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A COMPUTER METHOD FOR THE CALCULATION OF ENTHALPY CHANGES FOR ION ASSOCIATION IN SOLUTION FROM CALORIMETRIC DATA

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ABSTRACT

A general method for the determination of enthalpy changes in solution for systems containing an unlimited number of components, that can give rise to mononuclear, polynuclear, protonated, hydroxo and mixed species was set up.

A computer program, DOEC, able to elaborate data of a calorimetric titration such as concentrations, changes of the mole number of the various species, solution ionic strength and reaction enthalpy was written. The program can also correct the ionic strength changes, that can occur during a titration. Thanks to the analogy of the mathematical expressions, the program can also be used for the treatment of spectrophotometric data.

INTRODUCTION

For a while this research laboratory has been dealing with the determination of the thermodynamic parameters involved in complex formation in aqueous solution [1—5]. Thus we thought it useful to set up a computer program as general as possible, in other words, able to work out any problem from the simplest, such as the determination of the protonation enthalpy of a weak acid, to the most complicated, such as the determination of the formation enthalpy of ternary and protonated or hydroxo ternary complexes. To attain this object it is necessary to solve some important problems; first of all that concerning the determination of the species concentration in systems more or less complicated. This problem has been tackled by many authors by different methods [6—8]; we have chosen a modification of the method proposed by Ting Po I and Nancollas [8], which seems to be the most suitable for systems with no more than five mass balance equations.

Another problem is represented by the possible ionic strength change; in

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fact reagents comparatively concentrated are used for a calorimetric more often than for a potentiometric titration. Furthermore, a problem equivalent to the previous one is the determination of ΔH at different ionic strengths, in order to obtain the thermodynamic parameters at $I = 0$.

Moreover, it is necessary to take into account all possible methods employed when carrying out a titration; in other words, it must be specified whether the titrant is a strong or weak acid or base, a metal or a ligand. Furthermore, some of the species present in the titrant can undergo dissociation when added to the solution, with consequent thermic effects.

Working out most of these problems has been the aim of the present study. Several papers have been written on the various methods adopted to carry out the calorimetric (or mathematically equivalent spectrophotometric) data analysis [9—17]. In our opinion none of the methods reported in the literature are sufficiently general and simple. LETAGROP KALLE [11,18] represents the most relevant example of a computer program able to analyze calorimetric titration data. This program, however, besides being fairly complicated and slow, is not able to deal, in the present version, with systems having more than three mass balance equations and, moreover, it disregards possible ionic strength changes.

METHOD

If M components react in solution according to the equation

$$p_{1j}C_1 + p_{2j}C_2 + \cdots + p_{Mj}C_M = s_j \tag{1}$$

to form the j-th species, s_j, the stoichiometric coefficients of which are P_{ij} ($i = 1, 2 \cdots M$), the analytical concentrations, A_i, the free concentrations, a_i, the concentrations of the different species, s_j, and the formation constants, β_j, are bound by the following relations

$$\beta_j = s_j(\prod_i a_i^{p_{ij}})^{-1} \tag{2}$$

$$A_i = a_i + \sum_j p_{ij}s_j \tag{3}$$

The determination of the component free concentrations (and therefore, through eqn. (2), of the species concentration) consists in solving a system of M non-linear equations

$$A_i = a_i + \sum_j p_{ij}\beta_j(\prod_i a_i^{p_{ij}}) \tag{4}$$

Several methods have been used to solve the system of equations (4); the method proposed by Ting Po I and Nancollas [8] seems to be the most suitable for our problem, since we deal with systems having between two and five mass balance equations; this method, in turn, is based on a modified Newton—Raphson's method with scaling of the matrix and eigenvector analysis [8,19].

Its greater disadvantage lies in the necessity of having good initial values of the free concentrations in order to avoid the divergence of the iterative procedure. This obstacle can be overcome by calculating the free concentrations using the iterative formula

$$a_k = a_{k-1} \exp(\ln R q^{-1}) \tag{5}$$

where $R = A_{\text{given}} \times A_{\text{calc}}^{-1}$; $q = (|\log R| + 4)/2$; k = iteration index.

By resorting to eqn. (5), it is sufficient to make the initial approximation $a_i = A_i$. After a few iterations a value accurate enough to be used as the initial value for the Newton—Raphson method is obtained. We have made use of a combination of eqn. (5) with Newton—Raphson's method, giving up the idea of using (5) throughout because after the first iterations, it reaches the convergence slowly; a simplified form of eqn. (5) can be used [20] as the only iterative method only when M is greater than five. When, in a titration, several points are taken into consideration, the values of a_i obtained for the $k - 1$ point can be used as starting values for the k-th point, also using an interpolation method [21], thus saving iterations and therefore computing time.

Once the free concentrations, a_i, and therefore the species concentrations, s_j, are determined, the concentration changes during a titration can be calculated. These are expressed, in mmoles, by the relation

$$\delta n_{j,k} = s_{j,k} V_k - s_{j,k-1} V_{k-1} \tag{6}$$

where k is the index of the titration point and V is the total volume. At this point the following equation for the calculation of the reaction enthalpy changes can be formulated

$$-Q_{\text{corr},k} = \sum_j \Delta H_j \delta n_{jk} \tag{7}$$

If the titrant is not constituted by a single component, eqn. (6) must be changed to

$$\delta n_{j,k} = s_{j,k} V_k - s_{j,k-1} V_{k-1} - s_j'(v_k - v_{k-1}) \tag{6a}$$

where s_j' is the concentration of the j-th species in the titrant and v is the titrant volume.

Equation (7) can be solved by the linear least-squares method, by minimizing the function

$$U = \sum_k w_k (Q_{\text{corr},k} - Q_{\text{corr,calc},k})^2 \tag{8}$$

The weight w to be attributed to each experimental point is given statistically by $w = \sigma_Q^{-2}$. Unfortunately, the σ_Q value is hardly determinable. Thus a value of w equal to 1 is generally assumed for all points. We have seen that a different weighting can be advantageously used in some cases; thus, when the Q values differ markedly from each other, it can be assumed $w = Q^{-2}$, yet, when the δn values of the species, the ΔH of which is to be calculated, varies markedly from point to point, it can be set $w = f(\delta n)$. Although these two ways of weighting have no theoretical basis, they can be of considerable help towards the solution of this least-squares problem. Also in this case, the normal equations have been solved by scaling the coefficient matrix and calculating the inverse matrix through the calculation of the eigenvectors and eigenvalues [8—19].

As already mentioned, one often has to deal with titrations where more or less relevant changes of the ionic strength can take place. In this case, the following expressions giving $\log \beta$ and ΔH as functions of the ionic strength must be taken into account

$$\log \beta_{(I=0)} = \log \beta + g(z)f(I) \qquad (9)$$

$$\Delta H_{(I=0)} = \Delta H + RT^2 g(z)f'(I) \qquad (10)$$

where

$$g(z) = (\sum_i p_i z_i)^2 - \sum_i p_i z_i^2;\ f(I) = A(\sqrt{I}/(1 + B\sqrt{I}) - CI)$$

and $f'(I) = \partial f(I)/\partial T$ (A is the Debye—Huckel constant, $A = 0.511$ at 25°C). In eqns. (9 and 10) $B = 1.5$ and $C = 0$, and $B = 1$ and $C = 0.3$ according to Scatchard [22] and Davies [23], respectively. When using the above values for B and C, excellent approximations are obtained in the ionic strength range 0—0.2. The ionic strength of the solution is calculated iteratively as the $\log \beta$ values are corrected. At the end of the calculation also the ΔH values obtained are corrected if there are some changes in the ionic strength.

The program DOEC * (Determination Of Enthalpy Changes) is written in FORTRAN IV and consists of the MAIN, ten SUB ROUTINES and a FUNCTION. These parts of the program are briefly elucidated below.

MAIN reads the general data (number of components, number of species, formation constants, etc.) and controls all the program.

DATI reads the calorimetric titration data.

TERWA calculates the thermodynamic parameters relative to the water formation by means of the functions $\log K_w = f(T, I)$ and $\Delta H_w = f'(T, I)\, RT^2$-ln 10. If the approximation obtained through these equations is not sufficient ($0 < T < 60$°C or $I < 0.2$), ΔH_w and $\log K_w$ can be read by the program.

G calculates f(I) (see eqn. (9)).

GUESSA calculates the starting values of the free concentrations to be determined by FREE.

FREE calculates the free concentrations of the components. To solve the matrix of coefficients (inversion) recalls SCALE, JACOBI and MIAVA.

SCALE scales the coefficient matrix. It is recalled by FREE and LIREG.

JACOBI calculates the eigenvectors and eigenvalues of the coefficient matrix. It is recalled by FREE and LIREG.

MIAVA calculates the coefficients of the inverse matrix. It is recalled by FREE and LIREG.

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* The listing together with the input instructions are available on request.

DELTAN calculates δn, I and $Q_{corr} = Q_{exp} - Q_{dil} - Q$(formation of water) $- Q$(formation of species with known ΔH).

LIREG does the linear regression.

OUT prints out all the results.

RESULTS AND DISCUSSION

The program DOEC has already been used in our laboratory for some years [1—5]. To check the goodness of the results, some systems, reported in the literature [24,25], have been analyzed by our program; the results obtained were extremely consistent with those of the literature. Moreover, some of our systems have been elaborated also by the program CALOR [9]; also in this case we obtained quite coincident results.

The program DOEC allows the utilization of most of the data that can be obtained by calorimetric titrations. Both computing time and storage locations required are so modest as to allow the use of this program also on medium-sized computers. In fact, in the version with five mass balance equations 20 K storage locations are required; computing the reaction enthalpies of a system with five mass balance equations [26] (95 titration points, 15 species, 2 ΔH values to be calculated) requires less than 1′ on a CDC CY 7600 computer.

The possibility of correcting the ionic strength during a calorimetric titration has been proved to be particularly useful. In fact, under low ionic strength conditions, i.e., $I = 0.05$—0.2 mole dm^{-3}, fluctuations >10% often occur, with the consequent introduction of large errors in the ΔH determination.

The simultaneous determination of $\log \beta$ and ΔH has often been attempted more or less successfully; some comments on the limits of this kind of calculation have been reported [27,28]. It is our intention to tackle this problem again; for the present study, we paid attention to the correct calculation of ΔH values. We have also tried to determine simultaneously ΔH and $\log \beta$ for some very simple systems, by varying systematically $\log \beta$ and calculating the "best" value directly from the function $U = f(\log \beta)$ per $U = U_{min}$. Once defined the range, $RP = 2(5 - I)/5$, where $I = 1 \cdots 4$ (I is chosen depending on the degree of approximation of the $\log \beta$ values available), within starting value is $\log \beta_{in} = \log \beta - RP/2$, and the increments will be given by $\delta \log \beta = 0.4 \times 2^{(1-I)}$. From the minimum of the plot U vs. $\log \beta$ the "best" value of $\log \beta$ can be obtained. It has been useful in some cases to check the formation constant values by means of calorimetric data [5,29]. This simple method applied to a formation constant alone allows a good "internal check" of the calorimetric equipment when systems, the formation constants of which are well known, are investigated.

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