SUPERQUAD: An Improved General Program for Computation of Formation Constants from Potentiometric Data

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A new computer program has been developed in which formation constants are determined by minimisation of an error-square sum based on measured electrode potentials. The program also permits refinement of any reactant concentration or standard electrode potential. The refinement is incorporated into a new procedure which can be used for model selection.

The computer program MINIQUAD [1-3] has been widely used to calculate formation constants of species in solution equilibria from data obtained by potentiometric titration. As systems of ever increasing complexity have been examined, it has become apparent that improvements are needed in order to deal with some chemically significant problems of current interest.

First, there is a need to be able to treat data relating to substances which cannot be obtained in a state of high purity. These substances may be of biological origin, or may be extremely difficult to synthesise; in either case it is not unusual for the quantity available to be only a few milligrams, making purification difficult. Early attempts to allow for impurities were made by Sillén's group, including a contribution by one of us (A. V.),[4] and in the program ACBA [5] which applied to acid–base titrations, but no general approach has been implemented.

Secondly, the model selection criteria need to be improved. With MINIQUAD, application of statistical tests [6] based on the sum of squared residuals was hampered by the difficulty of relating calculated statistics to experimental errors. To remedy this, the program MIQUV [7] was developed in which the minimisation is based on measured electrode potentials. This program uses difference formulae to calculate certain derivatives, thus introducing non-experimental errors, which limit its usefulness.

A third and related problem concerns the treatment of formation constants which assume negative values during a refinement. Because a negative formation constant is physically meaningless, it has been the usual practice to 'reject' immediately formation constants which become negative during a refinement, and in so doing terminate and begin another with a different model. Experience has shown, however, that such rejection may be premature, as when MINIQUAD was modified to allow convergence under such circumstances.[8] It would be more logical to reject a model with a negative formation constant, than to reject the constant itself from a refinement.

Fourthly, it may be possible to take account of some systematic errors, as suggested by Sillén,[9] and others,[5,10] or to cater for non-standard electrode response.[11]

We have now developed a new program, SUPERQUAD,[12] which has been designed to SUPERcede miniQUAD by providing the facilities identified above in addition to those offered previously. The new program was evolved from MIQUV [7] *via* the unpublished program BETAREF in which analytical formulae were used for all derivatives, but modifications have been so extensive that little of the original code remains intact. A related paper gives an illustration of the use of SUPERQUAD with impure synthetic tetrapeptides;[13] those systems defied analysis with the MINIQUAD program.

Theory

Assumptions.—There are a number of assumptions underlying the whole treatment, and each needs to be considered explicitly.

1. For each chemical species $A_aB_b\ldots$ in the solution equilibria there is a chemical constant, the formation constant, which is expressed as a *concentration* quotient [equation (1)].

$$\beta_{ab}\ldots = \frac{[A_aB_b\ldots]}{[A]^a[B]^b\ldots} \quad (1)$$

A,B ... are the reactants (SUPERQUAD allows up to four of them) and [A], [B] are the concentrations of 'free' reactant; electrical charges may be attached to any species, but they are omitted for the sake of simplicity in this discussion. Since the thermodynamic definition of a formation constant is as an *activity* quotient, it is to be assumed that the quotient of activity coefficients is constant, an assumption usually justified by performing the experiments with a medium of high ionic strength.

2. Each electrode present exhibits a pseudo-Nernstian behaviour, equation (2), where [A] is the *concentration* of the

$$E = E^\circ + S_L \log [A] \quad (2)$$

electro-active ion, E is the measured potential, and E° the standard electrode potential. The ideal value of the slope, S_L, is of course RT/nF, but we assume only that it is a constant for a given electrode. The values of E° and S_L are usually obtained in a separate calibration experiment. If a glass electrode is calibrated in terms of hydrogen-ion *concentrations*, following Irving *et al.*,[14] we create an equivalent potential according to equation (3).

$$E = 10 + RT/nF \times \text{pH} \quad (3)$$

The alternative calibration method uses measurements in volts and determination of E° from a Gran plot derived from a titration of strong acid with strong base.[15] The electrode calibration problem has been reviewed recently.[16]

3. Systematic errors must be minimised by careful experimental work. Sources of systematic error include electrode calibration, sample weighings and dilutions, standardisation of reagents (use of carbonate-free alkali in particular), temperature variation and water quality. The last-named factor is more significant today than it was in the past, as water may be contaminated by titratable species which can pass through distillation columns by surface action. All statistical tests are based on the assumption that systematic errors are absent from the data.

4. The 'independent' variable is not subject to error. Errors in the dependent variable are assumed to have a normal distribution. If these assumptions are true use of the principle of least squares will yield a maximum likelihood result, and computed residuals should not show systematic trends.[17]

5. There exists a model of the equilibrium system, which adequately accounts for the experimental observations. The model is specified by a set of coefficients $a,b\ldots$, one for each species formed. All least-squares refinements are performed in terms of an assumed model. Examination of a sequence of models should yield a 'best' model which is not significantly different from the 'true' model. Choice of the best model is known as 'species selection'.

The Refinement Algorithm.—The independent variable is chosen as the titre volume, as in MINIQUAD. However, we now use the measured potential as the dependent variable, as in MIQUV. Now, it is well known that electrode readings in the region of an end-point are unreliable because a small titre error can have a significant effect on them. For each electrode we can use the standard error propagation formula, equation (4), to

$$\sigma^2 = \sigma_E{}^2 + \left(\frac{\partial E}{\partial V}\right)^2 \sigma_v{}^2 \qquad (4)$$

calculate the error in measured potential, where σ^2 is the calculated variance of the measurement, $\sigma_E{}^2$ and $\sigma_V{}^2$ are the estimated variances of the electrode and volume readings, taken individually, and $\partial E/\partial V$ is the slope of the titration curve. We can then assign a weight to each observed titration point, inversely proportional to the variance at that point given by equation (4). In this way data near the end point, where $\partial E/\partial V$ is large, are given less weight than the other data. If two electrodes are present we follow Deming[18] and assign an off-diagonal covariance term $(\partial E_1/\partial V)(\partial E_2/\partial V)\sigma_V{}^2$ to connect the potentials E_1 and E_2 at each point. Thus the introduction of weights based on ideas of error propagation makes the calculation a 'rigorous' least-squares minimisation, in the sense that we follow Deming's procedure for setting up the normal equations with a weight matrix W, which is the inverse of the variance–covariance matrix.

To calculate the weights we need an estimate of the derivative $\partial E/\partial V$ at each point. This derivative can be obtained from the experimental data by using a five-point cubic first-derivative convolution filter,[19] or by an analytical formula from a calculated titration curve. The first option is the one normally used. A third option, that of unit weights, is available; it is essential for 'batch' titration data. When the derivatives have been calculated, the weight matrix W is set up. It is diagonal when one electrode is present, and 2 × 2 block-diagonal when two electrodes are present. The weight matrix enters the standard normal equations used to minimise the error-square sum by iterative refinement from some initial parameter estimates [equation (5)]: s is a vector of shifts to be applied to

$$A^{\mathrm{T}}\, W\, A\, s = A^{\mathrm{T}}\, W\, \varepsilon \qquad (5)$$

the parameters, and ε a vector of residuals in potential; A^{T} is the transpose of the matrix A. The refinement is protected against divergence by Marquart's method using code based on that of Fletcher.[1,20]

The elements of the design matrix A are the partial derivatives of potentials with respect to the parameters. However the parameters do not appear explicitly in the expression for potential [equation (2)] so an implicit differentiation is required, equation (6), where $[X_i]$ is the concentration of the ion to which the ith electrode responds, and p_j is the jth parameter. The reason for the appearance of p_j on both sides of equation (6)

$$p_j\frac{\partial E_i}{\partial p_j} = p_j\frac{\partial E_i}{\partial [X_i]}\frac{\partial [X_i]}{\partial p_j} = p_j\frac{S_L}{[X_i]}\frac{\partial [X_i]}{\partial p_j} \qquad (6)$$

will shortly become clear. The values of $[X_i]$ are obtained in terms of the model by solving the set of non-linear equations of mass-balance (7) applicable to each reactant. $T_A, T_B\ldots$ are the

$$\begin{aligned} T_A &= [A] + \sum_k a_k \beta_{a_k b_k}\ldots [A]^a[B]^b\ldots \\ T_B &= [B] + \sum_k b_k \beta_{a_k b_k}\ldots [A]^a[B]^b\ldots \\ &\ldots \qquad\qquad \ldots \end{aligned} \qquad (7)$$

total concentrations of reactants A,B... and there are assumed to be k complex species formed. A different set applies at each titration point. They are solved iteratively by Newton's method. Initial estimates of the free concentrations [A],[B]... are obtained as follows.

At the first point in a titration curve, equation (2) is used to obtain an estimate of the free concentration of the electroactive ions. The other free concentrations are taken as one thousandth of the corresponding total concentration. Initial estimates at other titration points are taken as the values calculated at the preceding point. The refinement calculates the shifts δ[A],δ[B]... from the residuals in total concentration, $\delta T_A\ldots$, *via* equations (8). The derivatives on the left-hand side

$$\begin{bmatrix} [A]\dfrac{\partial T_A}{\partial [A]} & [B]\dfrac{\partial T_A}{\partial [B]} & \ldots \\ [A]\dfrac{\partial T_B}{\partial [A]} & [B]\dfrac{\partial T_B}{\partial [B]} & \ldots \\ \ldots & \ldots & \ldots \end{bmatrix} \begin{bmatrix} \delta[A]/[A] \\ \delta[B]/[B] \\ \ldots \end{bmatrix} = \begin{bmatrix} \delta T_A \\ \delta T_B \\ \ldots \end{bmatrix} \qquad (8)$$

are obtained easily from equations (7). The off-diagonal terms are given by expressions such as equation (9). Note that the

$$[B]\frac{\partial T_A}{\partial [B]} = [A]\frac{\partial T_B}{\partial [A]} = \sum_k a_k b_k \beta_{a_k b_k}\ldots [A]^a[B]^b\ldots \qquad (9)$$

matrix is symmetrical. The diagonal terms are given by an expression such as that given by equation (10).

$$[A]\frac{\partial T_A}{\partial [A]} = [A] + \sum_k a_k{}^2 \beta_{a_k b_k}\ldots [A]^a[B]^b\ldots \qquad (10)$$

In some circumstances, usually when one or more formation constants are negative, the true solution to the equations (7) requires one or more negative free concentrations. As this is physically meaningless, some action must be taken. We have decided to constrain the parameter refinement in such a way as to ensure that free concentrations are always positive.

To obtain the derivatives $\partial[X_i]/\partial p_j$ required in equation (6), we first identify $[X_i]$ with one of the entities [A],[B]... and then obtain the derivatives by implicit differentiation[21] of the equations (7). Consider first the case where the parameters concerned are the formation constants, *i.e.* put β_j in place of the generalised parameters p_j in equation (6). We must now solve a set of linear simultaneous equations (11).

There are a number of points to notice. First, the matrices of coefficients in equations (8) and (11) are the same. So, having solved the system (8) for [A],[B]... the coefficients do not need to be re-calculated. Furthermore in solving (8) the matrix has already been Choleski-factored. Next, only one or at most two derivatives $\partial[X_i]/\partial\beta_j$ are needed, so the whole system does not need to be solved. Lastly, we use the relative derivatives $\beta_j(\partial T_A/\partial\beta_j)\ldots$ because these are obtained from equation (7) as

$$\begin{bmatrix} [A]\frac{\partial T_A}{\partial [A]} & [B]\frac{\partial T_A}{\partial [B]} & \cdots \\ [A]\frac{\partial T_B}{\partial [A]} & [B]\frac{T_B}{\partial [B]} & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix} \begin{bmatrix} \frac{1}{[A]}\beta_j\frac{\partial [A]}{\partial \beta_j} \\ \frac{1}{[B]}\beta_j\frac{\partial [B]}{\partial \beta_j} \\ \cdots \end{bmatrix} = \begin{bmatrix} -\beta_j\frac{\partial T_A}{\partial \beta_j} \\ -\beta_j\frac{\partial T_B}{\partial \beta_j} \\ \cdots \end{bmatrix} \quad (11)$$

simple multiples of species concentrations. This is the reason for the appearance of p_j on both sides of equation (6).

Other parameters can be refined if we replace β_j by the more general parameter p_j in equation (11). For this we require the derivatives $\partial T_A/\partial p_j \ldots$. The total concentration T_A can be written as in equation (12), where n_A is the initial amount of

$$T_A = \frac{n_A + C_A v}{v_0 + v} \quad (12)$$

reactant A, C_A is the concentration of that reactant in the burette, v_0 is the initial volume of reaction mixture, and v is the titre volume. The derivatives $n_A(\partial T_A/\partial n_A)$ and $C_A(\partial T_A/\partial C_A)$ are easily obtained from equation (12), so that total quantity and burette concentrations are possible parameters. The derivative $v(\partial T_A/\partial v)$ permits us to calculate $\partial E/\partial v$, the slope of the calculated titration curve which can be used to set up the weights. Another parameter which can be refined is E° since direct differentiation of equation (2) gives $E^\circ(\partial E/\partial E^\circ) = E^\circ$.

When $n_A, C_A \ldots$ or E° are treated as variables, we term them *dangerous parameters*. Their use is clearly questionable unless their values cannot be established with sufficient accuracy by any known chemical method. Dangerous parameters may be refined individually or certain constraints may be introduced. We have in mind the situation in which a stock solution contains a reagent of uncertain purity. When two or more titration curves are obtained using this solution it is clear that the calculated concentration of that solution must be the same in all titration curves. The constraints are implemented by setting equal the *relative* shifts of constrained parameters. In this way the amount of a reactant present in each curve is the same proportion of the amount given at the beginning of the calculation, and we can determine the purity of a reactant. Burette concentrations are constrained to be equal by setting them equal at the start of the calculation, and then applying the same relative shift.

Other dangerous parameters could be implemented by utilising the general procedure for evaluating $\partial E/\partial p_j$, using explicit or implicit differentiation as required. In fact in MIQUV[7] there is a modified Nernst equation (13). This

$$E = E^\circ + S_L \log [H^+] + r[H^+] + s[H^+]^{-1} \quad (13)$$

equation was first suggested as a means of taking into account junction potentials in strongly acidic and strongly basic conditions.[22] Early versions of the new program included the r and s parameters, but after careful consideration we concluded that the corrections given by equation (11) are of such limited validity as to render them of little use, and these parameters were removed from the program.

General Strategy.—In most of our work the problem is to find a model which gives a satisfactory fit to the experimental data. To this end the refinement is but the central part of a scheme designed to facilitate the model selection process. A greatly simplified flow diagram of the scheme is shown in Figure 1. At (*i*) we read in the titration data and a 'basis set' of formation constants. Associated with each formation constant are the stoicheiometric coefficients *a,b* ... and a refinement key which may be 1, 0, or −1. If the key is zero then β is held constant. If it is 1, β is refined, and if it is −1, β is ignored. When a new model is read in at (*ii*) the refinement keys are changed. In this way a sequence of models can be examined comprising any combination of the formation constants in the basis set held constant, refined, or ignored. (In MINIQUAD[1] the zero keys could not be changed.) Each model is encoded into an integer and a check is made to ensure that no model is done (refined) twice (*iii*).

As the sequence of models progresses, the data for the best model are stored at (*iv*). The best model is taken as the one with the lowest sample standard deviation (see below) and no ill-defined formation constants. We say a formation constant is ill-defined if its calculated standard deviation is more than 33% of its value, or if its value is negative.

Each model examined uses as initial estimates the formation constants stored with the best model (*v*) before proceeding to the refinement (*vi*). The refinement is extensively protected against computer failures, but in the event of failure (*vii*) a new model is immediately requested. If the refinement converges successfully the parameter values, errors, and correlation coefficients are given in the first output routine (*viii*) together with a χ^2 statistic based on weighted residuals, as in MIQUV.[7] There is also an s statistic (the sample standard deviation) defined by equation (14), where m is the number of data observations, and n the

$$s = \left[\frac{\varepsilon^T W \varepsilon}{m - n}\right]^{\frac{1}{2}} \quad (14)$$

number of parameters in a refinement. In an ideal case s should be one, meaning that the data have been correctly weighted using appropriate values of σ_E and σ_V, and that the requirements of the assumptions *1*—*5* are fulfilled.

A check is then made to see if any formation constant is ill-defined (*ix*). If an ill-defined constant is found (it will be signalled by the word 'excessive' or 'negative' in place of the standard deviation value in the first output routine), the model is rejected, the refinement key of the 'worst' β is set to −1, and the new model thus generated becomes the next model for refinement (*x*). If no ill-defined formation constant is found, the second output routine (*xi*) is entered in which a full range of diagnostics, including plots of residuals and species distributions, is available. Note that these diagnostics are not available for models rejected at (*ix*), nor can such a model become the best one at (*iv*).

Discussion

SUPERQUAD is an extremely powerful general purpose computer program for stability constant work. It can handle data from all known systems of potentiometric titration. These include batch titrations,[23] electrode readings in pH or millivolts, alkali added or generated coulometrically, and determinate systems where the number of electrodes is equal to the number of reactants. It can cater for ion-selective electrodes whose response slope is other than Nernstian, and in principle could be modified for other non-Nernstian responses. Titration curves of different types can be mixed together.[2] Refinement of

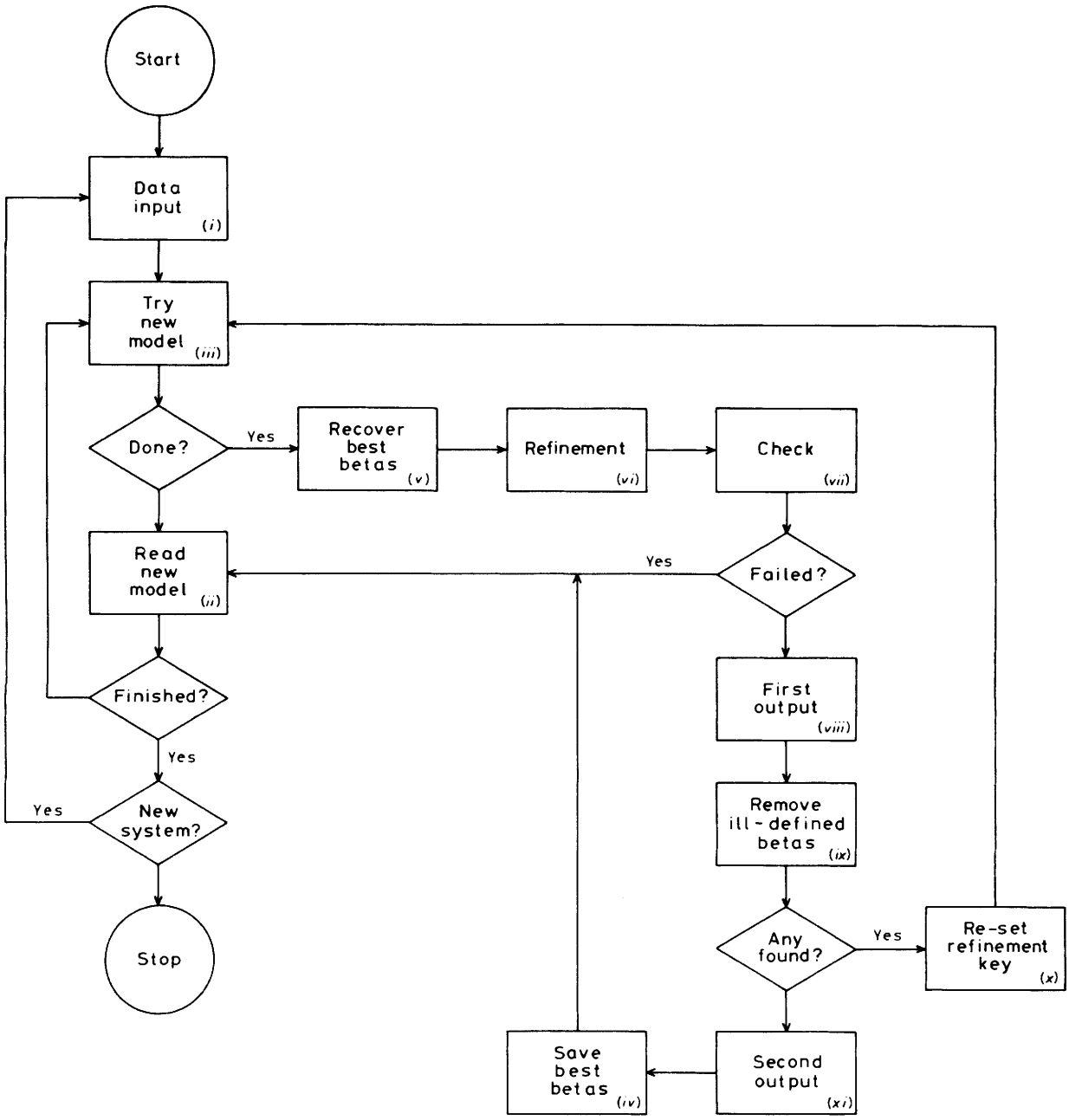

Figure 1. Simplifed flow-diagram of the species selector in SUPERQUAD

total and burette concentrations and standard potentials are individually possible, and concentrations can be constrained either equal, or of equal purity.

For the first time some model selection criteria are incorporated into the program. If, after refinement a formation constant is found to be ill-defined, a new model is automatically generated. We have found that when rejection of a single ill-defined constant takes place, the model generated converges rapidly (two or three cycles) to a very similar result, confirming the hypothesis that the formation constant was ill-defined because the corresponding species had little effect on measured potentials, due to its low overall concentrations. By not rejecting negative formation constants during a refinement it is possible that they may finish up positive again, and be well-defined. This has been observed to happen,[8] and aids the model-selection process.

Because the refinement is based directly on measured quantities, it is relatively easy to decide when a fit is satisfactory. It has been proposed that any fit with s less than 3 is satisfactory.[23] We re-iterate this proposal, although values nearer to one are often found when a single titration curve is involved. However, it is essential that σ_E and σ_V, equation (4), be estimated realistically, since the statistical interpretation of the results is absolutely dependent on these quantities. The error σ_E represents the error in the system comprising potentiometer, indicator and reference electrodes, and interconnections including any salt bridges that may be used. For a good experimental set-up a value of 0.1 mV or 0.002 pH units appears to be satisfactory. We have estimated σ_V by careful weighing of the liquid delivered by the microsyringe which serves as the burette.

By taking some explicit account of errors in burette readings it has become easier to treat data from complete titration

curves. When using MINIQUAD it was common practice to omit from the calculation data obtained near end-points. These points can now be included because they are assigned small weights.

Mathematically the program represents a major advance in its use of implicit differentiation[21] to obtain some derivatives. The method is a general one, and means that in future analytical formulae could be obtained for any desired derivatives.

The program has been extensively tested on experimental data of various types, and from various laboratories. Surprisingly it was always found that the residuals showed some systematic trends. The most surprising result came from a phthalic acid–alkali titration, in which the residuals obtained with both SUPERQUAD and MINIQUAD showed similar systematic trends.

We have also constructed various sets of synthetic data on the assumption that the only errors present were normally distributed errors in titre and potentiometer system. Refinements on these data gave residuals which did not show systematic trends. Since the synthetic data conformed to the assumptions *1*—*5*, we can only conclude that one or more of these assumptions is invalid for experimental data, and this results in systematic trends appearing in the residuals.

It might be thought that one could use the dangerous parameters to eliminate the systematic errors in concentrations and standard potentials. This is an extremely dangerous procedure because changes in concentration can mask or mimic other systematic errors in the data. We cannot stress too strongly that the use of dangerous parameters cannot be a substitute for careful experimental procedures. The case for treating $E^{\ominus}$ as a variable is different, because of the problems associated with electrode calibration.[16]

In developing this new program we have taken the opportunity to make data input more user-friendly, and have tailored all the output to a maximum width of 80 characters for ease of use with a variety of terminals and printers. The FORTRAN code conforms to the requirements of 'Compatible Fortran'[24] and has also been checked using the PFORT compiler.[25] We therefore expect that the program will run without difficulty on most computers, and this has been checked on various machines in Leeds and Florence. Details concerning the availability of the program, test data and results, and a comprehensive users manual can be obtained from P. G.

The Nickel–Glycine System.—This system has been studied in many laboratories and provides a useful benchmark by which to test experimental and computational techniques.[26] Further, Braibanti *et al.*[27] have suggested that systematic errors in one series of experiments may be considered as random when many series are considered.

In the titration of glycine (denoted as HL) with base there is a very sharp end-point. Fitting of two titration curves gave log

Table. Results from titrations of nickel(II) and glycine (HL) with alkali

Curve	$\log \beta_{NiL}$	$\log \beta_{NiL_2}$	$\log \beta_{NiL_3}$	s	χ^2
1	5.627(1)[a]	10.434(1)	13.992(1)	1.4	8.8
2	5.634(2)	10.400(2)	13.899(3)	2.1	12.6
1 + 2	5.630(5)	10.422(4)	13.963(4)	7.2	32.6
1 + 2[b]	5.629(5)	10.397(13)	13.846(41)	2.1	16.9
Literature[c]	5.631(10)	10.399(10)	13.907(23)[d]		

[a] Figures in parentheses are the computed standard deviations. [b] Included refinement of four dangerous parameters. [c] Ref. 27. Figures in parentheses are the standard deviations computed from seven independent determinations. [d] This value was obtained using some data up to pH 11.5 and with models that included other complexes.

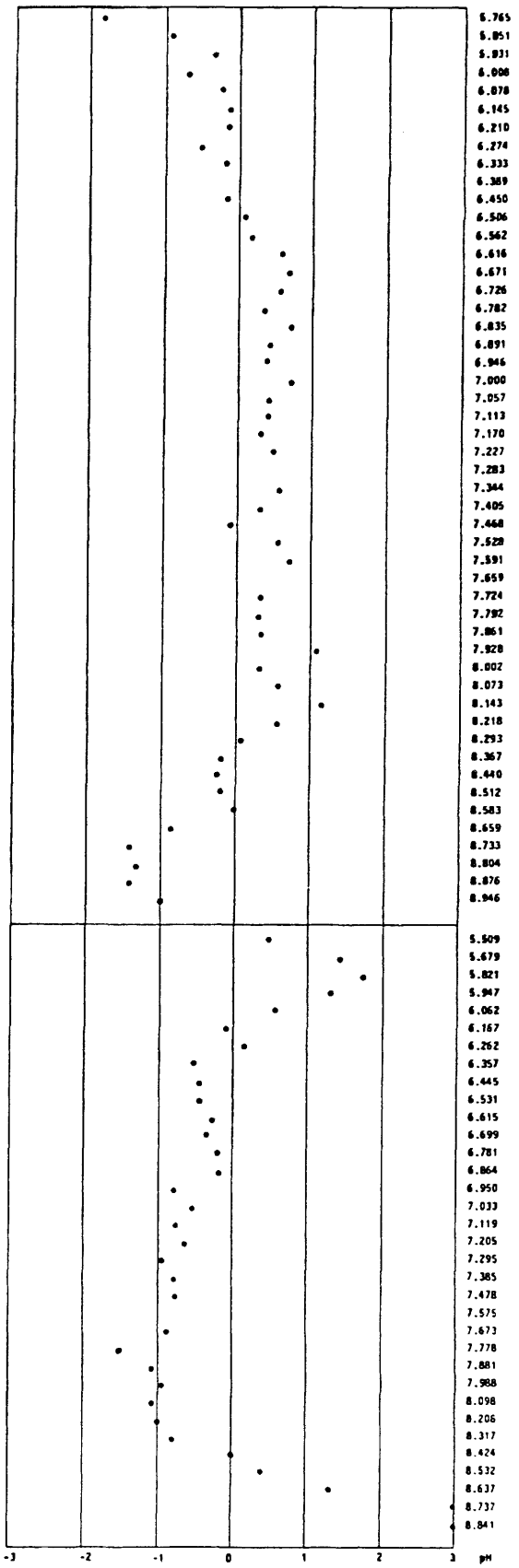

Figure 2. Plots of residuals corresponding to the result in the fourth line of the Table. The horizontal scale is in units of s (the sample standard deviation)

$\beta_{HL} = 9.645 \pm 0.003$ and $\log \beta_{H_2L} = 12.060 \pm 0.006$, in good agreement with published values.[27]

Samples of nickel(II) and glycine (mol ratio 1:3.24) were titrated with two different alkali solutions. Excellent fits were obtained when each curve was treated separately, as shown in the Table, though selection of the data range was important in obtaining good fits. At low pH it corresponds to *ca.* 20% formation of the complex $[NiL]^+$; data at pH 9 and above were omitted following published recommendations.[26]

When the two curves were refined together, however, the resultant statistics were unacceptable, and the residuals in both curves showed a marked overall slope (in opposite directions). It seemed likely that this might be caused by errors in the alkali standardisations, so these, and the amount of acid added initially, were refined. The alkali concentrations changed from 0.2454 to 0.2399 and from 0.3674 to 0.3644 mol dm^{-3}, and T_H changed by *ca.* 1%. These changes are just within the bounds of credibility. They resulted in a much improved set of statistics and a reasonable scatter of residuals, as shown in Figure 2. However, the residuals still show some systematic tendencies, despite the fact that the model is known with some certainty. This suggests some departure from the assumptions given in the Theory section. It is nothing to do with the weighting scheme, as the weights are virtually equal since the relationship of pH to titre is nearly linear. The source of the systematic tendencies remains a matter for speculation since we cannot identify systematic errors that might cause them, but it is important to recognise that the systematic errors must have a small effect on the accuracy to which a formation constant is known. When the fit is as good as that shown in Figure 2, we suggest that the accuracy is comparable to the precision, and this is confirmed by concordance of our results with the 'general grand averages' given by Braibanti *et al.*[27]

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