Thermochimica Acta, 138 (1989) 141–146
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COMPUTER ANALYSIS OF EQUILIBRIUM DATA IN SOLUTION. ES5CM FORTRAN AND BASIC PROGRAMS FOR COMPUTING FORMATION ENTHALPIES FROM CALORIMETRIC MEASUREMENTS

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(Received 4 March 1988)

ABSTRACT

A computer program was written in FORTRAN and BASIC languages for calculating enthalpy changes of complex formation in solution from direct calorimetric measurements. The program (ES5CM) can deal with any system in which mononuclear, polynuclear, protonated, hydroxo, mixed metal or mixed ligand complexes are formed. Particular attention has been paid to the robustness of the algorithm and to the possibility of using the program ES5CM with different machines, including small personal computers. Some test systems were used to check the efficiency of the program, and execution times for different machines are reported.

INTRODUCTION

For the last decade we, together with some other colleagues, have been dealing with the computer analysis of equilibrium data (potentiometric and calorimetric) of solutions [1–11].

The computation of enthalpy changes for ion association in solution from calorimetric data involves a series of problems that can be solved rigorously only by means of a general calculation method. Therefore, we have developed an algorithm, and some computer programs based on this algorithm, with the aim of providing a simple and general calculation method, valid for the different systems that may be studied in different laboratories where calorimetric measurements are performed.

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0040-6031/89/$03.50

Here, we report the simplest version of the program ES5CM (Equilibria in Solution, problem no. 5, Calorimetric Measurements).

METHOD

The main features of a general program for computing ΔH^0 values for reactions in solution are:

(a) calculation of the concentrations of all the species at each point of the titration;

(b) solution of the system of linear equations

$$-Q_{\text{corr},h} = \sum_i \Delta H_i^0 \delta n_{ih} \tag{1}$$

where Q_{corr} is the measured heat, corrected for the dilution and for heat contributions of reactions for which ΔH^0 is known, δn is the change (mmol) in the concentration of the ith species, and h is the index of the titration point;

(c) some optional calculations, such as the determination of the weight at each point, the correction of ΔH^0 and of formation constants when dealing with experimental conditions where the ionic strength cannot be kept constant, and the simultaneous calculation of enthalpy changes and formation constants.

For the calculation of species concentrations, we chose a simplified version of the ES4EC algorithm [9–11] devised for calculating free concentrations in large multimetal–multiligand systems, which makes use of a particular damped Newton–Raphson technique [9–12]. The problem is represented by the solution of the set of mass balance equations

$$f_k(c) = c_k + \sum_i p_{ik}\beta_i \prod_j c_j^{p_{ij}} - C_k = 0 \tag{2}$$

where c is the free concentration, C the analytical concentration, p the stoichiometric coefficient, β the formation constant, k and j indices for the component, and i the index for the species. Since in solving highly non-linear equations such as eqn. (2), the Newton–Raphson method may diverge, a damping factor R is used in the iterations

$$R_k^{(n)} = C_k / C_{k,\text{calcd}}^{(n)} \tag{3}$$

where n is the iteration index. If $R_k^{(n)}$ lies outside the range 0.25–4, then the free concentration of the kth component is damped by

$$c_{k,\text{damped}}^{(n)} = c_k^{(n)} \left(R_k^q \right)^{(n)} \tag{4}$$

where $q = | p_{ik} |_{\max}^{-\eta}$ (i.e. q is the reciprocal of the greatest stoichiometric coefficient of the species containing the kth component [9], η is an exponential correction for the damping factor R (in general $\eta = 1$, but in some cases

$\eta > 1$ speeds up calculations—see ref. 10). Other details concerning the procedure followed in computing free concentrations are reported in refs. 9–11.

Once c_k and x_i (concentration of the ith species) values are obtained, we can calculate the concentration changes δn by

$$\delta n_{ih} = x_{ih}V_h - x_{i(h-1)}V_{h-1} - x_i^{\mathrm{T}}(v_h - v_{h-1}) \tag{5}$$

(where V is the total volume, v the titrant volume, x_i^{T} the concentration of the ith species in the titrant, and h the index for the titration point). Equation (1) can then be solved by the linear least squares method, by minimizing the function

$$U = \sum_h w_h (Q_{\mathrm{corr},h} - Q_{\mathrm{corr,h,calcd}})^2 \tag{6}$$

The weight w can be obtained from variance propagation

$$w^{-1} = s^2 = s_Q^2 + \sum_i [\partial(\delta n_i)/\partial v]^2 s_v^2 \tag{7}$$

(where s_Q^2 and s_v^2 are estimates of variances in the measured heat and in the titrant volume, respectively) for each point. In practice, the weight can also be chosen as follows:

(i) $w^{-1} = s_Q^2$ when assuming $s_v^2 = 0$ (or negligible);

(ii) $w^{-1} = Q^2$ when the Q values differ markedly from each other;

(iii) $w = f(\delta n)$ when δn values vary markedly from point to point (see ref. 4);

(iv) $w = 1$ when all the points have the same weight;

(v) the weight can be read in for each point, i.e., the weight is given by user.

It is necessary to stress that the correct choice of weights is of fundamental importance in order to obtain reliable "best values" of the parameters to be refined. Although some of the proposed ways of weighting have no theoretical basis, they can be of help in certain particular cases; separate trials must be performed for each type of system considered. For the program ES5CM fairly good estimates of the partial derivatives $\partial(\delta n)/\partial v$ in eqn. (7) are obtained by a simple linear interpolation of the curve $\delta n = f(v)$.

RESULTS AND DISCUSSION

On the basis of the above method, two programs have been written in FORTRAN (ES5CM1) and BASIC (EC5CM2) languages. These programs (identical, apart from the language) consist of the MAIN routine and eleven subroutines:

MAIN	controls all the program (recalls INP, DNC, LINRE and OUT).

INP	reads all the input data.
DNC	calculates δn values (recalls GCL)
GCL	calculates initial estimates of free concentrations (recalls FES4).
FES4	calculates free concentrations (recalls SPECO, CTOL, SCALE, GAUSSC).
SPECO	calculates species concentrations and $C_{k,\text{calcd}}$ (see eqn. (3)).
CTOL	checks for R value (damping procedure, eqns. (3) and (4)) (recalls SPECO).
WCURV	calculates weights according to eqn. (7) by smoothing the curve $\delta n = f(v)$.
SCALE	for the scaling procedure before solving linear equations
GAUSSC	for solving the system of linear equations, by using the compact Gauss method [13]; this routine is recalled both for calculating free concentrations (Newton–Raphson technique) and for calculating ΔH^0 values (least squares method).
LINRE	for the linear least squares calculation (recalls SCALE and GAUSSC).
OUT	prints out all the results.

The programs ES5CM1 and ES5CM2 were run in the following machines:

(a) IBM PC (CPU i8086; operating systems MS DOS 2.10 and 3.10, mathematical coprocessor i8087, compilers BASCOM version 2.0, IBM FORTRAN version 2.0, FORTRAN Professional (PROFORT) version 1.0 and TURBO BASIC version 3.0);

(b) IBM PC AT (CPU i80286, operating system MS DOS 3.2, mathematical coprocessor i80287, compilers as for IBM PC);

(c) OLIVETTI M24 (CPU i8086, operating systems MS DOS 2.10 and 3.20, mathematical coprocessor i8087, compilers as for IBM PC).

TABLE 1

Test systems [14] used for checking the performances of the ES5CM program

Test system	NMBE [a]	NS [b]	NP [c]	NT [d]	No. of ΔH^0 calculated
I	3	7	180	7	6
II	3	11	177	11	10
III	3	5	40	4	4
IV	4	12	70	7	11
V	2	6	60	4	5
VI	2	6	60	4	5

[a] Number of mass balance equations.
[b] Number of species.
[c] Total number of points.
[d] Number of titrations.

TABLE 2

Some net execution times (s) [a]

System	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_8	τ_9	τ_{10}
I	58	32	405	39	37	29	114	28	17	192
II	178	98	1274	112	109	83	358	82	48	606
III	21	12	135	14	13	11	38	10	6	64
IV	125	67	876	82	78	58	246	61	34	418
V	27	16	192	18	18	13	54	13	8	91
VI	31	18	216	20	19	16	61	14	9	103

[a] See Table 3.

TABLE 3

Technical details concerning the execution times in Table 2

	Machine	Language	Compiler
τ_1	IBM PC	FORTRAN	IBM FORTRAN (i8087)
τ_2	IBM PC	FORTRAN	PROFORT (i8087)
τ_3	IBM PC	BASIC	BASCOM
τ_4	IBM PC	BASIC	TURBO BASIC (i8087)
τ_5	IBM PC AT	FORTRAN	IBM FORTRAN (i8087)
τ_6	IBM PC AT	FORTRAN	PROFORT (i80287)
τ_7	IBM PC AT	BASIC	BASCOM
τ_8	OLIVETTI M24	FORTRAN	IBM FORTRAN (i8087)
τ_9	OLIVETTI M24	FORTRAN	PROFORT (i8087)
τ_{10}	OLIVETTI M24	BASIC	BASCOM

Some preliminary trials were performed with a Honeywell Lev. 6 and a VAX 750. The robustness and the efficiency of ES5CM1 and ES5CM2 were checked by using the test systems [14] briefly described in Table 1. All the test systems were solved by both programs, and some execution times are reported in Table 2.

On the basis of the obtained results we can affirm that both programs are robust (the test systems reported in Table 1 are quite representative of the most complicated systems one can deal with in calorimetric studies), and fast (see Table 2). With respect to the DOEC program [4], the present programs are more compact, can deal with more weighting schemes, are more robust, and the FORTRAN version is by far the fastest. In the near future, development of this work will involve the simultaneous calculation of ΔH^0 and β, and the treatment of data in not constant ionic strength conditions.

Listings and input instructions of ES5CM1 and ES5CM2 will be supplied on request.

ACKNOWLEDGEMENTS

We thank CNR (Rome) and Ministero della Pubblica Istruzione for financial support, Mr. M. Grasso and Dr. R. Purrello (University of Catania) for comments and trials on the BASIC version and Prof. S. Sammartano for helpful discussion.

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