1964

Calculation of acid dissociation constants

Wayne Woodson Dunning
Iowa State University

CALCULATION OF ACID DISSOCIATION CONSTANTS

by

Wayne Woodson Dunning

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1964

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

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.[1] 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.

---

[1]Numerous 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-Huckel equation

$$-\log f_i = \frac{A z_i^2 \sqrt{\mu}}{1 + B a_i \sqrt{\mu}} - \beta\mu \qquad 1$$

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, β 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, μ, is defined by Lewis and Randall (8) as

$$\mu = \tfrac{1}{2} \Sigma\, m_i\, z_i^2 \qquad 2$$

where m_i is the molal concentration of ion i.[1]

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

$$pcH = -\log c_H \qquad 3$$

or

$$pcH = -\log m_H \qquad 3a$$

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,Soln. X/Salt bridge/ 0.1 N Calomel electrode,

$$psH = \frac{E - 0.3376}{0.05916} \quad \text{at } 25^\circ, \qquad 4$$

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 $a_c = a_m d^\circ$, where d° is the density of water. At 25° 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

$$paH = - \log a_H = - \log (f_H c_H) \qquad 5$$

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

$$pwH = - \log (f_H f_{Cl} m_H) \; . \qquad 6$$

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 paH, 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 $-\log f_H m_H$, 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.

---

[1]This 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

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

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

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

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

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

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

Equation 9 may be rearranged to

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

and proper substitution of successive terms will give

$$[H_{n-i}A^{-i}] = \frac{\gamma_o}{\gamma_i} \frac{[H_nA]}{(H^+)^i} \prod_{i=1}^{i} K_i . \qquad 11$$

Since the products of the dissociation constants will be encountered so frequently, it is useful to define

$$k_i = \prod_{q=1}^{i} K_q \qquad 12$$

and

$$k_o = 1. \qquad 13$$

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

$$C_a = [H_nA] \left(1 + \sum_{i=1}^{n} \frac{k_i}{\gamma_i (H^+)^i}\right) . \qquad 14$$

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

$$[H^+] + [Na^+] = [OH^-] + [Cl^-] + \sum_{i=1}^{n} i[H_{n-1}A^{-i}] \qquad 15$$

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

$$N = [H^+] + [Na^+] - [OH^-] - [Cl^-] \qquad 16$$

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

$$N = \frac{(H^+)}{\gamma_H} + [Na^+] - \frac{K_w}{(H^+)\gamma_{OH}} - [Cl^-] . \qquad 17$$

Combination of Equations 15 and 16 gives

$$N = \sum_{i=1}^{n} i\,[H_{n-i}A^{-i}] \qquad 18$$

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

$$N = \left(\sum_{i=1}^{n} \frac{ik_i}{\gamma_i (H^+)^i} \right) \left(\frac{Ca}{1 + \sum_{i=1}^{n} \frac{k_i}{\gamma_i (H^+)^i}} \right) . \qquad 19$$

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

$$N = \left(\sum_{i=1}^{n} \frac{ik_i\,(H^+)^{n-i}}{\gamma_i} \right) \left(\frac{Ca}{(H^+)^n + \sum_{i=1}^{n} \frac{k_i (H^+)^{n-i}}{\gamma_i}} \right) . \qquad 20$$

Rearrangement of terms gives

$$N \left[(H^+)^n + \sum_{i=1}^{n} \frac{k_i (H^+)^{n-i}}{\gamma_i} \right] = \sum_{i=1}^{n} \frac{ik_i\,(H^+)^{n-i} Ca}{\gamma_i} \qquad 21$$

and the separation and recombination of terms gives

$$N(H^+)^n = \sum_{i=1}^{n} k_i \left(\frac{i\,Ca - N}{\gamma_i} \right) (H^+)^{n-i} . \qquad 22$$

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

$$Y = A_1k_1 + A_2k_2 + \text{----------} A_nk_n \quad . \qquad 23$$

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

$$(\Sigma A_1Y) = (\Sigma A_1A_1)k_1 + \text{----------} (\Sigma A_1A_n)k_n \qquad 24$$

$$\vdots \qquad\qquad\qquad\qquad \vdots$$

$$(\Sigma A_nY) = (\Sigma A_nA_1)k_1 + \text{----------} (\Sigma A_nA_n)k_n \quad .$$

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.

$$K_i = \frac{k_i}{k_{i-1}} \quad . \qquad 25$$

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

$$k_j = \prod_{j=1}^{j} K_j \quad , \qquad 26$$

$$N = \sum_{i=1}^{n} i\,[H_{n-i}A^{-i}] + \sum_{j=1}^{m} j[H_{m-j}B^{-j}] \qquad 27$$

and

$$N = \left(\sum_{i=1}^{n} \frac{ik_i\,(H^+)^{n-i}}{\gamma_i}\right)\left(\frac{Ca}{(H^+)^n + \sum_{i=1}^{n} \frac{k_i(H^+)^{n-i}}{\gamma_i}}\right) + \left(\sum_{j=1}^{m} \frac{jk_j\,(H^+)^{m-j}}{\gamma_j}\right)\left(\frac{Cb}{(H^+)^m + \sum_{j=1}^{m} \frac{k_j(H^+)^{m-j}}{\gamma_j}}\right). \qquad 28$$

This equation may be reduced to

$$N(H^+)^{n+m} = \sum_{i=1}^{n} k_i\left(\frac{i\,Ca-N}{\gamma_i}\right)(H^+)^{n+m-i} + \sum_{j=1}^{m} k_j\left(\frac{jC_b-N}{\gamma_j}\right)(H^+)^{n+m-j} + \sum_{i=1}^{n}\sum_{j=1}^{m} k_ik_j\left(\frac{iCa + j\,C_b-N}{\gamma_i\,\gamma_j}\right)(H^+)^{n+m-i-j}. \qquad 29$$

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

$$Q = \Sigma(Y_C - Y_M)^2 \qquad 30$$

where

$$Y = N(H^+)^{n+m} \qquad 31$$

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, $(\vec{dk})$, in vector notation, to the variables would result in

$$Q + \Sigma\left(\frac{\partial Q}{\partial k}\right)(\vec{dk}) = 0. \qquad 32$$

From this, it follows that

$$\Sigma\left(\frac{\partial Q}{\partial k}\right)(\vec{dk}) = -Q \qquad 33$$

and

$$\Sigma\left(\frac{\partial Q}{\partial k}\right) = \Sigma\ 2(Y_C - Y_M)\left(\frac{\partial Y_C}{\partial k}\right) \quad . \qquad 34$$

Therefore

$$\Sigma\ 2(Y_C - Y_M)\left(\frac{\partial Y_C}{\partial k}\right)(\vec{dk}) = \Sigma\ -(Y_C - Y_M)^2 \qquad 35$$

or

$$\Sigma\ 2\left(\frac{\partial Y_C}{\partial k}\right)(\vec{dk}) = \Sigma\ (Y_M - Y_C). \qquad 36$$

This can be most conveniently solved by multiplying by $(\partial Y_C/\partial k)$ and expressing the entire equation in vector or matrix notation,

$$\left[\sum_{1=1}^{ND}\sum_{a=1}^{n+m}\left(\frac{\partial Y_{C(1)}}{\partial k_a}\right)^2\right][dk] = \left[\sum_{1=1}^{ND}\sum_{a=1}^{n+m}(Y_{M(1)} - Y_{C(1)})\left(\frac{\partial Y_{C(1)}}{\partial k_a}\right)\right] \qquad 37$$

where ND is the number of points on the titration curve.

This system,

$$[G][dk] = [R] \qquad 38$$

is solved for the vector [dk] by matrix inversion to yield improved values of the variables, $k_a = k_a^{\circ} + d\,k_a$.

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

$$N = \sum_{i=1}^{n} i[M(OH)_{n-i}^{+i}] \; . \qquad 39$$

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 $[Na^+]$ will generally be zero, and $[Cl^-]$ 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. $[Cl^-]$ equals the salt concentration, and $[Na^+]$ 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 $[Na^+]$ is obtained from the expression

$$[Na^+] = \frac{\text{Total volume of base added}}{\text{Total volume of solution}} \times \text{base normality.} \qquad 40$$

The difference, required $[Na^+]$ - Previous $[Na^+]$, 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

$$(\sigma R_L)^2 = \frac{G^{-1}(L,L) \times Q}{ND-NC-1} \qquad 41$$

where ND is the number of points on the titration curve, NC is the number or 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.

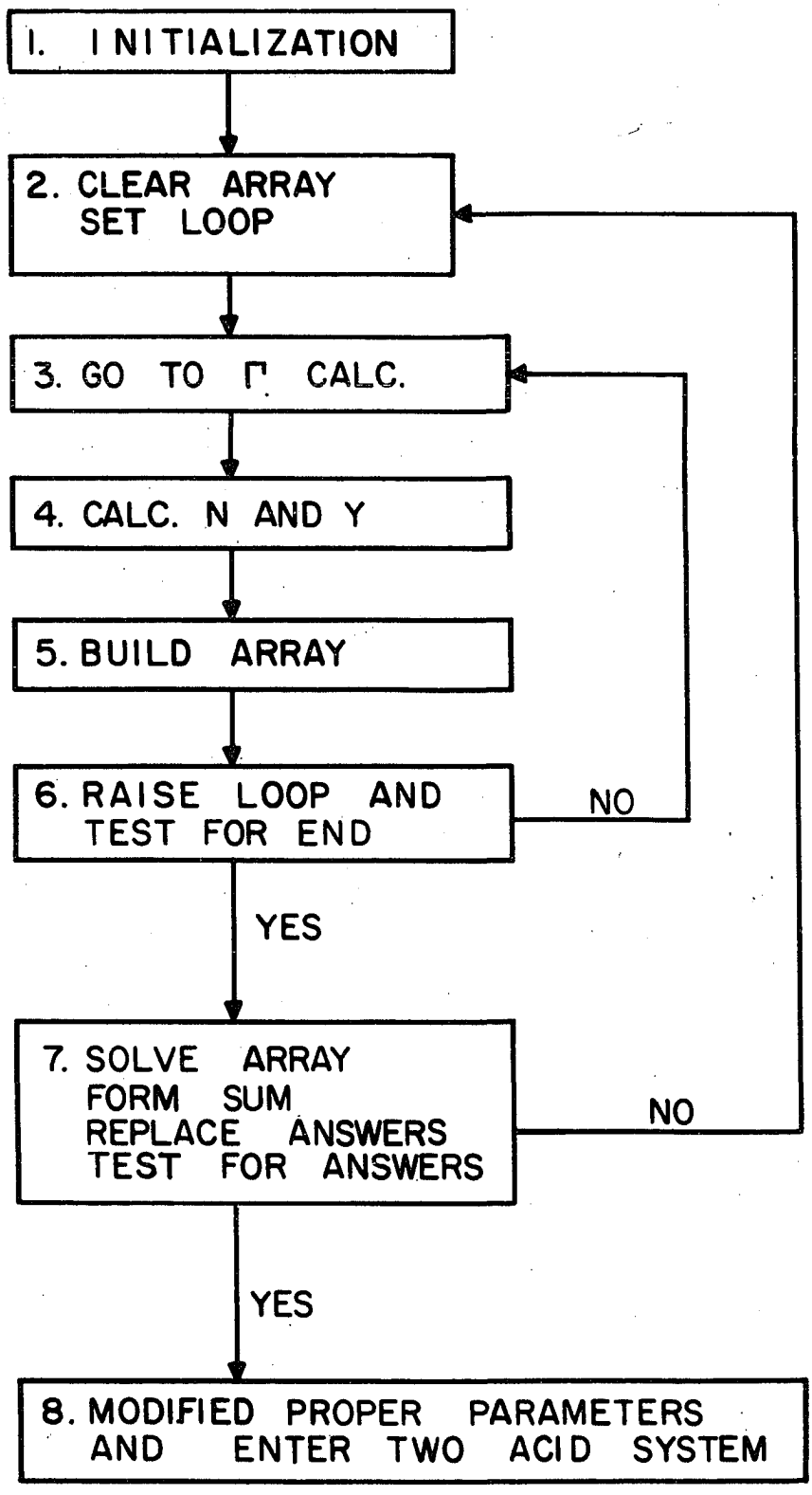
Utilization of the procedures developed in this work requires the availability of an electronic digital computer, preferably of large size. Much of the initial development and testing was done on an International Business MachinesType 650 computer. However, this machine is of insufficient size to contain 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 Γ CALC.
4. CALC. N AND Y
5. BUILD ARRAY
6. RAISE LOOP AND
TEST FOR END
NO
YES
7. SOLVE ARRAY
FORM SUM
REPLACE ANSWERS
TEST FOR ANSWERS
NO
YES
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 $Y = N(H^+)^n$ 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.

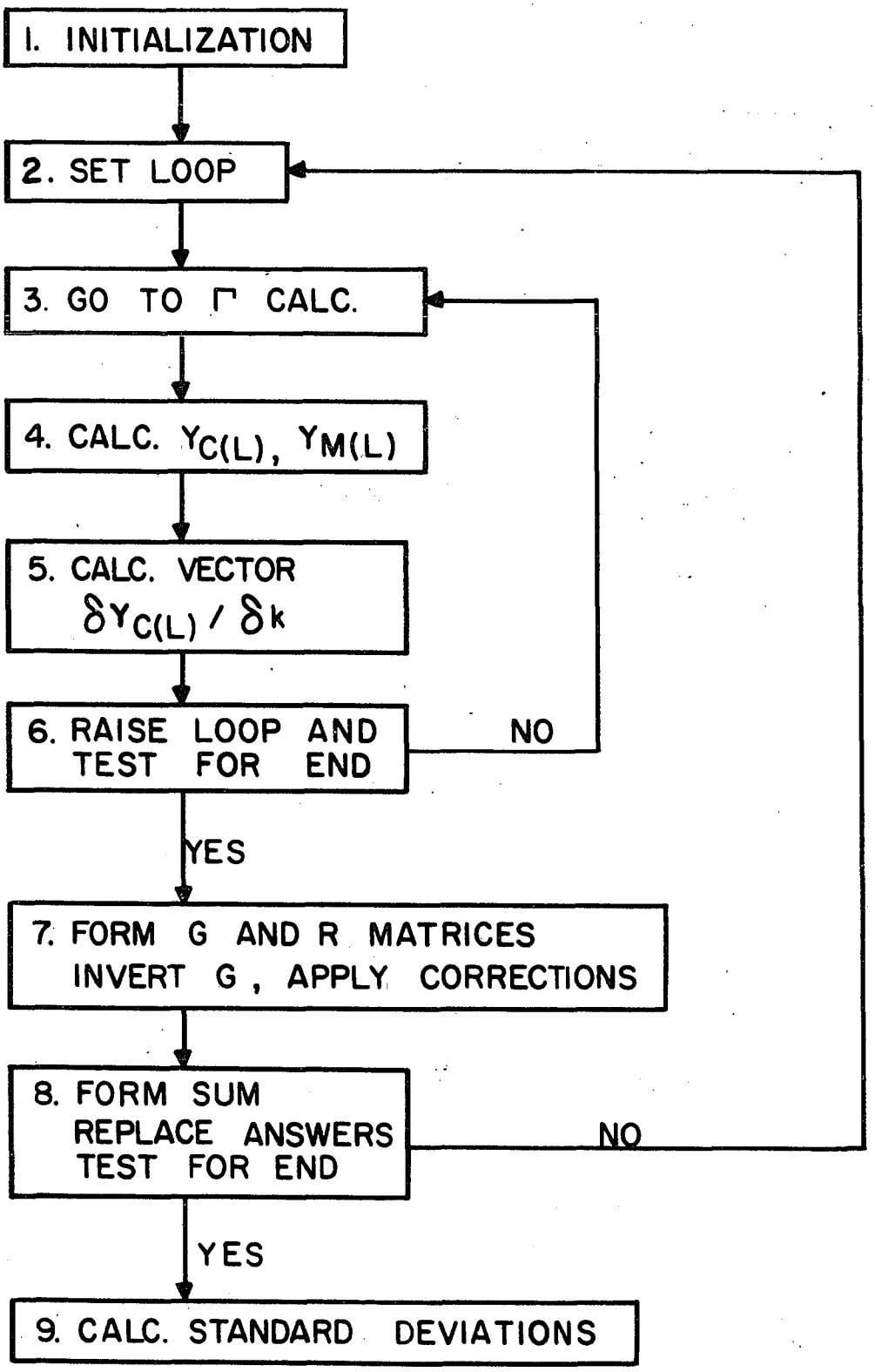
8. If the last answers obtained are satisfactory, the control parameters for the two acid system (Section B) are modified to allow one pass through that section in order to calculate the standard deviations.

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 Section A. Equation 26 is used in addition to Equation 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 treatment does not appear in this section.
3. See Section C.
4. From Equations 16, 29, and 31, Y_C and Y_M are calculated. These quantities are vectors, there being one value of each for every point on the titration curve.
5. The partial derivatives, $\partial Y_C/\partial k$, 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 Γ 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

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, dk_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-Huckel 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.

$$C_{corr} = C_{init} \times \frac{V_{init}}{V_{init} + V_{base}} \quad . \qquad 42$$

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

$$[Na^+] = \frac{V_{base} \times N_{base}}{V_{base} + V_{init}} \quad . \qquad 43$$

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 pcH, paH, or pwH.
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 β 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 constants is over sixteen. Since there exist several acids whose reported constants differ by even lesser amounts, it is important 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 determine 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 indicate 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 consuming, 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 activity 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 Table1.

Figure 3. Calculated titration curves for various hypothetical dibasic acids with varying ratios of K_1/K_2

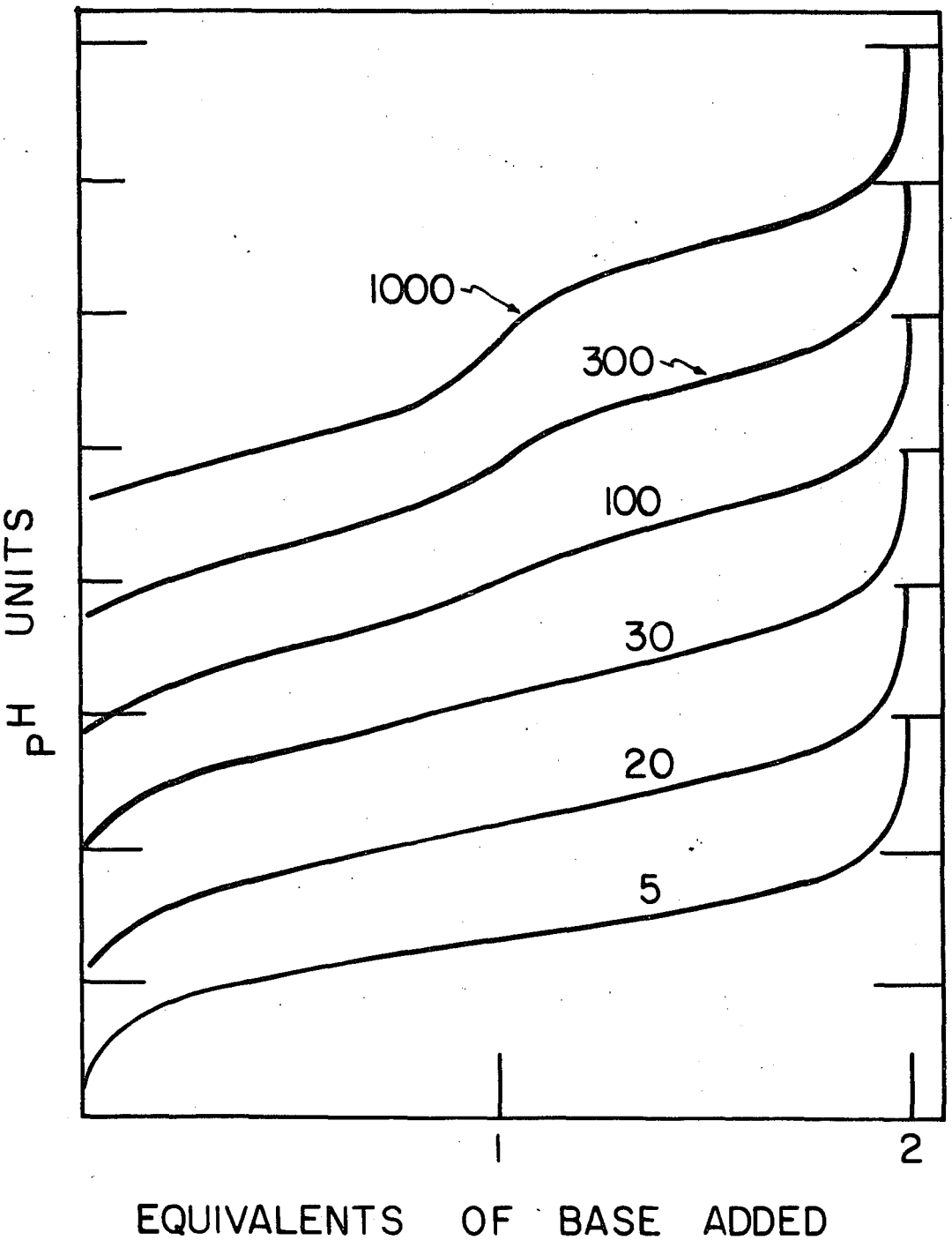

1000
300
100
30
20
5
pH UNITS
1
2
EQUIVALENTS OF BASE ADDED

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)

Initial constants		Ratio	Calculated constants		Fractional Standard deviations	
pK_1	pK_2		pK_1	pK_2	δK_1	δK_2
3.00	6.00	1000	3.00	5.99	1×10^{-5}	2×10^{-5}
3.52	6.00	300	3.52	6.00	5×10^{-6}	1×10^{-6}
4.00	6.00	100	4.00	6.00	9×10^{-6}	3×10^{-7}
4.52	6.00	30	4.52	6.01	2×10^{-5}	1×10^{-7}
4.60	6.00	25	4.60	6.00	1×10^{-5}	7×10^{-8}
4.70	6.00	20	4.70	6.00	4×10^{-5}	1×10^{-6}
4.82	6.00	15	4.82	6.00	2×10^{-5}	4×10^{-8}
5.00	6.00	10	5.00	6.01	7×10^{-5}	9×10^{-8}
5.30	6.00	5	5.30	5.99	1×10^{-4}	4×10^{-8}
5.52	6.00	3	5.52	6.00	1×10^{-4}	2×10^{-8}
5.00[a]	6.00	10	5.00	6.00	6×10^{-6}	6×10^{-9}
5.52[a]	6.00	3	5.52	6.00	5×10^{-4}	8×10^{-8}

[a]With 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

Initial constants		Calculated constants with +0.05 pH unit error		Calculated constants with -0.05 pH unit error	
pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
3.00	6.00	3.09	4.61	2.91	Neg.
3.52	6.00	3.61	4.80	3.43	"
4.00	6.00	4.08	5.04	3.91	"
4.52	6.00	4.61	5.25	4.44	"
4.60	6.00	4.69	5.18	4.51	"
4.70	6.00	4.77	5.65	4.63	"
4.82	6.00	4.90	5.58	-- [a]	-[a]
5.00	6.00	5.08	5.47	4.92	Neg.
5.30	6.00	5.37	5.74	5.23	"
5.52	6.00	5.60	5.63	5.44	"
5.00[b]	6.00	5.08	5.64	4.92	"
5.52[b]	6.00	5.60	5.76	5.44	"

[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 $\pm$ 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

Digits +	Digits -	Error
0	5	0.006
1	6	0.020
2	7	0.034
3	8	0.072
4	9	0.083

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

Initial constants pK_1	Initial constants pK_2	Calculated constants pK_1	Calculated constants pK_2
3.00	6.00	2.84	Neg.
3.52	6.00	3.54	6.33
4.00	6.00	4.10	4.30
4.52	6.00	4.49	5.45
4.60	6.00	4.57	5.49
4.70	6.00	4.60	Neg.
4.82	6.00	4.72	Neg.
5.00	6.00	4.88	Neg.
5.30	6.00	5.29	5.85
5.52	6.00	5.51	5.82
5.00[a]	6.00	4.89	Neg.
5.52[a]	6.00	5.51	5.92

[a]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 1.0×10^{-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

Molar concentrations		Dissociation constants x 10^5	
Acid 1	Acid 2	Acid 1	Acid 2
0.0500	0.0000	1.000	----
0.0495	0.0005	1.000	1.02
0.0490	0.0010	.999	1.05[a]
0.0475	0.0025	.999	1.02[a]
0.0450	0.0050	1.00	.995
0.0425	0.0075	.998	1.01
0.0400	0.0100	.999	1.00
0.0350	0.0150	1.00	.995
0.0300	0.0200	.991	1.01
0.0250	0.0250	1.00	.997

[a]Better 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 converge 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 mixture of a monobasic and a dibasic acid (Concentration of each acid = 0.01 M)

		Dissociation constants given	found
Acid 1	K_1	6.40×10^{-5}	6.41×10^{-5}
	K_2	2.70×10^{-6}	2.69×10^{-6}
Acid 2		1.77×10^{-4}	1.77×10^{-4}

C. Consistency

Experimental consistency was examined by titrating aliquots 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)

Dissociation constants		Standard deviations	
$K_1 \times 10^4$	$K_2 \times 10^5$	$K_1 \times 10^6$	$K_2 \times 10^{10}$
8.64	4.34	6.24	12.5
8.64	4.35	5.34	10.7
8.81	4.28	4.33	8.8
9.33	4.19	3.76	7.8
8.34	4.31	5.32	10.5
10.07	4.12	2.41	5.2
10.05	4.17	3.00	6.5

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 9.6×10^{-4}. The variations in K_2 are much smaller than those in K_1, but the values differ somewhat from the accepted one of 2.9×10^{-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

Initial constants		Calculated constants	
pK_1	pK_2	pK_1	pK_2
3.00	6.00	3.00	5.99
3.52	6.00	3.52	6.00
4.00	6.00	4.00	5.99
4.52	6.00	4.54	5.99
4.60	6.00	4.62	5.99
4.70	6.00	4.72	5.97
4.81	6.00	4.86	5.97
5.00	6.00	5.05	5.96
5.30	6.00	Neg.	3.72
5.52	6.00	5.39	Neg.

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

Acid	Constant	Experimental value	Literature value
Acetic	K	1.66×10^{-5}	1.75×10^{-5}
Succinic	K_1	5.96×10^{-5}	6.6×10^{-5}
	K_2	2.18×10^{-6}	2.8×10^{-6}
Tartaric + Succinic	Tar. K_1	9.81×10^{-4}	9.6×10^{-4}
	Tar. K_2	2.88×10^{-5}	2.9×10^{-5}
	Suc. K_1	Neg.	
	Suc. K_2	Neg.	

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

1. Dippy, J., S. Hughes, and A. Rozanski, J. Chem. Soc., 1959, 2492.

2. Jones, R. and D. Stock, J. Chem, Soc., 1960, 102.

3. Kolthoff, I., Chem. Weekblad, 16, 1154, (1918). [Original not available for examination; abstracted in Chem. Abstr. 14, 13 (1920).]

4. Paul, T., Z. physik. Chem., 110, 417 (1924).

5. Dhar, N., Z. anorg. allgem. Chem., 153, 323 (1926).

6. Bates, R., W. Hamer, G. Manov, and S. Acree, J. Res. Natl. Bur. Std., 29, 183 (1942).

7. Hamer, W. and S. Acree, J. Res. Natl. Bur. Std., 17, 605 (1936).

8. Lewis, G. and M. Randall. Thermodynamics and the Free Energy of Chemical Substitution. New York, N.Y., McGraw-Hill Co. 1923.

9. Britton, H. Hydrogen Ions. 3rd ed., Vol. 1. New York, N.Y., D. Van Nostrand Co. 1943.

10. Sorensen, S. and K. Linderstrom-Lang, Compt. Rend. Trav. Lab. Carlsberg, 15, No. 6 (1924).

11. Guggenheim, E., J. Phys. Chem., 34, 1758 (1930).

12. Hitchcock, D., J. Am. Chem. Soc., 58, 855 (1936).

13. Mori, Y., Mem. Coll. Sci. Eng., 1, 205. [Original not available for examination; abstracted in Chem. Abstr., 1, 2529 (1907).]

14. Auerbach, F. and E. Smolczyk, Z. physik. Chem., 110, 65 (1924).

15. Britton, H., J. Chem. Soc., 127, 1896 (1925).

16. Cohn, E., F. Heyroth, and M. Menkin, J. Am. Chem. Soc., 50, 696 (1928).

17. Speakman, J., J. Chem. Soc., 1940, 855.

18. Crosbie, E. and J. Monahan. A General Least Squares Fitting Procedure. (Typewritten) Argonne, Illinois, Argonne National Laboratory. 1959.

19. McComas, W. and W. Rieman, J. Am. Chem. Soc., 64, 2948 (1942).

20. The Rand Corporation. A Million Random Digits with 100,000 Normal Deviates. Glencoe, Illinois, The Free Press. 1955.

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.

Ml of base	Solution pH						
	1	2	3	4	5	6	7
4.00	2.98	2.98	2.97	2.96	2.99	2.94	2.94
8.50	3.45	3.45	3.45	3.44	3.46	3.43	3.43
12.50	3.94	3.94	3.93	3.93	3.94	3.91	3.90
16.50	4.47	4.46	4.47	4.47	4.49	4.45	4.45
19.00	5.04	5.02	5.05	5.03	5.05	5.01	5.01
20.00	5.66	5.67	5.70	5.67	5.70	5.67	5.68
20.20	5.99	5.98	6.07	6.00	6.06	5.99	6.00
20.30		6.34	6.43	6.30	6.48	6.32	6.38
20.40	6.95	7.00	7.11	7.01	7.20	7.01	7.00
20.45		7.55	7.58	7.50	7.87	7.70	7.55
20.50	8.17	8.39		8.30	8.55	8.40	8.30
20.52			8.56				

Table 11. Data for titration of acetic acid
Acid concentration = 0.02174 M; base concentration = 0.0501 N; initial solution volume = 50.00 ml.

Ml of base	Solution pH
1.00	3.56
3.00	3.99
6.00	4.32
10.00	4.67
14.00	5.00
18.00	5.45
20.00	5.85
21.00	6.34
21.30	6.70
21.50	7.26

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

Ml of base	Solution pH
2.00	3.63
4.50	4.05
7.50	4.46
10.50	4.87
13.50	5.28
16.50	5.70
18.50	6.08
19.60	6.41
20.20	6.73
20.60	7.17

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.)

Ml of base	Solution pH	Ml of base	Solution pH
1.00	2.77	26.00	4.63
2.00	2.84	27.00	4.70
3.00	2.92	28.00	4.80
4.00	3.00	29.00	4.89
5.00	3.09	30.00	4.99
6.00	3.15	31.00	5.09
7.00	3.23	32.00	5.20
8.00	3.31	33.00	5.30
9.00	3.40	34.00	5.40
10.00	3.48	35.00	5.53
11.00	3.55	36.00	5.65
12.00	3.62	37.00	5.80
13.00	3.70	38.00	5.95
14.00	3.77	39.00	6.18
15.00	3.86	39.50	6.31
16.00	3.92	40.00	6.50
17.00	4.00	40.20	6.60
18.00	4.05	40.40	6.71
19.00	4.12	40.60	6.84
20.00	4.19	40.80	7.05
21.00	4.26	41.00	7.35
22.00	4.32	41.10	7.55
23.00	4.40		
24.00	4.48		
25.00	4.55		

XI. APPENDIX B

```
C                                                                       WWD1100
C                                                                       WWD1026
C                                                                       WWD1002
C     WAYNE DUNNING,  IOWA STATE UNIVERSITY                             WWD
C     THIS PROGRAM CALCULATES DISSOCIATION CONSTANTS AND THEIR STANDARD
C     DEVIATIONS FOR A SINGLE ACID OR A MIXTURE OF TWO ACIDS.  PRINCIPAL
C     INPUT DATA CONSIST OF A PH TITRATION CURVE AND KNOWN ACID CONCEN-
C     TRATIONS.  IN ADDITION, CONCENTRATIONS MAY BE CALCULATED FROM A
C     TITRATION CURVE AND KNOWN CONSTANTS, OR A THEORETICAL TITRATION
C     CURVE MAY BE COMPUTED.  OPTIONS INCLUDE THE TITRATION OF A BASE,
C     OR OF A SALT OF A WEAK ACID OR BASE.
C
      DIMENSION  JUNK1(40), JUNK2(40,2), JUNK3(40)
00000 DIMENSION SIZION(6), CKPROD(6), CKIND(6), HAION(8), HYDACT(4),     WWD1003
000001 OHACT(4), CMU(51), PH(51), ACTCFH(51), GAMMA(6), TNTML(51),       WWD1004
000002 FACTOR(6), ACTSCL(7), RESULT(6), AR(50,6), E(14), FC(50), FM(50),WWD1005
000003 DF(50), G(40,40), R(40,1), U(6,6)                                WWD1006
      COMMON  JUNK1, JUNK2, JUNK3
00000 COMMON SIZION, CKPROD, CKIND, HAION, HYDACT, OHACT, CMU, PH,      WWD1007
000001 ACTCFH, GAMMA, TNTML, FACTOR, ACTSCL, RESULT, AR, E, FC, FM, DF, WWD1008
000002 G, R, U, ACID1, ACID2, CACID1, CACID2, NACIDS, NCON1, NCON2,     WWD1009
000003 NCONT, DENOM1, DENOM2, VNUM1, VNUM2, SCFTR, FN, Y, FB, MSCALE,   WWD1010
000004 SUM, Q, Q1, NOPTS, CMLTNT, RQDCL, VOLTL, CNA, VOLC, CLION        WWD1011
C     BEGINNING OF PROGRAM.  THIS SECTION IS PRIMARILY FOR PROPER
C     INITIALIZATION OF THE PROGRAM.  THE NECESSARY DATA IS READ IN, AND
C     THE VALUES OF CERTAIN CONSTANTS ARE SET.
C     SET ICN SIZE PARAMETERS, DISSOCIATION CONSTANTS, AND INDIVIDUAL   WWD1101
C     ION CONCENTRATIONS TO ZERO                                        WWD1102
00401 DO 403 I = 1, 6                                                   WWD1103
00000 SIZION(I) = 0.                                                    WWD1104
      RESULT(I) = 0.
00000 CKPROD(I) = 0.                                                    WWD1105
00403 CKIND(I) = 0.                                                     WWD1106
00000 DO 405 I = 1, 8                                                   WWD1107
00405 HAION(I) = 0.                                                     WWD1108
C                                                                       WWD1109
C     ZERO POWER OF HYDROGEN AND HYDROXIDE ACTIVITY EQUALS ONE          WWD1110
00000 HYDACT(1) = 1.                                                    WWD1111
00000 OHACT(1) = 1.                                                     WWD1112
C
C     UNLESS OTHERWISE SPECIFIED, HYDROGEN ION SIZE IS 5                WWD1113
      HIONSZ = 5.
C
C     UNLESS OTHERWISE SPECIFIED, TEMPERATURE IS 25 DEGREES, AND DEBYE  WWD1115
C     HUCKEL COEFFICIENTS ARE                                           WWD1116
00000 DBHFA = 0.5092                                                    WWD1117
00000 DBHFB = 0.3286                                                    WWD1118
C
C     UNLESS OTHERWISE SPECIFIED, BETA IN D-H FORMULA IS ZERO           WWD1119
      BETADH = 0.
C
C     WRITE HEADING, READ AND WRITE OPENING STATEMENT                   WWD1121
00000 WRITE OUTPUT TAPE 9, 8                                            WWD1122
00000 READ 10                                                           WWD1123
00000 WRITE OUTPUT TAPE 9, 10                                           WWD1124
      PUNCH 10
C
C     READ CONTROL PARAMETERS                                           WWD1125
00000 READ 12, NTYPE1, NTYPE2, NTYPE3, NTYPE4, NTYPE5, NTYPE6, NTYPE7,  WWD1126
000001  NTYPE8, NTYPE9                                                  WWD1127
C
C     WRITE TYPE OF CALCULATION TO BE DONE IN THIS PARTICULAR RUN
```

```
00407 GO TO (413, 411, 409), NTYPE1                                    WWD1129
00409 WRITE OUTPUT TAPE 9, 14                                          WWD1130
00000 GO TO 415                                                        WWD1131
00411 WRITE OUTPUT TAPE 9, 16                                          WWD1132
00000 GO TO 415                                                        WWD1133
00413 WRITE OUTPUT TAPE 9, 18                                          WWD1134
C                                                                      WWD1135
C
C     READ ACID CONCENTRATIONS, AND WRITE WITH APPROPRIATE COMMENT
C     DEPENDING UPON WHETHER CONCENTRATION IS EXACT, OR AN INITIAL
C     ESTIMATE.  IF THERE IS ONLY ONE ACID, THE CONCENTRATION OF THE
C     SECOND IS ZERO.
00415 READ 20, ACID1, ACID2                                            WWD1137
00417 GO TO (421, 421, 419), NTYPE1                                    WWD1138
00419 WRITE OUTPUT TAPE 9, 22, ACID1, ACID2                            WWD1139
00000 GO TO 423                                                        WWD1140
00421 WRITE OUTPUT TAPE 9, 24, ACID1, ACID2                            WWD1141
C                                                                      WWD1142
C
C     READ INITIAL VOLUME OF SOLUTION IN ML., NORMALITY OF TITRANT,
C     IONIC STRENGTH (AN ESTIMATE UNLESS VALUE IS CONSTANT), MOLAR CON-
C     CENTRATION OF ANY ADDED MONOVALENT SALT, DISSOCIATION CONSTANT OF
C     WATER, AND DESIRED CLOSENESS OF FIT OF RESULTS IN PERCENT
00423 READ 26, SOLNV, BASEN, GMU, CKNO3, WCON, ERROR                   WWD1147
C
C     WRITE THE ABOVE QUANTITIES
00000 WRITE OUTPUT TAPE 9, 28, SOLNV, BASEN, GMU, CKNO3, WCON, ERROR   WWD1149
C                                                                      WWD1150
C     READ THE INDIVIDUAL DISSOCIATION CONSTANTS OR THE ESTIMATED VALUES
C     OF THEM.  THE FIRST FOUR ARE FOR THE FIRST ACID, THE LAST TWO FOR
C     THE SECOND ACID.  ANY CONSTANT WHICH DOES NOT EXIST MUST HAVE A
C     VALUE OF ZERO.
00000 READ 30, (CKIND(I), I = 1, 6)                                    WWD1152
C
C     WRITE INDIVIDUAL DISSOCIATION CONSTANTS WITH COMMENTS
00425 GO TO (429, 427, 427), NTYPE1                                    WWD1154
00427 WRITE OUTPUT TAPE 9, 32, (CKIND(I), I = 1, 6)                    WWD1155
00000 GO TO 431                                                        WWD1156
00429 WRITE OUTPUT TAPE 9, 34, (CKIND(I), I = 1, 6)                    WWD1157
C
C     IF ACTIVITY CORRECTIONS ARE NOT TO BE MADE, WRITE THIS FACT, SET
C     ALL VALUES OF IONIC STRENGTH TO ZERO, AND DO NOT READ IN THE ION
C     SIZE PARAMETERS.
00431 GO TO (435, 433, 435), NTYPE2                                    WWD1158
00433 WRITE OUTPUT TAPE 9, 36                                          WWD1161
00000 DO 434 I = 1, 50                                                 WWD1162
00434 CMU(I) = 0.                                                      WWD1163
00000 GO TO 437                                                        WWD1164
C
C     READ AND WRITE THE ION SIZE PARAMETERS.  VALUES FOR NONEXISTENT
C     IONS SHOULD BE ZERO.
00435 READ 38, (SIZION(I), I = 1, 6)                                   WWD1166
00000 WRITE OUTPUT TAPE 9, 40, (SIZION(I), I = 1, 6)                   WWD1167
C
C     IF IONIC STRENGTH IS SPECIFIED AS CONSTANT, WRITE ITS VALUE AND
C     SET ALL STORAGE VALUES TO IT.
00437 GO TO (440, 439, 443), NTYPE3                                    WWD1168
00439 WRITE OUTPUT TAPE 9, 42, GMU                                     WWD1172
00440 DO 441 I = 1, 50                                                 WWD1173
00441 CMU(I) = GMU                                                     WWD1174
C
C     IF VOLUME IS SPECIFIED AS CONSTANT, WRITE THIS FACT AND THE VALUE
```

```
00443 GO TO (447, 445), NTYPE4                                          WWD1175
00445 WRITE OUTPUT TAPE 9, 44, SOLNV                                    WWD1177
C
C     WRITE THE TYPE OF PH READING SPECIFIED BY CONTROL PARAMETER 5
00447 GO TO (453, 451, 449), NTYPE5                                     WWD1178
C     WRITE THAT PWH IS USED
00449 WRITE OUTPUT TAPE 9, 46                                           WWD1180
00000 GO TO 455                                                         WWD1181
C     WRITE THAT PCH IS USED
00451 WRITE OUTPUT TAPE 9, 48                                           WWD1183
00000 GO TO 455                                                         WWD1184
C     WRITE THAT PAH IS USED
00453 WRITE OUTPUT TAPE 9, 50                                           WWD1186
C
C     READ AND WRITE ION SIZE PARAMETER FOR HYDROGEN IF VALUE IS NOT 5.0
00455 GO TO (459, 457), NTYPE6                                          WWD1187
00457 READ 52, HIONSZ                                                   WWD1190
00000 WRITE OUTPUT TAPE 9, 54, HIONSZ                                   WWD1191
C
C     READ AND WRITE NEW D-H COEFFICIENTS A AND B IF TEMPERATURE IS NOT
C     25 DEGREES
00459 GO TO (463, 461), NTYPE7                                          WWD1192
00461 READ 56, DBHFA, DBHFB                                             WWD1194
00000 WRITE OUTPUT TAPE 9, 58, DBHFA, DBHFB                             WWD1195
C
C     READ AND WRITE BETA IN D-H FORMULA IF BETA IS TO BE USED
00463 GO TO (467, 465), NTYPE8                                          WWD1196
00465 READ 60, BETADH                                                   WWD1198
00000 WRITE OUTPUT TAPE 9, 62, BETADH                                   WWD1199
C
C     WRITE THE TYPE OF TITRATION SPECIFIED BY CONTROL PARAMETER 9
00467 GO TO (475, 473, 471, 469), NTYPE9                                WWD1200
C     WRITE SALT OF BASE TITRATED WITH BASE
00469 WRITE OUTPUT TAPE 9, 64                                           WWD1203
00000 GO TO 477                                                         WWD1204
C     WRITE BASE TITRATED WITH ACID
00471 WRITE OUTPUT TAPE 9, 66                                           WWD1206
00000 GO TO 477                                                         WWD1207
C     WRITE SALT OF ACID TITRATED WITH ACID
00473 WRITE OUTPUT TAPE 9, 68                                           WWD1209
00000 GO TO 477                                                         WWD1210
C     WRITE ACID TITRATED WITH BASE
00475 WRITE OUTPUT TAPE 9, 70                                           WWD1212
C                                                                       WWD1213
C     COUNT NUMBER OF ACIDS                                             WWD1214
00477 NACIDS = 1                                                        WWD1215
00479 IF (ACID2) 901, 483, 481                                          WWD1216
00481 NACIDS = 2                                                        WWD1217
C
C     COUNT NUMBER OF DISSOCIATION CONSTANTS FOR FIRST ACID             WWD1218
00483 NCON1 = 0                                                         WWD1219
00000 DO 489 I = 1, 4                                                   WWD1220
00485 IF (CKIND(I)) 902, 489, 487                                       WWD1221
00487 NCON1 = NCON1 + 1                                                 WWD1222
00489 CONTINUE                                                          WWD1223
04911 NCON2 = 0                                                         WWD1224
C
C     COUNT DISSOCIATION CONSTANTS FOR SECOND ACID, IF ANY              WWD1225
04913 GO TO (4923, 4915), NACIDS                                        WWD1226
C     AN INITIALIZATION FOR NON-LINEAR LEAST SQUARES, IF THERE ARE
C     TWO ACIDS
04915 OOD = 1000.                                                       WWD1228
```

```
C     MAXIMUM NUMBER OF ITERATIONS ALLOWED PER PASS IN N-L LEAST SQS.    WWD1229
00000 NID = 5                                                            WWD1230
00000 DO 4921 I = 5, 6                                                   WWD1231
04917 IF (CKIND(I)) 913, 4921, 4919                                      WWD1232
04919 NCON2 = NCON2 + 1                                                  WWD1233
04921 CONTINUE                                                           WWD1234
C                                                                        WWD1235
C     TOTAL NUMBER OF CONSTANTS                                          WWD1236
04923 NCONT = NCON1 + NCON2                                              WWD1237
C
C     ABSOLUTE ERROR                                                     WWD1238
00000 ERROR = ERROR / 100.                                               WWD1239
C                                                                        WWD1240
C     OBTAIN PRODUCTS OF DISSOCIATION CONSTANTS                          WWD1241
C     RESET OVERFLOW TRIGGER
00000 IF ACCUMULATOR OVERFLOW 4925, 4925                                 WWD1242
04925 CKPROD(1) = CKIND(1)                                               WWD1243
00000 DO 4927 I = 2, NCON1                                               WWD1244
04927 CKPROD(I) = CKPROD(I - 1) * CKIND(I)                               WWD1245
04929 GO TO (4933, 4931), NACIDS                                         WWD1246
04931 CKPROD(5) = CKIND(5)                                               WWD1247
00000 CKPROD(6) = CKIND(5) * CKIND(6)                                    WWD1248
C     ERROR STOP IF A PRODUCT OF CONSTANTS IS OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 909, 4933                                  WWD1249
C     TRANSFER TO PROPER SECTION OF PROGRAM DEPENDING ON TYPE OF
C     CALCULATION BEING DONE
04933 GO TO (101, 201, 301), NTYPE1                                      WWD1250
C                                                                        WWD1398
C     SUBMASTER PROGRAM TO DETERMINE DISSOCIATION CONSTANTS              WWD1399
C                                                                        WWD1400
C     GO TO READ IN TITRATION CURVE                                      WWD1401
00101 GO TO 501                                                          WWD1402
C
C     RETURN FROM CURVE READ IN. DETERMINE MATRIX SIZE FOR SINGLE ACID   WWD1403
00103 NROWS = NCON1                                                      WWD1404
00000 NCOLMS = NROWS + 1                                                 WWD1405
C
C     SET ITERATION COUNTER AND SCALE CHANGE CHECKER TO ZERO             WWD1406
C     CHECKER PREVENTS AN ATTEMPT TO SCALE IN BOTH DIRECTIONS
C     SCALING IS NECESSARY TO KEEP DECIMAL POINT WITHIN ALLOWABLE RANGE
00000 MSCALE = 0                                                         WWD1407
00000 MCOUNT = 0                                                         WWD1408
      MCLLD = 0
C     INITIAL SCALING FACTOR EQUALS ZERO
00000 SCFTR = 0.                                                         WWD1410
C     SET NONLINEAR ERROR FACTOR                                         WWD1412
00000 ERQD = .0001 * FLOATF(NDPTS)                                       WWD1413
C
C     GET SCALING QUANTITY                                               WWD1414
00000 IF ACCUMULATOR OVERFLOW 105, 105                                   WWD1415
00105 ACTSCL(1) = 10. ** (SCFTR * FLOATF(NCONT))
C     ERROR STOP IF SCALING QUANTITY OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 906, 107                                   WWD1417
C
C     SET NONLINEAR ITERATION COUNTER TO ZERO                            WWD1418
00107 LLD = 0                                                            WWD1419
C     CLEAR RESULTS AND ARRAY FOR SINGLE ACID                            WWD1420
00109 GO TO (111, 115), NACIDS                                           WWD1421
00111 DO 113 I = 1, NROWS                                                WWD1422
00000 RESULT(I) = 0.                                                     WWD1423
00000 DO 113 J = 1, NCOLMS                                               WWD1424
00113 AR(I , J) = 0.                                                     WWD1425
```

```
C
C      INITIALIZE LOOP AND GO TO ACTIVITY CORRECTION SECTION (GAMMA
C      CALCULATOR)
00115 K = 1                                                          WWD1427
C      OPTIONAL OUTPUT
       IF (SENSE SWITCH 1) 116, 801
  116 WRITE OUTPUT TAPE 9, 61
00000 GO TO 801                                                      WWD1428
C                                                                    WWD1429
C      RETURN FROM GAMMA CALCULATOR AND BRANCH ON TITRATION TYPE     WWD1430
00117 GO TO (125, 125, 119, 119), NTYPE9                             WWD1431
C
C      OBTAIN SCALED HYDROXIDE ACTIVITIES                            WWD1432
00119 DO 123 I = 1, NCONT                                            WWD1433
00123 ACTSCL(I + 1) = ACTSCL(I) * OHACT(2)                           WWD1434
C      TOTAL NEGATIVE ION CONCENTRATION                              WWD1435
00000 FN = -HYDACT(2) / GHYDRO - CNA + COH + CLION                   WWD1436
00000 GO TO 131                                                      WWD1437
C
C      OBTAIN SCALED HYDROGEN ACTIVITIES                             WWD1438
00125 DO 129 I = 1, NCONT                                            WWD1439
00129 ACTSCL(I + 1) = ACTSCL(I) * HYDACT(2)                          WWD1440
C      TOTAL POSITIVE ION CONCENTRATION                              WWD1441
00000 FN = HYDACT(2) / GHYDRO + CNA - COH - CLION                    WWD1442
C
C      SCALED FN TIMES PROPER POWER OF ACTIVITY
00131 Y = FN * ACTSCL(NCONT + 1)                                     WWD1444
C      IF OUT OF RANGE, SCALE UP
00000 IF ACCUMULATOR OVERFLOW 161, 133                               WWD1445
C
C      TRANSFER OUT TO CALCULATE PROPER MATRIX ELEMENTS FOR THIS POINT
00133 GO TO (601, 1001), NACIDS                                      WWD1446
C                                                                    WWD1447
C      RETURN FROM OBTAINING ELEMENTS, SET LOOP FOR NEXT POINT       WWD1448
C      SINGLE ACID
00135 K = K + 1                                                      WWD1449
C      TEST FOR LAST POINT USED.  IF FINISHED, SOLVE MATRIX.
00137 IF (K - NDPTS) 801, 801, 701                                   WWD1451
C
C      RETURN FROM MATRIX SOLVE. OBTAIN DIFFERENCE FROM OLD ANSWERS  WWD1452
00139 SUM = 0.                                                       WWD1453
00141 DO 143 I = 1, NCON1                                            WWD1454
00000 SUM = SUM + ABSF((RESULT(I) - CKPROD(I)) / RESULT(I))          WWD1455
C      REPLACE OLD ANSWERS WITH NEW                                  WWD1456
00143 CKPROD(I) = RESULT(I)                                          WWD1457
00000 CKIND(1) = RESULT(1)                                           WWD1458
00145 IF (NCON1 - 1) 904, 151, 147                                   WWD1459
00147 DO 149 I = 2, NCON1                                            WWD1460
00149 CKIND(I) = RESULT(I) / RESULT(I - 1)                           WWD1461
C
C      WRITE ANSWERS AND DIFFERENCE FROM PREVIOUS SET                WWD1462
00151 WRITE OUTPUT TAPE 9, 72, (CKIND(I), I = 1, 4), SUM             WWD1463
       PUNCH 30, (CKIND(I), I = 1, 4), SUM
C      TEST FOR END.  IF ANSWERS SATISFACTORY, OBTAIN STANDARD DEVIATIONS
00000 MCOUNT = MCOUNT + 1                                            WWD1469
  153 IF (SUM - ERROR * FLOATF(NROWS)) 6001, 6001, 155
C
C      ANSWERS NOT GOOD ENOUGH. REPEAT IF NOT TOO MANY ITERATIONS    WWD1467
00155 MSCALE = 0                                                     WWD1468
00157 IF (MCOUNT - 10) 107, 6001, 6001                               WWD1470
C                                                                    WWD1471
C      SCALE UP                                                      WWD1472
```

```
00161 IF (MSCALE) 905, 163, 163                                          WWD1473
00163 MSCALE = 1                                                         WWD1474
00000 SCFTR = SCFTR + 1.                                                 WWD1475
00000 GO TO 105                                                          WWD1476
C                                                                        WWD1477
C     SCALE DOWN                                                         WWD1478
00171 IF (MSCALE) 173, 173, 905                                          WWD1479
00173 MSCALE = -1                                                        WWD1480
00000 SCFTR = SCFTR - 1.                                                 WWD1481
00000 GO TO 105                                                          WWD1482
C                                                                        WWD1483
C     TWO ACID, NON-LINEAR LEAST SQUARE SOLUTION                         WWD1484
C                                                                        WWD1485
C     SET MEASURED VALUE                                                 WWD1486
01001 FM(K) = Y                                                          WWD1487
C     CALCULATE ELEMENTS FOR SIXTH CONSTANT, IF ANY                      WWD1488
 1003 IF (CKPROD(6)) 1005, 1009, 1005
01005 DO 1007 I = 1, NCON1                                               WWD1490
00000 Z = I                                                              WWD1491
00000 L = NCONT - 1 - I                                                  WWD1492
01007 E(I+10)=((Z*CACID1+2.*CACID2-FN)*ACTSCL(L))/(GAMMA(I)*GAMMA(6))    WWD1493
00000 E(6) = ((2. * CACID2 - FN) * ACTSCL(NCONT - 1)) / GAMMA(6)         WWD1494
00000 GO TO 1011                                                         WWD1495
C     CALCULATE ELEMENTS FOR FIFTH CONSTANT, IF ANY                      WWD1496
 1009 IF (CKPROD(5)) 1011, 1015, 1011
01011 DO 1013 I = 1, NCON1                                               WWD1498
00000 Z = I                                                              WWD1499
00000 L = NCONT - I                                                      WWD1500
01013 E(I+6) = ((Z*CACID1 + CACID2 - FN)*ACTSCL(L))/(GAMMA(I)*GAMMA(5))  WWD1501
00000 E(5) = ((CACID2 - FN) * ACTSCL(NCONT)) / GAMMA(5)                  WWD1502
C     CALCULATE ELEMENTS FOR FIRST ACID                                  WWD1503
01015 DO 1017 I = 1, NCON1                                               WWD1504
00000 Z = I                                                              WWD1505
00000 L = NCONT + 1 - I                                                  WWD1506
01017 E(I) = ((Z * CACID1 - FN) * ACTSCL(L)) / GAMMA(I)                  WWD1507
C                                                                        WWD1508
C     OBTAIN DIFFERENTIAL ELEMENTS OF MATRIX                             WWD1509
01019 IF ACCUMULATOR OVERFLOW 1021, 1021                                 WWD1510
01021 AR(K, 1) = E(1) + E(7) * CKPROD(5) + E(11) * CKPROD(6)             WWD1511
00000 AR(K, 2) = E(2) + E(8) * CKPROD(5) + E(12) * CKPROD(6)             WWD1512
00000 AR(K, 3) = E(3) + E(9) * CKPROD(5) + E(13) * CKPROD(6)             WWD1513
00000 AR(K, 4) = E(4) + E(10) * CKPROD(5) + E(14) * CKPROD(6)            WWD1514
00000 AR(K, NCON1+1) = E(5) + E(7) * CKPROD(1) + E(8) * CKPROD(2)        WWD1515
000001 + E(9) * CKPROD(3) + E(10) * CKPROD(4)                            WWD1516
00000 AR(K, NCON1+2) = E(6) + E(11) * CKPROD(1) + E(12) * CKPROD(2)      WWD1517
000001 + E(13) * CKPROD(3) + E(14) * CKPROD(4)                           WWD1518
C     CALCULATE FC                                                       WWD1519
01023 FC(K) = CKPROD(1)*E(1)+CKPROD(2)*E(2)+CKPROD(3)*E(3)+CKPROD(4)*    WWD1520
010231 E(4)+CKPROD(5)*E(5)+CKPROD(6)*E(6)+CKPROD(1)*E(7)*CKPROD(5)+      WWD1521
010232 CKPROD(2)*E(8)*CKPROD(5)+CKPROD(3)*E(9)*CKPROD(5)+CKPROD(4)*      WWD1522
010233 E(10)*CKPROD(5)+CKPROD(1)*E(11)*CKPROD(6)+CKPROD(2)*E(12)*        WWD1523
010234 CKPROD(6)+CKPROD(3)*E(13)*CKPROD(6)+CKPROD(4)*E(14)*CKPROD(6)     WWD1524
00000 IF ACCUMULATOR OVERFLOW 161, 1025                                  WWD1525
C     SET LOOP FOR NEXT POINT                                            WWD1526
01025 K = K + 1                                                          WWD1527
C     TEST FOR LAST POINT USED                                           WWD1528
01027 IF (K - NDPTS) 801, 801, 1380                                      WWD1529
C                                                                        WWD1530
C     MODIFIED AN E 208 PROGRAM
C                                                                        WWD1532
01380 DO 1430 J = 1, NDPTS                                               WWD1533
01430 DF(J) = FM(J) - FC(J)                                              WWD1534
```

```
C     TESTING SWITCH FOR OPTIONAL OUTPUT
01450 IF (SENSE SWITCH 3) 1460, 1490                                    WWD1536
01460 DO 1480 J = 1, NDPTS                                              WWD1537
01480 WRITE OUTPUT TAPE 9, 74, (AR(J,K),K = 1, NCONT), DF(J)            WWD1538
C
C     CALCULATE                                                         WWD1539
01490 DO 1520 L = 1, NCONT                                              WWD1540
01500 R(L, 1) = 0.                                                      WWD1541
01510 DO 1520 J = 1, NDPTS                                              WWD1542
01520 R(L, 1) = R(L, 1) + AR(J, L) * DF(J)                              WWD1543
01530 DO 1570 L = 1, NCONT                                              WWD1544
01540 DO 1570 K = 1, NCONT                                              WWD1545
01550 G(L, K) = 0.                                                      WWD1546
01560 DO 1570 J = 1, NDPTS                                              WWD1547
01570 G(L,K) = G(L, K) + AR(J, L) * AR(J, K)                            WWD1548
00000 IF ACCUMULATOR OVERFLOW 161, 1580                                 WWD1549
C     TEST SWITCH FOR R AND G OPTIONAL OUTPUT
01580 IF (SENSE SWITCH 4) 1590, 1600                                    WWD1551
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                    WWD1553
C     BY Y AND G REPLACED BY G INVERSE                                  WWD1554
01600 MM = 1                                                            WWD1555
01610 CALL MATINV (G, NCONT, R, MM, DETERM)                             WWD1556
01615 GO TO (1620, 911, 1617), NTYPE1                                   WWD1557
01617 CKIND(1) = ACID1                                                  WWD1558
00000 CKIND(2) = ACID2                                                  WWD1559
00000 Q1 = 0.                                                           WWD1560
00000 DO 1619 J = 1, NDPTS                                              WWD1561
01619 Q1 = Q1 + (DF(J) ** 2.)                                           WWD1562
00000 GO TO 1760                                                        WWD1563
C
C     CHECK THE FIT                                                     WWD1564
01620 Q1 = 0.                                                           WWD1565
01625 DO 1630 J = 1, NDPTS                                              WWD1566
01630 Q1 = Q1 + (DF(J) ** 2.)                                           WWD1567
      IF ACCUMULATOR OVERFLOW 161, 1635
01635 Q = ABSF(QOD - Q1)                                                WWD1568
01640 QOD = Q1                                                          WWD1569
01645 LLD = LLD + 1                                                     WWD1570
      MCLLD = MCLLD + 1
C     IF FIT IS NOT GOOD ENOUGH, REPEAT IF NO. OF ITERATIONS IS         WWD1571
C     NOT TOO LARGE.  CKPROD(J) CORRECTED IN ANY CASE                   WWD1572
 1650 DO 1653 J = 1, NCON1
 1653 CKPROD(J) = CKPROD(J) + R(J,1)
      IF (NCON2) 911, 1660, 1655
 1655 DO 1659 J = 1, NCON2
 1657 JJ = J + NCON1
 1659 CKPROD(J + 4) = CKPROD(J + 4) + R(JJ, 1)
01660 IF (Q - ERQD) 1680, 1680, 1665                                    WWD1575
01665 IF (LLD - NID) 1670, 1680, 1760                                   WWD1576
C     TEST SWITCH FOR Y AND G INVERSE, OPTIONAL OUTPUT
01670 IF (SENSE SWITCH 4) 1675, 1677                                    WWD1578
01675 WRITE OUTPUT TAPE 9, 74, ((G(L,K), K = 1, NCONT), R(L, 1),        WWD1579
     1 L = 1, NCONT), (CKPROD(L2), L2 = 1, 6), Q1
01677 GO TO 107                                                         WWD1581
C
C     REPLACE DISSOCIATION CONSTANTS AND TEST FOR CLOSENESS,            WWD1582
C     RECORRECT FOR ACTIVITY AND REITERATE IF NECESSARY                 WWD1583
01680 SUM = 0.                                                          WWD1584
01685 RESULT(1) = CKPROD(1)                                             WWD1585
01690 IF (NCON1 - 2) 1705, 1695, 1695                                   WWD1586
```

```
01695 DO 1700 I = 2, NCON1                                              WWD1587
01700 RESULT(I) = CKPROD(I) / CKPROD(I - 1)                             WWD1588
01705 IF (NCON2 - 1) 1720, 1715, 1710                                   WWD1589
 1710 RESULT(6) = CKPROD(6) / CKPROD(5)
 1715 RESULT(5) = CKPROD(5)
01720 DO 1730 I = 1,    6                                               WWD1592
      IF (CKIND(I)) 914, 1730, 1725
01725 SUM = SUM + ABSF((RESULT(I) - CKIND(I)) / CKIND(I))               WWD1593
 1727 CKIND(I) = RESULT(I)
 1730 CONTINUE
00000 WRITE OUTPUT TAPE 9, 97, (CKIND(I), I = 1, 6), SUM                WWD159
      PUNCH 30, (CKIND(I), I = 1, 6)
01735 IF (SUM - ERROR * FLOATF(NCONT)) 1760, 1760, 1740                 WWD1596
01740 MSCALE = 0                                                        WWD1597
01745 MCOUNT = MCOUNT + 1                                               WWD1598
01750 IF (MCOUNT - 10) 107, 1760, 1760                                  WWD1599
C                                                                       WWD1600
C     CALCULATE THE CORRELATION MATRIX                                  WWD1601
01760 DO 1770 J = 1, NCONT                                              WWD1602
01765 DO 1770 K = 1, NCONT                                              WWD1603
01770 U(J, K) = G(J , K) / SQRTF( G(J, J) * G(K, K) )                   WWD1604
01775 DO 1780 L = 1, NCONT                                              WWD1605
01780 U(L, L) = SQRTF( G(L, L) * Q1 / FLOATF(NDPTS - NCONT - 1) )       WWD1606
C
C     WRITE FINAL RESULTS
01785 WRITE OUTPUT TAPE 9, 76, Q1, MCLLD, ACTSCL(1)
01790 WRITE OUTPUT TAPE 9, 78                                           WWD1609
01795 WRITE OUTPUT TAPE 9, 80, (J, CKIND(J), U(J,J), J = 1,  6)         WWD1610
01800 WRITE OUTPUT TAPE 9, 82                                           WWD1611
01810 DO 1820 L = 1, NCONT                                              WWD1612
01820 WRITE OUTPUT TAPE 9, 84, (U(L,K), K = 1, NCONT)                   WWD1613
01830 WRITE OUTPUT TAPE 9, 86                                           WWD1614
01840 WRITE OUTPUT TAPE 9, 88, (TNTML(J), PH(J), CMU(J), ACTCFH(J),     WWD1615
018401  FM(J), FC(J), DF(J), J = 1, NDPTS)                              WWD1616
00000 GO TO 401                                                         WWD1617
C                                                                       WWD1618
C     SUBMASTER PROGRAM FOR CALCULATION OF TITRATION CURVE
C                                                                       WWD1620
C     READ LIMITS OF PH AND STEPPING INTERVAL
00201 READ 90, PHLOWR, PHUPPR, PHSTEP                                   WWD1621
      WRITE OUTPUT TAPE 9, 91
C     INITIAL CONDITIONS                                                WWD1622
00000 K = 1                                                             WWD1623
00000 CMU(1) = GMU                                                      WWD1624
00000 TNTML(1) = 0.                                                     WWD1625
00000 PH(1) = PHLOWR                                                    WWD1626
C
C     SCALING FACTOR                                                    WWD1627
00203 ACTSCL(1) = 1.0E30                                                WWD1628
C     IF TWO ACIDS, MOVE CONSTANTS OVER TO MAKE THEM CONSECUTIVE
00205 GO TO (801, 207), NACIDS                                          WWD1629
00207 DO 209 I = 1, NCON2                                               WWD1631
00000 M = NCON1 + I                                                     WWD1632
00209 CKPROD(M) = CKPROD(I + 4)                                         WWD1633
C
C     GO TO ACTIVITY CORRECTION SECTION
00000 GO TO 801                                                         WWD1634
C
C     RETURN AND TRANSFER ACCORDING TO TYPE OF TITRATION
00211 GO TO (217, 217, 213, 213), NTYPE9                                WWD1635
C
C     TITRATIONS OF BASE                                                WWD1636
```

```
00213 DO 215 I = 1, 4                                                    WWD1637
00215 ACTSCL(I + 1) = ACTSCL(I) * OHACT(2)                               WWD1638
00000 GO TO 221                                                          WWD1639
C
C     TITRATIONS OF ACID                                                 WWD1640
00217 DO 219 I = 1, 4                                                    WWD1641
00219 ACTSCL(I + 1) = ACTSCL(I) * HYDACT(2)                              WWD1642
C                                                                        WWD1643
C     OBTAIN ELEMENTS OF EQUATION
00221 DO 223 I = 1, NCON1                                                WWD1645
00000 Z = I                                                              WWD1646
00223 E(I) = (HAION(1) * Z * ACTSCL(1)) / (GAMMA(I) * ACTSCL(I + 1))     WWD1647
00225 GO TO (231, 227), NACIDS                                           WWD1648
00227 DO 229 I = 1, NCON2                                                WWD1649
00000 Z = I                                                              WWD1650
00000 L = NCON1 + I                                                      WWD1651
00229 E(L) = (HAION(6) * Z * ACTSCL(1)) / (GAMMA(I + 4) * ACTSCL(I + 1))WWD1652
C
C     TRANSFER ACCORDING TO TYPE OF TITRATION
00231 GO TO (245, 241, 237, 233), NTYPE9                                 WWD1653
C
C     TYPE 4 TITRATION, SALT OF BASE WITH BASE
00233 RQDNA = -HYDACT(2) / GHYDRO + COH + CLION                          WWD1655
00000 DO 235 I = 1, NCONT                                                WWD1656
00235 RQDNA = RQDNA - (E(I) * CKPROD(I))                                 WWD1657
00000 CMLTNT = (RQDNA - CNA) * (VOLTL / BASEN)                           WWD1658
00000 GO TO 249                                                          WWD1659
C
C     TYPE 3 TITRATION, BASE WITH ACID
C     TYPE 3 TITRATION                                                   WWD1660
00237 RQDCL = HYDACT(2) / GHYDRO - COH                                   WWD1661
00000 DO 239 I = 1, NCONT                                                WWD1662
00239 RQDCL = RQDCL + (E(I) * CKPROD(I))                                 WWD1663
00000 CMLTNT = (RQDCL - CLION) * (VOLTL / BASEN)                         WWD1664
00000 GO TO 249                                                          WWD1665
C
C     TYPE 2 TITRATION, SALT OF ACID WITH ACID
C     TYPE 2 TITRATION                                                   WWD1666
00241 RQDCL = HYDACT(2) / GHYDRO + CNA - COH                             WWD1667
00000 DO 243 I = 1, NCONT                                                WWD1668
00243 RQDCL = RQDCL - (E(I) * CKPROD(I))                                 WWD1669
00000 CMLTNT = (RQDCL - CLION) * (VOLTL / BASEN)                         WWD1670
00000 GO TO 249                                                          WWD1671
C
C     TYPE 1 TITRATION, ACID WITH BASE
C     TYPE 1 TITRATION                                                   WWD1672
00245 RQDNA = COH - HYDACT(2) / GHYDRO                                   WWD1673
00000 DO 247 I = 1, NCONT                                                WWD1674
00247 RQDNA = RQDNA + (E(I) * CKPROD(I))                                 WWD1675
      CMLTNT = (RQDNA - CNA) * (VOLTL / BASEN)                           WWD1675A
  249 CONTINUE                                                           WWD1675B
C
C     ADD TITRANT AND TEST FOR LIMIT                                     WWD1676
00251 TNTML(1) = TNTML(1) + CMLTNT                                       WWD1677
      IF ((CMLTNT ** 2.) - 1.0E-6) 255, 255, 253
C     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
00255 WRITE OUTPUT TAPE 9, 92, TNTML(1), PH(1), CMU(1), GHYDRO           WWD1679
C
C     DO NEXT POINT, IF ANY LEFT                                         WWD1680
```

```
00257 PH(1) = PH(1) + PHSTEP                                          WWD1681
00259 IF (PH(1) - PHUPPR) 801, 801, 261
  261 PUNCH 92, TNTML(1), PH(1), CMU(1), GHYDRO
      GO TO 401
C                                                                     WWD1764
C     SUBMASTER PROGRAM TO CALCULATE CONCENTRATIONS OF ACIDS
C                                                                     WWD1766
C     GO TO READ IN TITRATION CURVE                                   WWD1767
00301 GO TO 501                                                       WWD1768
C
C     RETURN FROM READ IN.  DETERMINE MATRIX SIZE                     WWD1769
00303 NROWS = NACIDS                                                  WWD1770
00000 NCOLMS = NROWS + 1                                              WWD1771
C
C     SET ITERATION COUNTER AND INITIAL SUM                           WWD1772
00000 MCOUNT = 0                                                      WWD1773
00000 SUM = 1.                                                        WWD1774
C
C     CLEAR RESULTS AND ARRAY                                         WWD1775
00305 DO 307 I = 1, NROWS                                             WWD1776
00000 RESULT(I) = 0.                                                  WWD1777
00000 E(I) = 0.                                                       WWD1778
00000 DO 307 J = 1, NCOLMS                                            WWD1779
00307 AR(I, J) = 0.                                                   WWD1780
C
C     INITIALIZE LOOP                                                 WWD1781
00309 K = 1                                                           WWD1782
00000 GO TO 801                                                       WWD1783
C     RETURN FROM GAMMA CALCULATOR AND BRANCH ON TITRATION TYPE       WWD1784
00311 GO TO (315, 315, 313, 313), NTYPE9                              WWD1785
00313 FN = -1.                                                        WWD1786
00000 GO TO 317                                                       WWD1787
00315 FN = 1.                                                         WWD1788
00317 Y = FN * (HYDACT(2)/GHYDRO + CNA - COH - CLION)                 WWD1789
C
C     OBTAIN ELEMENTS OF MATRIX
00319 VNUM1 = 0.                                                      WWD1791
00000 DO 321 I = 1, NCON1                                             WWD1792
00000 Z = I                                                           WWD1793
00321 VNUM1 = VNUM1 + Z * FACTOR(I)                                   WWD1794
00000 E(1) = VNUM1 * VOLC / DENOM1                                    WWD1795
00323 GO TO (328, 325), NACIDS                                        WWD1796
C     ELEMENTS FOR SECOND ACID                                        WWD1797
00325 VNUM2 = 0.                                                      WWD1798
00000 DO 327 I = 1, NCON2                                             WWD1799
00000 Z = I                                                           WWD1800
00327 VNUM2 = VNUM2 + Z * FACTOR(I + 4)                               WWD1801
00000 E(2) = VNUM2 * VOLC / DENOM2                                    WWD1802
C
C     SOLVE FOR ANSWERS OR ERRORS                                     WWD1803
00328 IF (SUM - 1.0E-6) 345, 345, 329                                 WWD1804
C
C     BUILD MATRIX                                                    WWD1805
00329 DO 333 L = 1, NROWS                                             WWD1806
00000 AR(L, NCOLMS) = AR(L, NCOLMS) + E(L) * Y                        WWD1807
00331 DO 333 M = 1, L                                                 WWD1808
00333 AR(L, M) = AR(L, M) + E(L) * E(M)                               WWD1809
00000 K = K + 1                                                       WWD1810
00335 IF (K - NOPTS) 801, 801, 701                                    WWD1811
C
C     RETURN FROM MATRIX SOLVE                                        WWD1812
00337 SUM = ((ACID1 - RESULT(1)) / ACID1) ** 2.                       WWD1813
```

```
00000 ACID1 = RESULT(1)                                                 WWD1814
00339 GO TO (343, 341), NACIDS                                          WWD1815
00341 SUM = SUM + ((ACID2 - RESULT(2)) / ACID2) ** 2.                   WWD1816
00000 ACID2 = RESULT(2)                                                 WWD1817
00343 WRITE OUTPUT TAPE 9, 99, ACID1, ACID2, SUM                        WWD1818
      MCOUNT = MCOUNT + 1
      IF (MCOUNT - 10) 305, 344, 344
  344 SUM = -1.0E+10
      GO TO 309
C
C     DETERMINE STANDARD DEVIATIONS.  OBTAIN DIFFERENTIAL ELEMENTS
00345 FM(K) = Y                                                         WWD1821
00000 AR(K, 1) = E(1)                                                   WWD1822
00000 AR(K, 2) = E(2)                                                   WWD1823
00000 FC(K) = E(1) * CACID1 + E(2) * CACID2                             WWD1824
00000 K = K + 1                                                         WWD1825
C     TEST FOR LAST POINT USED                                          WWD1826
00347 IF (K - NDPTS) 801, 801, 349                                      WWD1827
C
C     SET NUMBER OF UNKNOWNS FOR ERROR TREATMENT                        WWD1828
00349 NCONT = NACIDS                                                    WWD1829
00000 NID = 0                                                           WWD1830
00000 ERQD = 0.                                                         WWD1831
00000 QOD = 0.                                                          WWD1832
      PUNCH 99, ACID1, ACID2, SUM
00000 GO TO 1380                                                        WWD1833
C                                                                       WWD1683
C     READ IN TITRATION CURVE                                           WWD1684
C                                                                       WWD1685
00501 I = 1                                                             WWD1686
00503 GO TO (505, 505, 507), NTYPE2                                     WWD1687
00505 GO TO (515, 515, 513), NTYPE3                                     WWD1688
00507 GO TO (511, 511, 509), NTYPE3                                     WWD1689
00509 READ 93, TNTML(I), PH(I), CMU(I), ACTCFH(I)                       WWD1690
00000 GO TO 517                                                         WWD1691
00511 READ 94, TNTML(I), PH(I), ACTCFH(I)                               WWD1692
00000 GO TO 517                                                         WWD1693
00513 READ 96, TNTML(I), PH(I), CMU(I)                                  WWD1694
00000 GO TO 517                                                         WWD1695
00515 READ 98, TNTML(I), PH(I)                                          WWD1696
C
C     TEST FOR END AT PH OF ZERO                                        WWD1697
00517 IF (PH(I)) 907, 521, 519                                          WWD1698
C
C     READ NEXT POINT                                                   WWD1699
00519 I = I + 1                                                         WWD1700
00000 GO TO 503                                                         WWD1701
C
C     COUNT NUMBER OF POINTS                                            WWD1702
00521 NDPTS = I - 1                                                     WWD1703
00523 GO TO (103, 401, 303), NTYPE1
C
C     FORMATION OF MATRIX
C                                                                       WWD1705
C     OBTAIN ELEMENTS OF EQUATION                                       WWD1706
C                                                                       WWD1707
00601 DO 605 I = 1, NCON1                                               WWD1708
00000 Z = I                                                             WWD1709
00000 L = NCON1 + 1 - I                                                 WWD1710
00603 E(I) = (((Z * CACID1) - FN) / GAMMA(I) ) * ACTSCL(L)              WWD1711
C     IF OVERFLOW, SCALE UP                                             WWD1712
00000 IF ACCUMULATOR OVERFLOW 161, 605                                  WWD1713
```

```
00605 CONTINUE                                                          WWD1714
C                                                                       WWD1715
C     BUILD MATRIX                                                      WWD1716
00607 DO 615 L = 1, NROWS                                               WWD1717
00000 AR(L, NCOLMS) = AR(L, NCOLMS) + E(L) * Y                          WWD1718
C     IF OVERFLOW, SCALE UP                                             WWD1719
00000 IF ACCUMULATOR OVERFLOW 161, 609                                  WWD1720
00609 DO 615 M = 1, L                                                   WWD1721
00000 AR(L, M) = AR(L, M) + E(L) * E(M)                                 WWD1722
00000 IF ACCUMULATOR OVERFLOW 613, 615                                  WWD1723
C     DETERMINE WHETHER TO SCALE UP OR DOWN                             WWD1724
00613 IF (ABSF(E(L)) - 1.0) 161, 161, 171                               WWD1725
00615 CONTINUE                                                          WWD1726
00617 GO TO 135                                                         WWD1727
C                                                                       WWD1728
C     SOLVE MATRIX                                                      WWD1729
C                                                                       WWD1730
C     RESET TRIGGERS                                                    WWD1731
00701 IF ACCUMULATOR OVERFLOW 703, 703                                  WWD1732
00703 J = NROWS - 1                                                     WWD1733
00705 IF(J) 912, 707, 711                                               WWD1734
C     IF ONLY ONE ROW, SOLVE DIRECTLY                                   WWD1735
00707 RESULT(1) = AR(1, 2) / AR(1, 1)                                   WWD1736
00709 GO TO (139, 912, 337), NTYPE1                                     WWD1737
C
C     FILL OUT MATRIX                                                   WWD1738
00711 DO 715 K = 2, NROWS                                               WWD1739
00000 M = K - 1                                                         WWD1740
00713 DO 715 L = 1, M                                                   WWD1741
00715 AR(L, K) = AR(K, L)                                               WWD1742
C     OPTIONAL OUTPUT
      IF (SENSE SWITCH 5) 716, 717
  716 WRITE OUTPUT TAPE 9, 51, ((AR(K,L), L = 1, 5), K = 1, NROWS)
C
C     SOLVE BY TRIANGULARIZATION
  717 DO 727 I = 1, J
00000 M = I + 1                                                         WWD1744
00719 DO 727 K = M, NROWS                                               WWD1745
00000 FB = -AR(I, I) / AR(K, I)                                         WWD1746
00723 DO 727 L = I, NCOLMS                                              WWD1747
00000 AR(K, L) = FB * AR(K, L) + AR(I, L)                               WWD1748
00000 IF ACCUMULATOR OVERFLOW 725, 727                                  WWD1749
00725 IF (FB - 1.0) 161, 161, 171                                       WWD1750
00727 CONTINUE                                                          WWD1751
C     OPTIONAL OUTPUT
      IF (SENSE SWITCH 5) 728, 729
  728 WRITE OUTPUT TAPE 9, 55, ((AR(K,L), L = 1, 5), K = 1, NROWS)
00729 DO 737 I = 1, NROWS                                               WWD1752
00000 SUM = 0.                                                          WWD1753
00000 K = I - 1                                                         WWD1754
00000 M = NCOLMS - I                                                    WWD1755
00731 IF (K) 912, 737, 733                                              WWD1756
00733 DO 735 L = 1, K                                                   WWD1757
00000 N = NCOLMS - L                                                    WWD1758
00000 SUM = SUM + RESULT(N) * AR(M, N)                                  WWD1759
00000 IF ACCUMULATOR OVERFLOW 161, 735                                  WWD1760
00735 CONTINUE                                                          WWD1761
00737 RESULT(M) = ( AR(M, NCOLMS) - SUM ) / AR(M , M)                   WWD1762
00739 GO TO (139, 912, 337), NTYPE1                                     WWD1763
C                                                                       WWD1251
C     ACTIVITY CORRECTION SECTION.   THIS SECTION CALCULATES ACTIVITY
C     COEFFICIENTS, VOLUME CORRECTIONS, IONIC CONCENTRATIONS, IONIC
```

```
C     STRENGTH, ETC.
C     THE SUBSCRIPT (K) IS SET OUTSIDE THIS SECTION FOR THE POINT UNDER
C     CONSIDERATION.
C                                                                      WWD1254
C     OBTAIN HYDROGEN ION ACTIVITY OR CONCENTRATION AT THIS POINT      WWD1255
00801 HYDACT(2) = 10. ** (-PH(K))                                      WWD1256
C                                                                      WWD1257
C     RESET OVERFLOW TRIGGER
00000 IF ACCUMULATOR OVERFLOW 803, 803                                 WWD1259
C
C     TRANSFER DEPENDING UPON WHETHER OR NOT ACTIVITY CORRECTIONS ARE TO
C     BE MADE.
00803 GO TO (809, 805, 809), NTYPE2                                    WWD1260
C
C     NO CORRECTIONS. ALL ACTIVITIES EQUAL ONE                         WWD1261
00805 GHYDRO = 1.                                                      WWD1262
00000 ACTCFH(K) = 1.                                                   WWD1263
00000 GOXIDE = 1.                                                      WWD1264
00000 DO 807 I = 1, 6                                                  WWD1265
00807 GAMMA(I) = 1.                                                    WWD1266
00000 GO TO 835                                                        WWD1267
C
C     ACTIVITY CORRECTIONS MADE. D-H FACTORS COMPUTED                  WWD1268
00809 SRMU = SQRTF(CMU(K))                                             WWD1269
00000 ASRMU = -DBHFA * SRMU                                            WWD1270
00000 BSRMU = DBHFB * SRMU                                             WWD1271
00000 BETAMU = BETADH * CMU(K)                                         WWD1272
C                                                                      WWD1273
C     ACTIVITY COEFFICIENTS FOR HYDROGEN AND HYDROXIDE IONS            WWD1274
C     IF HYDROGEN ACTIVITY READ IN, DO NOT CALCULATE                   WWD1275
00811 GO TO (815, 903, 813), NTYPE2                                    WWD1276
00813 GHYDRO = ACTCFH(K)                                               WWD1277
00000 GO TO 817                                                        WWD1278
00815 GHYDRO = 10. ** (ASRMU / (1. + BSRMU * HIONSZ) - BETAMU)         WWD1279
00000 ACTCFH(K) = GHYDRO                                               WWD1280
00817 GOXIDE = 10. ** (ASRMU / (1. + BSRMU * 3.5) - BETAMU)            WWD1281
C                                                                      WWD1282
C     ACTIVITY COEFFICIENTS FOR IONS OF FIRST ACID                     WWD1283
00819 DO 821 I = 1, NCON1                                              WWD1284
00000 Z = I * I                                                        WWD1285
00821 GAMMA(I) = 10. ** (ASRMU * Z / (1. + BSRMU * SIZION(I)) - BETAMU) WWD1286
C                                                                      WWD1287
C     ACTIVITY COEFFICIENTS FOR IONS OF SECOND ACID                    WWD1288
00823 GO TO (829, 825), NACIDS                                         WWD1289
00825 DO 827 I = 1, NCON2                                              WWD1290
00000 Z = I * I                                                        WWD1291
00827 GAMMA(I+4) = 10.**(ASRMU*Z / (1. + BSRMU * SIZION(I+4)) - BETAMU) WWD1292
C
C     CORRECT VALUE OF HYDROGEN ACTIVITY FOR CALCULATING USE DEPENDING
C     UPON TYPE OF PH MEASUREMENT MADE.
00829 GO TO (835, 833, 831), NTYPE5                                    WWD1293
00831 HYDACT(2) = HYDACT(2) / GHYDRO                                   WWD1294
00000 GO TO 835                                                        WWD1295
  833 HYDACT(2) = HYDACT(2) * GHYDRO                                   WWD1294
C                                                                      WWD1297
C     VOLUME CORRECTION SECTION                                        WWD1298
C     TEST FOR CONSTANT VOLUME                                         WWD1299
00835 GO TO (839, 837), NTYPE4                                         WWD1300
00837 VOLTL = SOLNV                                                    WWD1301
00000 GO TO 841                                                        WWD1302
C
C     CALCULATE TOTAL VOLUME                                           WWD1303
```

```
00839 VOLTL = SOLNV + TNTML(K)                                          WWD1304
C
C     HYDROXIDE ION CONCENTRATION                                       WWD1305
00841 COH = WCON / (HYDACT(2) * GOXIDE)                                 WWD1306
C
C     VOLUME CORRECTION FACTOR                                          WWD1307
00000 VOLC = SOLNV / VOLTL                                              WWD1308
C
C     CONCENTRATIONS OF ACIDS, CORRECTED                                WWD1309
00000 CACID1 = ACID1 * VOLC                                             WWD1310
00000 CACID2 = ACID2 * VOLC                                             WWD1311
C
C     BRANCH ACCORDING TO TYPE OF TITRATION                             WWD1312
00843 GO TO (867, 865, 847, 845), NTYPE9                                WWD1313
C                                                                       WWD1314
C     SALT OF BASE TITRATED WITH BASE                                   WWD1315
00845 CNA = TNTML(K) * BASEN / VOLTL                                    WWD1316
00000 CLION = CACID2 + CACID1                                           WWD1317
00000 GO TO 849                                                         WWD1318
C     BASE TITRATED WITH ACID                                           WWD1319
00847 CNA = 0.                                                          WWD1320
00000 CLION = TNTML(K) * BASEN / VOLTL                                  WWD1321
C                                                                       WWD1322
C     POWERS OF HYDROXIDE ION ACTIVITY                                  WWD1323
00849 OHACT(2) = WCON / HYDACT(2)                                       WWD1324
00000 OHACT(3) = OHACT(2) * OHACT(2)                                    WWD1325
00000 OHACT(4) = OHACT(3) * OHACT(2)                                    WWD1326
C     ERROR STOP IF PH OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 910, 850                                  WWD1327
C                                                                       WWD1328
C     ION CONCENTRATION CALCULATION SECTION                             WWD1329
00850 IF QUOTIENT OVERFLOW 851, 851                                     WWD1330
00851 DENOM1 = 1.                                                       WWD1331
00000 DO 853 I = 1, NCON1                                               WWD1332
00000 FACTOR(I) = CKPROD(I) / (GAMMA(I) * OHACT(I))                     WWD1333
00000 FACTOR(I) = FACTOR(I) / OHACT(2)                                  WWD1334
C     IF RESULT OUT OF RANGE, SET VALUE TO ZERO
00000 IF QUOTIENT OVERFLOW 852, 853                                     WWD1335
00852 FACTOR(I) = 0.                                                    WWD1336
00853 DENOM1 = DENOM1 + FACTOR(I)                                       WWD1337
C     CONCENTRATION OF UNIONIZED BASE NUMBER ONE                        WWD1338
00000 HAION(1) = CACID1 / DENOM1                                        WWD1339
C     CONCENTRATION OF IONIC SPECIES                                    WWD1340
00000 DO 855 I = 1, NCON1                                               WWD1341
00855 HAION(I + 1) = HAION(1) * FACTOR(I)                               WWD1342
00857 GO TO (885, 859), NACIDS                                          WWD1343
C     REPEAT ABOVE FOR SECOND BASE                                      WWD1344
00859 DENOM2 = 1.                                                       WWD1345
00000 DO 861 I = 1, NCON2                                               WWD1346
00000 FACTOR(I+4) = CKPROD(I + 4) / (GAMMA(I + 4) * OHACT(I + 1))       WWD1347
00861 DENOM2 = DENOM2 + FACTOR(I + 4)                                   WWD1348
00000 HAION(6) = CACID2 / DENOM2                                        WWD1349
00000 DO 863 I = 1, NCON2                                               WWD1350
00863 HAION(I + 6) = HAION(6) * FACTOR(I + 4)                           WWD1351
00000 GO TO 885                                                         WWD1352
C
C     TITRATION OF ACID SALT WITH ACID                                  WWD1353
00865 CNA = CACID1 + CACID2                                             WWD1354
00000 CLION = TNTML(K) * BASEN / VOLTL                                  WWD1355
00000 GO TO 869                                                         WWD1356
C     ACID TITRATED WITH BASE                                           WWD1357
00867 CNA = TNTML(K) * BASEN / VOLTL                                    WWD1358
```

```
00000 CLION = 0.                                                        WWD1359
C     POWERS OF HYDROGEN ION ACTIVITY                                   WWD1360
00869 HYDACT(3) = HYDACT(2) * HYDACT(2)                                 WWD1361
00000 HYDACT(4) = HYDACT(3) * HYDACT(2)                                 WWD1362
C     ERROR STOP IF PH OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 910, 870                                  WWD1363
C     ION CONCENTRATION CALCULATION SECTION                             WWD1364
00870 IF QUOTIENT OVERFLOW 871, 871                                     WWD1365
00871 DENOM1 = 1.                                                       WWD1366
00000 DO 873 I = 1, NCON1                                               WWD1367
00000 FACTOR(I) = CKPROD(I) / (GAMMA(I) * HYDACT(I))                    WWD1368
00000 FACTOR(I) = FACTOR(I) / HYDACT(2)                                 WWD1369
C     IF RESULT OUT OF RANGE, SET VALUE TO ZERO
00000 IF QUOTIENT OVERFLOW 872, 873                                     WWD1370
00872 FACTOR(I) = 0.                                                    WWD1371
00873 DENOM1 = DENOM1 + FACTOR(I)                                       WWD1372
C     CONCENTRATION OF UNIONIZED ACID NUMBER ONE                        WWD1373
00000 HAION(1) = CACID1 / DENOM1                                        WWD1374
C                                                                       WWD1375
C     CONCENTRATION OF IONIC SPECIES                                    WWD1376
00000 DO 875 I = 1, NCON1                                               WWD1377
00875 HAION(I + 1) = HAION(1) * FACTOR(I)                               WWD1378
00877 GO TO (885, 879), NACIDS                                          WWD1379
C     REPEAT ABOVE FOR SECOND ACID                                      WWD1380
00879 DENOM2 = 1.                                                       WWD1381
00000 DO 881 I = 1, NCON2                                               WWD1382
00000 FACTOR(I + 4) = CKPROD(I + 4) / (GAMMA(I + 4) * HYDACT(I + 1))    WWD1383
00881 DENOM2 = DENOM2 + FACTOR(I + 4)                                   WWD1384
00000 HAION(6) = CACID2 / DENOM2                                        WWD1385
00000 DO 883 I = 1, NCON2                                               WWD1386
00883 HAION(I + 6) = HAION(6) * FACTOR(I + 4)                           WWD1387
C
C     TRANSFER OUT IF NO ACTIVITY CORRECTIONS                           WWD1388
00885 GO TO (887, 891, 887), NTYPE2                                     WWD1389
C     TRANSFER OUT IF IONIC STRENGTH CONSTANT OR GIVEN AT EACH POINT    WWD1390
00887 GO TO (889, 891, 891), NTYPE3                                     WWD1391
C
C     COMPUTE NEW IONIC STRENGTH                                        WWD1392
00889 CMU(K) = .5 * ( HYDACT(2)/GHYDRO + CNA + COH + CLION + HAION(2)   WWD1393
008891 + 4. * HAION(3) + 9. * HAION(4) + 16. * HAION(5) + HAION(7)      WWD1394
008892 + 4. * HAION(8) ) + (CKNO3 * VOLC)                               WWD1395
C
C     TRANSFER OUT TO PROPER SECTION OF MAIN PROGRAM. OUTPUT OPTIONAL.  WWD1396
  891 IF (SENSE SWITCH 1) 893, 895
  893 WRITE OUTPUT TAPE 9, 63, K, HYDACT(2), GHYDRO, CMU(K), VOLC,
     1 (HAION(KS), KS = 1, 8)
  895 GO TO (117, 211, 311), NTYPE1
C                                                                       WWD1834
C     ERROR CALCULATION FOR DISSOCIATION CONSTANTS                      WWD1835
C     MUST SPECIFY TWO ACIDS TO ENTER NON-LINEAR TREATMENT AND CALCULATE
C     STANDARD DEVIATIONS
C                                                                       WWD1836
06001 NACIDS = 2                                                        WWD1837
00000 NID = 0                                                           WWD1838
00000 ERQD = 0.                                                         WWD1839
00000 QOD = 0.                                                          WWD1840
00000 GO TO 107                                                         WWD1841
C
C     ERROR STOPS                                                       WWD1842
C                                                                       WWD1843
00901 WRITE OUTPUT TAPE 9, 9010                                         WWD1844
      GO TO 483
```

```
00902 WRITE OUTPUT TAPE 9, 9020                                          WWD1846
      GO TO 487
00903 WRITE OUTPUT TAPE 9, 9030                                          WWD1848
      PUNCH 9030
      PRINT 9080
      STOP 33333
00904 WRITE OUTPUT TAPE 9, 9040                                          WWD1850
      WRITE OUTPUT TAPE 9, 97, (CKIND(I2), I2 = 1, 6), SUM
00000 GO TO 401                                                          WWD1851
00905 WRITE OUTPUT TAPE 9, 9050                                          WWD1852
00000 GO TO 401                                                          WWD1853
00906 WRITE OUTPUT TAPE 9, 9060                                          WWD1854
00000 GO TO 401                                                          WWD1855
00907 WRITE OUTPUT TAPE 9, 9070                                          WWD1856
      GO TO 503
00909 WRITE OUTPUT TAPE 9, 9090                                          WWD1860
      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                                          WWD1864
      PUNCH 9110
      PRINT 9080
      STOP 33333
00912 WRITE OUTPUT TAPE 9, 9120                                          WWD1866
00000 GO TO 401                                                          WWD1867
  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 CWWD1027
000081URVE DRAWER, AND CONCENTRATION FINDER  )                           WWD1028
00010 FORMAT (72H0                                                       WWD1029
000101                      )                                            WWD1030
00012 FORMAT (9I2)                                                       WWD1031
00014 FORMAT (44HOTHIS PROGRAM CALCULATES ACID CONCENTRATIONS)           WWD1032
00016 FORMAT (42HOTHIS PROGRAM CALCULATES A TITRATION CURVE)             WWD1033
00018 FORMAT (47HOTHIS PROGRAM CALCULATES DISSOCIATION CONSTANTS)        WWD1034
00020 FORMAT (F8.5, F10.5)                                               WWD1035
00022 FORMAT (48HOORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE   F9.6, WWD1036
000221 8H    AND  F9.6, 8H   MOLAR)
00024 FORMAT (35HOORIGINAL ACID CONCENTRATIONS ARE   F9.6,              WWD1038
000241 8H    AND  F9.6, 8H   MOLAR)
00026 FORMAT (F10.5, 3F10.7, E9.2, F6.1)                                 WWD1040
00028 FORMAT (25H INITIAL SOLUTION VOLUME F8.3, 19HML,  TITRANT CONC.    WWD1041
000281F7.4, 23HN, EST. IONIC STRENGTH F6.3, 18HMOLAR, ADDED SALT F6.3,   WWD1042
0002826HMOLAR,/ 32H DISSOCIATION CONSTANT OF WATER E9.2,                 WWD1043
00028328H,  DESIRED CLOSENESS OF FIT F5.1, 16H PERCENT AVERAGE)          WWD1044
00030 FORMAT (6E10.3)                                                    WWD1045
00032 FORMAT (47HOINITIAL VALUES OF DISSOCIATION CONSTANTS ARE  6E11.3)  WWD1046
00034 FORMAT (50HOINITIAL ESTIMATES OF DISSOCIATION CONSTANTS ARE        WWD1047
000341 6E11.3)                                                           WWD1048
00036 FORMAT (33HONO ACTIVITY CORRECTIONS ARE MADE )                     WWD1049
00038 FORMAT (F4.1, 5F5.1)                                               WWD1050
   40 FORMAT (25HOION SIZE PARAMETERS ARE 6F5.1)
00042 FORMAT (32HOIONIC STRENGTH IS CONSTANT AT   F6.3, 6H MOLAR)        WWD1052
00044 FORMAT (25HOVOLUME IS CONSTANT AT F8.3, 3H ML)                     WWD1053
```

```
00046 FORMAT (12HOPWH IS USED)                                          WWD1054
00048 FORMAT (12HOPCH IS USED)                                          WWD1055
00050 FORMAT (12HOPAH IS USED)                                          WWD1056
   51 FORMAT (50HOTHE FILLED OUT MATRIX, AFTER INSTRUCTION 715, IS     /
     1 ( 5E20.8 ))
00052 FORMAT (F4.1)                                                     WWD1057
00054 FORMAT (23H HYDROGEN ION SIZE IS  F4.1)                           WWD1058
   55 FORMAT (54HOTHE TRIANGULARIZED MATRIX, AFTER INSTRUCTION 727, IS /
     1 ( 5E20.8 ))
00056 FORMAT (F8.5, F10.5)                                              WWD1059
00058 FORMAT (26H D-H COEFFICIENTS ARE  A= F8.5,  6H,  B=  F8.5)        WWD1060
00060 FORMAT (F8.5)                                                     WWD1061
   61 FORMAT (119HO  K   HYDACT   GHYDRO  ION.ST.   VOLC  HAION(1)  HAIO
     1N(2)  HAION(3)  HAION(4)  HAION(5)  HAION(6)  HAION(7)  HAION(8) )
00062 FORMAT (14H D-H BETA IS   F8.5)                                   WWD1062
   63 FORMAT (1H I3, E11.2, F8.4, F9.5, F7.3, 8F10.6)
00064 FORMAT (32HOSALT OF BASE TITRATED WITH BASE)                      WWD1063
00066 FORMAT (24HOBASE TITRATED WITH ACID)                              WWD1064
00068 FORMAT (32HOSALT OF ACID TITRATED WITH ACID)                      WWD1065
   70 FORMAT (24HOACID TITRATED WITH BASE)
00072 FORMAT (29HODISSOCIATION CONSTANTS ARE    4E11.3,                 WWD1067
000721 20H   SUM OF SQUARES =  F8.5)                                    WWD1068
00074 FORMAT (1HO 8E14.7)                                               WWD1069
   76 FORMAT (4HOQ1=E16.8, 36H TOTAL NO. OF NON-LINEAR ITERATIONS= I4,
     1 18H  SCALING FACTOR=  E8.1)
00078 FORMAT (42HO  J  FINAL CKIND(J)    STANDARD DEVIATION  )          WWD1071
00080 FORMAT (1H I3, E13.4, E22.8)                                      WWD1072
00082 FORMAT (26HOTHE CORRELATION MATRIX IS)                            WWD1073
00084 FORMAT (1H  10E11.3)                                              WWD1074
00086 FORMAT (83HOTITRANT ML  PH  IONIC STRENGTH  H ACT COEF.  FM(MEAS.)WWD1075
000861   FC(CALC.)  DIFFERENCE       )
00088 FORMAT(1H F8.3, F7.2, F11.6, F14.4, E14.3, 2E12.3)                WWD1077
00090 FORMAT (F6.2, F10.2, F9.2)                                        WWD1078
   91 FORMAT (54HOTITRANT ML     PH      IONIC STRENGTH     H ACT COEF.)WWD1079
   92 FORMAT (1H  F8.4, F12.3, F12.6, F19.4)
00093 FORMAT (F7.3, F10.3, F12.6, F8.4)                                 WWD1081
00094 FORMAT (F7.3, F10.3, F10.4)                                       WWD1082
00096 FORMAT (F7.3, F10.3, F12.6 )                                      WWD1083
00097 FORMAT (29HODISSOCIATION CONSTANTS ARE    6E11.3,                 WWD1084
000971  20H   SUM OF SQUARES =   F8.5 )                                 WWD1085
00098 FORMAT (F7.3, F10.3)                                              WWD1086
   99 FORMAT (9HOACID1 = F8.5,  13H M., ACID2 = F8.5,
     1 22H M., SUM OF SQUARES = E11.4)
09010 FORMAT (73HOACID NUMBER TWO HAS NEGATIVE CONCENTRATION. ASSUME ONL
    1Y ONE ACID PRESENT)
09020 FORMAT (30HOA CKIND OR CKPROD IS NEGATIVE )                       WWD1089
09030 FORMAT (22HOWRONG TRANSFER IN 800 )                               WWD1090
09040 FORMAT (34HOFIRST ACID HAS NO DISC. CONSTANTS)                    WWD1091
09050 FORMAT (38HOATTEMPTED TO SCALE IN BOTH DIRECTIONS )               WWD1092
09060 FORMAT (35HOOVERFLOW IN GETTING SCALING FACTOR )                  WWD1093
09070 FORMAT (26HOA NEGATIVE PH ENCOUNTERED )                           WWD1094
 9080 FORMAT (45H  IMPOSSIBLE ERROR STOP. DISCONTINUE PROGRAM.)
09090 FORMAT (20HOCKPROD OUT OF RANGE )                                 WWD1096
09100 FORMAT (28HOPH OUT OF RANGE, 849 OR 869 )                         WWD1097
09110 FORMAT (23HOWRONG TRANSFER IN 1600 )                              WWD1098
09120 FORMAT (22HOWRONG TRANSFER IN 700 )                               WWD1099
```