

IONIC STRENGTH DEPENDENCE OF FORMATION CONSTANTS. XVII.  
THE CALCULATION OF EQUILIBRIUM CONCENTRATIONS AND  
FORMATION CONSTANTS.

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**Summary** - Calculation methods for the study of equilibria in solution, in non constant ionic strength conditions, are described. Two problems, in particular, are considered: (a) the calculation of equilibrium concentrations, and, (b) the calculation of formation constants from potentiometric measurements. For these problems, two computer programs, BSTAC and ES4ECI, have been written, and are discussed in detail.

**Riassunto** - In questo lavoro vengono descritti alcuni metodi di calcolo per lo studio di equilibri in soluzione in condizioni di forza ionica variabile. Due problemi, in particolare, vengono considerati: (a) il calcolo delle concentrazioni all'equilibrio, e, (b) il calcolo delle costanti di formazione da dati potenziometrici. Per questi problemi sono stati scritti due programmi, BSTAC ed ES4ECI, che sono discussi in dettaglio.

#### INTRODUCTION

In preceding papers we reported some calculation methods and computer programs for the study of equilibria in solution<sup>1-11</sup>. Moreover, in a series of investigations on ionic strength dependence of formation constants<sup>12-16</sup> and on the formation of weak complexes<sup>17-20</sup>, it was necessary to modify some computer programs in order to take into account non constant ionic strength experimental conditions. Since this problem implies fairly important

modifications, we thought it useful to report here the complete description of two computer programs (written in BASIC language) concerning the calculation of equilibrium concentrations and the calculation of formation constants. This paper collects the decennary experience of our research group on this matter, partially reported in several preceding works.

#### IONIC STRENGTH DEPENDENCE OF ACTIVITY COEFFICIENTS

Let us consider the generic reaction among components  $X_i$  to give the species S ( $p_i$  = stoichiometric coefficients;  $z_i$  = charges)



with  $i = 1 \dots n$ , and having the equilibrium constant

$$\beta = [S] \left\{ [X_1]^{p_1} [X_2]^{p_2} \dots [X_i]^{p_i} \dots [X_n]^{p_n} \right\}^{-1} \quad (2)$$

By taking into account activity coefficients  $f_i$  and  $f_s$  we can express the equilibrium constant at infinite dilution (thermodynamic equilibrium constant) as

$$\tau \beta = \beta f_s \left( f_1^{p_1} f_2^{p_2} \dots f_i^{p_i} \dots f_n^{p_n} \right)^{-1} \quad (3)$$

Activity coefficients can be expressed by

$$\log f_z = - z^2 A \frac{\sqrt{I}}{1 + \alpha B' \sqrt{I}} + C_z I + D_z I^{3/2} \quad (4)$$

i.e., by a Debye-Hückel type equation with two additional linear terms. A and  $B'$  are the Debye-Hückel parameters and  $\alpha$  is the ion-dimensional parameter.  $C_z$  and  $D_z$  are empirical coefficients. In general one uses  $\alpha B' = B$ ; and by setting  $\sqrt{I} = J$ , equation (4) becomes

$$\log f_z = - z^2 A \frac{J}{1 + BJ} + C_z J^2 + D_z J^3 \quad (5)$$

Equation (3) can be written

$$\log \tau \beta = \log \beta + \log f_s - \sum_1^n p_i \log f_i \quad (6)$$

and by substituting  $\log f_z$  [eq.(5)] into (6), we obtain

$$\log {}^T \beta = \log \beta - \left( z_s^2 - \sum p_i z_i^2 \right) A \frac{J}{1 + BJ} + \\ + \left( C_{z_s} - \sum p_i C_{z_i} \right) J^2 + \left( D_{z_s} - \sum p_i D_{z_i} \right) J^3 \quad (7)$$

Following the hypothesis that it is possible to express the dependence on ionic strength of formation constants by a simple equation independent of the type of reactants, and only dependent on the type of reaction, activity coefficients will thus depend on charge only. If the dependence of C and D on  $z^2$  is linear we have

$$\left. \begin{array}{l} C_{z_i} = c_0 + z_i^2 c_1 \\ D_{z_i} = d_0 + z_i^2 d_1 \end{array} \right\} \quad (8)$$

and therefore

$$\log {}^T \beta = \log \beta - \left( z_s^2 - \sum p_i z_i^2 \right) A \frac{J}{1 + BJ} + \\ + \left( c_0 + z_s^2 c_1 - c_0 \sum p_i - c_1 \sum p_i z_i^2 \right) J^2 + \\ + \left( d_0 + z_s^2 d_1 - d_0 \sum p_i - d_1 \sum p_i z_i^2 \right) J^3 \quad (9)$$

$$\log {}^T \beta = \log \beta + z^* A \frac{J}{1 + BJ} - (p^* c_0 + z^* c_1) J^2 - \\ - (p^* d_0 + z^* d_1) J^3 \quad (9a)$$

or

$$\log \beta = \log {}^T \beta - z^* A \frac{J}{1 + BJ} + C J^2 + D J^3 \quad (9b)$$

with

$$\left. \begin{array}{l} z^* = \sum p_i z_i^2 - z_s^2 \\ p^* = \sum p_i - 1 \end{array} \right\} \quad (10)$$

In general, if we take into account the formation of more than one species S, [i.e.  $S_j$  species, with  $p_j$  stoichiometric coefficients, that are on the right hand of equation (1)], equation (10) becomes

$$\left. \begin{array}{l} z^* = \sum p_i z_i^2 - \sum p_j z_j^2 \\ p^* = \sum p_i - \sum p_j \end{array} \right\} \quad (11)$$

Therefore, according to our model for the ionic strength dependence of formation constants, only  $c_0$ ,  $c_1$ ,  $d_0$  and  $d_1$  parameters must be known for any type of reaction in aqueous solution. Recently, we used a simplified version of equation (9a), i.e.

$$\log \beta = \log \tau_\beta - z^* \frac{J}{2 + 3J} + (p^* c_0 + z^* c_1) J^2 + z^* d_1 J^3 \quad (12)$$

Equation (12) comes from the following considerations: (a)  $A \approx 0.5$  (at 25 °C) and small differences are corrected in linear terms; (b)  $\Delta B' \approx 1.5$ , i.e.  $\Delta \approx 5\text{\AA}$ , as used by several authors in similar equations; (c)  $d_0 \approx 0$ . In Table 1, some values of empirical parameters for the ionic strength dependence of formation constants are reported.

TABLE 1. Values of empirical parameters for the ionic strength dependence of formation constants.

T	$c_0$	$c_1$	$d_1$	ref.
25	0.10	0.230	-0.10	(13) (a)
10	0.12	0.223	-0.10	(16) (b)
25	0.10	0.235	-0.10	
45	0.075	0.251	-0.10	
10	0.22	0.23	-0.12	(c)
25	0.20	0.215	-0.105	
45	0.17	0.19	-0.08	
10	0.20	0.213	-0.11	(18) (d)
25	0.18	0.208	-0.10	
40	0.16	0.204	-0.08	
10	0.16	0.222	-0.125	(14) (e)
25	0.10	0.209	-0.093	
37	0.05	0.199	-0.067	
45	0.03	0.192	-0.050	

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- a) Average values of preceding works on the dependence on ionic strength of formation constants.
  - b) Protonation of several carabolic acids,  $0 \leq I \leq 1M$ ,  $10 \leq T \leq 45^\circ C$
  - c) Ionic strength dependence of formation constants and of  $\Delta H^\circ$  of complex formation [A.De Robertis, C.De Stefano, C.Rigano and S.Sammartano, J.Chem.Res.,(S)194(1986)].
  - d) Studies of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  complexes of low molecular weight ligands,  $0 \leq I \leq 1M$ ,  $10 \leq T \leq 45^\circ C$ .
  - e) A review of our and literature findings.

Calculations on these data give:

$$\begin{aligned} c_0 &= 0.110 & \partial c_0 / \partial T &= -0.0016 \\ c_1 &= 0.224 & \partial c_1 / \partial T &= -0.0006 \\ d_1 &= -0.099 & \partial d_1 / \partial T &= 0.0012 \end{aligned} \quad (12a)$$

Alternative calculations give:

$$\log \beta = \log \beta^* [1 + 0.0015(T-25)] \left[ \frac{\sqrt{I}}{2+3\sqrt{I}} + 0.1 I^{3/2} \right] + I \left[ 0.11 + z^* 0.2245 - (T-25)(0.0016 - 0.001z^*) \right] \quad (12b)$$

Equation (12), with parameters (12a), and eqn. (12b) give the same fit and can be used to obtain corrections  $\Delta \log \beta = \log \beta - \log \beta^*$  with an estimated standard deviation given by

$$s(\Delta \log \beta) = (8.3 \times 10^{-4} + 6.3 \times 10^{-5}|T-25|) z^* I$$

For example, if considering the reaction  $Cu^{2+} + L^{2-} = CuL^\circ$  at 37 °C,  $s(\Delta \log \beta) = 0.007$ , when the formation constant is corrected from  $I=0$  to  $I=0.15$ . In Fig. 1,  $s(\Delta \log \beta)/z^* \times 10^3$  is plotted vs.  $I$ , at different temperatures.

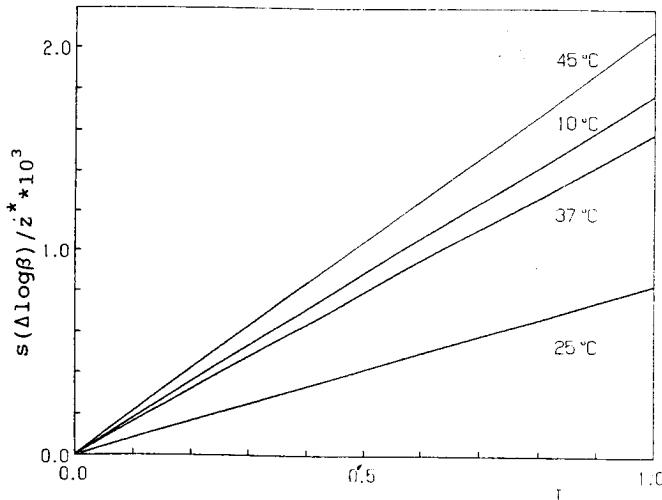


Fig. 1.  $s(\Delta \log \beta)/z^* \times 10^3$  vs.  $I$  at different temperatures.

## THE SOLUTION OF MASS BALANCE EQUATIONS

Calculation problems for equilibria in solution in general need the solution of a set of mass balance equations. This can be written

$$\mathbf{X} = \mathbf{x} + \mathbf{p} \mathbf{s} \quad (13)$$

$$\mathbf{x} = \begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix} \quad \text{vector of analytical concentrations}$$

$$\mathbf{x} = \begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix} \quad \text{vector of free concentrations}$$

$$\mathbf{p} = \begin{bmatrix} p_{11} & \cdots & p_{1m} \\ \vdots & \ddots & \vdots \\ p_{n1} & \cdots & p_{nm} \end{bmatrix} \quad \text{matrix of stoichiometric coefficients}$$

$$\mathbf{s} = \begin{bmatrix} s_1 \\ \vdots \\ s_m \end{bmatrix} \quad \text{vector of species concentrations}$$

$$\mathbf{L} = \mathbf{B} + \mathbf{p}^T \mathbf{l} \quad (14)$$

$$\mathbf{L} = \begin{bmatrix} \log s_1 \\ \vdots \\ \log s_m \end{bmatrix} \quad \mathbf{l} = \begin{bmatrix} \log x_1 \\ \vdots \\ \log x_n \end{bmatrix} \quad \mathbf{B} = \begin{bmatrix} \log \beta_1 \\ \vdots \\ \log \beta_m \end{bmatrix}$$

$n$  = number of components

$m$  = number of species

$\beta_j$  = overall formation constants of the species

The system of equation (13) can be solved by different methods, to obtain free concentrations, and therefore species concentrations. The most popular numerical methods used for this problem are briefly described below.

A. The 'ratio' method, first proposed by Perrin and Sayce<sup>21</sup>, for which the iteration formula is:

$$\mathbf{x}^{(i+1)} = \mathbf{x}^{(i)} \mathbf{R}^{(i)} \quad (15)$$

$$\mathbf{R} = \begin{bmatrix} R_1 \\ \vdots \\ R_n \end{bmatrix}$$

$$R = (X/X_{\text{calcd}})^{1/q} \quad (16)$$

i = iteration index, q = damping factor

This method has been used in several computer programs<sup>22, 23</sup>, in which the main differences consist in the choice of initial values of concentration (to be used for successive iterations) and in the formulation of damping. In program COMICS<sup>21</sup>,  $x_{\text{initial}} = X$  and  $1/q = 1/2$ .

#### B. The Newton-Raphson method<sup>24</sup>, for which the iteration formula is

$$\mathbf{x}^{(i+1)} = \mathbf{x}^{(i)} + \mathbf{B}^{-1} \mathbf{D} \quad (17)$$

where

$\mathbf{B}$  is the matrix with generic element  $b_{ij} = \partial X_i / \partial x_j$ ;

$\mathbf{D}$  is the vector with generic element  $d_i = X_{i,\text{exp}} - X_{i,\text{calcd}}$ ;

has been widely used in the computation of free concentrations, as well as in many nonlinear chemical problems. Recently we used quite an efficient method which consists in a Newton-Raphson type iteration procedure with a damping routine based on the 'ratio' method<sup>7</sup> (see also below).

When dealing with experimental conditions and/or species stability constants at different (and/or variable) ionic strengths, one must use activity coefficients in the mass balance equations. Therefore eq.(14) becomes

$$\mathbf{L} + \mathbf{F}_c = \mathbf{B}_T + \mathbf{p}^T \mathbf{l} + \mathbf{p}^T \mathbf{F}_a \quad (14a)$$

$$\mathbf{B}_T = \begin{bmatrix} \log^T \beta_1 \\ \vdots \\ \log^T \beta_m \end{bmatrix} \quad \begin{array}{l} \text{vector of thermodynamic (zero ionic strength)} \\ \text{overall formation constants (log)} \end{array}$$

$$\mathbf{F}_c = \begin{bmatrix} \log f_{x_1} \\ \vdots \\ \log f_{x_m} \end{bmatrix} \quad \text{vector of component activity coefficients (log)}$$

$$F_a = \begin{bmatrix} \log f_{s_1} \\ \vdots \\ \log f_{s_n} \end{bmatrix} \quad \text{vector of species activity coefficients (log)}$$

## THE ALGORITHM FOR THE CALCULATION OF EQUILIBRIUM CONCENTRATIONS

For a system containing N components and M species, the mass-balance equations can be written:

$$x_k = x_k + \sum_i p_{ik} \beta_i \prod_j x_j^{p_{ij}} \quad (18)$$

$$X_k = x_k + \sum_i p_{ik} s_i \quad (18a)$$

where  $x_k$  and  $X_k$  are the analytical and free concentrations of the k-th component, respectively,  $\beta_i$  and  $s_i$  are the formation constants and concentrations of i-th species, respectively,  $p_{ik}$  (or  $p_{ij}$ ) is the stoichiometric coefficients of the k-th component in the i-th species, and the indices are defined as  $k, j=1\dots N$ ;  $i=1\dots M$ . The problem for calculating free concentrations, once analytical concentrations and formation constants are known, is that of solving N nonlinear equations

$$f_k(x) = x_k + \sum_i p_{ik} \beta_i \prod_j x_j^{p_{ij}} - X_k = 0 \quad (19)$$

subject to constraints  $x_k > 0$ . The Newton-Raphson technique allows  $x_k$  values to be calculated by the iterative procedure

$$x^{(n+1)} = x^{(n)} - G^{-1} e \quad (20)$$

(n: iteration index)

$$x = \{x_1 \dots x_k \dots x_N\}, \quad G = \{\partial f_k(x)/\partial x_j\} = \{g_{kj}\}$$

$$e = \{e_1 \dots e_k \dots e_N\}, \quad e_k = X_{k, \text{calcd}} - x_k$$

at a certain stage n, the calculated analytical concentration is taken from eq.(18):

$$X_{k, \text{calcd}}^{(n)} = x_k^{(n)} + \left[ \sum_i p_{ik} \beta_i \prod_j x_j^{p_{ij}} \right]^{(n)} \quad (21)$$

This technique offers the important advantage that few iterations are generally needed to reach convergence, but there are two main

difficulties: (a) when  $G$  is singular or near-singular, inversion is impossible; (b) iteration is often very unstable and, at some stage, the correction  $G^{-1}e$  may lead to divergence. These difficulties must always be kept in mind when the Newton-Raphson technique is used, but are particularly severe when dealing with highly nonlinear equations and when  $N>5$ . In order to avoid underflow and/or overflow problems, logarithms are used in calculating species concentrations (22) and formation constants are divided appropriately (22a).

$$\log s_i = (\text{JB})_i \log \beta_i + \sum_j p_{ij} \log x_j \quad (22)$$

$$\log \beta_i = (\text{JB})_i^{-1} \log \beta_i^{\text{INPUT}} \quad (22a)$$

(if  $\log \beta > \text{ESPL}$  then  $\text{JB}=4$  else  $\text{JB}=1$ ). In order to overcome difficulty (a), scaling was applied to matrix  $G$  and to vector  $e$  according to the equations

$$g_{kj}^* = g_{kj} (g_{kk} g_{jj})^{-1/2}$$

$$e_k^* = e_k g_{kk}^{-1/2}$$

where  $g_{kj}^*$  and  $e_k^*$  are the elements of the scaled matrix and vector, respectively. In order to improve the stability of the iterations, proved the best the following procedure. If at a certain stage  $n$ , the ratio

$$R_k^{(n)} = X_k^{(n)} / X_{k,\text{calcd}}^{(n)}$$

for the  $k$ -th component lies outside the range

$$1/\rho < R_k^{(n)} < \rho \quad (22b)$$

( $\rho$  is a limit chosen in the range  $1<\rho<10$ ), then the free concentration of the  $k$ -th component is damped by the equation

$$x_{k,\text{damped}}^{(n)} = x_k^{(n)} \left[ R_k^{(n)} q \right]^{(n)} \quad (23)$$

where

$$q = (p_{ik})_{\text{max}}^{-1/\eta} \quad (24)$$

(i.e., if  $\eta=1$ ,  $q$  is the reciprocal of the largest stoichiometric coefficient of the species containing the  $k$ -th component). This procedure is applied to the component for which  $\ln|R_k|$  assumes the

maximum value, and is repeated until  $R_k$  for all components satisfies the condition  $1/\rho < R_k^{(n)} < \rho$ . Then a new Newton-Raphson iteration step is performed. For the solution of the system outlined in eq.(19), the compact Gauss method was chosen (modified Gauss elimination method, more easily programmable on computers). Initial estimates of free concentrations, for the first point, are chosen as  $x_k^{(0)} = X_k * 0.001$ . For the second and the third points, initial estimates are the output of the first and the second points. For the subsequent points ( $p \geq 4$ ) an extrapolation method [(25), (26)] is used. When simulating a titration curve

$$l_{k,p}^{(0)} = l_{k,p-1} + \left( \frac{l_{k,p-1} - l_{k,p-2}}{v_{p-1} - v_{p-2}} \right)^2 \left( \frac{v_{p-2} - v_{p-3}}{l_{k,p-2} - l_{k,p-3}} \right) (v_p - v_{p-1}) \quad (25)$$

with  $l_{k,p} = -\log x_{k,p}$ ;  $p$ =point index;  $v$ =titrant volume.

When calculating distribution diagrams (with constant intervals)

$$l_{k,p}^{(0)} = l_{k,p-1} + \frac{\left( l_{k,p-1} - l_{k,p-2} \right)^2}{\frac{1}{l_{k,p-2} - l_{k,p-3}}} \quad (26)$$

Errors in free concentrations (and, therefore, in species concentrations), arising from errors in formation constants and in analytical concentrations, are calculated by variance propagation (27) (more details are reported in ref.7).

$$\sigma_{X_j}^2 = \sum_i (\partial x_j / \partial \beta_i)^2 \sigma_{\beta_i}^2 + \sum_r (\partial x_j / \partial X_r)^2 \sigma_{X_r}^2 \quad (27)$$

$r=1, \dots, N$

Another parameter to be taken into account, in order to optimize execution time, is tolerance (TOLC in the program) for convergence. This parameter is defined by equation (28)

$$TOLC = 10^{-KEXP} \quad (28)$$

and convergence is defined by equation (29).

$$\sum_i \left( \frac{x_i - X_{i,calcd}}{X_i} \right)^2 < TOLC \quad (29)$$

## COMPUTER PROGRAM FOR THE CALCULATION OF EQUILIBRIUM CONCENTRATIONS

Special features of ES4ECI\* are as follows: (a) Only non-zero stoichiometric coefficients are memorized for calculations. (b) Only terms with non-zero  $p_{ik}$  are calculated. In equation (18) several terms reduce to zero and the procedure adopted speeds up calculations. (c) The calculations of free concentrations are damped using equation (23); our experience with hundreds of systems (in some cases very complicated ones) allows us to affirm that this procedure avoids divergence in all practical cases. (d) Some computer environments allow underflow or overflow to be avoided. For example, if  $x_j < 10^{-ESPL}$ , the program fixes  $x_j = 10^{-ESPL}$ . This procedure does not lead to any error in the final results. (e) Ill condition is avoided by scaling matrices and vectors<sup>7,29</sup>. Furthermore, the subroutines FREEC, GAUSSC, SPECO and CTOL can be easily used in other programs for computing the thermodynamic formation parameters. (f) ES4ECI has been written with the aim of offering a computing means valid for any machine. Particular attention has been paid to the use of small personal computers. Small personal computers are unsatisfactory (in terms of execution times) only in the calculation of errors. A comparison with other programs has shown that ES4ECI is the fastest computer program in this field (see text and tables, and ref.7).

Dependence on ionic strength of formation constants is taken into account by adding a linear term to log(formation constant), [eqn.(14a)]. In practice, eqn.(9a) is used in program ES4ECI in two different ways: (a) by considering general parameters  $c_0$ ,  $c_1$ ,  $d_0$  and  $d_1$  for all the species ; or (b) by considering different C and D values for each species. Output results can be represented graphically, both as distribution diagrams or titration curves. Data for graphical representation can also be printed on plotter (HP-GL) and/or recovered on HD using HP-GL code in order to be utilized with DTP (Desk Top Publishing) programs, such as VENTURA, PAGE MAKER, WINWORD, etc.

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\* With ES4EC we denote the general algorithm for the calculation of equilibrium constants (ref.7, and this work), and with ES4ECX the relative computer programs (X=1, FORTRAN version, ref. 9; X=2, BASIC version, ref. 10; X=3, PASCAL version, ref. 10; X=I, present BASIC version with variable ionic strength and graphic facilities).

## THE ALGORITHM FOR THE CALCULATION OF FORMATION CONSTANTS

Since the sixties some standard computer programs for the calculation of formation constants from potentiometric measurements have been published. Among others, the most popular (and powerful) are LETAGROP<sup>25</sup>, SCOGS<sup>26</sup>, MINIQUAD<sup>27</sup> and SUPERQUAD<sup>28</sup>. The first uses the 'pit-mapping' method and the others use the Gauss-Newton technique. A variety of utilities are implemented in these programs, such as the refinement of analytical and instrumental parameters (group parameters), selection of species, electrode response, etc. Some techniques to protect refinement against divergence have been used, as the well known Marquardt<sup>29</sup> one using code based on the Fletcher<sup>30</sup> one. Basically, the Gauss-Newton technique can be expressed by

$$\mathbf{s} = (\mathbf{A}^T \mathbf{W} \mathbf{A})^{-1} (\mathbf{A}^T \mathbf{W}) \mathbf{e}$$

$$\mathbf{A} = \begin{bmatrix} \partial y_1 / \partial p_1 & \dots & \partial y_1 / \partial p_n \\ \vdots & \ddots & \vdots \\ \partial y_k / \partial p_1 & \dots & \partial y_k / \partial p_n \end{bmatrix} \quad \text{matrix of partial derivatives } \partial y / \partial p \\ (y=\text{independent variable of } k\text{-th point})$$

$$\mathbf{W} = \begin{bmatrix} w_{11} & 0 & \dots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \dots & 0 & w_{kk} \end{bmatrix} \quad \text{weight matrix}$$

$$\mathbf{e} = \begin{bmatrix} e_1 \\ \vdots \\ e_k \end{bmatrix} \quad \text{residuals vector}$$

$$\mathbf{s} = \begin{bmatrix} s_1 \\ \vdots \\ s_n \end{bmatrix} \quad \text{shifts vector}$$

Different independent variables,  $y$ , have been chosen in the refinement of formation constants, such as  $E$  (electrode potential),  $v$  (titrant volume),  $X$  (analytical concs.),  $\bar{n}$  (average number of ligands bound to the metal),  $Z$  (average number of protons displaced per metal ion). When dealing with experimental data at a variable ionic strength, formation constants must be given together with their dependence on ionic strength, according to the eqn.(12).

## COMPUTER PROGRAM FOR THE CALCULATION OF FORMATION CONSTANTS

Computer program BSTAC is derived from the well known SUPERQUAD. The main minimization procedure and the calculation of free concentration routine is practically unaltered. Modifications are as follows: i) translation from FORTRAN to BASIC (Compiler QuickBASIC version 4.5); ii) input and output; iii) mass balance equations are modified to take into account the dependence on ionic strength of formation constants; iv) parameters for ionic strength dependence of formation constants are also refined.

In the original program (SUPERQUAD) the independent variable is chosen as the titre volume and the measured potential is the dependent variable. Since the parameters do not appear explicitly in the expression for potential ( $S_L$ =slope;  $j_a$ =coefficient for junction potential,  $E_j = j_a [H]$ )

$$E = E^{\circ} + S_L \log[x] + j_a [H] \quad (30)$$

an implicit differentiation is required:

$$p_j \frac{\partial E}{\partial p_j} = p_j \frac{\partial E}{\partial [x]} \frac{\partial [x]}{\partial p_j} = p_j \frac{S_L}{[x]} \frac{\partial [x]}{\partial p_j} \quad (31)$$

where  $[x]$  is the concentration of the ion to which the electrode responds, and  $p_j$  is the  $j$ -th parameter. The mass balance equation to which the dependent variable,  $E$ , refers is generally that of the proton (last MBE). In BSTAC it is also possible to choose other MBEs (for each titration), so that titrations performed by using different electrodes (pH, pNa, pCu, ...) can be analyzed simultaneously. The values of  $[x_i]$  are obtained in terms of the model by solving the set of non-linear equations of mass balance (32) applicable to each reactant.

$$X_k = x_k + \sum_i p_{ik} \beta_i \prod_j x_j^{p_{ij}} \quad (32)$$

where  $X_k$  and  $x_k$  are the analytical and free concentrations of the  $k$ -th component, respectively,  $\beta_i$  is the formation constant of  $i$ -th species,  $p_{ik}$  (or  $p_{ij}$ ) is the stoichiometric coefficient of the  $k$ -th component in the  $i$ -th species, and the indices are defined as  $k, j=1\dots N$ ;  $i=1\dots M$ . The system of mass balance equations is solved iteratively by Newton's method. In order to spare matrix inversion

calculations, relative shifts of refining parameters are calculated. A detailed description of the original algorithm can be found in ref. 28. The program refines the formation constants  $\beta$ , the ionic strength parameters  $c_0$ ,  $c_1$ ,  $d_0$ ,  $d_1$ , the parameters of Debye-Hückel equation C and D, the initial concentration in the titration vessel  $C^0$ , the standard potential  $E^\circ$ , the linear coefficient of junction potential  $j_a$  and slope  $S_L$ . Dependence on ionic strength of formation constants is taken into account by equation (12).  $E^\circ$  and  $j_a$  [eq. (30)] are dependent on I too. Function  $E^\circ = f(I)$  used in BSTAC is the one proposed in a paper for the dependence on ionic strength of proton activity coefficients<sup>31</sup>

$$E^\circ(I) = E^\circ(I') + S_L g(I) \quad (33)$$

$$g(I) = z_E^2 \left[ \frac{-\sqrt{I}}{2+3\sqrt{I}} - \frac{-\sqrt{I'}}{2+3\sqrt{I'}} \right] + (c_0 + c_1 z_E^2)(I-I') + (d_0 + d_1 z_E^2)(I^{3/2} - I'^{3/2})$$

( $z_E$ =charge of the ion to which the electrode responds). According to Sillén<sup>32</sup> in most cases  $j_a I$  must be a constant, and the program calculates  $j_a' = j_a I$  ( $j_a'$  can be refined). Weights for each point of titration curves are given as (v=titrant volume)

$$w=1/s^2$$

$$s^2 = s_E^2 + \left( \frac{\partial E}{\partial v} \right)^2 s_v^2$$

In some cases it is convenient to give unit weight for each point. An additional possibility in BSTAC consists in the following procedure: (1) refinement of parameters ( $\log \beta$ ,  $E^\circ$ , etc.) using  $w=1$ ; (2) second refinement procedure using  $w=1/\delta^\varepsilon$ , where  $\delta = |E_{exp} - E_{calcd}|$ ,  $\varepsilon$  = an empirical factor ( $\varepsilon=0.5$  is a good value for most cases). Though this procedure has no theoretical basis, it has been tested for several systems and in some cases is quite useful. For example, if some points are affected by an abnormal error, with the above procedure these points are in practice neglected in the second refinement step. The various dimensions are not fixed a priori but, with a simple procedure, the program uses all the memory by fixing dimensions in dependence of the system under study. In the present version of BSTAC (compiler QuickBASIC version 4.5) the maximum available memory is 64K for each vector.

## DISCUSSION

Computer programs ES4ECI and BSTAC have been used with several systems (protonation, metal complex formation, hydrolysis, mixed metal complexes, mixed ligand complexes) and always showed very good performances both in calculation times and robustness. The machines used for testing these programs were the following: a) PC IBM compatible, CPU i80486 (50 MHz); b) PC IBM compatible, CPU i80486 (33 MHz); c) COMPAQ, CPU i80386 (25 MHz), math. coprocessor i80387; d) PC IBM compatible XT, CPU i8088 (4.77 MHz), math. coprocessor i8087. In machines a), b), d) the operating system was MS DOS version 5.0, in machine c) the operating system was MS DOS version 4.0, the compiler used for all the machines was QuickBASIC version 4.5. Test systems for checking performances and for giving execution times are as reported in Tables 2 and 3, for ES4ECI and BSTAC, respectively. Execution times can be compared with the standard ESTIME program<sup>9</sup>, which allow a comparison among different machines. The version ESTIME5 (compiler QuickBASIC ver. 5.0) give  $\tau = 2.86$ , 4.28, 14.86, 131.56 sec. for the above machines, respectively. Execution times for both programs are reported in Tables 4 and 5. As can be seen, though some systems are quite complicated (several points, several MBE),  $\tau$  values for faster machines are very reasonable. Note that system CABTC contains titrations performed with an ( $H^+$ )-glass electrode and titrations performed with ISE-Ca electrode; the simultaneous analysis of these two different types of potentiometric titrations gave very encouraging results. The main conclusions, referring to the characteristics of the computer programs above reported, are as follows.

ES4ECI program: (a) it is probably the fastest computer program available for calculating equilibrium concentrations; (b) no other program is available for computing concentrations at different ionic strengths; (c) its robustness is demonstrated by the different test systems used for checking.

BSTAC program: (a) no other program is available for refining formation constants in non constant ionic strength conditions (even parameters for the dependence on ionic strength can be refined); (b) different kinds of potentiometric titrations can be analyzed simultaneously; (c) it is fast, robust and easy to use.

In order to see performances and characteristics of other

computer programs in this field, one can refer to refs. 35-37, which contain details and a fairly abundant bibliography.

In the Appendices we report: I) Input instructions of ES4ECI; II) Input instructions of BSTAC; III) an example of file input and output for ES4ECI; IV) an example of file input and output for BSTAC.

Files .BAS and .EXE of both programs can be obtained on request (please previously contact one of authors, for details on the type of disk and on reimbursement of expenses).

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TABLE 2. Characteristics of Test Systems used to check performances (further details are reported in refs.7,9,22,33).

System	Description	No. of MBE	No. of species	IOP <sup>a)</sup>	No. of points	ref:
I	Hydrolysis of Al <sup>3+</sup> (3 different analytical concentrations)	2	10	0	36(12x3)	7
IIa	K <sup>+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> -citrate complexes	5	18	0	41	7
IIIa	Mixture of Na <sup>+</sup> , K <sup>+</sup> ,	14	75	0	20	7
IIIb	Ca <sup>2+</sup> and 10 low molecular weight ligands			1	10	
IVa	Hydrolysis of six metal ions (synthetic system)	7	35	0	14	7
IVb				1	21	
V	Synthetic system with formation of mixed metal species (5 different analytical concentrations)	5	35	0	165(33x5)	9
VIa	Hydrolysis of iron(III)	2	5	0	61	(*)
VIb		2	5	1	10	
VII	SSWE (synthetic sea water) (3 different analytical concentrations)	7	14	1	36(12x3) .	(*)
IL	One metal-one ligand <sup>b)</sup>	3	12	0	37	33
III L	One metal-one ligand <sup>b)</sup>	3	13	0	31	33
IIIL	One metal-two ligands <sup>b)</sup>	4	13	0	36	33
IVL	Two metals-two ligands <sup>b)</sup>	5	15	0	31	33
VL	Two metals-three ligands <sup>b)</sup>	6	22	0	31	33
VIL	Hg <sup>2+</sup> -iodide-cyanide <sup>b)</sup> (4 different analytical concentrations)	4	9	0	20(5x4)	33
IG	Cd <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> -NTA, NH <sub>3</sub> (pH=7.5,8,8.5,9) <sup>c)</sup>	6	26	0	4	22

<sup>a)</sup> IOP=0: distribution of species; IOP=1: titration curves.

<sup>b)</sup> Systems proposed by Leggett.

<sup>c)</sup> System proposed by Ginsburg.

(\*) This research group: work in progress.

TABLE 3. Characteristics of Test Systems used to check BSTAC performances (further details are reported in refs.7,34).

System		No. of comps.	No. of species	No. of tit.	No. of points	ref.
CALLETNA	(+)	(a)	4	10	41	3027
S1P		(b)	3	6	6	97
S1PC		(b)	3	6	6	97
S1PI	(+)	(b)	3	6	22	354
S5P		(b)	5	23	8	200
CABTC	(+)	(c)	6	25	28	1035

(a) Tricarballylic acid in tetraethylammonium iodide and in NaCl: protonation and  $\text{Na}^+$  complexes.

(b) Synthetic system.

(c) Butanetetracarboxylic acid - calcium complexes. Measurements performed with ( $\text{H}^+$ )-glass and ISE-Ca electrodes.

(\*) This work.

(+) Not constant ionic strength conditions.

TABLE 4. Test systems and calculation times for BSTAC.

System	$\beta^a)$	tit. <sup>b)</sup>	calculation times (sec)			
			(1) <sup>c)</sup>	(2) <sup>c)</sup>	(3) <sup>c)</sup>	(4) <sup>c)</sup>
CALLETNA	8	84	545	1086	4046	
S1P	5	0	3.5	6	24	
S1PC	5	6	3.7	7	28	226
S1PI	5	0	23	37	148	2566
S5P	16	0	47	78	312	3000
CABTC	6	15	196	321	1164	

In system CALLETNA  $c_1$  and  $d_1$  parameters are refined.

In system S1PI C and D parameters for each  $\beta$  are refined.

In system CABTC  $c_1$  parameter is refined.

<sup>a)</sup> number of  $\beta$  refined

<sup>b)</sup> number of titration parameters refined

<sup>c)</sup> (1) PC IBM compatible (50 MHz); (2) PC IBM compatible (33 MHz);  
 (3) COMPAQ; (4) PC IBM compatible XT.

TABLE 5. Test systems and calculation times for ES4ECI.

System	calculation times (sec)			
	(1) <sup>a)</sup>	(2) <sup>a)</sup>	(3) <sup>a)</sup>	(4) <sup>a)</sup>
IIIa	14.67	22.01	76.28	936
IVb	3.46	5.19	17.99	202
V	4.70	7.00	20.45	257
VIIa	0.39	0.59	2.03	21
VII	2.00	4.00	10.00	114
VL	0.61	0.92	3.17	35
IG	0.16	0.24	0.83	8

<sup>a)</sup> (1) PC IBM compatible (50 MHz); (2) PC IBM compatible (33 MHz);  
 (3) COMPAQ; (4) PC IBM compatible XT.

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## APPENDIX I

## Input instructions of ES4ECI program.

BASIC version 1.0 - February, 1993  
 Compiler QuickBASIC version 4.5

Equilibria in solution, problem n.4  
 Equilibrium concentrations, program n.4

## \*\*\* Equilibrium concentrations and titration curves \*\*\*

## Program characteristics:

- 1) Calculation of species distribution together with the errors in the calculated concentrations arising from the errors in formation constants values and in analytical concentrations
- 2) Calculation of titration curves together with errors, such as in (1)
- 3) Input formation constants can be given at different ionic strengths and titration curves and distribution diagrams can be calculated at ionic strengths different from those for which the formation data are valid: the program calculates the opportune corrections [text eqn.(12)]

\*\*\*\*\* I N P U T      D A T A \*\*\*\*\*

## 1) TITLE

TITLE = descriptive title of the job

## 2) NCT, NS, IOP, IOUT, ESPL, RCAN, ETA, KEXP, ION

NCT: no. of components

NS: no. of species

IOP = 0: distribution of species

with this option the program calculates the free concentrations of (NCT-1) components and NS species for a number of given -log(free concentrations) values of the last component. A very common case is represented by the distribution of the species vs. pH

= 1: titration curves

with this option the program simulates a titration curve by calculating the free concentrations of NCT components and NS species. In this option the concentrations and the volume(s) of titrant must be given (output for graphic = v, pH)

= 2: titration curves (see IOP=1)

(output for graphic = pH, %species)

IOUT = 0: prints out concentrations

= 1: prints out concentrations and the relative errors

<sub>ESPL</sub>

ESPL: a limit of the machine used: 10 does not overflow

RCAN: a damping factor for which when the ratio R (given analytical concentration / calculated analytical concentration) is <1/RCAN or >RCAN the procedure is forced to converge by a particular algorithm [text eqn.(22b)];

normally RCAN=4.

ETA:  $Q=P_{max}(-1/\text{ETA})$  [generally ETA=1] [text eq.(24)]

KEXP: TOLC=10 [generally KEXP=10] [text eq.(28)]

ION = 0: calculations are performed at constant ionic strength  
= 1: not constant ionic strength conditions are considered

3) COMP [NCT times]

COMP=symbols of components

\*\*\* if ION = 0 goto item (6) \*\*\*

4) IBT, c0, c1, d0, d1, AA, BB, (Z [NCT times])

IBT = reference ionic strength

c0,c1,d0,d1 = parameters of ionic strength dependence (note [1])

AA,BB = Debye-Hückel parameters (A,B) [eqn.(9a)]

(if AA=BB=0 the program sets AA=0.5, BB=1.5)

Z = charges of components

5) [NS times]

BET, SIGMA, IB, AG, BG, CG, DG, NX, (KX, IX [NX times]), IA

\*\*\* if IOP=0 goto item (15) else goto item (8) \*\*\*

6) [NS times]

BET, SIGMA, NX, (KX, IX [NX times]), IA

BET,SIGMA =  $\log\beta$  and  $s(\log\beta)$

$\beta$ =formation constant;  $s(\log\beta)$ =standard deviation

IB = reference ionic strength

AG,BG,CG,DG = A,B,C,D [see ISDFC equation (9b)]; note [1]

if A=0, the program sets A=AA

if B=0, the program sets B=BB

if C=0, the program sets  $C=c_0 p + c_1 z$

if D=0, the program sets  $D=d_0 p + d_1 z$

NX = no. of stoichiometric coefficients ≠ zero

KX = index of stoichiometric coefficient ≠ zero

IX = stoichiometric coefficient

for example in a ten components system the species  
(A1)(A3)<sub>2</sub> is described by the indexes 21132 instead of

1 0 2 0 0 0 0 0 0 0

IA: the percentages of species are calculated with respect to  
the component IA

(different IA values can be used for different species)

\*\*\* if IOP = 0 goto item (15) \*\*\*

reads INPUT data of titration curves

8) V0, VV, DV, NPV

V0 = initial volume

VV = volume of the first point of the titration

DV = increment of volume for the subsequent points

[if DV=0 reads titrant volume for each point, see item

(14)]

NPV = no. of points in the titration

\*\*\* if V0 = 0 end of file \*\*\*

9) CO [NCT times]

10) CTT [NCT times]

CO = initial concentration in the titration vessel

CTT = concentration in the titrant

\*\*\* if IOUT = 0 goto item (13) \*\*\*

11) SIGCO [NCT times]

12) SIGCT [NCT times]

SIGCO,SIGCT = std.dev.(%) in CO and CTT respectively

13) COI, CTI (only if ION=1)

COI,CTI = concentrations in the vessel and in the titrant solution, respectively, of ionic species that do not take part in the considered reactions, note [2]

14) V [NPV times] (only if DV=0)

V=volume

\*\*\* goto item (8) \*\*\*

reads INPUT data of distribution of species

15) CAN [NCT-1 times]

CAN = analytical concentrations

\*\*\* if all CAN=0 end of file \*\*\*

16) SIGC [NCT-1 times] (only if IOUT=1)

SIGC = std.dev.(%) in analytical concentrations (IOUT=1)

17) BS (only if ION=1)

BS = concentration of background ions

18) PA, PAFIN, DPA

PA= initial value of -log[A]

PAFIN=final value of -log[A]

DPA = increment of -log[A] for the subsequent points  
A is the last component [i.e. the distribution diagrams  
are plotted vs. -log(free concs.) of last component]

\*\*\* goto item (15) \*\*\*

**Notes**

- [1] The program ES4ECI can run either with general parameters for ISDFC, i.e.  $c_0$ ,  $c_1$ ,  $d_0$  and  $d_1$  [eqn.(9a)], or with parameters C and D [eqn.(9b)] for each formation constant.
- [2] If some components, such as  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ , etc., which influence the value of I, are not taken into account in the mass balance equations, their concentration is considered in  $C_0$  and  $C_1$ .

---

At the end of calculations the program asks for graphics.  
Interactive instructions are given on screen.

## APPENDIX II

## Input instructions of BSTAC program.

BASIC version 1.2 - February, 1993  
Compiler QuickBASIC version 4.5

Calculation of stability constants and other parameters related to potentiometric titrations

## Program characteristics:

- a) Calculation of formation constants.
- b) Calculation of ionic strength dependence of formation constants.
- c) Calculation of analytical concentrations and other titration parameters.

## INPUT INSTRUCTIONS

1') NFILE - Name of the input file

2') OFILE - Name of the output file

Input File

## 1) TITLE

TITLE: title of the job (one row)

## 2) MAXIT, NMBE, NKM, MODE, ICD, WESP, PERC

MAXIT: maximum no. of refinement cycles (normally ≤15)

NMBE: no. of components (no. of Mass Balance Equations)

NKM: no. of species

MODE=1: weights=1 (unit weight for each experimental point)  
=0: weights=1/SIGMA<sub>2</sub>

(SIGMA=estimated standard deviations)

ICD=0: the constant medium method is used in the job (see items)

=1: the titrations in the job are at different ionic strengths (see items)

WESP: weights=1/DE<sup>WESP</sup> (see note [1])

PERC: limit of the shifts % (PERC=0 no limit for shifts)

## 3) IPRIN, JCY, IDAT

IPRIN=0: final table (some calculated quantities, formation percentages, etc.) and correlation matrix are not printed out

=1: final table is printed out

=2: correlation matrix is printed out

=3: final table and correlation matrix are printed out

JCY=0: intermediate calculations are not printed out

=1: " " are printed out

IDAT=0: titration data are not printed out  
 =1: general titration data are printed out

## 4) KEMIC (NMBE times)

KEMIC: symbol for mass balance equation

## 5) TEMP, PHI, PHF

TEMP: temperature in degrees cent.

PHI,PHF: pH range to be considered in the job (last MBE)  
 (if PHI=PHF=0 all the points are considered)

## 6) (only if ICD=1, i.e., variable ionic strength)

IREF, AT, BT, c0, c1, d0, d1, Z (NMBE times), KCD (4 times)

IREF: reference ionic strength

[if IREF<0, then IB for each formation constant must be given, see item (8)]

AT,BT: A and B parameters of Debye-Hückel type equation [text eqn.(9a)]

(if AT=BT=0 then program fixes AT=0.5, BT=1.5)

c0,c1,d0,d1: parameters for the ionic strength dependence of formation constants [see text, eqn.(9a)]

Z: charge of components

KCD(1) = 0: c0 constant  
 = 1: c0 refined

KCD(2) = 0: c1 constant  
 = 1: c1 refined

KCD(3) = 0: d0 constant  
 = 1: d0 refined

KCD(4) = 0: d1 constant  
 = 1: d1 refined

## 7) (if ICD=0) (NK times)

BLOG, JQR (NMBE times), KEY

(for explanation see item 8)

## 8) (if ICD=1) (NK times)

BLOG, (IB), C, D, JQR (NMBE times), KEY

BLOG: log(formation constant)

IB: reference ionic strength (to be given only if IREF<0)

C,D: parameters of Debye-Hückel equation [see text, eqn.(9b)]  
 (if program reads c0,c1,d0,d1 set C=D=0)

JQR: stoichiometric coefficients

KEY: index for refinement

KEY = 0: parameters BETA,C,D constant

= 1: refines BETA

= 2: " C

= 3: " D

= 4: " BETA,C

= 5: " BETA,D

= 6: " C,D  
 = 7: " BETA,C,D  
 = -1: species ignored in the model

## 9) NAMET

NAMET: title of the titration (one row)  
 (if EOF then stop)

## 10) JP, MBET

JP: percentages (final table) are calculated with respect to  
 the component JP  
 MBET: the e.m.f. (or  $pX=-\log[X]$ ) read in for the titration  
 refers to the component MBET  
 (if MBET=0 then the program sets MBET=NMBE)

## 11) TOTMM, ADDC, LOK (NMBE times)

TOTMM: initial concentration in the titration vessel (mol/L)  
 ADDC: concentration in the titrant (mol/L)  
 LOK = 0: TOTMM constant  
 = 1: TOTMM refined  
 (for constraints see note [3])

## 12) (only if ICD=1)

COI, CTI, IREFT

COI: concentration of ionic species which does not take place  
 in complexation reactions (reaction vessel)  
 CTI: idem in the titrant solution  
 IREFT: initial value of ionic strength (see note [2])

## 13) VO, SIGMAV

VO: initial volume ( $\text{cm}^3$ )  
 SIGMAV: estimated standard deviation in the titrant volume

## 14) EO, SIGMAE, JA, SLOPE, LOK(1), LOK(2), LOK(3)

EO: standard potential  $E^\circ$  of the electrode in mV  
 (EO=0 if reads pH)

SIGMAE: estimated standard deviation in e.m.f. (EO=0) or pH  
 (EO=0)

JA: linear coefficient of junction potential

SLOPE: slope  
 (if SLOPE=0 the program calculates SLOPE=Nernstian  
 value)

LOK = 0: EO (JA,SLOPE) constant  
 = 1: EO (JA,SLOPE) refined  
 (for constraints see note [3])

## 15) TITV, EMFC, IND

TITV: titrant volume

EMFC: potential (or pH, if EO=0)

IND = 0: normal  
 = 1: for the last point of the titration

```
if IND=1 goto item (9)
```

---

#### Notes

- [1] If WESP $\neq$ 0, calculations are performed two steps. The first is the normal one - according to the given input instructions -. The second step, the calculations are performed giving each point a new weight  $W = \delta E^{WESP}$  on the basis of the residual calculated in the first step:  $W = \delta E^{WESP}$
- [2] IREFT is used by the program:
  - a) as initial guess of ionic strength
  - b) as reference ionic strength for  $E^0$  [see text, eqn.(33)].
- [3] Titration parameters can be constrained to refine together. For example,  $C^0$  (initial analytical concentration) for a ligand of uncertain purity used in various titration curves may be constrained so that the final purity is the same in all curves. This is achieved by setting the refinement keys of all constrained titration parameters equal to some number greater than 1. When constrained, parameters will changed by the same proportion. This means that their initial values need not necessarily be equal.

## APPENDIX III

Input and output example for ES4ECI.

## INPUT EXAMPLE: SIST7

SSWE 20,35,45 %. 25 .C (speciation of synthetic sea water)

7 14 0 1 75 4 1 10 1

Na

K

Mg

Ca

Cl

SO4

H

0 .1 .209 0 -.093 0 0

1 1 2 2 -1 -2 1

-13.834 .01 .15 0 0 0 0 1 7 -1 0

-13.93 .1 .15 0 0 0 0 2 1 1 7 -1 1

-14.2 .2 0 0 0 0 0 2 2 1 7 -1 2

-11.44 .1 0 0 0 0 0 2 3 1 7 -1 3

-12.90 .1 .15 0 0 0 0 2 4 1 7 -1 4

-.60 .20 .5 0 0 .1 0 2 1 1 5 1 5

.50 .05 .5 0 0 0 0 2 1 1 6 1 6

-.5 .2 .5 0 0 .26 0 2 2 1 5 1 5

.61 .05 .5 0 0 0 0 2 2 1 6 1 6

.07 .2 .5 0 0 .36 0 2 3 1 5 1 5

1.55 .05 .5 0 0 0 0 2 3 1 6 1 6

-.02 .2 .5 0 0 .53 0 2 4 1 5 1 5

1.53 .05 .5 0 0 0 0 2 4 1 6 1 6

1.69 .01 .5 0 0 0 0 2 6 1 7 1 6

.2712 .0062 .031 .0063 .3194 .0163

.00001 .00001 .00001 .00001 .00001 .00001

0

1 12 1

.4797 .011 .0548 .0111 .5649 .0288

.00001 .00001 .00001 .00001 .00001 .00001

0

1 12 1

.6211 .0142 .0710 .0143 .7313 .0373

.00001 .00001 .00001 .00001 .00001 .00001

0

1 12 1

## OUTPUT EXAMPLE

program ES4ECI - BASIC version 18/2/1993

INPUT filename: SIST7

OUTPUT device/filename: SIST7.O

SSWE 20,35,45 %. 25 .C (speciation of synthetic sea water)

day 02-18-1993

IB= 0.000 A = 0.5000 B = 1.500  
 CO= 0.100 C1= 0.209 D0= 0.0000 D1=-0.093

components charge

1) Na 1  
 2) K 1  
 3) Mg 2  
 4) Ca 2  
 5) Cl -1  
 6) SO4 -2  
 7) H 1

	log.BETA	sigma	IB	A	B	C	D	Z	IA	species
1	-13.834	0.010	0.2	0.500	1.500	-0.618	0.186	-1	0	(H)-1
2	-13.930	0.100	0.2	0.500	1.500	-0.100	0.000	0	1	(Na)(H)-1
3	-14.200	0.200	0.0	0.500	1.500	-0.100	0.000	0	2	(K)(H)-1
4	-11.440	0.100	0.0	0.500	1.500	0.318	-0.186	1	3	(Mg)(H)-1
5	-12.900	0.100	0.2	0.500	1.500	0.318	-0.186	1	4	(Ca)(H)-1
6	-0.600	0.200	0.5	0.500	1.500	0.100	0.000	0	5	(Na)(Cl)
7	0.500	0.050	0.5	0.500	1.500	0.936	-0.372	-1	6	(Na)(SO4)
8	-0.500	0.200	0.5	0.500	1.500	0.260	0.000	0	5	(K)(Cl)
9	0.610	0.050	0.5	0.500	1.500	0.936	-0.372	-1	6	(K)(SO4)
10	0.070	0.200	0.5	0.500	1.500	0.360	0.000	1	5	(Mg)(Cl)
11	1.550	0.050	0.5	0.500	1.500	1.772	-0.744	0	6	(Mg)(SO4)
12	-0.020	0.200	0.5	0.500	1.500	0.530	0.000	1	5	(Ca)(Cl)
13	1.530	0.050	0.5	0.500	1.500	1.772	-0.744	0	6	(Ca)(SO4)
14	1.690	0.010	0.5	0.500	1.500	0.936	-0.372	-1	6	(SO4)(H)

ESPL = 75 RCAN = 4.0  
 ETA = 1.0 KEXP = 10

analyt.concs.	(sigma%)
Na	0.2712000 ( 0.00)
K	0.0062000 ( 0.00)
Mg	0.0310000 ( 0.00)
Ca	0.0063000 ( 0.00)
Cl	0.3194000 ( 0.00)
SO4	0.0163000 ( 0.00)
BS	0.0000000

BS=concentration of background ions

initial -log(free concentrations) for the first point

1 3.566710  
 2 5.207608  
 3 4.508638  
 4 5.200659  
 5 3.495665  
 6 4.787812

legenda:

- 1) analytical concentrations of components
- 2) free concentrations of components
- 3) -log(free concentrations of components)
- 4) errors in -log(free concentrations of components)
- 5) % free concentrations

- 6) errors in % free concentrations
- 7) species concentrations
- 8) errors in species concentrations
- 9) % species concentrations with respect to the component IA
- 10) errors in % species concentrations
- 11) log(BETA) value corrected for the current ionic strength

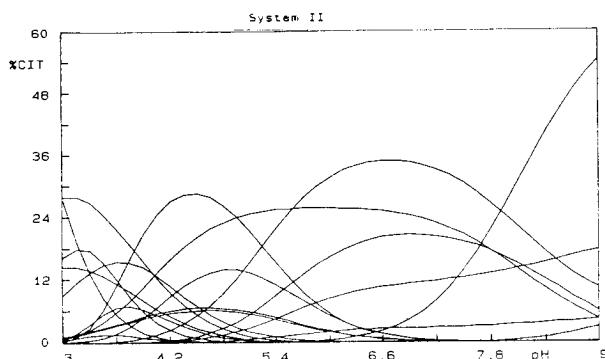
time 16:39:23 timer 59962.922

point no	1	no of iterations	4			
		function evaluations	11	I=	0.392	
	1	2	3	4	5	6
	7	8	9	10	11	12
	13	14				
2)	0.251D+00	0.564D-02	0.219D-01	0.471D-02	0.291D+00	0.222D-02
	0.100D+00					
3)	0.6007	2.2487	1.6601	2.3272	0.5356	2.6527
	1.0000					
4)	0.0131	0.0165	0.0480	0.0401	0.0116	0.0107
5)	92.463	90.980	70.555	74.731	91.220	13.650
6)	2.785	3.451	7.797	6.897	2.445	0.337
7)	0.135D-12	0.279D-13	0.325D-15	0.453D-12	0.546D-14	0.188D-01
	0.168D-02	0.510D-03	0.488D-04	0.752D-02	0.161D-02	0.126D-02
	0.331D-03	0.104D-01				
8)	0.310D-14	0.647D-14	0.150D-15	0.116D-12	0.135D-14	0.760D-02
	0.183D-03	0.216D-03	0.598D-05	0.258D-02	0.228D-03	0.464D-03
	0.471D-04	0.223D-03				
9)	0.000	0.000	0.000	0.000	0.000	5.873
	10.329	0.160	0.299	2.353	9.890	0.395
	2.033	63.799				
10)	0.000	0.000	0.000	0.000	0.000	2.379
	1.120	0.068	0.037	0.806	1.400	0.145
	0.289	1.367				
11)	-13.871	-13.954	-14.239	-11.684	-12.936	-0.591
	0.480	-0.508	0.590	0.072	1.520	-0.037
	1.500	1.670				

time 16:39:23 timer 59962.980

etc.

#### EXAMPLE OF GRAPHIC-OUTPUT



## APPENDIX IV

Input and output example for BSTAC.

INPUT EXAMPLE: file CABTC

Ca-BTC (pH and pCa measurements)

50 6 25 1 1 0 0  
0 0 0

Na

Ca

Cl

BTC

NO3

H

25 0 6.5

0 0 0 .1 .23 0 -.1 1 2 -1 -4 -1 1 0 1 0 0

-14 0 0 0 0 0 0 -1 0

-.6 0 0 1 0 1 0 0 0 0

.4 0 0 0 1 1 0 0 0 0

.75 0 0 0 1 0 0 1 0 0

-.05 0 0 1 0 0 0 1 0 0

7.18 0 0 0 0 0 1 0 1 0

13.01 0 0 0 0 0 1 0 2 0

17.54 0 0 0 0 0 1 0 3 0

20.92 0 0 0 0 0 1 0 4 0

8.67 0 0 1 0 0 1 0 1 0

13.94 0 0 1 0 0 1 0 2 0

17.76 0 0 1 0 0 1 0 3 0

1.82 0 0 1 0 0 1 0 0 0

3.45 0 0 2 0 0 1 0 0 0

3.3 0 0 3 0 0 1 0 0 0

9.31 0 0 2 0 0 1 0 1 0

13.1 0 0 2 0 0 1 0 2 0

4.50 0 0 0 1 0 1 0 0 1

10.83 0 0 0 1 0 1 0 1 1

15.56 0 0 0 1 0 1 0 2 1

19.16 0 0 0 1 0 1 0 3 1

7.66 0 0 0 2 0 1 0 0 1

12.7 0 0 0 2 0 1 0 1 1

5.65 0 0 1 1 0 1 0 0 0

11.2 0 0 1 1 0 1 0 1 0

cabtc2 (glass electrode)

2 0

1.0015 1 0

.0100 0 0

1.0215 0 0

.0150 0 0

0 0 0

.0600 -1 1

0 0 .9999999

25 .005

367.03 .15 0 0 0 0 0

0 220.7 0

.025 216.9 0

.05 212.9 0

.075 208.7 0

.087 206.7 0

.111 202.8 0

.....

.....

etc.

Ca/BTC 1mis (ISE-Ca electrode)

2 2

0 0 0

.0042 0 0

0 0 0

0 .1232 0

.1071 0 0

0 0 0

.1033 .4928 .05

20.254 .005

122.2 .3 0 20.9 0 0 0

.05 68.4 0

.10 67.6 0

.15 67.0 0

.20 66.2 0

.25 65.4 0

.30 64.8 1

etc.

#### OUTPUT EXAMPLE

program BSTAC

BASIC version 2.2 - 19/1/1993

filename dati: cabtc

day 02-19-1993

Ca-BTC (pH and pCa measurements)

Temperature 25.00 deg.cent.

weights 1

range pH 0.00- 6.50

Reference ionic strength 0.000

Ionic strength parameters

A= 0.5000 B= 1.5000

c0= 0.10 c1= 0.23

d0= 0.00 d1= -0.10

according to the equation:

logK=logK(Iref)-AJ/(1+BJ)+I(c0p\*+c1z\*)+JI(d0p\*+d1z\*)

J=SQRT(I)

reactant 1 - Na (+)

reactant 2 - Ca ( 2+)

reactant 3 - Cl (-)

reactant 4 - BTC ( 4- )  
 reactant 5 - NO<sub>3</sub> (-)  
 reactant 6 - H (+)

	log beta	Iref	C	D	Z*	P*	species
1	-14.0000	0.000	-0.6600	0.2000	-2	-2	(H)-1
2	-0.6000	0.000	0.5600	-0.2000	2	1	(Na)(Cl)
3	0.4000	0.000	1.0200	-0.4000	4	1	(Ca)(Cl)
4	0.7500	0.000	1.0200	-0.4000	4	1	(Ca)(NO <sub>3</sub> )
5	-0.0500	0.000	0.5600	-0.2000	2	1	(Na)(NO <sub>3</sub> )
6	7.1800	0.000	1.9400	-0.8000	8	1	(BTC)(H)
7	13.0100	0.000	3.4200	-1.4000	14	2	(BTC)(H)2
8	17.5400	0.000	4.4400	-1.8000	18	3	(BTC)(H)3
9	20.9200	0.000	5.0000	-2.0000	20	4	(BTC)(H)4
10	8.6700	0.000	3.4200	-1.4000	14	2	(Na)(BTC)(H)
11	13.9400	0.000	4.4400	-1.8000	18	3	(Na)(BTC)(H)2
12	17.7600	0.000	5.0000	-2.0000	20	4	(Na)(BTC)(H)3
13	1.8200	0.000	1.9400	-0.8000	8	1	(Na)(BTC)
14	3.4500	0.000	3.4200	-1.4000	14	2	(Na)2(BTC)
15	3.3000	0.000	4.4400	-1.8000	18	3	(Na)3(BTC)
16	9.3100	0.000	4.4400	-1.8000	18	3	(Na)2(BTC)(H)
17	13.1000	0.000	5.0000	-2.0000	20	4	(Na)2(BTC)(H)2
18	4.5000*	0.000	3.7800	-1.6000	16	1	(Ca)(BTC)
19	10.8300*	0.000	4.8000	-2.0000	20	2	(Ca)(BTC)(H)
20	15.5600*	0.000	5.3600	-2.2000	22	3	(Ca)(BTC)(H)2
21	19.1600*	0.000	5.4600	-2.2000	22	4	(Ca)(BTC)(H)3
22	7.6600*	0.000	5.7200	-2.4000	24	2	(Ca)2(BTC)
23	12.7000*	0.000	5.8200	-2.4000	24	3	(Ca)2(BTC)(H)
24	5.6500	0.000	4.8000	-2.0000	20	2	(Na)(Ca)(BTC)
25	11.2000	0.000	5.3600	-2.2000	22	3	(Na)(Ca)(BTC)(H)

\* value to be refined

total no. of points = 1035

ionic strength parameters to be refined:

C1= 0.2300

15 titration parameters to be refined

curve	value
1	C06 0.06000
2	C06 0.04000
3	C06 0.02030
4	C06 0.04030
5	C06 0.02000
6	C06 0.07970
7	C06 0.06010
8	C06 0.04000
9	C06 0.02000
10	C06 0.04000
11	C06 0.02000
12	C06 0.03000
13	C06 0.03000
14	C06 0.03000
15	C06 0.03000

time 20:32:55 timer 73974.531

time 20:36:11 timer 74170.563

net time 0: 3:16.03  
 5 iterations  
 refinement terminated successfully

sigma = 0.6800  
 mean dev. = 0.491

value std.dev.

BETA18	1.10447D+04	2.38334D+03	(Ca) (BTC)
log BETA18	4.04315	0.09372	
BETA19	3.18232D+10	2.55274D+09	(Ca) (BTC) (H)
log BETA19	10.50274	0.03484	
BETA20	5.35284D+15	1.92814D+14	(Ca) (BTC) (H) 2
log BETA20	15.72858	0.01564	
BETA21	1.72857D+19	1.18399D+18	(Ca) (BTC) (H) 3
log BETA21	19.23769	0.02975	
BETA22	5.72557D+07	2.87986D+06	(Ca) 2(BTC)
log BETA22	7.75782	0.02184	
BETA23	8.82756D+12	9.90434D+11	(Ca) 2(BTC) (H)
log BETA23	12.94584	0.04873	
C1	0.20083	0.00366	

curve

		old value	refined value	std.dev.
1	CO6	0.0600000	0.0592121	0.0000700
2	CO6	0.0400000	0.0394038	0.0000472
3	CO6	0.0203000	0.0199572	0.0000251
4	CO6	0.0403000	0.0400429	0.0000474
5	CO6	0.0200000	0.0197603	0.0000270
6	CO6	0.0797000	0.0787080	0.0000625
7	CO6	0.0601000	0.0594859	0.0000490
8	CO6	0.0400000	0.0394460	0.0000377
9	CO6	0.0200000	0.0196975	0.0000235
10	CO6	0.0400000	0.0395871	0.0000329
11	CO6	0.0200000	0.0196422	0.0000314
12	CO6	0.0300000	0.0295027	0.0000210
13	CO6	0.0300000	0.0298957	0.0000231
14	CO6	0.0300000	0.0295133	0.0000209
15	CO6	0.0300000	0.0296916	0.0000232