A New Method for Least-squares Refinement of Stability Constants

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Formation constants of metal complexes have been determined from pH titration data by use of a new method of calculation. In this method the sum of the squared residuals of all the mass balance equations is minimised with respect to the unknown parameters, the partial derivatives being evaluated analytically. The shifts of the adjustable parameters, calculated from a least-squares cycle, are optimised so that the maximum decrease of the error square sum is obtained for that cycle. A computer programme, based on this method, has been written and its performance has been compared with those obtained using other programmes previously described.

MANY procedures have been described to calculate stability constants of metal complexes and recently two reviews have been published.[1,2] Digital computers have been increasingly used for computing stability constants and many programmes are now available, which are generally based on the non-linear Gauss–Newton least-squares method.[3] This method is used in the procedure introduced by Tobias and Yasuda [4] and developed by Perrin's school. The computer programme SCOGS [5] is the most recent one based on this procedure and uses the conventional least-squares approach to calculate the shifts in the constants, the partial derivatives being obtained numerically by incrementing the constants. Another method, due to Sillén and his co-workers,[6] is employed in programmes, as LETAGROP, which use the 'pit-mapping' approach. In these programmes an error square sum is still minimised: this sum is assumed to be a quadratic function of n unknowns, which may be represented as a paraboloid in $(n + 1)$-dimensional space and the procedure is designed to find the minimum of this paraboloid.

Both methods require a process of numerical differentiation, either for calculating the elements of the design matrix (in SCOGS) or for calculating the coefficients of the second-degree function (in LETAGROP). Numerical differentiation presents two main disadvantages, *i.e.*, it is slow and it lacks precision owing to the finite increment used in the differentiation.

This paper describes a new method for the least-squares refinement of stability constants, where the derivatives are evaluated analytically. In this method, which may use either the Gauss–Newton or the Newton–Raphson [7] least-squares approach, the optimisation of the calculated shifts [8] is introduced. It has been claimed [9] that in non-linear problems the Newton–Raphson method is more powerful than the conventional Gauss–Newton method. It has been shown, further, that the optimisation of the shifts reduces the number of cycles needed to reach the minimum and, in some cases, is able to overcome problems of divergence.[9]

THEORY

Least-squares Method.—The least-squares method is employed to calculate the set of m parameters $x_1, x_2, \dots x_m$, which minimise the error square sum (1)

$$U = \sum_{i=1}^{n} w_i[f^\circ_i - f_i(x_1, x_2, \dots x_m)]^2 \quad (n \geqslant m) \qquad (1)$$

where f°_i are observed quantities, $f_i(x_1, x_2, \dots x_m)$ are the corresponding calculated values, according to functional relationships which are assumed to be known, and w_i are the weights assigned to each observation. The above equation can be expressed in matrix notation as (2) where $\boldsymbol{v}$ is a column vector, whose n elements v_i

$$U = \tilde{\boldsymbol{v}}\boldsymbol{W}\boldsymbol{v} \qquad (2)$$

are the residuals $f^\circ_i - f_i(x_1, x_2, \dots x_m)$ and $\boldsymbol{W} = \mathrm{diag}(w_1, w_2, \dots w_n)$ is the diagonal weight matrix.

Let $\boldsymbol{g}$ be the gradient vector, whose elements g_j [equation (3)] are equal to $\partial U/\partial x_j$, or, in matrix notation,

$$g_j = -2\sum_{i=1}^{n} w_i v_i \partial f_i/\partial x_j \quad (j = 1, 2, \dots m) \qquad (3)$$

equation (4) where the $n \times m$ matrix $\boldsymbol{A}$ is the design

$$\boldsymbol{g} = -2\tilde{\boldsymbol{A}}\boldsymbol{W}\boldsymbol{v} \qquad (4)$$

matrix, whose elements a_{ij} are the partial derivatives $\partial f_i/\partial x_j$. In the minimum of U, $\boldsymbol{g}$ must be a zero vector, that is $g_j = 0$ $(j = 1, 2, \dots m)$.

If the functions f_i are linear in the parameters, a set of m linear equations is obtained and the m unknown parameters can be evaluated directly by simultaneous solution of these equations.

Should the functions be non-linear, a starting vector of the parameters $\boldsymbol{x} = \{x_k\}$ close to the solution of the problem is needed. The elements g_j will be not equal to zero. A first-order Taylor expansion about the starting vector $\boldsymbol{x}$ leads to equation (5).

$$\Delta g_j = \sum_{k=1}^{m} (\partial g_j/\partial x_k)\Delta x_k \quad (j = 1, 2, \dots m) \qquad (5)$$

The m shifts Δx_k can be evaluated by solving the

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[1] C. W. Childs, P. S. Hallman, and D. D. Perrin, *Talanta*, 1969, **16**, 1119.

[2] F. J. C. Rossotti, H. S. Rossotti, and R. J. Whewell, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2051.

[3] W. C. Hamilton, 'Statistics in Physical Sciences,' The Roland Press Company, New York, 1964, p. 150.

[4] R. S. Tobias and M. Yasuda, *Inorg. Chem.*, 1963, **2**, 1307.

[5] I. G. Sayce, *Talanta*, 1968, **15**, 1397.

[6] L. G. Sillén, *Acta Chem. Scand.*, 1962, **16**, 159; 1964, **18**, 1085; N. Ingri and L. G. Sillén, *Arkiv Kemi*, 1964, **23**, 97.

[7] J. B. Scarborough, 'Numerical Mathematical Analysis,' The John Hopkins Press, Baltimore, 1930, p. 187.

[8] H. O. Hartley, *Technometrics*, 1961, **3**, 269.

[9] T. G. Strand, D. A. Kohl, and R. A. Bonham, *J. Chem. Phys.*, 1963, **39**, 1307.

system of m linear equations (6), or, in matrix notation,

$$\sum_{k=1}^{m} (\partial g_j/\partial x_k)\Delta x_k = -g_j \quad (j = 1, 2, \ldots m) \tag{6}$$

equation (7), where $\boldsymbol{H}$ is a $m \times m$ matrix, whose elements

$$\boldsymbol{Hs} = -\boldsymbol{g} = 2\tilde{\boldsymbol{A}}\boldsymbol{Wv} \tag{7}$$

h_{jk} are the partial derivatives $\partial g_j/\partial x_k$ and $\boldsymbol{s}$ is the correction vector $\{\Delta x_k\}$. The elements of the matrix $\boldsymbol{H}$ are (8).

$$h_{jk} = 2 \sum_{i=1}^{n} w_i[(\partial f_i/\partial x_j)(\partial f_i/\partial x_k) - v_i\partial^2 f_i/\partial x_j\partial x_k] \tag{8}$$

Let $\boldsymbol{C}$ be a $m \times m$ matrix, whose elements c_{jk} are given by equation (9) and, considering equations (4)

$$c_{jk} = \sum_{i=1}^{n} w_i v_i \partial^2 f_i/\partial x_j \partial x_k \tag{9}$$

and (7), we can write equations (10) or (11) where $\boldsymbol{B}$ is

$$(\tilde{\boldsymbol{A}}\boldsymbol{WA} - \boldsymbol{C})\boldsymbol{s} = \tilde{\boldsymbol{A}}\boldsymbol{Wv} \tag{10}$$

$$\boldsymbol{Bs} = \tilde{\boldsymbol{A}}\boldsymbol{Wv} \tag{11}$$

given by equation (12).

$$\boldsymbol{B} = \tilde{\boldsymbol{A}}\boldsymbol{WA} - \boldsymbol{C} = \tfrac{1}{2}\boldsymbol{H} \tag{12}$$

Equation (11) gives the set of normal equations of the Newton–Raphson least-squares method. In the well known Gauss–Newton method the second derivatives $\partial^2 f_i/\partial x_j\partial x_k$ are neglected, that is, the matrix $\boldsymbol{C}$ is considered to be a zero matrix.

The correction vector s is obtained [equation (13)] by

$$\boldsymbol{s} = \boldsymbol{B}^{-1}\tilde{\boldsymbol{A}}\boldsymbol{Wv} \tag{13}$$

multiplying both sides of equation (11) from the left by $\boldsymbol{B}^{-1}$. Because of the approximation due to the truncation of the Taylor expansion, the correction $\boldsymbol{s}$ to the starting vector $\boldsymbol{x}$ will only lead to a better approximation to the solution. With an iterative procedure convergence towards the minimum will be obtained.

When the minimum value of the function U, $U_{\text{min.}}$, has been reached, the standard deviations of the parameters are the square-roots of the diagonal elements of the variance–covariance matrix $\boldsymbol{M}_x$ of the parameters[10] [equation (14)].

$$\boldsymbol{M}_x = \frac{U_{\text{min.}}}{n - m}\boldsymbol{B}^{-1} \tag{14}$$

Application to the Refinement of Stability Constants.— A method, widely used in the determination of stability constants of metal complexes in aqueous solution, employs pH titration data for systems containing one metal M and one ligand L. At each point of the titration curve an equilibrium is established among different species whose general formula is $H_pM_qL_r$ (charges are omitted for clarity and generality; for details on the symbolism, see ref. 11). The concentration of $H_pM_qL_r$ is given by equation (15), where β_{pqr}

$$[H_pM_qL_r] = \beta_{pqr}[H]^p[M]^q[L]^r \tag{15}$$

is the formation constant of the species under consideration and [H], [M], and [L] are the concentrations at the equilibrium of the hydrogen ion, of the free metal ion, and of the free ligand, respectively.

For each point the mass-balance equations (16)—(18)

$$T_M = [M] + \Sigma q\beta_{pqr}[H]^p[M]^q[L]^r \tag{16}$$

$$T_L = [L] + \Sigma r\beta_{pqr}[H]^p[M]^q[L]^r \tag{17}$$

$$T_H = [H] + \Sigma p\beta_{pqr}[H]^p[M]^q[L]^r \tag{18}$$

must hold, where T_M, T_L, and T_H are the analytical concentrations of the metal, ligand, and acid respectively, the sum being extended over all the species $H_pM_qL_r$, which are assumed to be present in solution.

The unknown parameters in these equations are [M] and [L] for each point and the stability constants β_{pqr}. The values of [H] are obtained from the potentiometric measurement. If a set of n points is considered, $3n$ equations will result with $2n + m$ unknowns, where m is the number of stability constants to be determined.

Let f°_1, f°_2, and f°_3 denote the analytical concentrations (T_M, T_L, and T_H, respectively) for the first point, f°_4, f°_5, and f°_6 those relative to the second point, and so on. Similarly the unknown concentrations [M] and [L] for the first point will be denoted by x_1 and x_2, those for the second point by x_3 and x_4, and so on. The m unknown constants will be denoted by x_{2n+1}, x_{2n+2}, $\ldots x_{2n+m}$.

The error square sum is defined as in equation (19)

$$U = \sum_{i=1}^{3n} w_i(f^\circ_i - f_i)^2 = \sum_{i=1}^{3n} w_i v_i^2 \tag{19}$$

where w_i is the weight assigned to the ith experimental analytical concentration and f_i is the corresponding value calculated according to equations (16—18). Since f_i are explicit functions, their derivatives with respect to the parameters x_j can be analytically evaluated.

The unknown parameters may take values in a wide range of order of magnitude. Hence, for the practical application of the method, all the partial derivatives $\partial f_i/\partial x_j$ and $\partial^2 f_i/\partial x_j\partial x_k$ are multiplied by the values of the parameters, x_j, and x_j and x_k, respectively. As a consequence, the elements of the matrices $\boldsymbol{A}$ and $\boldsymbol{C}$ will be (20) and (21) and the correction vector, $\boldsymbol{s}$, which is

$$a_{ij} = x_j\partial f_i/\partial x_j \tag{20}$$

$$c_{ij} = \sum_{k=1}^{3n} w_k v_k x_i x_j \partial^2 f_k/\partial x_i\partial x_j \tag{21}$$

obtained by solving equation (13), will contain the relative shifts of the parameters given by (22). For

$$s_i = \frac{1}{x_i}\Delta x_i \tag{22}$$

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[10] Ref. 3, p. 130.

[11] A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, 1966, **5**, 1384.

each point the analytical concentrations are only functions of [M] and [L] at that point and of the constants β_{pqr}. Thus the derivatives of f_1, f_2, and f_3 will be non-vanishing only with respect to $x_1, x_2, x_{2n+1}, \dots x_{2n+m}$, those of f_4, f_5, and f_6 will be non-vanishing only with respect to $x_3, x_4, x_{2n+1}, \dots x_{2n+m}$, and so on. Therefore, the design matrix $\boldsymbol{A}$ takes the form shown in Figure 1.

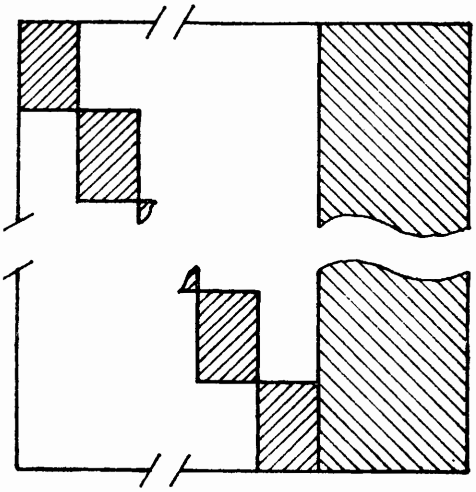

FIGURE 1 Form of the design matrix $\boldsymbol{A}$ of order $3n \times (2n + m)$. The non-zero elements are in the shaded blocks. There are n 3×2 blocks and one $3n \times m$ block

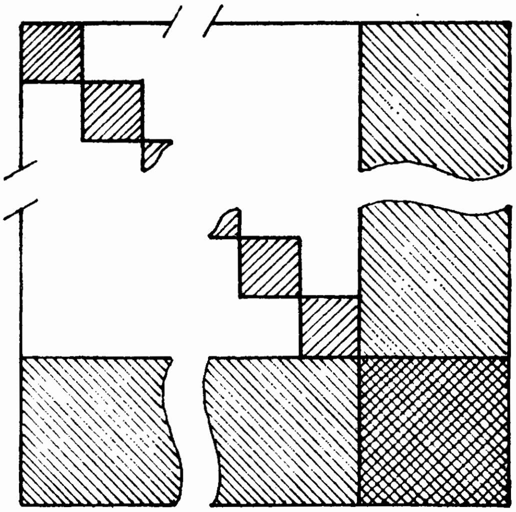

FIGURE 2 Form of the symmetric matrix of the normal equations. Along the diagonal there are n 2×2 blocks and one $m \times m$ block. The non-vanishing elements are in the shaded blocks

The matrix $\tilde{\boldsymbol{A}}\boldsymbol{W}\boldsymbol{A}$ contains the coefficients of the normal equations for the Gauss–Newton method and has the form shown in Figure 2. For the Newton–Raphson approach, the matrix $\boldsymbol{C}$, previously defined, must be subtracted from the matrix $\tilde{\boldsymbol{A}}\boldsymbol{W}\boldsymbol{A}$. The elements, which are zero in the matrix $\tilde{\boldsymbol{A}}\boldsymbol{W}\boldsymbol{A}$, are zero also in the matrix $\boldsymbol{C}$. Therefore, the matrix $\boldsymbol{B}$ of the normal equations in the Newton–Raphson method [obtained from equation (12)] has the same form as the matrix $\tilde{\boldsymbol{A}}\boldsymbol{W}\boldsymbol{A}$ (Figure 2).

According to equation (13), inversion of the matrix $\boldsymbol{B}$ must be performed to obtain the vector $\boldsymbol{s}$ of the corrections of the set of input parameters. Owing to the considerable dimensions of the matrix $\boldsymbol{B}$, whose order is $(2n + m) \times (2n + m)$, the inversion of this matrix is not feasible with medium-size computers. This trouble can be easily overcome, if the matrix $\boldsymbol{B}$ is transformed into a block-diagonal matrix: in this case the problem is reduced to the inversion of each block along the diagonal. Taking advantage of the particular form of the matrix $\boldsymbol{B}$, which contains a large number of zero-elements, we can find a new matrix $\boldsymbol{D}$, such that $\tilde{\boldsymbol{D}}\boldsymbol{B}\boldsymbol{D}$ will be a strictly block-diagonal matrix. The matrix $\boldsymbol{D}$ is a triangular matrix with unit diagonal and contains a $2n \times m$ block of non-zero elements above the diagonal (submatrix $\boldsymbol{D}_1$); all the other elements are equal to zero.

For the calculation of the elements of the matrix $\boldsymbol{D}$, it is convenient to consider the partitioning (23) of the

$$\boldsymbol{B} = \begin{vmatrix} \boldsymbol{B}_1 & \boldsymbol{B}_2 \\ \tilde{\boldsymbol{B}}_2 & \boldsymbol{B}_3 \end{vmatrix} \tag{23}$$

matrix $\boldsymbol{B}$ into the $2n \times 2n$, $2n \times m$, $m \times 2n$, and $m \times m$ submatrices, $\boldsymbol{B}_1$, $\boldsymbol{B}_2$, $\tilde{\boldsymbol{B}}_2$, and $\boldsymbol{B}_3$, respectively.

Let us take a square matrix $\boldsymbol{D}$ of the same order of $\boldsymbol{B}$ and identically partitioned, as in (24), where $\boldsymbol{I}_{2n}$ and

$$\boldsymbol{D} = \begin{vmatrix} \boldsymbol{I}_{2n} & \boldsymbol{D}_1 \\ \boldsymbol{O} & \boldsymbol{I}_m \end{vmatrix} \tag{24}$$

$\boldsymbol{I}_m$ are two unit submatrices of order $2n \times 2n$ and $m \times m$, respectively, and $\boldsymbol{O}$ a zero $m \times 2n$ submatrix.

The product $\tilde{\boldsymbol{D}}\boldsymbol{B}\boldsymbol{D}$ is given by (25). By imposing the

$$\begin{vmatrix} \boldsymbol{B}_1 & \boldsymbol{B}_1\boldsymbol{D}_1 + \boldsymbol{B}_2 \\ \tilde{\boldsymbol{D}}_1\boldsymbol{B}_1 + \tilde{\boldsymbol{B}}_2 & \boldsymbol{B}_3 + \tilde{\boldsymbol{B}}_2\boldsymbol{D}_1 + \tilde{\boldsymbol{D}}_1(\boldsymbol{B}_1\boldsymbol{D}_1 + \boldsymbol{B}_2) \end{vmatrix} \tag{25}$$

condition (26) the matrix $\tilde{\boldsymbol{D}}\boldsymbol{B}\boldsymbol{D}$ becomes (27) which is a

$$\boldsymbol{B}_1\boldsymbol{D}_1 + \boldsymbol{B}_2 = \boldsymbol{O} \tag{26}$$

$$\begin{vmatrix} \boldsymbol{B}_1 & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{B}_3 + \tilde{\boldsymbol{B}}_2\boldsymbol{D}_1 \end{vmatrix} \tag{27}$$

block-diagonal matrix with n 2×2 blocks (submatrix $\boldsymbol{B}_1$) and one $m \times m$ block (submatrix $\boldsymbol{B}_3 + \tilde{\boldsymbol{B}}_2\boldsymbol{D}_1$).

The above procedure is illustrated schematically in Figure 3. From equation (26), equation (28) follows,

$$\boldsymbol{D}_1 = -\boldsymbol{B}_1^{-1}\boldsymbol{B}_2 \tag{28}$$

and the inversion of the submatrix $\boldsymbol{B}_1$ is readily executable owing to its block-diagonal form.

Equation (11) can be written as (29) which leads to

$$(\tilde{\boldsymbol{D}}\boldsymbol{B}\boldsymbol{D})(\boldsymbol{D}^{-1}\boldsymbol{s}) = \tilde{\boldsymbol{D}}\tilde{\boldsymbol{A}}\boldsymbol{W}\boldsymbol{v} \tag{29}$$

(30). The correction vector $\boldsymbol{s}$ is obtained as (31).

$$\boldsymbol{D}^{-1}\boldsymbol{s} = (\tilde{\boldsymbol{D}}\boldsymbol{B}\boldsymbol{D})^{-1}\tilde{\boldsymbol{D}}\tilde{\boldsymbol{A}}\boldsymbol{W}\boldsymbol{v} \tag{30}$$

$$\boldsymbol{s} = \boldsymbol{D}(\boldsymbol{D}^{-1}\boldsymbol{s}) \tag{31}$$

The shifts $\boldsymbol{s}$ obtained after each cycle of iteration are multiplied by a scalar t, such that the largest decrease of U for that cycle is obtained (shift optimisation). If it is assumed that $U(t) = U(\boldsymbol{x} + t\boldsymbol{s})$ is a parabolic function of t, values of U are calculated for three different values of t. It is then possible to obtain the value of t for which $U(t)$ is a minimum. The corrected parameters are used to obtain the starting vector for the next cycle of the iteration. The iterative procedure is stopped when each partial derivative $(\partial U/\partial x_j)x_j$ is less than a pre-established small quantity (usually 10^{-9}).

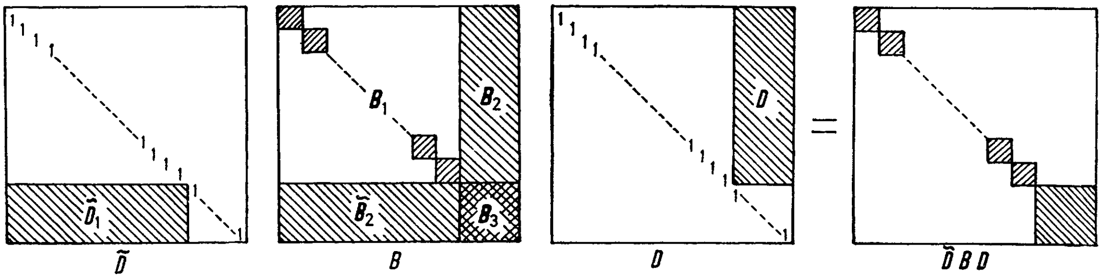

FIGURE 3 Transformation of the matrix $\boldsymbol{B}$ into a block-diagonal matrix. The matrix $\boldsymbol{\tilde{D}BD}$ presents only n 2×2 blocks and one $m \times m$ block along the diagonal

For evaluating the standard deviations of the stability constants (parameters $x_{2n+1}, \ldots x_{2n+m}$) according to equation (14), the last m diagonal elements of the matrix $\boldsymbol{B}^{-1}$ are requested. The matrix $\boldsymbol{B}^{-1}$ can be obtained as (32) or, by use of a partitioning which is identical to that

$$\boldsymbol{B}^{-1} = \boldsymbol{D}(\boldsymbol{\tilde{D}BD})^{-1}\boldsymbol{\tilde{D}} \tag{32}$$

described above, one has (33).

$$\begin{aligned}\boldsymbol{B}^{-1} &= \begin{vmatrix} \boldsymbol{I}_{2n} & \boldsymbol{D}_1 \\ \boldsymbol{O} & \boldsymbol{I}_m \end{vmatrix} \begin{vmatrix} \boldsymbol{B}_1^{-1} & \boldsymbol{O} \\ \boldsymbol{O} & (\boldsymbol{B}_3 + \boldsymbol{\tilde{B}}_2\boldsymbol{D}_1)^{-1} \end{vmatrix} \begin{vmatrix} \boldsymbol{I}_{2n} & \boldsymbol{O} \\ \boldsymbol{\tilde{D}}_1 & \boldsymbol{I}_m \end{vmatrix} \\ &= \begin{vmatrix} \boldsymbol{B}_1^{-1} + \boldsymbol{D}_1(\boldsymbol{B}_3 + \boldsymbol{\tilde{B}}_2\boldsymbol{D}_1^{-1})\boldsymbol{\tilde{D}}_1 & \boldsymbol{D}_1(\boldsymbol{B}_3 + \boldsymbol{\tilde{B}}_2\boldsymbol{D}_1)^{-1} \\ (\boldsymbol{B}_3 + \boldsymbol{\tilde{B}}_2\boldsymbol{D}_1)^{-1}\boldsymbol{\tilde{D}}_1 & (\boldsymbol{B}_3 + \boldsymbol{\tilde{B}}_2\boldsymbol{D}_1)^{-1} \end{vmatrix}\end{aligned} \tag{33}$$

This shows that the last $m \times m$ block along the diagonal of the matrix $(\boldsymbol{\tilde{D}BD})^{-1}$ is identical to the corresponding block of the matrix $\boldsymbol{B}^{-1}$. The diagonal elements of this block are used for computing the standard deviations of the stability constants.

As previously described, a starting vector $\boldsymbol{x}$, containing initial estimates of the parameters, must be available for a non-linear least-squares method. In the present case, the vector $\boldsymbol{x}$ must contain approximate values of [M] and [L] for each data point and of the complex formation constants. This vector is obtained by considering a set of plausible values for the stability constants and by calculating then the starting values of [M] and [L] from equations (16) and (17) for each point.

The importance of the introduction of weighting factors in least-squares adjustment of stability constants has often been claimed.[2,4] However, in the most recent computer programmes (like SCOGS and LETAGROP) the approximation of unit weights is generally employed. A statistically correct weighting scheme is possible only if good estimates of the elements of the variance–covariance matrix of the observations are available. In our case the variances associated with the quantities f°_i (T_M, T_L, and T_H for each point) can be calculated from estimates of the variances of all the experimental quantities with use of the usual variance propagation rules. These experimental quantities are the number of moles of the metal ion, ligand, and acid (or base), the volume and the concentration of the titrating solution, the experimental e.m.f., the standard potential, and the initial volume of the solution. It must be noted, however, that for a given titration curve, the errors associated with some of these quantities, even if originally random, become systematic for all points of the curve under consideration. For example, the random error on the standard potential for a curve leads to a constant systematic error on all the pH values of this curve. Therefore, the calculated variances on the observations f°_i, because of these systematic errors, will not be correct.

For this reason, the usual application of unit weights, while not statistically sound, has the advantage of simplifying the problem.

Alternatively, by analogy with force-constant determinations and, sometimes, with crystallographic calculations, a diagonal weighting matrix $\boldsymbol{W}$, where $w_i = 1/f^\circ{}_i^2$, might be used. This procedure leads to the minimisation of the sum of the squares of the relative residuals and it is justifiable when the observed quantities differ noticeably in order of magnitude and when the error expected on each observation is presumed to be a constant percentage of the observed quantity.

RESULTS

The FORTRAN IV programme, LEAST,[12] * for the determination of stability constants, based on the present method, has been written for the IBM 1130 computer (16 K, one disk). This programme allows the alternative use of the Gauss–Newton or of the Newton–Raphson method and

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* This programme has been deposited with the National Lending Library under Supplementary Publication No. SUP 20416 (18 pp., 1 microfiche), for details of this see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No 20.

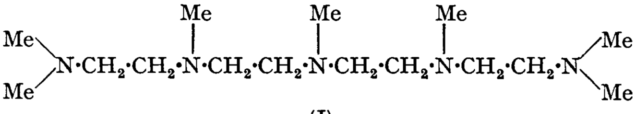
[12] Complete deck listing and instructions of the programme LEAST may be obtained by writing to the authors.

the application of either unit weights or weights equal to the squared reciprocals of the observed quantities. The results, which we have obtained using this programme in the solution of three complex-formation equilibria, are reported here and compared with those obtained by use of two other programmes, SCOGS1 and LG/3. SCOGS1 Has been obtained from the original programme SCOGS[5] by substituting the subroutine COGSNR with another equivalent subroutine designed for a system of one metal and one ligand; the values of [M] and [L] for all the points, obtained at each cycle, are stored as a matrix and then used as starting values in the next cycle of the iteration. These modifications have speeded up the calculations and have overcome troubles due to non-convergence of the iterative calculation of [M] and [L]. The programme LG/3, which uses the same basic approach as the programme LETAGROP, has been described.[13]

The experimental data used in the calculations were taken from potentiometric investigations on metal complex formation, carried out in this laboratory and whose results have been already published.

System Nickel(II)–*Tri*-(3-*aminopropyl*)*amine* (tpt).—This system was the subject of a previous investigation[13] and the existence of two complexes was established: $Ni(Htpt)^{3+}$ and $Ni(tpt)^{2+}$. The calculations have been performed employing 89 data points taken from three titration curves.

System Copper(II)–(Me_7tetren).—The five-dentate ligand (Me_7tetren) has the formula (I). In previous work the



$$\begin{array}{c} Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{Me}{\overset{|}{N}}{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{Me}{\overset{|}{N}}{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{Me}{\overset{|}{N}}{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2 \end{array}$$

(I)

following four complexes have been characterised:[14] $Cu(H_2Me_7tetren)^{4+}$, $Cu(HMe_7tetren)^{3+}$, $CuMe_7tetren^{2+}$, and $Cu(OH)Me_7tetren^+$. In the calculations 105 data points, belonging to five titration curves, were used.

System Copper(II)–NNN′N′-*Tetramethylethylenediamine* (Me_4en).—This system has been already investigated[15] with a previous version of the programme LEAST. The formation of the following six complex species at the equilibrium has been ascertained: $CuMe_4en^{2+}$, $Cu(OH)(Me_4en)^+$, $Cu_2(OH)_2(Me_4en)_2{}^{2+}$, $Cu_2(OH)_2(Me_4en)^{2+}$, $Cu_3(OH)_4(Me_4en)_2{}^{2+}$, and $Cu(OH)_2(Me_4en)$. The experimental data consisted of a set of 151 readings taken from seven different titration curves.

The results of the calculation are shown in the Table. The column headed INPUT contains the starting values of the logarithms of the stability constants. In the following two columns the results obtained using the programmes SCOGS1 and LG/3 are listed. The results in the columns LEAST NR and LEAST GN have been obtained by the programme LEAST with unit weights and by use of the Newton–Raphson and Gauss–Newton methods respectively. The last column, LEAST WGN, contains the results of the programme LEAST, based on the Gauss–Newton method, with a diagonal weight matrix, whose elements w_i are equal to $1/f^{\circ}{}_i{}^2$.

Logarithms of formation constants obtained by use of different methods of refinement[a,b]

	Complex	INPUT	SCOGS1	LG/3	LEAST NR	LEAST GN	LEAST WGN
L = (tpt)							
	$NiHL^{3+}$	15·7	15·78(3)	15·78(3)	15·76(4)	15·76(4)	15·77(3)
	NiL^{2+}	8·8	8·702(2)	8·702(2)	8·702(2)	8·702(2)	8·702(2)
Time[c]			0·81	0·51	0·36	0·25	0·50
L = (Me_7tetren)							
	CuH_2L^{4+}	24·6	24·618(6)	24·619(4)	24·613(4)	24·613(4)	24·616(4)
	$CuHL^{3+}$	20·0	20·05(2)	20·05(2)	20·07(1)	20·07(1)	20·06(1)
	CuL^{2+}	12·2	12·34(3)	12·32(4)	12·32(3)	12·32(3)	12·33(3)
	$Cu(OH)L^+$	3·0	3·06(3)	3·02(2)	3·04(3)	3·04(3)	3·04(3)
Time[c]			1·65	0·86	0·84	0·31	0·58
L = (Me_4en)							
	CuL^{2+}	7·4	7·376(1)	7·377(2)	7·376(1)	7·376(1)	7·378(2)
	$Cu(OH)L^+$	−0·4	−0·65(6)	−0·65(7)	−0·66(7)	−0·66(7)	−0·46(4)
	$Cu_2(OH)_2L^{2+}$	−3·8	−3·66(5)	−3·65(5)	−3·65(5)	−3·65(5)	−3·69(7)
	$Cu_2(OH)_2L_2{}^{2+}$	2·5	2·59(2)	2·59(2)	2·59(2)	2·59(2)	2·54(2)
	$Cu_3(OH)_4L_2{}^{2+}$	−7·9	−8·18(3)	−8·14(6)	−8·15(6)	−8·15(6)	−8·16(8)
	$Cu(OH)_2L$	−10·9	−10·91(2)	−10·91(2)	−10·91(2)	−10·91(2)	−10·81(2)
Time[c]			7·02	4·99	3·60	0·93	1·83

[a] $\log \beta_{pqr} = \log([H_pM_qL_r][H]^{-p}[M]^{-q}[L]^{-r})$. [b] Values in parentheses are standard deviations on the last significant figure. [c] Time/h required for convergence starting from the values reported in the column INPUT (calculations performed on an IBM 1130 computer).

DISCUSSION

The values of the stability constants, obtained using different methods and reported in the Table, agree in general within one standard deviation. It follows also that the calculations (LEAST NR, LEAST GN, and LEAST WGN) based on the method described in this paper require shorter running time to reach the minimum than the other programmes (LG/3 and SCOGS1).

It must be pointed out that the number of cycles and, then, the time required for convergence, using the two last programmes, are critically dependent on the values of the increments assigned to each constant in the procedure of numerical differentiation. Sometimes, if these increments have not been suitably chosen, the refinement procedure may diverge.

The Gauss–Newton method with unit weights (LEAST

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[15] E. Arenare, P. Paoletti, A. Dei, and A. Vacca, *J.C.S. Dalton*, 1972, 736.

GN) appears to be by far the most rapid method, particularly when a large number of stability constants are to be refined. Surprisingly, the Gauss–Newton method converges in fewer cycles than the Newton–Raphson one even if, as shown previously in this paper, the first method is less rigorous than the second. The introduction of weights equal to the reciprocals of the squares of the observed quantities increases the number of cycles required to reach the minimum. Moreover the values of the stability constants obtained sometimes do not agree within one standard deviation with those computed using all the other programmes.

The method of calculation, here described, differs from the other methods reported [4-6] in a basic point, *i.e.*, the concentrations of the free metal ion and free ligand of each point are considered as independent variables at the same level as the stability constants. In the previous methods, the minimisation of the function U is carried out by considering only the stability constants as adjustable parameters, while [M] and [L] are calculated by simultaneous solution of the mass balance equations (16) and (17) for each point. In this way, only the mass balance equation (18) of the acid carries the error whereas the other two are rigorously satisfied. This is wrong in principle, as the values of T_M and T_L are experimental quantities affected by an error as well as the values of T_H.

Further, by considering [M] and [L] as adjustable parameters, the analytical differentiation of the function U is feasible, making the computation faster and more rigorous.

From the above discussion, we can conclude that the Gauss–Newton method with unit weights is the procedure to be preferred in the computer refinement of stability constants.

[1/2445 *Received*, 21*st December*, 1971]