

APPLICATIONS SECTION

DEC FAM—A NEW COMPUTER ORIENTED ALGORITHM FOR THE DETERMINATION OF EQUILIBRIUM CONSTANTS FROM POTENTIOMETRIC AND/OR SPECTROPHOTOMETRIC MEASUREMENTS—I

BASIC PRINCIPLES OF THE METHOD AND CALCULATIONS OF EQUILIBRIUM CONCENTRATIONS

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Abstract—A new algorithm for the evaluation of equilibrium constants from potentiometric and/or spectrophotometric data, based on the least-squares method has been worked out. The mathematical formalism elaborated enables a very suitable description of the equilibrium problem and provides an analytical expression for all the quantities. In the present paper this formalism and a new method for calculation of equilibrium concentrations are presented. Comparison is made with earlier methods and a generalization is given using this formalism.

Many computer programmes for evaluation of equilibrium constants have been worked out (Gaizer, 1979; Legett & Mc Bryde, 1977). Unfortunately they are applicable only to special types of reactions like acidbase, complex formation or combinations of both. They cannot be readily generalized to other types of equilibria. Some, like SCOGS (Sayce, 1968), need good initial approximations of equilibrium constants. Most of the methods are based on the Gauss-Newton version of the nonlinear least-squares algorithm. By introducing appropriate modifications this method generally becomes stable, but local convergence is only first order. The Newton-Raphson method of minimization gives second order convergence, but the global convergence becomes worse because the Hessian is positive definite only in the region of local convergence. Both methods require computation of derivatives of the type $\partial\psi_i/\partial X_j$; where ψ_i is the result of i th measurement, and X_j the j th parameter to be determined, the Newton-Raphson method needs also $\partial^2\psi_i/\partial X_j\partial X_k$. In programmes published till now, which minimize the sum of the squares of the differences between measured and theoretical absorbances or electromotive forces these derivatives were approximated by divided differences (Alcock, 1978). Programmes applying analytical expressions for the derivatives minimize the sum of squares of other quantities (Sabatini *et al.*, 1974; Zuberbuhler & Kaden, 1982). Our method utilizes analytical expressions of the derivatives of absorbances or of electromotive forces. A general iterative scheme for the determination of equilibrium constants is as shown on the following page.

As shown in the scheme below, it is necessary to compute the equilibrium concentrations in each iter-

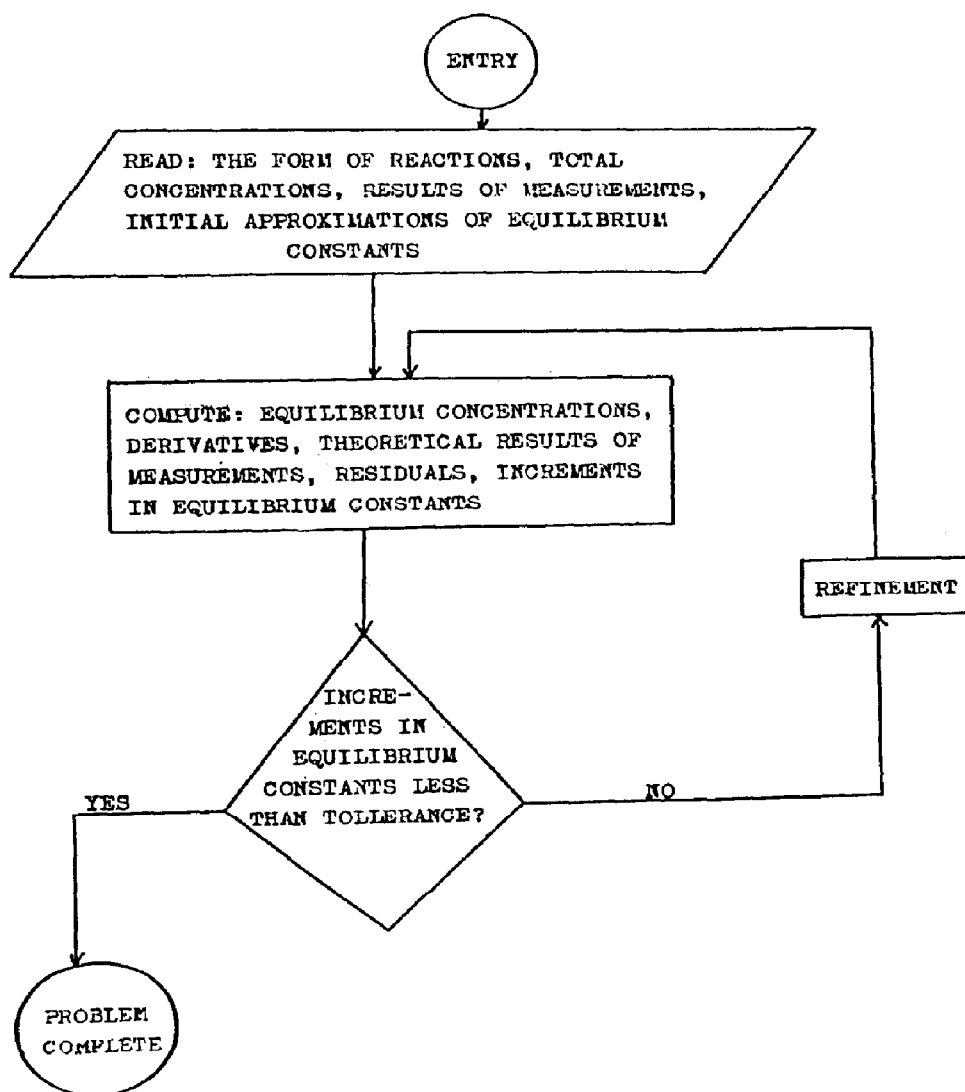
ation. In the following part of our work we describe a formalism which is very convenient in dealing with chemical equilibrium systems, especially electrolytic solutions. We also show how to use this formalism to compute equilibrium concentrations, including cases for which the ionic strength should be considered. In the second part we describe the evaluation of equilibrium constants using nonlinear least-squares.

Let an equilibrium system be composed of n chemical species and assume that there are m reactions. We may describe the state of the system in terms of the concentration (number of moles, mole fraction etc.) of each component:

$$C = [C_1, C_2, \dots, C_n]^T \quad (1)$$

The reactions may be described by a matrix whose elements are the algebraic stoichiometric coefficients, reactants having been transferred to the right side (Bauder & Gunthard, 1972; Petho, 1967). This matrix will be called the stoichiometric matrix, and indicated by a symbol A ; a_{ij} will denote the stoichiometric coefficient of the i th reaction and the j th species. Each a_{ij} is positive for a product, negative for a reactant and zero for a species which does not partake in the i th reaction (Alcock *et al.*, 1978; Bauder & Gunthard, 1972; Petho, 1967). The change in the concentration of the j th species is then expressed by the product $a_{ij}\epsilon_i$ where ϵ_i is the reaction number assigned to the i th reaction (Bauder & Gunthard, 1972). The total change of concentration for the j th species is given by (Bauder & Gunthard, 1972):

$$\Delta C_j = \sum_{i=1}^m a_{ij}\epsilon_i \quad (2)$$



or in matrix notation:

$$\Delta C = A^T \epsilon. \quad (2')$$

The initial state (C^0) will be the set of concentrations resulting from the input value and the equilibrium state (C^*) is a set of concentrations which satisfy equations of equilibrium:

$$\ln K_i = \sum_{j=1}^n a_{ij} \ln C_j \quad i = 1, 2, \dots, m \quad (3)$$

or

$$\ln K = A \ln C. \quad (3')$$

The linear independence of the reactions means the linear independence of the rows of the matrix A : $\det AA^T \neq 0$. Each system of reactions may be replaced by an equivalent system of linearly indepen-

dent linear combinations of those reactions. Mathematically this means that the matrix UA and the vector $U \ln K$ describe the same system as A and that $\ln K(U_{m \times m}, \det U \neq 0)$ (Bauder & Gunthard, 1972; Petho, 1967). The material balance is described by linear equations which may be written as (Alcock *et al.*, 1978; Bauder & Gunthard, 1972):

$$T_i = \sum_{j=1}^n q_{ij} C_j \quad i = 1, 2, \dots, n - m \quad (4)$$

or

$$T = QC. \quad (4')$$

The coordinates of vector T will be called the balance constants, and the matrix Q —the balance matrix. Obviously, the matrix $Q' = VQ$ and the vector $T' = VT(V_{(n-m) \times (n-m)}, \det V \neq 0)$ describe the same situation as Q and T .

The A and the Q matrices are not independent of each other. They satisfy the following matrix equation (Bauder & Gunthard, 1972):

$$AQ^T = 0 \quad (5)$$

The proof of (5) is as follows:

Let $C = C^0 + A^T \epsilon$ where ϵ is a chosen vector. Then $QC = QC^0 = T$ because the balance constants remain the same before and after the reaction. Then we can write:

$$0 = Q(C - C^0) = QA^T \epsilon = (AQ^T)^T \epsilon, \quad \text{for each } \epsilon.$$

This last equation is satisfied if and only if $AQ^T = 0$. The proof is complete.

When A is given, we can find Q using the following formula:

$$Q = [-(^0A^{-1}A^0)^T; I_{(n-m) \times (n-m)}] \quad (6)$$

where $A = [{}^0A_{m \times m}; A_{m \times (n-m)}^0]$, $\det {}^0A \neq 0$. It can be easily proved that (5) holds. Furthermore, in a similar manner, knowing Q we can find A :

$$A = [I_{m \times m}; -(Q^{0-1}Q^0)^T] \quad (7)$$

where

$$Q = [{}^0Q_{(n-m) \times m}; Q_{(n-m) \times (n-m)}^0], \quad \det Q^0 \neq 0.$$

The most convenient way is to reduce $A(Q)$ to such a form that

$${}^0A(Q^0) = I_{m \times m}(I_{(n-m) \times (n-m)}).$$

The balance matrix may be employed to give very convenient parametrical description of the equilibrium state:

$$\ln C_j = \ln C_j^* + \sum_{i=1}^{n-m} q_{ij} \tau_i, \quad j = 1, 2, \dots, n \quad (8)$$

or

$$\ln C = \ln C^* + Q^T \tau, \quad (8')$$

C^* —a state satisfying (3), $\tau_1, \dots, \tau_{n-m}$ —parameters corresponding to the chemical potentials of species.

Obviously:

$$A \ln C = A(\ln C^* + Q^T \tau) = A \ln C^* = \ln K.$$

Derivation

In the equilibrium state:

$$\sum_{j=1}^n a_{ij} \mu_j = 0, \quad i = 1, 2, \dots, m \quad (9)$$

or

$$A\mu = 0$$

(μ_j is the chemical potential of the j th species) so, the vector μ must be a linear combination of the rows of Q :

$$\mu = RTQ^T \tau \quad (10)$$

On the other hand:

$$\mu = \mu^\ominus + RT \ln C \quad (11)$$

then $\ln C = -\mu^\ominus/RT + Q^T \tau = \ln C^* + Q^T \tau$.

Note. In the case of non-ideal solutions the equations (3), (3'), (8), (8') and (11) are not exact, and we must write:

$$\ln K_i = \sum_{j=1}^n a_{ij} \ln \gamma_j C_j \quad (12)$$

$$\mu_i = \mu_i^\ominus + RT \ln \gamma_i C_i \quad (13)$$

$$\ln \gamma_j C_j = \ln(\gamma_j C_j)^* + \sum_{i=1}^{n-m} q_{ij} \tau_i \quad (14)$$

where γ_j is the activity coefficient of the j th species. We want to find the equilibrium concentrations of all species when equilibrium and balance constants are given. Mathematically this means that we must solve the following system of equations:

$$\sum_{j=1}^n a_{ij} \ln C_j = \ln K_i, \quad i = 1, 2, \dots, m \quad (15')$$

$$\sum_{j=1}^n q_{ij} C_j = T_i, \quad i = 1, 2, \dots, n - m. \quad (15'')$$

The following three methods can be used to solve the above system:

(I) Solution of the whole system (15) treating C_j 's as the unknowns. The Newton-Raphson method can be used, as described in the literature (Alcock *et al.*, 1978). We regard this approach as unsuitable because of the large number of unknowns and we have not employed it. The iteration formulas are given in literature (Alcock *et al.*, 1978).

(II) We find the solution of the subsystem (15'') among those concentrations which satisfy (15'). The concentrations satisfy (15') if and only if they satisfy (8), therefore we may insert (8) into (15'') obtaining the following system:

$$\sum_{j=1}^n q_{ij} \exp\left(\ln C_j^* + \sum_{k=1}^{n-m} q_{kj} \tau_k\right) = T_i \quad (16)$$

or

$$f_i(\tau) = \sum_{j=1}^n q_{ij} \exp\left(\ln C_j^* + \sum_{k=1}^{n-m} q_{kj} \tau_k\right) - T_i = 0$$

$$i = 1, 2, \dots, n - m.$$

The system (16) contains $n - m$ unknowns (τ_i) and $n - m$ nonlinear equations, so it can be solved by the Newton-Raphson method. The iteration formulas are:

$$\tau^{(p+1)} = \tau^{(p)} - [Df(\tau^{(p)})]^{-1} f(\tau^{(p)}) \quad (17)$$

$$\ln C^{(p+1)} = \ln C^{(p)} + Q^T \Delta \tau^{(p)}. \quad (18)$$

$$[Df(\tau^{(p)})]_{ij} = \sigma_{ij}^{(p)} = \sum_{k=1}^n q_{ik} q_{jk} C_k^{(p)} = (Q^T \mathcal{L} Q^T)_{ij}^{(p)} \quad (19)$$

where $\mathcal{L} = \text{diag}[C_j]$, p is the number of the iteration,

so $\Delta\tau^{(p)}$ is the solution of the following linear equations system:

$$\sigma^{(p)}\Delta\tau^{(p)} = T - QC^{(p)} \quad (20)$$

$\Delta\tau^{(p)} = \tau^{(p+1)} - \tau^{(p)}$, $\tau^{(0)} = 0$. As the convergence criterion we may take

$$\|\Delta\tau^{(p)}\|_1 = \sum_{i=1}^{n-m} |\Delta\tau_i^{(p)}| < \epsilon$$

(ϵ is a chosen tolerance, usually $\epsilon = 10^{-4}$). Clearly $\|\Delta\tau^{(p)}\|_1$ may become unreasonably large during the iteration process and then the evaluation of $\ln C^{(p+1)}$ according to (18) may be practically impossible. In this case several modifications must be introduced. Define:

$$L_{\phi}x = x \quad (21)$$

$$L_{n+1}x = \text{sgn } x \cdot \ln(1 + |L_n(x)|)$$

Then the modification of $\Delta\tau^{(p)}$ is:

$$\Delta\tau_i^{(p)} \leftarrow L_k(\Delta\tau_i^{(p)}). \quad (22)$$

Usually $k = 1$ enables satisfactory damping. In practice, however, no modifications of $\Delta\tau^{(p)}$ are needed. The problem of solvability of (20) may be considered further. To start the iteration process a positive state satisfying (3) is required. We can easily find it. It has the following form:

$$C_i = 10^{\alpha_i}$$

where

$$\alpha_i = \begin{cases} \beta \sum_{k=1}^{n-m} ({}^0A^{-1}A^0)_{ik} + ({}^0A^{-1} \log_{10} K)_i, & i = 1, \dots, m \\ -\beta & i = m+1, \dots, n. \end{cases} \quad (23)$$

β should be chosen so that the orders of magnitude of all C_i 's are comparable. The method described above corresponds to methods which have been applied to find equilibrium concentrations. Let A , $\Delta\tau$, Q and C be of the form as in the literature (Ting-Po & Nancolas, 1972)

$$A = [I_{m \times m} \quad -P^T] \quad Q = [P^T; I_{(n-m) \times (n-m)}]$$

$$C = [C_1, C_2, \dots, C_m, a_1, a_2, \dots, a_{n-m}]^T \quad (24)$$

$$\Delta\tau = [\Delta \ln a_1, \dots, \Delta \ln a_{n-m}]^T.$$

The iteration formulas according to Eqs. (17)–(19) are as described in Ting-Po & Nancolas, (1972):

$$\sigma_{ij} = a_j \delta_{ij} + \sum_{k=1}^m P_{ik} P_{jk} C_k$$

$$a_j^{(p+1)} = a_j^{(p)} \exp \Delta \ln a_j \quad (25)$$

$$C_j^{(p+1)} = C_j^{(p)} \exp \sum_{k=1}^{n-m} P_{kj} \Delta \ln a_k = K_j \prod_{k=1}^{n-m} [a_k^{(p+1)}]^{c_{kj}}$$

The greatest limitation of the above method is that it cannot readily be applied to the case of non-ideal solutions. If formula (18) were generalized to that

case, it would give activities and not concentrations of components (formula (14)). Since activities are nonlinear functions of concentrations (for example formula (29)), the latter quantities could usually be found only by iterative methods. Concentrations are needed for computing the modified matrix σ , which is now of the following form:

$$\sigma' = Q(\mathcal{L}^{-1} + D\kappa\kappa^T)^{-1}Q^T \quad (26)$$

where

$$D = -\frac{\hat{A} \ln 10}{2} \left(\frac{1}{2\sqrt{\mu}(1 + B\hat{a}\sqrt{\mu})^2} - \hat{C} \right) \quad (27)$$

$$\mu = \frac{1}{2} \sum_{j=1}^n C_j z_j^2$$

is the ionic strength of the solution

$$\kappa_k = z_k^2 \quad (28)$$

z_k is the charge number of the k th species (28) when using the Davies equation.

$$\ln \gamma_j = -\hat{A} \ln 10 z_j^2 \left(\frac{\sqrt{\mu}}{1 + B\hat{a}\sqrt{\mu}} - \hat{C}\mu \right) \quad (29)$$

(III) We find the solution of subsystem (15') among those concentrations that simultaneously satisfy (15''). Concentrations satisfy (15'') if and only if they satisfy (2), so we can insert (2) into (15'), obtaining the following system of m nonlinear equations in m unknowns:

$$\ln K_i = \sum_{j=1}^n a_{ij} \ln \left(C_j^0 + \sum_{k=1}^m a_{kj} \epsilon_k \right) \quad (30)$$

or

$$f_i(\epsilon) = \sum_{j=1}^n a_{ij} \ln \left(C_j^0 + \sum_{k=1}^m a_{kj} \epsilon_k \right) - \ln K_i = 0$$

$$i = 1, 2, \dots, m.$$

Solving these by the Newton-Raphson method, we obtain:

$$\epsilon^{(p+1)} = \epsilon^{(p)} - [Df(\epsilon^{(p)})]^{-1} f(\epsilon^{(p)}) \quad (31)$$

$$C^{(p+1)} = C^{(p)} + A^T \Delta \epsilon^{(p)} \quad (32)$$

where

$$\Delta \epsilon^{(p)} = \epsilon^{(p+1)} - \epsilon^{(p)}$$

$$\rho^{(p)} \Delta \epsilon^{(p)} = \ln K - A \ln C^{(p)} \quad (33)$$

$$\rho_{ij} = \frac{\partial f_i}{\partial \epsilon_j} = \sum_{k=1}^n a_{ik} a_{jk} / C_k = (A \mathcal{L}^{-1} A^T)_{ij}. \quad (34)$$

Clearly formula (32) can lead to negative concentrations. To overcome this we reduce the vector $\Delta \epsilon^{(p)}$ in the following manner (since usually $\Delta \epsilon^{(p)} \ll 1$, (22) is not applicable):

$$\Delta \epsilon^{(p)} \leftarrow \lambda^{(p)} \Delta \epsilon^{(p)} \quad (35)$$

$$\lambda^{(p)} = \min_{i, C_j^{(p)} > 0} \{ \lambda_i^{(p)} \}, \quad \lambda_i^{(p)} = \frac{(1-w)C_i^{(p)}}{C_i^{(p)} - C_i^{(p+1)}} \quad (36)$$

where w is a small positive number; we have used $w = 0.01$. The convergence criterion is:

$$\| \ln K - A \ln C \|_1 < \epsilon, \text{ usually } \epsilon = 10^{-4}. \quad (37)$$

The state used to start the iterative process must satisfy $C^0 > 0$ and $QC = T$. Usually we are given the state satisfying $C \geq 0$ and $QC = T$. Let C satisfy $QC = T$. We must then solve the following system of linear inequalities:

$$C^0 = C + A^T \epsilon^0 > 0. \quad (38)$$

Let $C \geq 0$. The general method for solving (38) is as follows:

Divide the vector C in the following manner:

$$[C_1, C_2, \dots, C_p, 0, 0, \dots, 0]^T = [(C^L)^T; 0]^T \quad (39)$$

where $C_1, C_2, \dots, C_p > 0$.

Then the stoichiometric matrix becomes:

$$A = [L_{m \times p}^T; R_{m \times (n-p)}^T] \quad (40)$$

and (38) becomes:

$$C^L + L\epsilon > 0 \quad (41')$$

$$R\epsilon > 0. \quad (41'')$$

Assume that ϵ^s is the solution of (41''). Clearly, there is such a $\lambda (0 < \lambda \leq 1)$ that $\lambda \epsilon^s$ is also the solution of (41') (since $C^L > 0$), being the solution of (41''). So all the difficulties are connected with the solution of (41'). The algorithm is as follows:

(1) Find such a column of the matrix R whose elements have different signs. Let it be the j th column. If such a j exists then go to (2). If such a column does not exist then for each i :

$$\epsilon_i = \begin{cases} 1 & \text{if the non-zero elements of } i\text{th column of } R \\ & \text{are positive} \\ -1 & \text{otherwise.} \end{cases} \quad (42)$$

Then go to (3).

(2) For such i that $R_{ij} \neq 0$, divide the i th row of R by $|R_{ij}|$, obtaining the matrix R' . Form the reduced system from such inequalities that $R_{ij} = 0$, and from all the possible sums of such pairs of k th and l th inequalities that R'_{kj} and R'_{lj} have opposite signs. In order to simplify the system eliminate all the inequalities which are equal or proportional to those found previously. The number of unknowns is now diminished by one. If the number is equal to unity, the reduced system can easily be solved or its insolubility can be proved. Otherwise go to (1) with the reduced system.

(3) We proceed to the inequalities with an increasing number of unknowns, inserting into them the variables found previously and thus finding the succeeding variable.

A simpler, but not general method for solving (38) can be used when the state satisfies the conditions $C \geq 0$ and $QC = T$.

Divide A and C as given by (39) and (40). In order to solve the system (41) assume $\epsilon = [0, \dots, \epsilon_k, \dots, 0]^T$.

The k th column of the matrix R should contain at least one non-zero element and its non-zero elements should all be negative or all should be positive. If so, the system $R_{ik}\epsilon_k \geq 0, i = 1, 2, \dots, n - p$ can be solved and at least for one $i: R_{ik}\epsilon_k > 0$. Then ϵ_k should have the following form:

$$\epsilon_k = \begin{cases} \alpha \min \left\{ \min_{h: L_{hk} < 0} |C_h^L / L_{hk}|, 1 \right\} \\ \quad \text{if } R_{ik} \text{ are non-negative, } i = 1, \dots, n - p \\ -\alpha \min \left\{ \min_{h: L_{hk} > 0} |C_h^L / L_{hk}|, 1 \right\} \\ \quad \text{if } R_{ik} \text{ are non-positive, } i = 1, \dots, n - p. \end{cases} \quad (43)$$

Then

$$0 < \alpha < 1,$$

$$C_i \leftarrow C_i + a_{ik}\epsilon_k \quad i = 1, 2, \dots, n,$$

Of course, all the coordinates of C^L remain positive after such an operation, and some of C^R coordinates become positive. If all the coordinates of C are already positive the system has been solved, else the procedure should be repeated. (Of course such coordinates of C^R which have become positive and corresponding columns of A should be transferred to C^L and L^T respectively.)

Although this procedure is not a general algorithm for solving (38), it has given very good results in practice.

Another method is to substitute all zero-coordinates of C by small positive numbers less than or equal to the balance error. This is, however, a little risky because even a small error in some coordinates of C may cause a great error in the final results. We are now in a position to generalize the above iteration formulas to the non-ideal solutions. The formulas (30), (33) and (34) become:

$$\ln K_i = \sum_{j=1}^n a_{ij} \ln \gamma_j + \sum_{j=1}^n a_{ij} \ln \left(C_j^0 + \sum_{k=1}^m a_{kj} \epsilon_k \right) \quad i = 1, 2, \dots, m \quad (44)$$

$$\rho_{ij}^{(\nu)} = \rho_{ij}^{(\nu)} + 0.5 \lambda_j \sum_{k=1}^n a_{ik} \frac{\partial \ln \gamma_k}{\partial \mu} \Big|_{\mu^{(\nu)}} \quad \begin{matrix} i = 1, 2, \dots, m \\ j = 1, 2, \dots, m \end{matrix} \quad (45)$$

$$\rho^{(\nu)} \Delta \epsilon^{(\nu)} = \ln K - A (\ln C^{(\nu)} + \ln \gamma^{(\nu)}) \quad (46)$$

where: $\mu^{(\nu)}$ is the ionic strength of the solution in the ν th iteration,

$$\lambda_j = \sum_{k=1}^n a_{jk} \kappa_k, \quad \kappa \text{ is defined by (28)} \quad (47)$$

For example using Davies' equation (see (29)) we obtain:

$$\rho_{ij} = \rho_{ij} + D \lambda_j \rho_j \quad (48)$$

where D is defined by (27), which is not very complicated.

Solvability of the systems (20), (33) and (46):
The matrices of (20) and (33) are of the form:

$$B = SDS^T$$

where D is a positive diagonal matrix. Consider the quadratic form:

$$\begin{aligned} X^T B X &= X^T S D S^T X = X^T S D^{1/2} D^{1/2} S^T X \\ &= (D^{1/2} S^T X)^T \times D^{1/2} S^T X \\ &= \|D^{1/2} S^T X\|_2^2 > 0 \end{aligned} \quad (49)$$

when $X \neq 0$ since S has the full rank. It means that B is a positive definite matrix and therefore has the inverse. So the systems (20) and (33) are solvable.

Examine now the matrix of (48). Consider the quadratic form:

$$X^T \rho' X = \|\mathcal{L}^{-1/2} A^T X\|_2^2 + D(\lambda^T X)^2.$$

In the case of dilute solutions $D \sim -1/\sqrt{C_{\max}}$ and

$$\|\mathcal{L}^{-1/2} A^T X\|_2^2 \sim 1/C_{\min}. \quad \text{Since } C_i \ll 1 (i = 1, \dots, n)$$

the quadratic form is greater than zero, and (46) is solvable. Otherwise the quadratic form becomes zero for $X \neq 0$, and the matrix ρ' may have no inverse. When ρ' loses its positive definite property the iteration process can diverge (Byrne & Hall, 1970).

Note. Since ρ and σ are, for $C > 0$, for positive definite matrices, it is convenient to use the Choleski decomposition to solve (20) and (33).

Practical considerations and numerical examples

Calculations have been carried out using ODRA 1204 and ODRA 1305 computers. The programmes have been written in an ALGOL-60 (version for the ODRA 1204) and in FORTRAN (for the ODRA 1305). Methods (II) and (III) have been written as procedures UMDESTau and UMDES (Universal Method for the Determination of Equilibrium States). UMDES is able to deal with non-ideal solutions. Several versions of the above mentioned programmes have been tested using a number of different examples. Our conclusions are as follows:

(1) Methods (II) and (III) both give rapid quadratic local convergence. Global convergence is also very good, except for several ill-conditioned examples which will be considered later, and is not greatly dependent on the initial guesses. A typical run of (III) is as follows:

(a) *Calculations for a solution of ferrous sulphide in water.* The stoichiometric matrix and the equilibrium constants are:

H ⁺	OH ⁻	Fe ²⁺	FeOH ⁺	S ⁻	HS ⁻	H ₂ S	K
1	1	0	0	0	0	0	10 ⁻¹⁴
0	0	1	0	1	0	0	5.1 × 10 ⁻¹⁸
1	0	0	0	0	1	-1	8.9 × 10 ⁻⁸
1	0	0	0	1	-1	0	1.3 × 10 ⁻¹³
1	0	-1	1	0	0	0	1.2 × 10 ⁻⁶

Table 1.

Number of iteration	log ₁₀ C _i			
	1	2	3	4
0	-7.0000	-6.9893	-8.3010	-8.3010
1	-7.0345	-6.9600	-8.1107	-7.9366
2	-7.1626	-6.8638	-7.5686	-7.2382
3	-8.4245	-6.5615	-7.0799	-6.4511
4	-8.0796	-6.2481	-7.0918	-5.8407
5	-7.9685	-6.0828	-7.2068	-5.4315
6	-7.9547	-6.0470	-7.1813	-5.2126
7	-7.9518	-6.0482	-7.1715	-5.1458
8	-7.9516	-6.0484	-7.1707	-5.1400
9	-7.9516	-6.0484	-7.1707	-5.1399

Number of iteration	log ₁₀ C _i		
	5	6	7
0	-8.3010	-8.6021	-8.6021
1	-10.3010	-8.0136	-8.0186
2	-12.3010	-7.3592	-7.3866
3	-11.6150	-6.6027	-6.7269
4	-10.9860	-5.9794	-6.3228
5	-10.5029	-5.5213	-6.1229
6	-10.2241	-5.2696	-6.0859
7	-10.1316	-5.1938	-6.0880
8	-10.1218	-5.1873	-6.0883
9	-10.1217	-5.1873	-6.0883

For the explanation of the form of the stoichiometric matrix see APPENDIX.

An example of results of calculations for non-ideal solutions is as follows (obviously method (III) has been used):

(b) *Calculations for the solution of Co(OH)₂ in 0.5 M glutamic acid.* The stoichiometric matrix and the equilibrium constants are:

The stoichiometric matrix has been transformed into form (24). Methods (II) and (III) have been used to calculate equilibrium concentrations. Execution time is 12 s for method (II) and 21 s for method (III). The equilibrium concentrations are:

$$[H^+] = 2.4169 \times 10^{-11} \quad [A_2H^-] = 8.1003 \times 10^{-5}$$

OH ⁻	L ²⁻	Co ²⁺	Co(OH) ⁺	Co(OH) ₂	CoL	CoL ₂ ²⁻	H ₃ L ⁺	HL ⁻	H ₂ L	H ⁺	log ₁₀ K
1	0	0	0	0	0	0	0	0	0	1	-14.00
-1	0	-1	1	0	0	0	0	0	0	0	4.10
-2	0	-1	0	1	0	0	0	0	0	0	9.20
2	0	1	0	0	0	0	0	0	0	0	-14.80
0	-1	-1	0	0	1	0	0	0	0	0	5.06
0	-2	-1	0	0	0	1	0	0	0	0	8.46
0	-1	0	0	0	0	0	1	0	0	-3	16.25
0	-1	0	0	0	0	0	0	1	0	-1	9.67
0	-1	0	0	0	0	0	0	0	1	-2	13.95

The Davies equation has been used to calculate the activity coefficients. We have assumed $\bar{A} = 0.51$, $B\bar{a} = 1.0$, $\bar{C} = 0.3$.

The result is as follows:

Species	log ₁₀ C _i	log ₁₀ C _i γ _i
OH ⁻	-6.5509	-6.6855
L ²⁻	-3.7073	-4.2456
Co ²⁺	-0.8908	-1.4291
Co(OH) ⁺	-3.8800	-4.0145
Co(OH) ₂	-5.6000	-5.6000
CoL	-0.6147	-0.6147
CoL ₂ ²⁻	-0.9219	-1.4602
H ₃ L ⁺	-9.8046	-9.9392
HL ⁻	-1.7555	-1.8901
H ₂ L	-4.9246	-4.9246
H ⁺	-7.1799	-7.3145

where H₂L denotes glutamic acid.

(2) If the number of reactions is less than the number of balance equations, method (III) is preferred because there are fewer unknowns. Otherwise method (II) is preferred. But for the calculations for non-ideal solutions we must always use method (III). The following example illustrates these points:

Calculations for the solution of 2.475 × 10⁻⁴ M picric acid and 9.9 × 10⁻⁴ M triethylamine in acetonitrile. Methods (II) and (III) have been used. Initial states have been defined using formulas (23) with β = 5 for (II) and (43) for (III) respectively.

The stoichiometric matrix and the equilibrium constants are as follows (Ralph, E. K. & Gilbertson W. R.; Kolthoff & Chantooni, 1966):

$$[BH^+] = 1.1121 \times 10^{-4} \quad [BHA] = 1.3629 \times 10^{-4}$$

$$[HA] = 6.6150 \times 10^{-4} \quad [B] = 2.2050 \times 10^{-13}$$

$$[B_2H^+] = 2.1263 \times 10^{-14} \quad [A^-] = 3.0209 \times 10^{-5}$$

(B denotes triethylamine and HA picric acid).

(3) The calculation of the matrices ρ and σ. The calculation of the matrix ρ needs, according to (34) $\frac{1}{2} \times n \times m \times (m+1)$ multiplications. For $\sigma \frac{1}{2} \times n \times (n-m) \times (n-m+1)$ multiplications are required. The number of multiplications can considerably be reduced if we transform the A(Q) matrix into the form (24). (In K or T must be transformed simultaneously). Then we need only $\frac{1}{2} \times (n-m) \times m \times (m+1)$ for the calculation of ρ and $\frac{1}{2} \times m \times (n-m) \times (n-m+1)$ for σ matrix. Let n = 8, m = 5 (as in a real situation). Without modification the number of multiplications is equal to 360 for ρ and 144 for σ matrix. After employing the transformation the number of multiplications reduces to 135 for the ρ and 90 for the σ matrix. This is a very considerable reduction. The reduction of time required for the calculations is illustrated by the following examples:

(a) The example is like (2). Without the transformation of the stoichiometric matrix the execution time is 36 s, with transformation time in 23 s. The method (III) has been used.

(b) In the case (1b) the execution time was 103 s without transformation and 56 s with transformation.

(4) The use of the Choleski factoring instead of the Gauss decomposition for the solution of (20) or (33) also reduces the execution time. The reduction is however not as considerable as in the case of the

H ⁺	BH ⁺	HA	B ₂ H ⁺	A ₂ H ⁻	BHA	B	A ⁻	K
1	-1	0	0	0	0	1	0	4.792 × 10 ⁻²⁰
1	0	-1	0	0	0	0	1	1.1037 × 10 ⁻¹²
0	-1	0	1	0	0	-1	0	8.6715 × 10 ²
0	0	-1	0	1	0	0	-1	4.0536 × 10 ³
0	-1	0	0	0	1	0	-1	4.0568 × 10 ⁴

modification (3). In the case of (3a) the execution time was 21 s when applying the Choleski method.

(5) Consider the following example:

$$(i) \quad A = \begin{matrix} & \text{H}^+ & \text{BH}^+ & \text{B} & \text{HA} & \text{A}^- & \text{BHA} \\ \begin{bmatrix} 1 & -1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & -1 & 1 & 0 \\ 0 & -1 & 0 & 0 & -1 & 1 \end{bmatrix} \end{matrix}$$

$$(ii) \quad A' = \begin{matrix} & \text{H}^+ & \text{BH}^+ & \text{B} & \text{HA} & \text{A}^- & \text{BHA} \\ \begin{bmatrix} 1 & -1 & 1 & 0 & 0 & 0 \\ 0 & -1 & 1 & 1 & -1 & 0 \\ 0 & -1 & 0 & 0 & -1 & 1 \end{bmatrix} \end{matrix}$$

where B denotes triethylamine and HA picric acid. The initial concentrations and the equilibrium constants for i and ii are:

H ⁺	7.8950 × 10 ⁻⁶	
BH ⁺	6.3950 × 10 ⁻⁵	
B	5.1921 × 10 ⁻³	
HA	7.1055 × 10 ⁻⁴	[mole × dm ⁻³]
A ⁻	7.1845 × 10 ⁻⁵	
BHA	7.1055 × 10 ⁻⁶	

$$(i) \quad \begin{matrix} K_1 = 10^{-18.46} \\ K_2 = 10^{-11} \\ K_3 = 10^3 \end{matrix} \quad (ii) \quad \begin{matrix} K'_1 = 10^{-18.46} \\ K'_2 = 10^{-7.46} \\ K'_3 = 10^3 \end{matrix}$$

(in acetonitrile)

Method (III) has been used for the calculation of equilibrium concentrations. The results are as follows:

(i) Diverged. 100 iterations were allowed.

$$\|\ln K - A \ln C^{(100)}\|_1 = 28.7$$

(ii) Converged in 16 iterations.

$$\begin{matrix} [\text{H}^+] = 4.0269 \times 10^{-20} \\ [\text{BH}^+] = 5.1956 \times 10^{-4} \\ [\text{B}] = 4.4737 \times 10^{-3} \\ [\text{HA}] = 2.0922 \times 10^{-12} \\ [\text{A}^-] = 5.1956 \times 10^{-4} \\ [\text{BHA}] = 2.6994 \times 10^{-4} \end{matrix}$$

Description (i) and (ii) are for the same system, so the calculations should have given the same result. But problem (i) diverges; this is due to the finite machine accuracy. Write:

$$\begin{matrix} \tilde{\rho}_{11} = \beta(\tilde{C}_{\text{H}^+}^{-1} + \tilde{C}_{\text{B}^-}^{-1} + \tilde{C}_{\text{BH}^+}^{-1}) \\ \tilde{\rho}_{12} = \tilde{C}_{\text{H}^+}^{-1} \end{matrix}$$

Clearly, near the final solution the hydrogen ion concentration becomes much smaller than the other concentrations (see the results of the calculations for (ii)). Thus:

$$\tilde{\rho}_{11} = \tilde{C}_{\text{H}^+}^{-1} = \tilde{\rho}_{12}$$

since ODRS carries 11 significant digits only. Thus the ρ matrix is ill-conditioned for system (i). This difficulty has been overcome in (ii) since the matrix A contains only one non-zero element in the column of the stoichiometric matrix corresponding to H^+ . In conclusion, when the iteration process diverges because of the fact that more than one non-zero element is in the column corresponding to the smallest C_i , the stoichiometric matrix should be transformed into the form in which only one non-zero element is in that column. As for matrix σ , it is possible for one concentration to be much greater than the others when the corresponding column of the matrix Q contains more than one non-zero element. If such is the case then transform Q and T as A and $\ln K$ in the above case. This is, however, a very rare situation.

(6) As we have shown above, introducing the ionic strength may lead to divergence of the iteration process. The following example illustrates this:

Calculations for the mixture of 0.1 M $\text{Fe}(\text{SCN})_3$, 0.1 M $\text{Fe}(\text{SCN})_2$ and 0.1 M H_2O_2 . Complex formation, redox and acid-base reactions are taken into consideration. The calculations have been carried out using method (III) with and without introducing activity coefficients. The equilibrium constants presented in the literature have been used (Inczedy, 1974):

(i) with activity coefficients Davies' equation with

$$\hat{A} = 0.5, B_a = 1.0, \hat{C} = 0.3$$

has been used.

$$\|A \ln C^{(100)} - \ln K\|_1 = 442$$

$$\mu^{(100)} = 4.23$$

(ii) without activity coefficients

$$\begin{matrix} \log_{10}[\text{H}^+] = -5.8711 \\ \log_{10}[\text{OH}^-] = -8.1289 \\ \log_{10}[\text{Fe}^{3+}] = -4.5844 \\ \log_{10}[\text{Fe}(\text{SCN})^{2+}] = -3.0838 \\ \log_{10}[\text{Fe}(\text{SCN})_2^+] = -1.9812 \\ \log_{10}[\text{Fe}(\text{SCN})_3] = -1.3837 \\ \log_{10}[\text{Fe}(\text{SCN})_4^-] = -1.3883 \\ \log_{10}[\text{Fe}(\text{SCN})_5^{2-}] = -2.1887 \\ \log_{10}[\text{Fe}^{2+}] = -15.0705 \\ \log_{10}[\text{FeSCN}^+] = -14.8709 \\ \log_{10}[\text{FeO}_2\text{H}^{2+}] = -2.4873 \\ \log_{10}[\text{H}_2\text{O}_2] = -1.3303 \\ \log_{10}[\text{HO}_2^-] = -7.2039 \\ \log_{10}[c_{\text{aq}}] = -23.4638 \\ \log_{10}[\text{SCN}^-] = -0.8005 \\ \log_{10}[\text{FeOH}^+] = -1.0144 \end{matrix}$$

As is shown above, the ionic strength became unreasonably large during the iteration process, a situation that is unphysical. The remedy is to calculate first without the ionic strength corrections until the region of the final solution is attained, and then to introduce the correction.

APPENDIX

(1) *The number of balance equations.* It is clear (see (5)) that the rows of the matrix A are orthogonal to those of Q . The rows of A span a m -dimensional space which is a subspace of a n -dimensional space. Thus the dimension of the space orthogonal to that spanned by the rows of A (which moreover is a subspace of the same n -dimensional space) is $n - m$. Thus the rank of Q , and consequently the number of linearly independent balance equations is $n - m$.

(2) *Uniqueness of the solution of (15).* Obviously, one initial state C^0 precisely corresponds to one particular state of equilibrium C^* (it is the result of thermodynamical considerations). But it should be shown that the system (15) has no other physical, that is positive solutions. Let C^\square be a solution of (15). Every other solution must satisfy:

$$C_j = C_j^\square + \sum_{i=1}^m a_{ij} \epsilon_i$$

$$\ln C_j = \ln C_j^\square + \sum_{i=1}^{n-m} q_{ij} \tau_i$$

and therefore:

$$C_j^\square + \sum_{k=1}^m a_{kj} \epsilon_k = C_j^\square \exp\left(\sum_{k=1}^{n-m} q_{kj} \tau_k\right) \quad j = 1, 2, \dots, n. \quad (50)$$

Clearly, the system (50) has the zero-solution. Assume that there are non-zero solutions, that is $\epsilon \neq 0$ and $\tau \neq 0$:

$$\sum_{k=1}^m a_{kj} \epsilon_k = C_j^\square \left(\exp\left(\sum_{k=1}^{n-m} q_{kj} \tau_k\right) - 1 \right).$$

Since

$$\text{sign}\left(\exp\left(\sum_{k=1}^{n-m} q_{kj} \tau_k\right) - 1\right) = \text{sign} \sum_{k=1}^{n-m} q_{kj} \tau_k$$

and for each j $C_j^\square > 0$, the following inequalities hold:

$$\left(\sum_{k=1}^m a_{kj} \epsilon_k\right) \left(\sum_{i=1}^{n-m} q_{ij} \tau_i\right) \geq 0 \quad j = 1, 2, \dots, n. \quad (51)$$

Since $\epsilon \neq 0$, there is such j' that $\sum_{k=1}^m a_{kj'} \epsilon_k \neq 0$ and $\sum_{k=1}^{n-m} q_{kj'} \tau_k \neq 0$. Then:

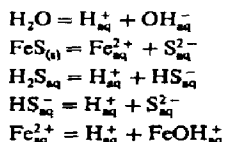
$$\left(\sum_{k=1}^m a_{kj'} \epsilon_k\right) \left(\sum_{i=1}^{n-m} q_{ij'} \tau_i\right) > 0,$$

and summing (51) over all j 's:

$$\sum_{j=1}^n \sum_{k=1}^m a_{kj} \epsilon_k \sum_{i=1}^{n-m} q_{ij} \tau_i = \sum_{k=1}^m \sum_{i=1}^{n-m} \epsilon_k \tau_i \sum_{j=1}^n a_{kj} q_{ij} > 0. \quad (52)$$

Since $\sum_{j=1}^n a_{kj} q_{ij} = (AQ^T)_{ki} = 0$, then (52) gives a contradiction. Then there are no non-zero solutions.

(3) *Some practical aspects of the stoichiometric matrix.* Consider the system of the example 1a. The reactions have the following form:



and then the full stoichiometric matrix is:

H_{aq}^+	OH_{aq}^-	$\text{Fe}_{\text{aq}}^{2+}$	$\text{FeOH}_{\text{aq}}^+$	$\text{S}_{\text{aq}}^{2-}$	HS_{aq}^-	$\text{H}_2\text{S}_{\text{aq}}$	H_2O	$\text{FeS}_{(\text{s})}$
1	1	0	0	0	0	0	-1	0
0	0	1	0	1	0	0	0	-1
1	0	0	0	0	1	-1	0	0
1	0	0	0	1	-1	0	0	0
1	0	-1	1	0	0	0	0	0

The relative change of $C_{\text{H}_2\text{O}}$ is negligible, then the expressions containing $\ln C_{\text{H}_2\text{O}}$ are approximately constant and can therefore be transferred to the right of eqns (3). After that operation we obtain a simplified system $A' \ln C' = \ln K'$ such that the matrix A' does not contain the column corresponding to H_2O and $\ln C'$ does not contain $\ln C_{\text{H}_2\text{O}}$. Although the change of $\ln C_{\text{H}_2\text{O}}$ is negligible, the change of $C_{\text{H}_2\text{O}}$ is not. Therefore a similar procedure cannot be applied to the balance equations. The matrix Q (and the vector T) should be transformed into such a form which contains only one non-zero element in the column corresponding to H_2O (see p. 5), and then the row containing that element should be removed. Then the column corresponding to H_2O can be removed from the balance matrix (since it contains only zero-elements). A similar operation can be performed in order to remove $\text{FeS}_{(\text{s})}$. Because $C_{\text{FeS}_{(\text{s})}} = \text{const}$ one can remove the column corresponding to $\text{FeS}_{(\text{s})}$ from the stoichiometric matrix, as in the case of H_2O . Since the system is heterogenous, the quantity of moles should, instead of concentrations be inserted into the balance equations. Removing of $\text{FeS}_{(\text{s})}$ from the balance matrix is like in the case of H_2O . The reduced balance matrix corresponds yet to a homogenous system and the balance equations may therefore be divided by the volume of the liquid phase, giving equations which contain concentrations.

The equations system to be solved is:

$$\begin{aligned} \ln C_1 + \ln C_2 &= \ln K_1 \\ \ln C_3 + \ln C_5 &= \ln K_2 \\ \ln C_1 + \ln C_6 - \ln C_7 &= \ln K_3 \\ \ln C_1 + \ln C_3 - \ln C_6 &= \ln K_4 \\ \ln C_1 - \ln C_3 + \ln C_4 &= \ln K_5 \end{aligned}$$

where:

$$\begin{aligned} C_1 &= C_1^0 + \epsilon_1 + \epsilon_3 + \epsilon_4 + \epsilon_5 \\ C_2 &= C_2^0 + \epsilon_1 \\ C_3 &= C_3^0 + \epsilon_2 - \epsilon_5 \\ C_4 &= C_4^0 + \epsilon_3 \\ C_5 &= C_5^0 + \epsilon_2 + \epsilon_4 \\ C_6 &= C_6^0 + \epsilon_3 - \epsilon_4 \\ C_7 &= C_7^0 - \epsilon_3. \end{aligned}$$

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