulting in a set of equations in n unknowns for a given titration. There will most generally be more than n data points, and in order that the best possible use may be made of all the experimental data for a titration, the method of least-squares, or multiple regression, is employed in solving the set of equations.

The particular treatment used in this work may be best
illustrated by simplifying the coefficients of Equation 22 to give

\[ Y = A_1 k_1 + A_2 k_2 + \cdots + A_n k_n \]  

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The coefficients of the numerous individual equations are multiplied and summed to form the following set of equations:

\[(\sum A_1 Y) = (\sum A_1 A_1) k_1 + \cdots (\sum A_1 A_n) k_n \]  

24

\[(\sum A_n Y) = (\sum A_n A_1) k_1 + \cdots (\sum A_n A_n) k_n \]  

25

This set may be solved for the \( k_i \) by any of several standard methods. The dissociation constants, \( K_i \), are then obtained from an equation analogous to Equation 12.

\[ K_i = \frac{k_i}{k_{i-1}} \]  

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B. Mixture of Two Acids

The addition of a second acid, \( H_mB \), to the system introduces certain complications. Dissociation constants for the second acid are \( K_j \), and the equations which differ significantly from those for a single acid are

\[ k_j = \prod_{j=1}^{\infty} K_j \]  

26

\[ N = \sum_{i=1}^{n} [H_{n-i} A^{-i}] + \sum_{j=1}^{m} j[H_{m-j} B^{-j}] \]  

27

and
\[ N = \left( \sum_{i=1}^{n} \frac{ik_i (H^+)^{n-i}}{\eta_i} \right) \left( \frac{Ca}{(H^+)n + \sum_{i=1}^{n} \frac{k_i (H^+)^{n-i}}{\eta_i}} \right) + \left( \sum_{j=1}^{m} \frac{j k_j (H^+)^{m-j}}{\delta_j} \right) \left( \frac{C_b}{(H^+)m + \sum_{j=1}^{m} \frac{k_j (H^+)^{m-j}}{\delta_j}} \right). \]

This equation may be reduced to
\[ N(H^+)^{n+m} = \sum_{i=1}^{n} k_i (\frac{i Ca - N}{\delta_i}) (H^+)^{n+m-i} + \sum_{j=1}^{m} k_j \left( \frac{j C_b - N}{\delta_j} \right) (H^+)^{n+m-j} + \sum_{i=1}^{n} \sum_{j=1}^{m} k_i k_j (\frac{i Ca + j C_b - N}{\delta_i \delta_j}) (H^+)^{n+m-i-j}. \]

A non-linear method must be employed in the solution of this system due to the fact that products of the variables are present. So far as is known, all methods for solving non-linear systems of equations on digital computers are iterative and have one of two disadvantages: either reasonably good initial estimates of the variables are required to assure convergence, or else the equations are expanded at each iteration and the program may bog down of sheer complexity. In this work, the Newton-Raphson method of iteration, as employed by Crosbie and Monahan (18), was chosen as the most suitable and convenient.

The method of least-squares requires the minimization of Q in the equation
\[ Q = \Sigma (Y_c - Y_m)^2 \]

where
\[ Y = N(H^+)^{n+m} \]

and may be either a measured value, \( Y_m \), by virtue of Equation 16, or a calculated value, \( Y_C \), from Equation 29 and the estimates of the \( k_{i,j} \).

The appropriate corrections, \( \delta k \), in vector notation, to the variables would result in

\[ Q + \Sigma \left( \frac{\partial Q}{\partial k} \right)(\delta k) = 0. \]

From this, it follows that

\[ \Sigma \left( \frac{\partial Q}{\partial k} \right)(\delta k) = -Q \]

and

\[ \Sigma \left( \frac{\partial Q}{\partial k} \right) = \Sigma 2(Y_c - Y_m) \left( \frac{\partial Y_c}{\partial k} \right). \]

Therefore

\[ \Sigma 2(Y_c - Y_m) \left( \frac{\partial Y_c}{\partial k} \right)(\delta k) = \Sigma -(Y_c - Y_m)^2 \]

or

\[ \Sigma 2\left( \frac{\partial Y_c}{\partial k} \right)(\delta k) = \Sigma (Y_m - Y_c). \]

This can be most conveniently solved by multiplying by \( \left( \frac{\partial Y_c}{\partial k} \right) \) and expressing the entire equation in vector or matrix notation,

\[
\begin{bmatrix}
\Sigma \Sigma \left( \frac{\partial Y_c(1)}{\partial k_a} \right)^2 \\
\end{bmatrix}
\begin{bmatrix}
\delta k
\end{bmatrix}
= 
\begin{bmatrix}
\Sigma \Sigma \left( Y_m(1) - Y_c(1) \right) \left( \frac{\partial Y_c(1)}{\partial k_a} \right)
\end{bmatrix}
\]

where ND is the number of points on the titration curve.
This system,

\[ [G][dk] = [R] \]

is solved for the vector \([dk]\) by matrix inversion to yield improved values of the variables, \(k_a = k_a^0 + d k_a\).

C. Modified Titrations

The principal variation that will be encountered is probably the titration of a weak base with a strong acid. In addition, the free acid (or base) may occasionally be unobtainable, necessitating the titration of a sodium or potassium salt of the acid with strong acid. Fortunately, modifications to the equations already developed are either slight or unnecessary, and the changes in computer programming required to handle all four situations are minor.

1. Salt of weak acid titrated with strong acid

The only changes needed are that \([Na^+]\) be made equal to the salt concentration, and \([Cl^-]\) is now the concentration of the acid titrant.

2. Weak base titrated with strong acid

For the titration of a base, \(M(OH)_n\), with acid, Equation 18 is changed to

\[ N = \sum_{i=1}^{n} i[M(OH)^{+i}]_{n-i} \]
Equation 16 remains the same, except for a change in sign, since \( N \) will now represent the total concentration of all simple negative ions. The value of \([\text{Na}^+]\) will generally be zero, and \([\text{Cl}^-]\) will be the concentration of the acid titrant.

3. **Salt of weak base titrated with strong base**

This case is very similar to that of Section 1 above. \([\text{Cl}^-]\) equals the salt concentration, and \([\text{Na}^+]\) is the concentration of the base titrant. The quantity \( N \) has the same sign as in Section 2.

**D. Calculation of Titration Curves**

It is sometimes useful to calculate an exact titration curve from known dissociation constants and concentrations.

An iterative process is necessary for curve calculation, due to the continual corrections for volume change. The required sodium ion concentration (or chloride ion, depending upon the type of titration) at each desired pH on the titration curve is calculated from Equation 19 and 16. The previous value of \([\text{Na}^+]\) is obtained from the expression

\[
[\text{Na}^+] = \frac{\text{Total volume of base added}}{\text{Total volume of solution}} \times \text{base normality.}
\]

40

The difference, required \([\text{Na}^+]\) - Previous \([\text{Na}^+]\), is multiplied by the total solution volume and divided by the concentration of the base to obtain the volume of base that must be added.
This calculated amount is added to the solution, and then a test is made to determine whether or not sufficient accuracy has been achieved. Generally, if the amount of base added (or subtracted, since the quantity may have either sign) is less than 0.001 ml, no further adjustments are made to the particular point on the curve in question.

E. Calculation of Acid Concentrations

The concentration of an acid can be readily obtained from its titration curve and dissociation constants by means of Equations 20 or 28 and the linear least-squares treatment. For a single acid, this is of doubtful utility since standard analytical analysis of the titration curve will generally give a value of completely satisfactory accuracy. For a mixture of acids, however, this calculation may be of some importance as there may be no break in the curve.

F. Determination of Errors

The method of least-squares can be reasonably depended upon to do a good job of fitting a particular equation to a given set of data. It does not, however, necessarily indicate how well the answers obtained satisfy the equation and data. It is therefore highly advantageous to determine the standard deviations of the final results; these will give indications of the random errors in the data, or perhaps evidence that the
chosen equation was not the proper one. In the latter case, this would be due to improper choice of the initial parameters specifying the number of acids or dissociation constants.

In all cases in this work, the same procedure is used to obtain the standard deviations of the particular results. The systems of linear equations are solved by the method for non-linear equations on the last iteration. The diagonal elements of the inverse matrix $G^{-1}$, from Equation 38, are transformed into the standard deviations by the expression

$$ (\sigma_{RL})^2 = \frac{G^{-1}(L,L) \times Q}{ND-NC-1} $$

where $ND$ is the number of points on the titration curve, $NC$ is the number of variables in the problem, and $Q$ is defined as in Equation 30.
IV. CALCULATIONS

The development of the equations in Chapter III, and, in particular, the reduction to practice of these equations, actually constituted the major portion of this research. For this reason, the applications of the equations for the titration of a single acid, and for a mixture of acids, will be described in some detail. The applications of the equations in the remaining sections do not differ sufficiently from the above to warrant detailed descriptions.

Utilization of the procedures developed in this work requires the availability of an electronic digital computer, preferably of large size. Much of the initial development and testing was done on an International Business Machines Type 650 computer. However, this machine is of insufficient size to contain the complete program, and final assembly and operation was done on an IBM Type 704. In general, the Fortran Automatic Coding System was used to code the programming for both machines. The program is listed in Appendix B.

A. Calculation of the Dissociation Constants for a Single Acid

A simplified flow sheet for this section is given in Figure 1. The individual steps are explained below.

1. Read in the titration curve, estimates of dissociation constants, control parameters, and any other
Figure 1. Flow diagram for the calculation of dissociation constants for a single acid
1. INITIALIZATION

2. CLEAR ARRAY
   SET LOOP

3. GO TO 4. CALC.

4. CALC. N AND Y

5. BUILD ARRAY

6. RAISE LOOP AND
   TEST FOR END

7. SOLVE ARRAY
   FORM SUM
   REPLACE ANSWERS
   TEST FOR ANSWERS

8. MODIFIED PROPER PARAMETERS
   AND ENTER TWO ACID SYSTEM
necessary information. The control parameters specify which of the numerous program options are to be used, and control the introduction of additional information necessary to satisfy those options. The products of the dissociation constants are formed by means of Equation 12.

2. The array specified by Equation 24 is set to zero since it is to be built up by a summation process in each iteration. The "loop" will control the successive processing of each point on the titration curve as the array is built up.

3. The "Gamma Calculator" and the operations it performs are described in detail in Section C.

4. The quantity N is calculated by means of Equation 17, and \( Y = N(H^+) \) as shown in Equations 22 and 23.

5. The elements of the array are formed by means of Equations 22 and 23, and are added to the previous values, as indicated by Equation 24.

6. The "loop" is increased to process the next point, and a test is made to determine whether or not any points remain.

7. The array is solved by the conventional method of triangularization. The answers replace the previous values of \( k_i \), and the sum of the absolute values of the fractional differences between the new results
and the previous results is compared with the desired
closeness of fit to determine the necessity for
another iteration.

8. If the last answers obtained are satisfactory, the
control parameters for the two acid system (Section
B) are modified to allow one pass through that sec-
tion in order to calculate the standard deviations.

B. Calculation of Dissociation Constants for a Two
Acid Mixture

Figure 2, detailed below, shows the basic steps employed in this treatment.

1. This step is essentially the same as Step 1 in Sec-
tion A. Equation 26 is used in addition to Equa-
tion 12 to form the products of the constants.

2. The looping operation is the same as the one used in
Section A. The array used in the single acid treat-
ment does not appear in this section.

3. See Section C.

4. From Equations 16, 29, and 31, $Y_Q$ and $Y_M$ are calcu-
lated. These quantities are vectors, there being one
value of each for every point on the titration curve.

5. The partial derivatives, $\partial Y_Q / \partial k$, are calculated by
means of Equations 29 and 31. These will form a
matrix whose dimensions are determined by the total
number of dissociation constants and the number of
Figure 2. Flow diagram for the calculation of dissociation constants for a mixture of two acids
1. **INITIALIZATION**

2. **SET LOOP**

3. **GO TO Π CALC.**

4. **CALC. \( Y_C(L), Y_M(L) \)**

5. **CALC. VECTOR**
   
   \[ \delta Y_C(L)/\delta k \]

6. **RAISE LOOP AND TEST FOR END**

   **NO**

   **YES**

   7. **FORM G AND R MATRICES**

   **INVERT G, APPLY CORRECTIONS**

8. **FORM SUM**

   **REPLACE ANSWERS**

   **TEST FOR END**

   **NO**

   **YES**

9. **CALC. STANDARD DEVIATIONS**
27

points on the titration curve.

6. Same as step 6 in Section A.

7. The G and R matrices, given by Equations 37 and 38, are formed and G is inverted by a standard procedure. The corrections, $d_{k_a}$, are added to the dissociation constants.

8. The previous values of $k_{i,j}$ are replaced and the sum of the absolute values of the fractional changes is calculated to determine the necessity for any further iterations.

9. The standard deviations are calculated from the inverse matrix, $G^{-1}$, by means of Equation 41.

C. Calculation of Intermediate Quantities

This section, previously referred to as the "Gamma Calculator", computes, in addition to the activity coefficients for the various ions in solution, a large number of other necessary factors. Since the operations in this section are performed in sequence, they will be described without reference to a flow sheet.

1. The activity coefficients for the hydrogen and hydroxide ions, and for all the ionic species derived from the acids, are calculated by means of the Debye-Hückel formula, Equation 1. In the first calculation for each point, the estimated ionic strength is used.
Successive calculations use the ionic strength previously determined at the end of this section.

2. The concentrations of the acids are corrected for the volume change, caused by the addition of base, by means of the following equation.

\[ C_{\text{corr}} = C_{\text{init}} \times \frac{V_{\text{init}}}{V_{\text{init}} + V_{\text{base}}} \]  

3. The sodium ion concentration is calculated from the volume of base added, its normality, and the initial solution volume.

\[ [\text{Na}^+] = \frac{V_{\text{base}} \times N_{\text{base}}}{V_{\text{base}} + V_{\text{init}}} \]  

4. The concentrations of all the ionic species of the acids are calculated from the current estimates of the dissociation constants. Equation 14 is first employed to obtain the concentration of the unionized acid. Equation 11, which relates the ionic species to the unionized acid, is then utilized to obtain the individual ion concentrations.

5. The new value of ionic strength is calculated by means of Equation 2.

D. Options and Considerations

As previously mentioned, Sections C through F of Chapter III do not warrant detailed description in this work. They
do, however, add considerably to the complexity of the program because of the many branches and multiple paths of similar calculations that must be provided.

In addition to the options previously described, a number of minor options have been incorporated in the final program to increase its flexibility and utility. They include the following.

1. Hydrogen ion concentration may be in the form of pH, pαH, or pωH.

2. Ionic strength may be calculated at each point, specified for each point, or constant.

3. Hydrogen ion activity coefficients may be calculated or specified at each point.

4. Total solution volume may be calculated or constant.

5. The coefficients, A, B, and θ in Equation 1 may be altered. Also, the ion size parameter for hydrogen ion, normally set at 5.0, may be changed.

The permissible decimal range of quantities in programs coded by Fortran is $10^{-38}$ to $10^{+38}$. This range is generally sufficient, but in some problems may be greatly exceeded, causing meaningless results. Considerable attention was therefore given to providing means by which certain quantities would be automatically scaled in the proper direction when necessary, without changing the validity of any equations.
V. RESULTS

Much of the testing of the computational methods developed herein could be done only with theoretical titration curves. For the most part, these curves were calculated from various hypothetical dibasic acids. The problem of the monobasic acid is considerably less complex in many respects, and has been largely ignored since any method capable of handling dibasic acids is almost certain to be more than sufficient for monobasic acids.

Likewise, once the problem of the dibasic acid has been solved without resorting to graphical or other two dimensional limitations, additional hydrogen ions give no particular complications, in theory. In practice, the limited accuracy of experimental data will likely be the greatest problem in the treatment of polybasic acids. For these reasons, dibasic acids are the principal ones considered in this work.

A. Resolution of Successive Constants

One of the greatest problems in the calculation of acid dissociation constants has been the differentiation of successive constants whose values differ only slightly. Generally, if the ratio of the values of successive constants has been less than about 500, previous calculations have employed mathematical artifices involving questionable assumptions. It
has been calculated (14) that a break will appear in the
titration curve of a dibasic acid only if the ratio of con-
stants is over sixteen. Since there exist several acids whose
reported constants differ by even lesser amounts, it is im-
portant to test the differentiating ability, or "resolving
power" of any new computational method. This has been done
using theoretical data, to test the ultimate limits, and with
modifications to simulate experimental data in order to de-
termine the results likely to be obtained in practice.

A series of titration curves was calculated for dibasic
acids with ratios of dissociation constants varying from 1000
to 3. The initial parameters used are given in Table 1.
Several of these curves have been plotted in Figure 3 to indi-
cate the general curve shape obtained with various ratios of
constants. These calculated curves are precise in pH, and
within 0.001 ml of base at each point. Activity corrections
were not made, since such corrections are somewhat time con-
suming, and ideally should have no effect on this part of the
investigation. However, as a safeguard, several of the curves
with low ratios of constants were also calculated with activ-
ity corrections to see if there were any effects peculiar to
such corrections.

1. Ultimate resolution

   These calculated curves were then processed to determine
the dissociation constants, and the results are given in Table 1.
Figure 3. Calculated titration curves for various hypothetical dibasic acids with varying ratios of $k_1/k_2$. 
Table 1. Conditions and results for the theoretical test of resolving power upon titration curves of dibasic acids (Acid concentration = 0.05 M, base concentration = 0.10 N, and initial solution volume = 100.0 ml)

<table>
<thead>
<tr>
<th>Initial constants</th>
<th>Ratio</th>
<th>Calculated constants</th>
<th>Fractional Standard deviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>P%1 PK2</td>
<td>P%1 PK2</td>
<td>P%1 PK2</td>
<td>P%1 PK2</td>
</tr>
<tr>
<td>3.00</td>
<td>6.00</td>
<td>1000</td>
<td>3.00</td>
</tr>
<tr>
<td>3.52</td>
<td>6.00</td>
<td>300</td>
<td>3.52</td>
</tr>
<tr>
<td>4.00</td>
<td>6.00</td>
<td>100</td>
<td>4.00</td>
</tr>
<tr>
<td>4.52</td>
<td>6.00</td>
<td>30</td>
<td>4.52</td>
</tr>
<tr>
<td>4.60</td>
<td>6.00</td>
<td>25</td>
<td>4.60</td>
</tr>
<tr>
<td>4.70</td>
<td>6.00</td>
<td>20</td>
<td>4.70</td>
</tr>
<tr>
<td>4.82</td>
<td>6.00</td>
<td>15</td>
<td>4.82</td>
</tr>
<tr>
<td>5.00</td>
<td>6.00</td>
<td>10</td>
<td>5.00</td>
</tr>
<tr>
<td>5.30</td>
<td>6.00</td>
<td>5</td>
<td>5.30</td>
</tr>
<tr>
<td>5.52</td>
<td>6.00</td>
<td>3</td>
<td>5.52</td>
</tr>
<tr>
<td>5.00a</td>
<td>6.00</td>
<td>10</td>
<td>5.00</td>
</tr>
<tr>
<td>5.52a</td>
<td>6.00</td>
<td>3</td>
<td>5.52</td>
</tr>
</tbody>
</table>

*aWith activity corrections*
It is evident from these results that this method is inherently capable of excellent resolution. It is instructive to note, however, that the answers obtained are not always exactly equal to the constants used to calculate the titration curves. An error of 0.01 in $pK$ is equivalent to an error of about 2% in $K$, and in several cases such errors were obtained. These errors are not reflected in the standard deviations, since this latter quantity is merely a measure of how well the answers fit the data, and not a measure of how accurate the answers are.

The inclusion of corrections for activity caused no difficulties.

2. **Effects of errors**

A consistent error in experimental data may result in a titration curve that is smooth and satisfactory in appearance when plotted, but is nevertheless inaccurate. An error of up to 0.05 units in the standardization of a pH meter might not be unexpected under certain circumstances. To determine the effects of such an error, the pH values of the calculated curves were all changed by the same amount, and the resulting data processed to obtain the constants. The results are given in Table 2.

The changes in $pK_1$ are quite consistent and not alarmingly large. The changes in $pK_2$ are considerable, and no posi-
Table 2. Conditions and results for the test of the effect upon dissociation constants of a consistent error in the titration curve

<table>
<thead>
<tr>
<th>Initial constants</th>
<th>Calculated constants with +0.05 pH unit error</th>
<th>Calculated constants with -0.05 pH unit error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$pK_1$</td>
<td>$pK_2$</td>
</tr>
<tr>
<td>3.00</td>
<td>6.00</td>
<td>3.09</td>
</tr>
<tr>
<td>3.52</td>
<td>6.00</td>
<td>3.61</td>
</tr>
<tr>
<td>4.00</td>
<td>6.00</td>
<td>4.08</td>
</tr>
<tr>
<td>4.52</td>
<td>6.00</td>
<td>4.61</td>
</tr>
<tr>
<td>4.60</td>
<td>6.00</td>
<td>4.69</td>
</tr>
<tr>
<td>4.70</td>
<td>6.00</td>
<td>4.77</td>
</tr>
<tr>
<td>4.82</td>
<td>6.00</td>
<td>4.90</td>
</tr>
<tr>
<td>5.00</td>
<td>6.00</td>
<td>5.08</td>
</tr>
<tr>
<td>5.30</td>
<td>6.00</td>
<td>5.37</td>
</tr>
<tr>
<td>5.52</td>
<td>6.00</td>
<td>5.60</td>
</tr>
<tr>
<td>5.00$^b$</td>
<td>6.00</td>
<td>5.08</td>
</tr>
<tr>
<td>5.52$^b$</td>
<td>6.00</td>
<td>5.60</td>
</tr>
</tbody>
</table>

$^a$This calculation was not completed

$^b$With activity corrections
tive values were obtained when the pH values were lowered. Activity corrections gave no change in $pK_1$, but did affect $pK_2$. The reason for this is not known.

Experimental titration curves are unlikely to exhibit the precision demanded of the calculated curves, nor, it is hoped, will they have a consistent error of disturbing magnitude. What will be found are random errors of multiple origin. A precise determination of the effects of such errors is more than likely impossible. Since acids with suitably spaced constants are not readily available (if at all), and experimental titrations are not sufficiently accurate, attempts to determine the effects of random errors must be made with calculated data suitably modified to include such errors. Ideally, the errors should be applied to both pH and titrant volume readings, but this would seem to be an unnecessary complication for what can at best be only an approximation. Thus, only the pH data were modified. McComas and Rieman (19) estimated the accuracy of pH measurements with a glass electrode as ± 0.03 units. Although other electrodes may be subject to less error, it was considered reasonable to subject the pH data to a standard deviation of 0.05 units. A table of random digits, in conjunction with the standard Gaussian Distribution Curve, was used to calculate the error to be applied. Table 3 gives the direction and magnitude of the error assigned for each digit.
Table 3. Errors in pH assigned by random digit table for Sigma = 0.05

<table>
<thead>
<tr>
<th>Digits</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
</tr>
</tbody>
</table>

All calculated curves were treated identically, and for a 28 point curve, the average deviation applied was -0.01 units. The results of the dissociation constant determinations from these modified curves are given in Table 4.

Table 4. Conditions and results for the test of the effect upon dissociation constants of random errors in the titration curve

<table>
<thead>
<tr>
<th>Initial constants</th>
<th>Calculated constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>pK₁</td>
<td>pK₂</td>
</tr>
<tr>
<td></td>
<td>pK₁</td>
</tr>
<tr>
<td>3.00</td>
<td>6.00</td>
</tr>
<tr>
<td>3.52</td>
<td>6.00</td>
</tr>
<tr>
<td>4.00</td>
<td>6.00</td>
</tr>
<tr>
<td>4.52</td>
<td>6.00</td>
</tr>
<tr>
<td>4.60</td>
<td>6.00</td>
</tr>
<tr>
<td>4.70</td>
<td>6.00</td>
</tr>
<tr>
<td>4.82</td>
<td>6.00</td>
</tr>
<tr>
<td>5.00</td>
<td>6.00</td>
</tr>
<tr>
<td>5.30</td>
<td>6.00</td>
</tr>
<tr>
<td>5.52</td>
<td>6.00</td>
</tr>
<tr>
<td>5.00a</td>
<td>6.00</td>
</tr>
<tr>
<td>5.52a</td>
<td>6.00</td>
</tr>
</tbody>
</table>

*With activity corrections*
Once again, it is $pK_2$ that is predominantly affected, both with and without activity corrections. However, the errors are consistent neither in direction nor magnitude.

B. Resolution of Mixtures

The mathematical resolution of a mixture of acids is considerably more difficult than the resolution of successive constants of a single acid. The first test was made upon a calculated curve for a monobasic acid, $pK = 5$, treating this curve as a mixture of monobasic acids in varying concentration ratios, with the total concentration equal to that used in calculating the curve. Ideally, the computations should result in values of $1.0 \times 10^{-5}$ for both constants. The results given in Table 5 indicate that this ideal was approached rather closely.

Table 5. Conditions and results for the mathematical treatment of a single monobasic acid as a mixture of two monobasic acids

<table>
<thead>
<tr>
<th>Molar concentrations</th>
<th>Dissociation constants x $10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid 1</td>
<td>Acid 2</td>
</tr>
<tr>
<td>0.0500</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0495</td>
<td>0.0005</td>
</tr>
<tr>
<td>0.0490</td>
<td>0.0010</td>
</tr>
<tr>
<td>0.0475</td>
<td>0.0025</td>
</tr>
<tr>
<td>0.0450</td>
<td>0.0050</td>
</tr>
<tr>
<td>0.0425</td>
<td>0.0075</td>
</tr>
<tr>
<td>0.0400</td>
<td>0.0100</td>
</tr>
<tr>
<td>0.0350</td>
<td>0.0150</td>
</tr>
<tr>
<td>0.0300</td>
<td>0.0200</td>
</tr>
<tr>
<td>0.0250</td>
<td>0.0250</td>
</tr>
</tbody>
</table>

*aBetter values were obtained in these runs
As mentioned in Chapter IV, this part of the program is
reiterative. Such methods may occasionally oscillate around
the correct answer, or perhaps even diverge, rather than con­
verge to a final solution. In the runs in Table 5, oscillation
was encountered. Ten iterations were permitted in each run,
and the answers were taken from the iteration which gave the
smallest least-squares parameter. This was usually the best
answer, although there were exceptions in two cases.

A calculated curve for what might be considered a typical
acid mixture was then processed; the results are given in
Table 6. No difficulties were encountered in this calculation.

Table 6. Conditions and results for the resolution of a mix­
ture of a monobasic and a dibasic acid (Concenra­
tion of each acid = 0.01 M)

<table>
<thead>
<tr>
<th>Dissociation constants</th>
<th>given</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid 1 ( K_1 )</td>
<td>( 6.40 \times 10^{-5} )</td>
<td>( 6.41 \times 10^{-5} )</td>
</tr>
<tr>
<td>( K_2 )</td>
<td>( 2.70 \times 10^{-5} )</td>
<td>( 2.69 \times 10^{-5} )</td>
</tr>
<tr>
<td>Acid 2</td>
<td>( 1.77 \times 10^{-4} )</td>
<td>( 1.77 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

C. Consistency

Experimental consistency was examined by titrating ali­
quots of a tartaric acid solution with sodium hydroxide, using
a glass electrode. The pH meter was standardized against 0.05
M potassium biphthalate at the beginning of each titration.
There was no significant drift. The constants obtained from these titrations, with activity corrections applied, are given in Table 7.

Table 7. Conditions and results for repetitive titrations of tartaric acid (Initial volume = 100.0 ml, acid concentration = 0.1031 M, base concentration = 0.05 N)

<table>
<thead>
<tr>
<th>Dissociation constants</th>
<th>Standard deviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1 \times 10^4$</td>
<td>$K_2 \times 10^5$</td>
</tr>
<tr>
<td>8.64</td>
<td>4.34</td>
</tr>
<tr>
<td>8.64</td>
<td>4.35</td>
</tr>
<tr>
<td>8.81</td>
<td>4.28</td>
</tr>
<tr>
<td>9.33</td>
<td>4.19</td>
</tr>
<tr>
<td>8.34</td>
<td>4.31</td>
</tr>
<tr>
<td>10.07</td>
<td>4.12</td>
</tr>
<tr>
<td>10.05</td>
<td>4.17</td>
</tr>
</tbody>
</table>

Although 12 to 14 pH measurements were made in each titration, and all reasonable care was taken, there are considerable variations in the results. Here, unlike the tests with calculated data, it is $K_1$ that shows the greatest variation, with values that bracket the commonly accepted $9.6 \times 10^{-4}$. The variations in $K_2$ are much smaller than those in $K_1$, but the values differ somewhat from the accepted one of $2.9 \times 10^{-5}$. Once again, the standard deviation is obviously not a valid indication of the accuracy of the computed constants.

D. Improper Calculations

The errors introduced by treating a dibasic acid as a mixture of monobasic acids were investigated by processing the
single acid calculated data as mixtures. From the results given in Table 8, it can be seen that this procedure will produce very good results when the ratio of constants is 100 or more, and reasonably good results are obtained at even lower ratios. Below a ratio of 10, results were unsatisfactory.

Table 8. Conditions and results for the test of the effect upon dissociation constants of the treatment of a dibasic acid as a mixture of two monobasic acids

<table>
<thead>
<tr>
<th>Initial constants</th>
<th>Calculated constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>pK₁</td>
<td>pK₂</td>
</tr>
<tr>
<td>3.00</td>
<td>6.00</td>
</tr>
<tr>
<td>3.52</td>
<td>6.00</td>
</tr>
<tr>
<td>4.00</td>
<td>6.00</td>
</tr>
<tr>
<td>4.52</td>
<td>6.00</td>
</tr>
<tr>
<td>4.60</td>
<td>6.00</td>
</tr>
<tr>
<td>4.70</td>
<td>6.00</td>
</tr>
<tr>
<td>4.81</td>
<td>6.00</td>
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<tr>
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</tr>
<tr>
<td>5.30</td>
<td>6.00</td>
</tr>
<tr>
<td>5.52</td>
<td>6.00</td>
</tr>
</tbody>
</table>

E. Experimental Titrations

In addition to the titrations of tartaric acid previously mentioned, titrations were made on acetic acid, succinic acid, and on mixtures of tartaric and acetic, succinic and acetic, and tartaric and succinic acids. The last three would provide a severe experimental test of the resolving power of the method for mixtures. Unfortunately, of these three, only the last produced any positive results. From Table 9, it can be seen that the single acids approached the literature values fairly
closely, and the values for tartaric acid in the mixture are very close to the commonly accepted values. However, negative constants were obtained for succinic acid in this mixture.

Table 9. Results of experimental titrations of various single acids and mixtures

<table>
<thead>
<tr>
<th>Acid</th>
<th>Constant</th>
<th>Experimental value</th>
<th>Literature value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>K</td>
<td>$1.66 \times 10^{-5}$</td>
<td>$1.75 \times 10^{-5}$</td>
</tr>
<tr>
<td>Succinic</td>
<td>$K_1$</td>
<td>$5.96 \times 10^{-5}$</td>
<td>$6.6 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$K_2$</td>
<td>$2.18 \times 10^{-6}$</td>
<td>$2.8 \times 10^{-6}$</td>
</tr>
<tr>
<td>Tartaric + Succinic</td>
<td>Tar. $K_1$</td>
<td>$9.81 \times 10^{-4}$</td>
<td>$9.6 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Tar. $K_2$</td>
<td>$2.88 \times 10^{-5}$</td>
<td>$2.9 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Suc. $K_1$</td>
<td>Neg.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Suc. $K_2$</td>
<td>Neg.</td>
<td></td>
</tr>
</tbody>
</table>

Data for the titrations giving successful results are tabulated in Appendix A.
VI. DISCUSSION

The computational procedures developed in this work have been shown, it is believed, to be fundamentally sound and inherently extremely accurate. However, the accuracy that can be attained in practice, by any method, may be far poorer than generally expected.

Successive dissociation constants of small ratio, a major obstacle in most former methods, have been shown to present no difficulties attributable to such ratios. The thoroughly satisfactory manner in which closely spaced constants are resolved is not, however, accompanied by equally satisfactory accuracy. It is this latter fact which casts some suspicion upon all constants previously determined by titration methods. It should be emphasized that the matter of accuracy is largely an experimental problem, and neither necessarily nor probably a fundamental limitation of the method. Since the "titrations" used for testing were calculated by reiterative methods, some tolerance had to be allowed. This was in the volume of base, which was within 0.001 ml at every point in a titration requiring 100.0 ml. Such accuracy in practice would be attainable only with exceptional care, even in weight titrations. Although, as shown, this may lead to a 2% error in dissociation constants, it is not unusual to find literature values expressed to three significant figures when even the
second is probably uncertain. Other experimental methods may involve less error, but they can not be judged in this work.

Consistent pH errors produce effects somewhat greater than anticipated. For a monobasic acid, it might be expected that the change in pK would essentially equal the change in pH. Such a test was not made, but it now appears that the effect might not be quite so simple. The dibasic acid tests demonstrate that a simple displacement of the titration curve gives a not so simple displacements of pKs. An analysis of the mathematical niceties involved in these displacements would have little practical value. However, two simple and constructive conclusions can be drawn. First, the magnitude of errors to be expected, if the work if performed with care, has been overestimated. Second, the effect of such errors as may be present can be considerable. These conclusions are also consistent with the experimental titrations done in this work.

When considering the results of introducing random errors into the titration curves, it is well to remember that the curves do not retain their original shape, nor are they altered identically in two dimensions. With this in mind, one may conclude that the rather random results indicate excessive pessimism in the estimation of likely experimental error; this is then essentially the same result as obtained for consistent errors.

Mixtures of acids proved to be no more difficult to re-
solve than single acids, within limits. Certainly the results given in Tables 5 and 6 are as good as one could reasonably expect. However, more severe examples, such as mixtures of dibasic acids with overlapping constants, proved to be insoluble. Inaccuracies in the data are the most reasonable explanation for this failure. It is possible that titration data accurate to more significant figures would enable satisfactory resolution to be attained, but there would be no practical application. The almost total failure of the experimental titrations of mixtures to be properly resolved is not surprising. The solitary exception cannot be explained. In general, titration of acid mixtures does not appear to be a fruitful undertaking, unless there is considerable separation of constants.

The multiple titrations of tartaric acid give an indication of the results likely to be obtained by ordinary analytical procedures. These titrations were not the ultimate in refinement nor accuracy, but were typical of ordinary laboratory practice. Better results would be desired, but the range of $pK_1$, 3.00 - 3.08, is not unreasonable in view of the previous tests, and $pK_2$, 4.36 - 4.39, covers an almost remarkably small range.

The "accepted" values, to which these results were compared in section V, are not to be considered as ultimate standards for comparison. They are perhaps the most widely accepted, but a cursory search of published constants will re-
veal both higher and lower values than those obtained in this work. For this reason, consistency is considered to be a more important criterion than conformance to any other particular work. On that basis, and in view of the effects of errors, these titrations may be considered quite satisfactory.

The errors that resulted by assuming a dibasic acid to be a mixture of monobasic acids were not as extensive as anticipated. If all other factors are equal, the ratio of constants may apparently be as small as 100 without introducing appreciable errors. There is no merit in such an assumption if computing methods and facilities of the type used in this work are available, (in fact the mixture involves more work), but it does indicate that the limits of 500 to 1000 used by others are rather conservative. And that is, perhaps, the only assumption in previous calculations that is conservative.
VII. SUMMARY

The primary goal of this work has been attained; dissociation constants have been calculated without use of simplifying assumptions, and with full consideration of all available data. Errors in the data have a considerable effect on the answers obtained, and some calculations are simply not possible due to experimental inaccuracies.

Many literature values must now be accepted with reservation for several reasons. These include unjustified or unnecessary simplifications in calculations, and the use of different pH scales in older work.

Extremely accurate titrations are required to obtain dissociation constants of two or more significant figures, particularly for polybasic acids. If good data are available, however, the mathematical means to make full use of them are now at hand.
VIII. LITERATURE CITED


IX. ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. Don S. Martin for the advice, encouragement, and patient understanding received during and after the course of the research.

He would further like to acknowledge the assistance of the Statistical Laboratory in making computer facilities available.
X. APPENDIX A

Table 10. Data for titrations of tartaric acid
Acid concentration = 0.01031 M; base concentration = 0.0501 N; initial solution volume = 50.00 ml.

<table>
<thead>
<tr>
<th>Ml of base</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<tr>
<td>4.00</td>
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<td>2.98</td>
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<td>2.96</td>
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<td>2.94</td>
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<td>8.50</td>
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<td>3.45</td>
<td>3.45</td>
<td>3.44</td>
<td>3.46</td>
<td>3.43</td>
<td>3.43</td>
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<tr>
<td>12.50</td>
<td>3.94</td>
<td>3.94</td>
<td>3.93</td>
<td>3.93</td>
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<td>4.47</td>
<td>4.47</td>
<td>4.49</td>
<td>4.45</td>
<td>4.45</td>
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<td>19.00</td>
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<td>5.05</td>
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<td>5.01</td>
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<td>5.70</td>
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<td>6.32</td>
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<td>7.01</td>
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<td>7.01</td>
<td>7.00</td>
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<td>20.45</td>
<td>7.55</td>
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<td>7.87</td>
<td>7.70</td>
<td>7.55</td>
<td></td>
</tr>
<tr>
<td>20.50</td>
<td>8.17</td>
<td>8.39</td>
<td>8.30</td>
<td>8.55</td>
<td>8.40</td>
<td>8.30</td>
<td></td>
</tr>
<tr>
<td>20.52</td>
<td>8.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 11. Data for titration of acetic acid  
Acid concentration = 0.02174 M; base concentration = 0.0501 N; initial solution volume = 50.00 ml.

<table>
<thead>
<tr>
<th>Ml of base</th>
<th>Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>3.56</td>
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<tr>
<td>3.00</td>
<td>3.99</td>
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<tr>
<td>6.00</td>
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<td>10.00</td>
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<td>21.00</td>
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<tr>
<td>21.30</td>
<td>6.70</td>
</tr>
<tr>
<td>21.50</td>
<td>7.26</td>
</tr>
</tbody>
</table>

Table 12. Data for titration of succinic acid 
Acid concentration = 0.01051 M; base concentration = 0.0501 N; initial solution volume = 50.00 ml.

<table>
<thead>
<tr>
<th>Ml of base</th>
<th>Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>3.63</td>
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<td>7.50</td>
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<td>13.50</td>
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<tr>
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<tr>
<td>18.50</td>
<td>6.08</td>
</tr>
<tr>
<td>19.60</td>
<td>6.41</td>
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<td>6.73</td>
</tr>
<tr>
<td>20.60</td>
<td>7.17</td>
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</tbody>
</table>
Table 13. Data for titration of tartaric and succinic acid mixture (Acid concentrations = 0.01031 M and 0.010437 M; base concentration = 0.0501 N; initial solution volume = 100.00 ml.)

<table>
<thead>
<tr>
<th>Ml of base</th>
<th>Solution pH</th>
<th>Ml of base</th>
<th>Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>2.00</td>
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<td>3.00</td>
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<td>7.00</td>
<td>3.23</td>
<td>32.00</td>
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<tr>
<td>8.00</td>
<td>3.31</td>
<td>33.00</td>
<td>5.30</td>
</tr>
<tr>
<td>9.00</td>
<td>3.40</td>
<td>34.00</td>
<td>5.40</td>
</tr>
<tr>
<td>10.00</td>
<td>3.48</td>
<td>35.00</td>
<td>5.53</td>
</tr>
<tr>
<td>11.00</td>
<td>3.55</td>
<td>36.00</td>
<td>5.65</td>
</tr>
<tr>
<td>12.00</td>
<td>3.62</td>
<td>37.00</td>
<td>5.80</td>
</tr>
<tr>
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<td>5.95</td>
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<td>6.31</td>
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<td>16.00</td>
<td>3.92</td>
<td>40.00</td>
<td>6.50</td>
</tr>
<tr>
<td>17.00</td>
<td>4.00</td>
<td>40.20</td>
<td>6.60</td>
</tr>
<tr>
<td>18.00</td>
<td>4.05</td>
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<td>6.71</td>
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<tr>
<td>19.00</td>
<td>4.12</td>
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</tr>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>25.00</td>
<td>4.55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
XI. APPENDIX B

WAYNE DUNNING, IOWA STATE UNIVERSITY

This program calculates dissociation constants and their standard deviations for a single acid or a mixture of two acids. Principal input data consist of a pH titration curve and known acid concentrations. In addition, concentrations may be calculated from a titration curve and known constants, or a theoretical titration curve may be computed. Options include the titration of a base, or of a salt of a weak acid or base.

DIMENSION JUNK1(40), JUNK2(40), JUNK3(40)
DIMENSION SIZION(6), CKPROD(6), CKIND(6), HAION(8), HYDACT(4), WWD1003
DIMENSION CMU(51), PH(51), ACTCFH(51), GAMMA(6), TNTML(51), WWD1004
DIMENSION FACTOR(6), ACTSL(7), RESULT(6), AR(50,6), E(14), FC(50), FM(50), WWD1005
DIMENSION FACTOR, ACTSCL(17), RESULT, AR, E, FC, FM, OF(50), WWD1006
COMMON JUNK1, JUNK2, JUNK3
COMMON SIZION, CKPROD, CKIND, HAION, HYDACT, OHACT, CMU, PH, WWD1007
COMMON ACTCFH, GAMMA, TNTML, FACTOR, ACTSL, RESULT, AR, E, FC, CMU, PH, WWD1008
COMMON G, R, U, ACID1, ACID2, CAC10, CAC10, NACIDS, NCON1, NCON2, WWD1009
COMMON NCON(9), VNUM1, VNUM2, SCFTR, FN, Y, FD, MSCALE, WWD1010
COMMON SUM, Q, O1, NOPTS, CMLNT, RQDCL, VOLTL, CNA, VOLG, CLION WWD1011

Beginning of program. This section is primarily for proper initialization of the program. The necessary data is read in, and the values of certain constants are set.

Set ion size parameters, dissociation constants, and individual ion concentrations to zero

DO 403 I = 1, 6
RESULT(I) = 0.

DO 405 I = 1, 8
HAION(I) = 0.

H exponent of hydrogen and hydroxide activity equals one

HYDACT(1) = 1.

UNLESS OTHERWISE SPECIFIED, HYDROGEN ION SIZE IS 5
HIONSZ = 5.

UNLESS OTHERWISE SPECIFIED, TEMPERATURE IS 25 DEGREES, AND DEBYE-HUCKEL COEFFICIENTS ARE

DBHFA = 0.5092
DBHFB = 0.3268

UNLESS OTHERWISE SPECIFIED, BETA IN D-H FORMULA IS ZERO
BETADH = 0.

WRITE HEADING, READ AND WRITE OPENING STATEMENT

WRITE OUTPUT TAPE 9, 8
READ 10
WRITE OUTPUT TAPE 9, 10
PUNCH 10

READ CONTROL PARAMETERS
READ 12, NTYPE1, NTYPE2, NTYPE3, NTYPE4, NTYPE5, NTYPE6, NTYPE7, NTYPE8

WRITE TYPE OF CALCULATION TO BE DONE IN THIS PARTICULAR RUN
READ ACID CONCENTRATIONS, AND WRITE WITH APPROPRIATE COMMENT
DEPENDING UPON WHETHER CONCENTRATION IS EXACT, OR AN INITIAL E
STIMATE. IF THERE IS ONLY ONE ACID, THE CONCENTRATION OF THE SECOND IS ZERO.

READ INITIAL VOLUME OF SOLUTION IN ML., NORMALITY OF TITRANT, IONIC STRENGTH (AN ESTIMATE UNLESS VALUE IS CONSTANT), MOLAR CONCENTRATION OF ANY ADDED MONOVALENT SALT, DISSOCIATION CONSTANT OF WATER, AND DESIRED CLOSENESS OF FIT OF RESULTS IN PERCENT.

READ THE INDIVIDUAL DISSOCIATION CONSTANTS OR THE ESTIMATED VALUES OF THEM. THE FIRST FOUR ARE FOR THE FIRST ACID, THE LAST TWO FOR THE SECOND ACID. ANY CONSTANT WHICH DOES NOT EXIST MUST HAVE A VALUE OF ZERO.

READ THE INDIVIDUAL DISSOCIATION CONSTANTS WITH COMMENTS

IF ACTIVITY CORRECTIONS ARE NOT TO BE MADE, WRITE THIS FACT, SET ALL VALUES OF IONIC STRENGTH TO ZERO, AND DO NOT READ IN THE ION SIZE PARAMETERS.

IF IONIC STRENGTH IS SPECIFIED AS CONSTANT, WRITE ITS VALUE AND SET ALL STORAGE VALUES TO IT.

IF VOLUME IS SPECIFIED AS CONSTANT, WRITE THIS FACT AND THE VALUE
GO TO (447, 445), NTYPE4
C
WRITE OUTPUT TAPE 9, 44, SOLNV
C
WRITE THE TYPE OF PH READING SPECIFIED BY CONTROL PARAMETER 5
GO TO (453, 451, 449), NTYPE5
C
WRITE THAT PWH IS USED
GO TO (453, 451, 449), NTYPE5
C
WRITE OUTPUT TAPE 9, 46
00000 GO TO 455
C
WRITE THAT PCH IS USED
GO TO (453, 451, 449) , NTYPE5
C
WRITE THAT PAH IS USED
GO TO 455
C
READ AND WRITE ION SIZE PARAMETER FOR HYDROGEN IF VALUE IS NOT 5.0
GO TO (459, 457), NTYPE6
READ 52, MIONSZ
WRITE OUTPUT TAPE 9, 54, MIONSZ
C
READ AND WRITE NEW D-H COEFFICIENTS A AND B IF TEMPERATURE IS NOT 25 DEGREES
READ 56, DBHFA, DBHFB
WRITE OUTPUT TAPE 9, 58, DBHFA, DBHFB
C
READ AND WRITE BETA IN D-H FORMULA IF BETA IS TO BE USED
READ 60, BETADH
WRITE OUTPUT TAPE 9, 62, BETADH
C
WRITE THE TYPE OF TITRATION SPECIFIED BY CONTROL PARAMETER 9
GO TO (475, 473, 471, 469), NTYPE9
C
WRITE SALT OF BASE TITRATED WITH BASE
WRITE OUTPUT TAPE 9, 64
GO TO 477
C
WRITE ACID TITRATED WITH ACID
WRITE OUTPUT TAPE 9, 66
00000 GO TO 477
C
WRITE SALT OF ACID TITRATED WITH ACID
C
WRITE ACID TITRATED WITH BASE
C
COUNT NUMBER OF ACIDS
NACIDS = 1
GO TO (491, 497), NACIDS
C
COUNT NUMBER OF DISSOCIATION CONSTANTS FOR FIRST ACID
NCON1 = 0
00000 DD 489 I = 1, 4
00485 IF (CKINDI I ) ) NCON1 = NCON1 + 1
00487 CONTINUE
04911 NCON2 = 0
C
COUNT DISSOCIATION CONSTANTS FOR SECOND ACID, IF ANY
GO TO (493, 495), NACIDS
C
AN INITIALIZATION FOR NON-LINEAR LEAST SQUARES, IF THERE ARE
C TWO ACIDS
DDDD = 1000.
MAXIMUM NUMBER OF ITERATIONS ALLOWED PER PASS IN N-L LEAST SQS.
00000 NID = 5
00000 DO 4921 I = 5, 6
04917 IF (CKIND(I)) 913, 4921, 4919
04919 NCNN = NCON1 + 1
04921 CONTINUE
C
C TOTAL NUMBER OF CONSTANTS
04923 NCON = NCON1 + NCON2
C
C ABSOLUTE ERROR
00000 ERROR = ERROR / 100.
C
C OBTAIN PRODUCTS OF DISSOCIATION CONSTANTS
C
C RESET OVERFLOW TRIGGER
00000 IF ACCUMULATOR OVERFLOW 4925, 4925
04925 CKPROD(I) = CKIND(I)
00000 DO 4927 I = 2, NCON1
04927 CKPROD(I) = CKPROD(I-1) * CKIND(I)
04929 GO TO (4933, 4931), NACIDS
04931 CKPROD(1) = CKIND(1)
00000 IF ACCUMULATOR OVERFLOW 4925, 4925
C ERROR STOP IF A PRODUCT OF CONSTANTS IS OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 4933
C TRANSFER TO PROPER SECTION OF PROGRAM DEPENDING ON TYPE OF
C CALCULATION BEING DONE
04933 GO TO (101, 201, 301), NTYPE1
C
C SUBMASTER PROGRAM TO DETERMINE DISSOCIATION CONSTANTS
C
C GO TO READ IN TITRATION CURVE
00101 GO TO 501
C
C RETURN FROM CURVE READ IN. DETERMINE MATRIX SIZE FOR SINGLE ACID
00103 NROWS = NCON1
00000 NCOLMS = NROWS + 1
C
C SET ITERATION COUNTER AND SCALE CHANGE CHECKER TO ZERO
C CHECKER PREVENTS AN ATTEMPT TO SCALE IN BOTH DIRECTIONS
C SCALING IS NECESSARY TO KEEP DECIMAL POINT WITHIN ALLOWABLE RANGE
00000 MSCALE = 0
00000 MCOUNT = 0
00000 MCLLD = 0
C
C INITIAL SCALING FACTOR EQUALS ZERO
00000 SCFTR = 0.
C
C SET NONLINEAR ERROR FACTOR
00000 ERROR = .0001 * FLOATFINPNTS
C
C GET SCALING QUANTITY
00000 IF ACCUMULATOR OVERFLOW 105, 105
00105 ACSCL(I) = 10. ** (SCFTR * FLOATFINPNTS)
C ERROR STOP IF SCALING QUANTITY OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 106, 107
C
C SET NONLINEAR ITERATION COUNTER TO ZERO
00107 LLD = 0
C
C CLEAR RESULTS AND ARRAY FOR SINGLE ACID
00109 GO TO (111, 115), NACIDS
00111 DO 113 I = 1, NROWS
00000 RESULT(I) = 0.
00000 DD 113 J = 1, NCOLMS
00113 AR(I, J) = 0.
C  INITIALIZE LOOP AND GO TO ACTIVITY CORRECTION SECTION (GAMMA CALCULATOR)
C
00115 K = 1
C
C  OPTIONAL OUTPUT
C  IF (SENSE SWITCH 1) 116, 801
C
116 WRITE OUTPUT TAPE 9, 61
00000 GO TO 801
C
C  RETURN FROM GAMMA CALCULATOR AND BRANCH ON TITRATION TYPE
C
00117 GO TO (125, 125, 119, 119), NTYPE9
C
C
00119 DO 123 I = 1, NCONT
C
123 ACTSCL(I + 1) = ACTSCL(I) * QHACT(2)
C
00125 DO 129 I = 1, NCONT
C
129 FN = -HYDACT(2) / GHYDRO - CNA + COH + CLION
00000 GO TO 131
C
C  OBTAIN SCALED HYDROXIDE ACTIVITIES
C
00129 ACTSCL(I + 1) = ACTSCL(I) * HYDACT(2)
C
00131 Y = FN * ACTSCL(NCONT + 1)
C
00000 IF ACCUMULATOR OVERFLOW 161, 133
C
C  TRANSFER OUT TO CALCULATE PROPER MATRIX ELEMENTS FOR THIS POINT
C
00133 GO TO (601, 1001), NACIDS
C
C  RETURN FROM OBTAINING ELEMENTS, SET LOOP FOR NEXT POINT
C
C  SINGLE ACID
C
00135 K = K + 1
C
C  TEST FOR LAST POINT USED. IF FINISHED, SOLVE MATRIX.
C
00137 IF (K - NDPTS) 801, 801, 701
C
C  RETURN FROM MATRIX SOLVE. OBTAIN DIFFERENCE FROM OLD ANSWERS
C
00139 SUM = 0.
00141 DO 143 I = 1, NCONI
C
143 SUM = SUM + ABS(RESULT(I) - CKPROD(I)) / RESULT(I))
00000 REPLACE OLD ANSWERS WITH NEW
00143 CKPROD(I) = RESULT(I)
00000 CKIND(I) = RESULT(I)
00145 IF (NCONI - 1) 904, 151, 147
00147 DO 149 I = 2, NCONI
C
149 CKIND(I) = RESULT(I) / RESULT(I) - 1)
C
C  WRITE ANSWERS AND DIFFERENCE FROM PREVIOUS SET
C
00151 WRITE OUTPUT TAPE 9, 72, (CKIND(I), I = 1, 4), SUM
C
PUNCH 30, (CKIND(I), I = 1, 4), SUM
C
C  TEST FOR END. IF ANSWERS SATISFACTORY, OBTAIN STANDARD DEVIATIONS
C
00000 MDOUNT = MDOUNT + 1
C
153 IF (SUM - ERROR * FLOAT(FROWS)) 6001, 6001, 155
C
C  ANSWERS NOT GOOD ENOUGH. REPEAT IF NOT TOO MANY ITERATIONS
C
00155 MSCE = 0
C
00157 IF (MDOUNT - 10) 107, 6001, 6001
C
C  SCALE UP
C
00161 IF (MSCALE) 905, 163, 163
00163 MSCALE = 1
00000 SCFTR = SCFTR + 1.
00000 GO TO 105
C
00171 IF (MSCALE) 173, 173, 905
00173 MSCALE = -1
00000 SCFTR = SCFTR - 1.
00000 GO TO 105
C
C TWO ACID NON-LINEAR LEAST SQUARE SOLUTION
C
C SET MEASURED VALUE
01001 FM(J) = Y
C
C CALCULATE ELEMENTS FOR SIXTH CONSTANT, IF ANY
01003 IF (CKPROD(6)) 1005, 1009, 1005
01005 DO 1007 I = 1, NCON1
00000 Z = 1
00000 L = NCONT - 1 - 1
01007 E(I+10) = ((Z*CACI1+2) + (CACID2-FN) + ACTSCL(L))/ (GAMMA(1) * GAMMA(6))
00000 E(6) = ((2 * CACID2 - FN) * ACTSCL(NCONT - 1)) / GAMMA(6)
00000 GO TO 1011
C
C CALCULATE ELEMENTS FOR FIFTH CONSTANT, IF ANY
01015 DO 1017 I = 1, NCON1
00000 Z = 1
00000 L = NCONT + 1 - 1
01017 E(I) = ((Z * CACI1 - FN) * ACTSCL(L)) / GAMMA(1)
C
OBTAIN DIFFERENTIAL ELEMENTS OF MATRIX
01019 IF ACCUMULATOR OVERFLOW 1021, 1021
01021 AR(K, 1) = E(1) + E(7) * CKPROD(5) + E(11) * CKPROD(6)
00000 AR(K, 2) = E(2) + E(8) * CKPROD(5) + E(12) * CKPROD(6)
00000 AR(K, 3) = E(3) + E(9) * CKPROD(5) + E(13) * CKPROD(6)
00000 AR(K, 4) = E(4) + E(10) * CKPROD(5) + E(14) * CKPROD(6)
000001 E(9) * CKPROD(3) + E(10) * CKPROD(4)
000000 AR(K, NCON1+2) = E(6) + E(11) * CKPROD(1) + E(12) * CKPROD(2)
000001 + E(13) * CKPROD(3) + E(14) * CKPROD(4)
C
C CALCULATE FC
01023 FC(K) = CKPROD(1)*E(1)+CKPROD(2)*E(2)+CKPROD(3)*E(3)+CKPROD(4)*E(4)
010231 E(4) + CKPROD(5)*E(5) + CKPROD(6)*E(6) + CKPROD(11)*E(7) + CKPROD(5)*E(8) + CKPROD(5)*E(9) + CKPROD(5)*E(10) + CKPROD(5)*E(11) + CKPROD(2)*E(12)
010234 CKPROD(6)*CKPROD(3)*E(13) + CKPROD(6) + CKPROD(1)*E(11) + CKPROD(1)*E(15) + CKPROD(4)*E(14) + CKPROD(6)
00000 IF ACCUMULATOR OVERFLOW 161, 1025
C
SET LOOP FOR NEXT POINT
01025 K = K + 1
C
C TEST FOR LAST POINT USED
01027 IF (K - NDPTS) 801, 801, 1380
C
C MODIFIED AN E ZCO PROGRAM
C
01380 DO 1430 J = 1, NDPTS
01430 D(F(J)) = FM(J) - FC(J)
C
C
C TESTING SWITCH FOR OPTIONAL OUTPUT
01450 IF (SENSE SWITCH 3) 1460, 1490 WWD1536
01460 DD 1460 J = 1, NDPTS WWD1537
01480 WRITE OUTPUT TAPE 9, 74, (AR(J,K), K = 1, NCONT), DF(J) WWD1538
C
C CALCULATE
01490 DD 1520 L = 1, NCONT WWD1539
01500 R(L, 1) = 0. WWD1540
01510 DD 1520 J = 1, NDPTS WWD1541
01520 R(L, 1) = R(L, 1) + AR(J, L) * DF(J) WWD1542
01530 DD 1570 L = 1, NCONT WWD1543
01540 DD 1570 K = 1, NCONT WWD1544
01550 G(L, K) = 0. WWD1545
01560 DD 1570 J = 1, NDPTS WWD1546
01570 G(L,K) = G(L, K) + AR(J, L) * AR(J, K) WWD1547
00000 IF ACCUMULATOR OVERFLOW 161, 1680 WWD1549
C TEST SWITCH FOR R AND G OPTIONAL OUTPUT
01580 IF (SENSE SWITCH 4) 1590, 1600 WWD1550
01590 WRITE OUTPUT TAPE 9, 74, (G(L,K), K=1,NCONT), R(L,1), L=1,NCONT) WWD1552
C
C IF G Y =R, THEN MATINV RETURNS WITH R REPLACED
C BY Y AND G REPLACED BY G INVERSE
01600 MM = 1 WWD1553
01610 CALL MATINV (G, NCONT, R, MM, DETERM) WWD1554
01615 GO TO (1620, 911, 1617), NTYPE1 WWD1555
01617 CKIND(1) = ACID1 WWD1556
00000 CKIND(2) = ACID2 WWD1557
00000 Q1 = 0. WWD1558
00000 DD 1619 J = 1, NDPTS WWD1559
01619 Q1 = Q1 + (DF(J) ** 2.) WWD1560
00000 GO TO 1760 WWD1562
C CHECK THE FIT
01620 Q1 = 0. WWD1563
01625 DD 1630 J = 1, NDPTS WWD1564
01630 Q1 = Q1 + (DF(J) ** 2.) WWD1565
IF ACCUMULATOR OVERFLOW 161, 1635
01635 Q = ABSFIOOD - Q1 WWD1566
01640 QDD = Q1 WWD1567
01645 LLD = LLD + 1 WWD1568
MLLD = MLLD + 1
C IF FIT IS NOT GOOD ENOUGH, REPEAT IF NO. OF ITERATIONS IS
C NOT TOO LARGE. CKPROD(J) CORRECTED IN ANY CASE
1650 DD 1653 J = 1, NCON1 WWD1569
1653 CKPROD(J) = CKPROD(J) + R(J,1)
IF (NCON2) 911, 1660, 1655
1655 DD 1659 J = 1, NCON2
1657 JJ = J + NCON1
1659 CKPROD(J + 4) = CKPROD(J + 4) + R(JJ, 1)
01660 IF (Q - ERQD) 1680, 1680, 1685 WWD1570
01665 IF (LLD = NID) 1670, 1680, 1760 WWD1571
C TEST SWITCH FOR Y AND G INVERSE, OPTIONAL OUTPUT
01670 IF (SENSE SWITCH 4) 1675, 1677 WWD1572
01675 WRITE OUTPUT TAPE 9, 74, ((G(L,K), K = 1, NCONT), R(L,1),
1 L = 1, NCONT), (CKPROD(L2), L2 = 1, 6), Q1 WWD1573
01677 GO TO 107 WWD1574
C
C REPLACE DISSOCIATION CONSTANTS AND TEST FOR CLOSENES,
C RECORRECT FOR ACTIVITY AND REITERATE IF NECESSARY
01680 SUM = 0. WWD1575
01685 RESULT(1) = CKPROD(1) WWD1576
01690 IF (NCON1 = 2) 1705, 1695, 1695 WWD1577
C
01695 DO 1700 I = 2, NCONI
01700 RESULT(I) = CKPROD(I) / CKPROD(I - 1)
01705 IF (NCON2 - I) 1720, 1715, 1710
1710 RESULT(6) = CKPROD(6) / CKPROD(5)
1715 RESULT(5) = CKPROD(5)
01720 DO 1730 I = 1, 6
1721 IF (CKIND(I)) 914, 1730, 1725
1725 RESULT(I) = CKPROD(I) / CKPROD(I - 1)
1727 CKIND(I) = RESULT(I)
1730 CONTINUE
00000 WRITE OUTPUT TAPE 9, 97, (CKIND(I), I = 1, 6), SUM
PUNCH 30, (CKIND(I), I = 1, 6)
01735 IF (SUM - ERROR * FLOAT(NCONT)) 1760, 1760, 1740
01740 MSCALE = 0
01745 MCOUNT = MCOUNT + 1
01750 IF (MCOUNT - 10) 107, 1760, 1760
C CALCULATE THE CORRELATION MATRIX
01760 DO 1770 J = 1, NCONT
01765 DO 1770 K = 1, NCONT
G(J, K) / SQRT(G(J, J)) = 1, NCONT
SQRT(G(L, L)) = 1, NCONT
1770 U(J, K) / FLOAT(NDPTS - NCONT - II)
1780 U(J, J) = 1, NCONT
1785 WRITE OUTPUT TAPE 9, 76, Q1, MCLLD, ACTSCL(I)
01790 WRITE OUTPUT TAPE 9, 78
01795 WRITE OUTPUT TAPE 9, 80, (J, CKIND(J), U(J, J), J = 1, 6)
01800 WRITE OUTPUT TAPE 9, 82
01810 DO 1820 L = 1, NCONT
01820 WRITE OUTPUT TAPE 9, 84, (U(L, K), K = 1, NCONT)
01830 WRITE OUTPUT TAPE 9, 86
01840 WRITE OUTPUT TAPE 9, 88, (TNML(J), PH(J), CMU(J), ACTCFH(J),
018401 PHM(J), FC(J), DF(J), J = 1, NDPTS)
00000 GO TO 401
C WRITE FINAL RESULTS
00000 SUBMASTER PROGRAM FOR CALCULATION OF TITRATION CURVE
C READ LIMITS OF PH AND STEPPING INTERVAL
00201 READ 90, PHLOWR, PHUPPR, PHSTEP
00202 INITIAL CONDITIONS
00000 K = 1
00000 CMU(1) = GMU
00000 TNML(1) = 0.
00000 PH(1) = PHLOWR
C C SCALING FACTOR
00203 ACTSCL(1) = 1.0E30
C IF TWO ACIDS, MOVE CONSTANTS OVER TO MAKE THEM CONSECUTIVE
00205 GO TO (801, 207), NACIDS
00207 DD 209 I = 1, NCON2
00000 M = NCON1 + 1
00209 CKPROD(M) = CKPROD(I + 4)
C GO TO ACTIVITY CORRECTION SECTION
00000 GO TO 801
C RETURN AND TRANSFER ACCORDING TO TYPE OF TITRATION
00211 GO TO (217, 217, 213, 213), NTYPE9
C C TITRATIONS OF BASE
WWD1587
WWD1588
WWD1589
WWD1592
WWD1593
WWD1594
WWD1595
WWD1596
WWD1597
WWD1598
WWD1599
WWD1600
WWD1601
WWD1602
WWD1603
WWD1604
WWD1605
WWD1606
WWD1607
WWD1608
WWD1609
WWD1610
WWD1611
WWD1612
WWD1613
WWD1614
WWD1615
WWD1616
WWD1617
WWD1618
WWD1619
WWD1620
WWD1621
WWD1622
WWD1623
WWD1624
WWD1625
WWD1626
WWD1627
WWD1628
WWD1629
WWD1630
WWD1631
WWD1632
WWD1633
WWD1634
WWD1635
WWD1636
TITRATIONS OF ACID
DO 215 I = 1, 4
ACTSCL(I + 1) = ACTSCL(I) + OHACT(2)
GO TO 221
00000 DO 221 I = 1, 4
ACTSCL(I + 1) = ACTSCL(I) + HYDACT(2)
00219 DO 223 I = 1, NCON1
E(I) = (HAION(I) * Z * ACTSCL(I)) / (GAMMA(I) * ACTSCL(I + 1))
GO TO (231, 227), NACIDS
00225 DO 229 I = 1, NCON2
Z = I
00000 Z = NCON1 + I
E(I) = (HAION(I) * Z * ACTSCL(I)) / (GAMMA(I + 4) * ACTSCL(I + 1))
00229 TYPE 4 TITRATION, SALT OF BASE WITH BASE
TRANFER ACCORDING TO TYPE OF TITRATION
GO TO (245, 241, 237, 233), NTYPE9
00231 TYPE 4 TITRATION, SALT OF BASE WITH BASE
RQDNA = -HYDACT(2) / GHYDRO + COH + CLION
GO TO 255
00000 DD 235 I = 1, NCONT
RQDNA = -HYDACT(2) / GHYDRO + COH
00000 DD 239 I = 1, NCONT
RQDNA = -HYDACT(2) / GHYDRO + COH
00000 DD 243 I = 1, NCONT
RQDNA = -HYDACT(2) / GHYDRO + COH
00000 DD 247 I = 1, NCONT
RQDNA = -HYDACT(2) / GHYDRO + COH
CMLNT = (RQDNA - CNA) * (VOLTL / BASEN)
GO TO 249
C TYPE 3 TITRATION, BASE WITH ACID
RQDCL = HYDACT(2) / GHYDRO + CNA - COH
GO TO 249
C TYPE 2 TITRATION, SALT OF ACID WITH ACID
RQDNA = HYDACT(2) / GHYDRO + CNA - COH
GO TO 249
C TYPE 1 TITRATION, ACID WITH BASE
RQDNA = HYDACT(2) / GHYDRO
GO TO 249
C ADD TITRANT AND TEST FOR LIMIT
TNTML(1) = TNTML(1) + CMLNT
IF (CMLNT < 2.) - 1.0E-6 255, 255, 253
OPTIONAL OUTPUT
253 IF (SENSE SWITCH 2) 254, 803
254 WRITE OUTPUT TAPE 9, 92, TNTML(1), PH(1), CMU(1), GHYDRO
GO TO 803
C WRITE OUTPUT TAPE 9, 92, TNTML(1), PH(1), CMU(1), GHYDRO
C DO NEXT POINT, IF ANY LEFT
DO NEXT POINT, IF ANY LEFT
PH(I) = PH(I) + PHSTEP
IF (PH(I) - PHUPPR) = 801, 801, 261
PUNCH 92, TMTNL(I), PH(I), CMUL(I), GHYDRO
GO TO 401

SUBMASTER PROGRAM TO CALCULATE CONCENTRATIONS OF ACIDS
GO TO READ IN TITRATION CURVE
GO TO 501
RETURN FROM READ IN. DETERMINE MATRIX SIZE
NROWS = NACIDS
NCOLMS = NROWS + 1
SET ITERATION COUNTER AND INITIAL SUM
MCOUNT = 0
SUM = 1.
CLEAR RESULTS AND ARRAY
RESULTd) = 0.
E) = 0.
DO 307 J = 1, NCOLMS
ARIJ, J) = 0.
INITIALIZE LOOP
K = 1
GO TO 801
RETURN FROM GAMMA CALCULATOR AND BRANCH ON TITRATION TYPE
FN = -1.
Y = FN * (HYDACT(2)/GHYDRO + CNA - COH - CLION)
OBTAIN ELEMENTS OF MATRIX
VNUM1 = 0.
DO 321 I = 1, NCON1
Z = I
VNUM1 = VNUM1 + Z * FACTOR(I)
E(I) = VNUM1 * VOLC / DENOM1
DO 325 I = 1, NACIDS
ELEMENTS FOR SECOND ACID
VNUM2 = 0.
DO 327 I = 1, NCON2
Z = I
VNUM2 = VNUM2 + Z * FACTOR(I + 4)
E(2) = VNUM2 * VOLC / DENOM2
SOLVE FOR ANSWERS OR ERRORS
IF (SUM = 1.0E-6) = 345, 345, 329
BUILD MATRIX
DO 333 L = 1, NROWS
DO 333 M = 1, L
ARIL, M) = ARIL, M) + E(L) * E(M)
K = K + 1
IF (K = NPTS) = 801, 801, 701
RETURN FROM MATRIX SOLVE
SUM = ((ACID1 - RESULTd) / ACID1) ** 2.
00000 ACID1 = RESULT(1)
00039 GO TO (343, 341), NACIDS
000341 SUM = SUM + ((ACID2 - RESULT(2)) / ACID2) ** 2.
00000 ACID2 = RESULT(2)
000343 WRITE OUTPUT TAPE 9, 99, ACID1, ACID2, SUM
MCCOUNT = MCCOUNT + 1
IF (MCCOUNT = 10) 305, 344, 344
344 SUM = -1.0E+10
GO TO 309
C
D DETERMINE STANDARD DEVIATIONS. OBTAIN DIFFERENTIAL ELEMENTS
00345 FM(K) = Y
00000 AR(K, 1) = E(1)
00000 AR(K, 2) = E(2)
00000 FC(K) = E(1) * CACID1 + E(2) * CACID2
00000 K = K + 1
C
TEST FOR LAST POINT USED
00347 IF (K - NDPST) 801, 801, 349
C
SET NUMBER OF UNKNOWNS FOR ERROR TREATMENT
00349 NCON= NACIDS
00000 NID = 0
00000 EROD = 0.
00000 QOD = 0.
PUNCH 99, ACID1, ACID2, SUM
00000 GO TO 1380
C
READ IN TITRATION CURVE
00501 I = 1
00503 GO TO (505, 505, 507), NTYPE2
00505 GO TO (515, 515, 513), NTYPE3
00507 GO TO (511, 511, 509), NTYPE3
00509 READ 93, TNTML1(I), PH1(I), CMU1(I), ACTCFH1(I)
00000 GO TO 517
00511 READ 94, TNTML1(I), PH1(I), ACTCFH1(I)
00000 GO TO 517
00513 READ 95, TNTML1(I), PH1(I), CMU1(I)
00000 GO TO 517
00515 READ 96, TNTML1(I), PH1(I)
C
TEST FOR END AT PH OF ZERO
00517 IF (PH1(I)) 907, 521, 519
C
READ NEXT POINT
00519 I = I + 1
00000 GO TO 503
C
COUNT NUMBER OF POINTS
00521 NDPST = I - 1
00523 GO TO (103, 401, 303), NTYPE1
C
FORMATION OF MATRIX
C
OBTAIN ELEMENTS OF EQUATION
C
00601 DD 605 I = 1, NCON1
00000 Z = I
00000 L = NCON1 + 1 - I
00603 E(I) = (((Z * CACID1) - FN) / GAMMA(I)) * ACTSCL(I)
C
IF OVERFLOW, SCALE UP
00000 IF ACCUMULATOR OVERFLOW 161, 605
00605 CONTINUE
00607 DO 615 L = 1, NROWS
00609 DO 615 M = 1, L
00611 AR(L, M) = AR(L, M) + E(L) * E(M)
00613 IF (ABS(E(L)) > 1.0) 161, 609
00615 CONTINUE
00617 GO TO 135
CONTINUE
BUILD MATRIX
DO 615 L = 1, NROWS
ARIL, NCOLMS) = ARIL, NCOLMS) + EtL) * Y
IF OVERFLOW, SCALE UP
DO 613, 615
ARIL, M) = ARIL, M) + EIL) * EIM)
IF ACCUMULATOR OVERFLOW 613, 615
DETERMINE WHETHER TO SCALE UP OR DOWN
00701 IF ACCUMULATOR OVERFLOW 703, 703
00703 J = NROWS - 1
00705 IF(J) 717, 711
SOLVE MATRIX
RESET TRIGGERS
IF ACCUMULATOR OVERFLOW 703, 703
J = NROWS - 1
IF !J) 912, 707, 711
IF ONLY ONE ROW, SOLVE DIRECTLY
RESULT(I) = AR(1, 2) / AR(1, 1)
GO TO (139, 912, 337), NTYPE1
FILL OUT MATRIX
DO 715 K = 2, NROWS
M = K - 1
DO 715 L = 1, M
AR(K, L) = AR(K, L) + EIL) * EIM)
OPTIONAL OUTPUT
IF (SENSE SWITCH 5) 716, 717
WRITE OUTPUT TAPE 9, 51, ((AR(K,L), L = 1, 5), K = 1, NROWS)
SOLVE BY TRIANGULARIZATION
DO 727 I = 1, J
M = I + 1
DO 727 L = 1, M
RESULT(L) = (AR(M, L)) / AR(M, M)
GO TO (139, 912, 337), NTYPE1
OPTIONAL OUTPUT
IF (SENSE SWITCH 5) 728, 729
WRITE OUTPUT TAPE 9, 55, ((AR(K,L), L = 1, 5), K = 1, NROWS)
ACTIVITY CORRECTION SECTION. THIS SECTION CALCULATES ACTIVITY
COEFFICIENTS, VOLUME CORRECTIONS, IONIC CONCENTRATIONS, IONIC
STRENGTH, ETC.

THE SUBSCRIPT (K) IS SET OUTSIDE THIS SECTION FOR THE POINT UNDER
CONSIDERATION.

OBTAIN HYDROGEN ION ACTIVITY OR CONCENTRATION AT THIS POINT
HYDAC T(2) = 10. ** (-PH(K))
RESET OVERFLOW TRIGGER
00000 IF ACCUMULATOR OVERFLOW 803, 803
TRANSFER DEPENDING UPON WHETHER OR NOT ACTIVITY CORRECTIONS ARE TO
BE MADE.
00803 GO TO (809, 805, 809), NTYPE2
NO CORRECTIONS. ALL ACTIVITIES EQUAL ONE
00805 GHYDRO = 1.
00800 ACTCFH(K) = 1.
00800 GOXIDE = 1.
00800 DO 807 I = 1, 6
00807 GAMMA(I) = 1.
00800 GO TO 835
ACTIVITY CORRECTIONS MADE. D-H FACTORS COMPUTED
00809 SRMU = SQRTF(CMU(K))
00000 ASRMU = -DBHFA * SRMU
00000 BSRMU = DSHFB * SRMU
00000 BETAML = BETADH * CMU(K)
ACTIVITY COEFFICIENTS FOR HYDROGEN AND HYDROXIDE IONS
IF HYDROGEN ACTIVITY READ IN, DO NOT CALCULATE
00811 GO TO (915, 903, 813), NTYPE2
00815 GHYDRO = ACTCFH(K)
00000 GO TO 817
00815 GHYDRO = 10. ** (ASRMU / (1. + BSRMU * SIZION(I)) - BETAMU)
00000 ACTCFH(K) = GHYDRO
00817 GOXIDE = 10. ** (ASRMU / (1. + BSRMU * 3.5) - BETAMU)
ACTIVITY COEFFICIENTS FOR IONS OF FIRST ACID
DO 821 I = 1, NCON1
00000 Z = 1 * I
00821 GAMMA(I) = 10. ** (ASRMU * Z / (1. + BSRMU * SIZION(I)) - BETAMU)
ACTIVITY COEFFICIENTS FOR IONS OF SECOND ACID
DO 827 I = 1, NCON2
00825 DO 827 I = 1, NCON2
00000 Z = 1 * I
00827 GAMMA(I+4) = 10. ** (ASRMU*Z / (1. + BSRMU * SIZION(I+4)) - BETAMU)
CORRECT VALUE OF HYDROGEN ACTIVITY FOR CALCULATING USE DEPENDING
UPON TYPE OF PH MEASUREMENT MADE.
00829 GO TO (835, 833, 831), NTYPE5
00831 HYDAC T(2) = HYDAC T(2) / GHYDRO
00000 GO TO 839
833 HYDAC T(2) = HYDAC T(2) * GHYDRO
VOLUME CORRECTION SECTION
TEST FOR CONSTANT VOLUME
00835 GO TO (839, 837), NTYPE4
00837 VOLT = SOLNV
00000 GO TO 841
CALCULATE TOTAL VOLUME
VOLTL = SOLNV + TNTML(K)

HYDROXIDE ION CONCENTRATION
\[ \text{COH} = \frac{\text{WCON}}{(\text{HYDACT}(2) \cdot \text{GOXIDE})} \]

VOLUME CORRECTION FACTOR
\[ \text{VOLC} = \frac{\text{SOLNV}}{\text{VOLTL}} \]

CONCENTRATIONS OF ACIDS, CORRECTED
\[ \text{CACID1} = \frac{\text{ACID1} \cdot \text{VOLC}}{\text{VOLC}} \]
\[ \text{CACID2} = \frac{\text{ACID2} \cdot \text{VOLC}}{\text{VOLC}} \]

BRANCH ACCORDING TO TYPE OF TITRATION

BASE TITRATED WITH BASE
\[ \text{CNA} = \frac{\text{TNTML}(K) \cdot \text{BASEN}}{\text{VOLTL}} \]
\[ \text{CLION} = \text{CACID2} + \text{CACID1} \]

Powers of Hydroxide Ion Activity
\[ \text{OHACT}(2) = \frac{\text{WCON}}{\text{HYDACT}(2)} \]
\[ \text{OHACT}(3) = \text{OHACT}(2) \cdot \text{OHACT}(2) \]
\[ \text{OHACT}(4) = \text{OHACT}(3) \cdot \text{OHACT}(2) \]

ERROR STOP IF pH OUT OF RANGE
\[ \text{IF accumulator overflow}, \text{GO TO} (867, 865, 847, 845) \]

ION CONCENTRATION CALCULATION SECTION

IF QUDITION OVERFLOW 851, 851
\[ \text{DENOM1} = 1. \]
\[ \text{DENOM1} = \text{DENOM1} \cdot \text{FACTOR}(I) \]
\[ \text{CONCENTRATION OF UNIONIZED BASE NUMBER ONE} \]
\[ \text{HAION}(1) = \frac{\text{CACID1}}{\text{DENOM1}} \]

REPEAT ABOVE FOR SECOND BASE
\[ \text{DENOM2} = 1. \]
\[ \text{DENOM2} = \text{DENOM2} \cdot \text{FACTOR}(I + 4) \]
\[ \text{HAION}(5) = \frac{\text{CACID2}}{\text{DENOM2}} \]

TITRATION OF ACID SALT WITH ACID
\[ \text{CNA} = \text{CACID1} + \text{CACID2} \]
\[ \text{CLION} = \frac{\text{TNTML}(K) \cdot \text{BASEN}}{\text{VOLTL}} \]

ACID TITRATED WITH BASE
\[ \text{CNA} = \frac{\text{TNTML}(K) \cdot \text{BASEN}}{\text{VOLTL}} \]
CLION = 0.

POWERS OF HYDROGEN ION ACTIVITY

HYDACT(3) = HYDACT(2) * HYDACT(2)

HYDACT(4) = HYDACT(3) * HYDACT(2)

ERROR STOP IF PH OUT OF RANGE

IF ACCUMULATOR OVERFLOW 910, 870

ION CONCENTRATION CALCULATION SECTION

IF QUOTIENT OVERFLOW 871, 871

DENOM1 = 1.

DO 873 I = 1, NCON1

FACTOR(I) = CKPROD(I) / (GAMMA(I) * HYDACT(I))

IF RESULT OUT OF RANGE, SET VALUE TO ZERO

DO 872 FACTOR(I) = 0.

DENOM1 = DENOM1 * FACTOR(I)

HAION(I) = CACID1 / DENOM1

CONCENTRATION OF IONIC SPECIES

DO 875 I = 1, NCON2

HAION(I + 1) = HAION(I) * FACTOR(I)

REPEAT ABOVE FOR SECOND ACID

DENOM2 = 1.

DO 881 I = 1, NCON2

FACTOR(I + 4) = CKPROD(I + 4) / (GAMMA(I + 4) * HYDACT(I + 1))

HAION(I + 6) = HAION(I) * FACTOR(I + 4)

TRANSFER OUT IF NU ACTIVITY CORRECTIONS

ERROR STOPS

WRITE OUTPUT TAPE 9, 9010

ERROR CALCULATION FOR DISSOCIATION CONSTANTS

MUST SPECIFY TWO ACIDS TO ENTER NON-LINEAR TREATMENT AND CALCULATE

STANDARD DEVIATIONS

NACIDS = 2

NID = 0

ERQ = 0.

GOD = 0.

GO TO 107

TRANSFER OUT TO PROPER SECTION OF MAIN PROGRAM. OUTPUT OPTIONAL.

CMU(K) = .5 * (HYDACT(2)/HYDRO + CNA + COH + CLION + HAION(2))

HAION(3) + 9., HAION(4) + 16., HAION(5) + HAION(7)

HAION(8) 1 + (CKNO3 * VOLC)

TRANSFER OUT TO PROPER SECTION OF MAIN PROGRAM. OUTPUT OPTIONAL.

WRITE OUTPUT TAPE 9, 9010

GO TO 483
00902 WRITE OUTPUT TAPE 9, 9020
GO TO 487
00903 WRITE OUTPUT TAPE 9, 9030
PUNCH 9030
PRINT 9080
STOP 33333
00904 WRITE OUTPUT TAPE 9, 9040
WRITE OUTPUT TAPE 9, 97, (CKIND(12), I2 = 1, 6), SUM
00000 GO TO 401
00905 WRITE OUTPUT TAPE 9, 9050
00000 GO TO 401
00906 WRITE OUTPUT TAPE 9, 9060
00000 GO TO 401
00907 WRITE OUTPUT TAPE 9, 9070
GO TO 503
00909 WRITE OUTPUT TAPE 9, 9090
NTYPE1 = 2
GO TO 501
910 GO TO (920, 920, 930), NTYPE6
920 WRITE OUTPUT TAPE 9, 9010
NTYPE6 = 3
930 GO TO (135, 401, 940), NTYPE1
940 K = K + 1
IF (SUM - 1.0E-6) 347, 347, 335
00911 WRITE OUTPUT TAPE 9, 9110
PUNCH 9110
PRINT 9080
STOP 33333
00912 WRITE OUTPUT TAPE 9, 9120
00000 GO TO 401
913 WRITE OUTPUT TAPE 9, 9020
GO TO 4919
914 WRITE OUTPUT TAPE 9, 9020
GO TO 1760
C
00008 FORMAT ( 92H1DUNNING DISSOCIATION CONSTANT CALCULATOR, TITRATION CURVE, CONCENTRATION FINDER )
000081 FORMAT (/)
000082 FORMAT (72H0)
000083 FORMAT (912)
000084 FORMAT (44H0THIS PROGRAM CALCULATES ACID CONCENTRATIONS)
000085 FORMAT (42H0THIS PROGRAM CALCULATES A TITRATION CURVE)
000086 FORMAT (47H0THIS PROGRAM CALCULATES DISSOCIATION CONSTANTS)
000087 FORMAT (F8.5, F10.5)
000088 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000089 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000090 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000091 FORMAT (F8.5, F10.5)
000092 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000093 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000094 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000095 FORMAT (F8.5, F10.5)
000096 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000097 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000098 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000099 FORMAT (F8.5, F10.5)
000100 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000101 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000102 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000103 FORMAT (F8.5, F10.5)
000104 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000105 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000106 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000107 FORMAT (F8.5, F10.5)
000108 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000109 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000110 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000111 FORMAT (F8.5, F10.5)
000112 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000113 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000114 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000115 FORMAT (F8.5, F10.5)
000116 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000117 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000118 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000119 FORMAT (F8.5, F10.5)
000120 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000121 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000122 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000123 FORMAT (F8.5, F10.5)
000124 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000125 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000126 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000127 FORMAT (F8.5, F10.5)
000128 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000129 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000130 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000131 FORMAT (F8.5, F10.5)
000132 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000133 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000134 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000135 FORMAT (F8.5, F10.5)
000136 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000137 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000138 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000139 FORMAT (F8.5, F10.5)
000140 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000141 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000142 FORMAT (F10.5, 3F10.7, E9.2, F6.1)
000143 FORMAT (F8.5, F10.5)
000144 FORMAT (48H0ORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
000145 FORMAT (35H0ORIGINAL ACID CONCENTRATIONS ARE F9.6, F9.6, MOLAR)
<table>
<thead>
<tr>
<th>Line</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>00046</td>
<td>FORMAT (12HOPWH IS USED)</td>
</tr>
<tr>
<td>00048</td>
<td>FORMAT (12HOPCH IS USED)</td>
</tr>
<tr>
<td>00050</td>
<td>FORMAT (12HOPAM IS USED)</td>
</tr>
<tr>
<td>00051</td>
<td>FORMAT (5D00 THE FILLED OUT MATRIX, AFTER INSTRUCTION 715, IS /</td>
</tr>
<tr>
<td>1</td>
<td>( 5E20.8 ) ]</td>
</tr>
<tr>
<td>00052</td>
<td>FORMAT (F4.1)</td>
</tr>
<tr>
<td>00054</td>
<td>FORMAT (12H HYDROGEN ION SIZE IS F4.1)</td>
</tr>
<tr>
<td>00055</td>
<td>FORMAT (34H THE TRIANGULARIZED MATRIX, AFTER INSTRUCTION 727, IS /</td>
</tr>
<tr>
<td>1</td>
<td>( 5E20.8 ) ]</td>
</tr>
<tr>
<td>00056</td>
<td>FORMAT (F8.5, F10.5)</td>
</tr>
<tr>
<td>00058</td>
<td>FORMAT (26H D-H COEFFICIENTS ARE A=F8.5, B=F8.5)</td>
</tr>
<tr>
<td>00060</td>
<td>FORMAT (F8.5)</td>
</tr>
<tr>
<td>00061</td>
<td>FORMAT (119H K HYDACT GYDRO ION.ST. VOLC HAION1)</td>
</tr>
<tr>
<td>011(2)</td>
<td>HAION3) HAION4) HAION5) HAION6) HAION7) HAION8)</td>
</tr>
<tr>
<td>00062</td>
<td>FORMAT (14H D-H BETA IS F8.5)</td>
</tr>
<tr>
<td>00063</td>
<td>FORMAT (1H I3, E11.2, F8.4, F9.5, F7.3, 8F10.6)</td>
</tr>
<tr>
<td>00064</td>
<td>FORMAT (32HOSALT OF BASE TITRATED WITH BASE)</td>
</tr>
<tr>
<td>00066</td>
<td>FORMAT (26HBASE TITRATED WITH ACID)</td>
</tr>
<tr>
<td>00068</td>
<td>FORMAT (32HOSALT OF ACID TITRATED WITH ACID)</td>
</tr>
<tr>
<td>00070</td>
<td>FORMAT (26HACID TITRATED WITH BASE)</td>
</tr>
<tr>
<td>00072</td>
<td>FORMAT (26MADISSOCIATION CONSTANTS ARE 4E11.3,</td>
</tr>
<tr>
<td>00073</td>
<td>20H SUM OF SQUARES = F8.5)</td>
</tr>
<tr>
<td>00074</td>
<td>FORMAT (1H0 8E14.7)</td>
</tr>
<tr>
<td>00076</td>
<td>FORMAT (4H0Q1=E16.8, 36H TOTAL NO. OF NON-LINEAR ITERATIONS= 14,</td>
</tr>
<tr>
<td>1</td>
<td>18H SCALING FACTOR= E8.1)</td>
</tr>
<tr>
<td>00078</td>
<td>FORMAT (1H0 J FINAL CKIND(I) STANDARD DEVIATION )</td>
</tr>
<tr>
<td>00080</td>
<td>FORMAT (4H0 I3, E11.2, F8.4, F9.5, F7.3, 8F10.6)</td>
</tr>
<tr>
<td>00082</td>
<td>FORMAT (26HTHE CORRELATION MATRIX IS)</td>
</tr>
<tr>
<td>00084</td>
<td>FORMAT (1H I3, E11.2, F8.4, F9.5, F7.3, 8F10.6)</td>
</tr>
<tr>
<td>00086</td>
<td>FORMAT (12HOTITRANT ML PH IONIC STRENGTH H ACT COEF, FM1 MEAS.)</td>
</tr>
<tr>
<td>00087</td>
<td>FORMAT (26H TITRANT ML PH IONIC STRENGTH H ACT COEF, FM1 MEAS.)</td>
</tr>
<tr>
<td>00088</td>
<td>FORMAT (1H F8.3, F7.2, F2.3, F2.3, F2.3, 8F10.6)</td>
</tr>
<tr>
<td>00090</td>
<td>FORMAT (F8.2, F10.2, F9.2)</td>
</tr>
<tr>
<td>00091</td>
<td>FORMAT (1H F8.4, F12.6, F12.6, F12.6, F12.6)</td>
</tr>
<tr>
<td>00092</td>
<td>FORMAT (1H F8.4, F12.6, F12.6, F12.6, F12.6)</td>
</tr>
<tr>
<td>00093</td>
<td>FORMAT (F7.3, F10.3, F10.3, F10.3, F10.3)</td>
</tr>
<tr>
<td>00094</td>
<td>FORMAT (F7.3, F10.3, F10.3, F10.3, F10.3)</td>
</tr>
<tr>
<td>00095</td>
<td>FORMAT (F7.3, F10.3, F10.3, F10.3, F10.3)</td>
</tr>
<tr>
<td>00097</td>
<td>FORMAT (26HDISSOCIATION CONSTANTS ARE 4E11.3,</td>
</tr>
<tr>
<td>00098</td>
<td>20H SUM OF SQUARES = F8.5 )</td>
</tr>
<tr>
<td>00099</td>
<td>FORMAT (F7.3, F10.3)</td>
</tr>
<tr>
<td>99</td>
<td>FORMAT (9H0ACID1 = F8.5, 13H M., ACID2 = F8.5,</td>
</tr>
<tr>
<td>1</td>
<td>22H M., SUM OF SQUARES = E11.4)</td>
</tr>
<tr>
<td>09010</td>
<td>FORMAT (73H0ACID NUMBER TWO HAS NEGATIVE CONCENTRATION. ASSUME ONL</td>
</tr>
<tr>
<td>1</td>
<td>1Y ONE ACID PRESENT)</td>
</tr>
<tr>
<td>09020</td>
<td>FORMAT (30H0A CKIND OR CKPROD IS NEGATIVE )</td>
</tr>
<tr>
<td>09030</td>
<td>FORMAT (22H0WRONG TRANSFER IN 800 )</td>
</tr>
<tr>
<td>09040</td>
<td>FORMAT (34H0FIRST ACID HAS NO DISC. CONSTANTS)</td>
</tr>
<tr>
<td>09050</td>
<td>FORMAT (38H0ATTEMPTED TO SCALE IN BOTH DIRECTIONS )</td>
</tr>
<tr>
<td>09060</td>
<td>FORMAT (35H0OVERFLOW IN GETTING SCALING FACTOR )</td>
</tr>
<tr>
<td>09070</td>
<td>FORMAT (26H0A NEGATIVE PH ENCLOSED )</td>
</tr>
<tr>
<td>09080</td>
<td>FORMAT (4H0 IMPOSSIBLE ERROR STOP DISCONTINUE PROGRAM.)</td>
</tr>
<tr>
<td>09090</td>
<td>FORMAT (20H0CKPROD OUT OF RANGE )</td>
</tr>
<tr>
<td>09100</td>
<td>FORMAT (28H0PH OUT OF RANGE, 869 OR 869 )</td>
</tr>
<tr>
<td>09110</td>
<td>FORMAT (23H0WRONG TRANSFER IN 1600 )</td>
</tr>
<tr>
<td>09120</td>
<td>FORMAT (22H0WRONG TRANSFER IN 700 )</td>
</tr>
</tbody>
</table>