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MINITERM, A DESK-COMPUTER PROGRAM FOR EVALUATION OF COMPLEX EQUILIBRIA FROM THERMOMETRIC DATA

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ABSTRACT

The program MINITERM is designed to run on a desk-computer with 32 kbytes of memory. It can calculate the optimum values of the overall enthalpies and stability constants of a maximum of eight species with composition $M_qL_pH_r$ (r or q can be zero), or the mixed-ligand complexes formed in the system $MA_N + MB_N$ ($N = 2,\ 3$ or 4), from thermometric data.

INTRODUCTION

Although thermometric titrations have only been used for enthalpy calculations, it has been proved that they can also be used for the simultaneous determination of both reaction enthalpies and equilibria constants (ΔG). In this case, therefore, the entropies of the reactions can be calculated, and then the technique is known as "entropic titration" [1].

Several excellent general programs for potentiometric and/or spectrophotometric data refinement can be found in the literature [2–5]. Nevertheless, programs for the refinement of thermodynamic parameters obtained from thermometric titrations are scarce.

The good results obtained in using MINISPEF [6] and MINIPOT [7], and the similarity in the basic foundations of thermometry, have encouraged us to use their algorithms in the simultaneous refinement of reaction enthalpies and equilibrium constants.

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EXPERIMENTAL

Calorimetric equipment

A thermometric titrator was built according to the design of Lumbiarres et al. [8] with several modifications. It consists (Fig. 1) of an automatic 5-ml Metrohm Herisau Dosimat E 535 burette, a temperature-measuring bridge with thermistor, an adiabatic titration cell, an electric calibration system and an OmniScribe B-5000 recorder (Houston Instruments).

To measure temperature, a miniature thermistor of the thermometer type, with a nominal value of 100 kΩ at 25°C, was selected. Its experimental calibration indicates that it follows the equation [9]

$$\ln R_T(\mathrm{k}\Omega) = A\exp[B/(T + C)]$$

where $A = 1.30E - 5$, $B = 5668$ K, $C = 61.8$ K.

The temperature scale of the enthalpygrams is modified by varying both the attenuation of the register and the input voltage of the bridge. We have usually used a scale of 0.1° (≡ 10 mV full scale).

The behaviour of the apparatus has been determined by the titration of 80.0 ml of several NaOH solutions of increasing concentration, with 0.9933 N HCl.

Heat capacity of the cell

In all the titrations 80.0 ml of the sample were used and the heat capacity of the system was determined under the same experimental conditions, by

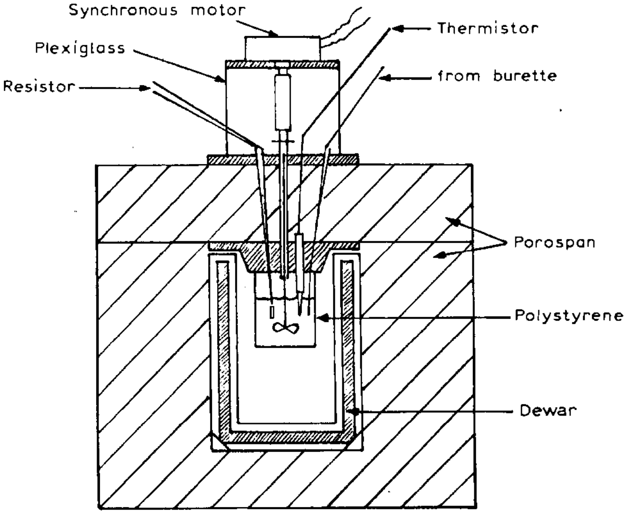

Fig. 1. Thermometric cell.

introducing a known quantity of heat by means of the electric calibration system or through a chemical reaction of well-known enthalpy (i.e., the neutralization of NaOH with HCl). The two methods have given concordant results, whose mean value is 89.3 cal $°C^{-1}$.

Procedure

Several independent samples of thioether acids and amidoximes were titrated at 20°C with 0.9020 N NaOH.

Calculations

A Hewlett-Packard HP-85 desk-computer with 32 kbytes of RAM was used for the calculations. The program, in BASIC, together with the entry data are available on request.

THE PROGRAM BASIS

In MINITERM the overall enthalpies and the logarithms of the overall stability constants are treated as unknown parameters, and the values which give the minimum of the non-weighted sum of the squares of the residuals (U) of the measured (ΔT_{meas}) and calculated (ΔT_{calc}) temperature increments are calculated, together with the probable errors

$$U=\sum_i(\Delta T_{\mathrm{meas},i}-\Delta T_{\mathrm{calc},i})^2=\sum_i\Bigg[\Delta T_{\mathrm{meas},i}+\Bigg(\Delta H_{\mathrm{M}}[\mathrm{M}]+\Delta H_{\mathrm{L}}[\mathrm{L}]$$

$$+\sum_j\Delta H_j\beta_j[\mathrm{M}]^{q_j}[\mathrm{L}]^{p_j}[\mathrm{H}^+]^{r_j}\Bigg)V_0/C_0\times 1000\Bigg]^2$$

Where $\sum_j$ and $\sum_i$ mean the summing of all (q,p,r) complex species and experimental points, respectively, ΔH_{M} and ΔH_{L} “apparent” dilution enthalpies of the metal and ligand, respectively, ΔH_j the enthalpies of the complex species (all enthalpies in cal mol^{-1}), V_0 the initial volume (ml^{-1}) and C_0 the initial heat capacity (in cal $°C^{-1}$).

As for MINISPEF, the following equilibria can be considered

$$q\mathrm{M}+p\mathrm{L}+r\mathrm{H}^+\rightleftarrows \mathrm{M}_q\mathrm{L}_p\mathrm{H}_r^+(\equiv C_j)$$

$$\beta=[\mathrm{M}_q\mathrm{L}_p\mathrm{H}_r^+]/([\mathrm{M}]^q[\mathrm{L}]^p[\mathrm{H}^+]^r)$$

$$\Delta H_j=-n_jQ_j=-n_j(C_0V_{\mathrm{Tot}}/V_0)\Delta T$$

($\Delta H_j<0$ for exothermic reactions, $\Delta H_j>0$ for endothermic ones).

Since zero values for q or r are allowed, four types of equilibria can be identified.

(1) Equilibria involving only the protonation ($+r$, $+\log \beta^{H}$) or deprotonation ($-r$, $-\log \beta^{H}$) of species L (i.e., only complexes H_rL_p are formed).

(2) Equilibria of protonated/deprotonated metal complexes.

(3) Equilibria involving metal complexes with compositions M_qL_p, or any association process which can be dealt with mathematically in the same way.

(4) Formation of mixed-ligand complexes from the parent complexes MA_N and MB_N

$$qMA_N + pMB_N \rightleftarrows M_{q+p}A_{Nq}B_{Np};\ \beta = [M_{q+p}A_{Nq}B_{Np}]/([MA_N]^q[MB_N]^p)$$

($N = 2$, 3 or 4).

THE PROGRAM DESCRIPTION

Introductory part

In this part the experimental data are read first and prepared for the subsequent calculations, followed by the stoichiometric coefficients and the starting values of the parameters with their increments. The quantities to be read in this part of the program are listed in Table 1.

Search for and refinement of parameters

This part of the program is identical with MINIPOT and MINISPEF. However, some small alterations had to be made to it, because the enthalpy values can be either positive or negative (difference with respect to molar absorptivities that must be put equal to zero when they become negative).

Variables and arrays

In the construction of MINITERM we have tried to keep the same meanings for the variables and arrays as for MINISPEF. Some small changes and new variables had to be introduced.

Variables

V0: initial volume in the thermometric cell (V_0)
C0: initial heat capacity of the titrand (C_0)
X8, X9: T_M and T_L in titrand
X6, X7: T_M and T_L in titrant.

Arrays

V7: added volume of titrant
E: temperature increment.

TABLE 1

Input for the program MINITERM

Input step	Input quantities	Comment
I	W,N1,N2,N3,N4,R,M, L,V0,C0,X8,X9,X6, X7	W: type no. of problem; N1: no. of measured points; N2: no. of parameters; N3: no. of complexes; N4: if equal to 1, then the percentage distribution of T_M, if equal to 2, then that of T_L in the complexes is calculated; R: printing instruction (if R = 0, then do not print): M,L: multiplication factors for T_M and T_L, respectively, to produce starting values for [M] and [L] (e.g. = 0.01); V0: initial volume in the thermometric cell; C0: initial heat capacity; X8, X9: T_M and T_L in titrand; X6, X7: T_M and T_L in titrant
II	if W = 1, then: ($V7_i$,E_i,$V1_i$) if W = 2, then: ($V7_i$,E_i,$V1_i$) if W = 3, then: ($V7_i$,E_i) if W = 4, then: ($V7_i$,E_i)	$V7_i$: added volume of titrant; E_i: ΔT_i; $V1_i$: pH
III	$(Q1_i,P1_i,R1_i)_{N3}$	Stoichiometric coefficients of the complexes $M_qL_pH_r$ or mixed-ligand complexes $M_{q+p}A_{Nq}B_{Np}$
IV	$(P_i,T_i)_{N2}$	$(\log \beta, \text{increment})_{N3}$ $(\Delta H, \text{increment})_{N3}$ ΔH_M, increment ΔH_L, increment
V	K, V, N, T1	K, V: first and last experimental points to be evaluated; N: step between two consecutive experimental points; T1: 0 or 1, depending on whether or not there are roots for solution of the mass-balance equations

Some remarks on the use of the program

The program will run on a desk-computer with 32 kbytes of RAM. The program can treat a maximum of 80 experimental points measured at a titration curve and a maximum of eight complex species formed. Consequently, the maximum number of parameters is 18, because the last two parameters are always the "dilution enthalpies" of the reacting species M and L, in that order. First the log β values, and then ΔH values must be fed in.

The handling of MINITERM is the same as that of MINISPEF and MINIPOT, and therefore is not illustrated or discussed here.

Like the other two programs, MINITERM allows the simultaneous refinement of a maximum of only four arbitrarily chosen parameters. When log β and ΔH values are refined simultaneously, the serial numbers of the ΔH values must always precede those of the log β values.

For stoichiometric coefficients not present in complexes a value of zero must be fed in.

RESULTS

Our experience with MINITERM has been very favourable. Its convergence is reliable, even if four parameters are refined simultaneously.

We have used MINITERM to refine the pK and ΔH values of (methylthio)acetic, thiodiacetic and 3,3′-thiodipropanoic acids, as well as 3,3′-imino-, 3,3′-oxy- and 3,3′-thiodipropioamidoxime [10–12].

In Table 2 the good agreement between the calculated and measured temperatures after refinement is shown. In Table 3 the values of U and s (standard deviation) can be seen, calculated with a linear least-squares method (point-by-point heat capacity method of ref. 12) and the same values after refinement with MINITERM.

TABLE 2

Refinement of pK and ΔH values of thiodipropionic acid with MINITERM: experiment 1; initial heat capacity 89.3 cal °C^{-1}; $T_L = 6.1167E-3$M; $T_M = 0$

mL	pH	Tot.M	Tot.L	T_{meas}	T_{calc}	D
0.286	3.779	$1.000E+0$	$6.095E-3$	+0.03813	+0.03877	−0.00065
0.357	3.932	$1.000E+0$	$6.090E-3$	+0.04813	+0.04802	+0.00010
0.428	4.078	$1.000E+0$	$6.084E-3$	+0.05813	+0.05767	+0.00045
0.500	4.222	$1.000E+0$	$6.079E-3$	+0.06750	+0.06762	−0.00012
0.571	4.366	$1.000E+0$	$6.073E-3$	+0.07813	+0.07778	+0.00034
0.714	4.664	$1.000E+0$	$6.063E-3$	+0.09813	+0.09835	−0.00023
0.785	4.827	$1.000E+0$	$6.057E-3$	+0.10813	+0.10859	−0.00046
0.857	5.011	$1.000E+0$	$6.052E-3$	+0.11875	+0.11869	+0.00006
0.928	5.238	$1.000E+0$	$6.047E-3$	+0.12875	+0.12861	+0.00014
1.000	5.576	$1.000E+0$	$6.041E-3$	+0.13825	+0.13831	−0.00006

q	p	r	log β	ΔH (cal mol^{-1})
0.00	1.00	−1.00	−3.8309	$-12.862E+3$
0.00	1.00	−2.00	−8.5672	$-24.460E+3$

$\Delta H_M = +00.000E-1$ cal mol^{-1}
$\Delta H_L = +00.000E-1$ cal mol^{-1}

Square of residuals $= 1.066E-6$°C^2
Standard deviation = 0.00037°C
Error of parameter no. 3 = $5.5784E+1$
Error of parameter no. 4 = $5.5607E+1$

TABLE 3

Thermodynamic values of several compounds before and after refinement with MINITERM

Compound	Method [a]	pK_1	pK_2	pK_3	$-\Delta H_1$(kcal mol^{-1})	$-\Delta H_2$(kcal mol^{-1})	$-\Delta H_3$(kcal mol^{-1})	U(°C^2)	s(°C)
S-Methylthioacetic	L	3.50	–	–	14.70	–	–	$385.7E-6$	$8.73E-3$
acid	R	3.64	–	–	14.72 ± 0.14	–	–	$13.4E-6$	$1.64E-3$
Thiodiacetic	L	3.14	4.11	–	12.16	16.48	–	$118.0E-6$	$4.44E-3$
acid	R	3.14	4.17	–	12.67 ± 0.01	14.94 ± 0.01	–	$2.6E-6$	$0.72E-3$
Thiodipropionic	L	3.87	4.68	–	12.36	16.47	–	$210.0E-6$	$4.83E-3$
acid	R	3.82	4.74	–	12.83 ± 0.06	14.70 ± 0.06	–	$1.4E-6$	$0.42E-3$
3,3′-Iminodipro-	L	3.54	4.58	8.47	6.96	6.29	8.78	$48.4E-6$	$2.84E-3$
pioamidoxime	R	3.55	4.53	8.84	6.38 ± 0.11	7.81 ± 0.05	8.81 ± 0.02	$1.1E-6$	$0.44E-3$
3,3′-Oxydipropio-	L	4.61	5.83	–	7.85	6.62	–	$177.7E-6$	$5.44E-3$
amidoxime	R	4.62	5.81	–	6.09 ± 0.11	8.05 ± 0.08	–	$1.8E-6$	$0.61E-3$
3,3′-Thiodipropio-	L	4.95	5.89	–	7.43	7.27	–	$56.8E-6$	$2.51E-3$
amidoxime	R	5.04	5.83	–	6.71 ± 0.12	7.68 ± 0.13	–	$12.2E-6$	$1.23E-3$

[a] L, least-squares method; R, refined by MINITERM.

REFERENCES

1 J.J. Christensen, D.D. Wrathall, J.O. Oscarson and R.M. Izatt, Anal. Chem., 40 (1968) 1713.
2 A. Sabatini, A. Vacca and P. Gans, Talanta, 21 (1974) 53.
3 N. Ingri and L.G. Sillén, Ark. Kem., 23 (1964) 47.
4 D.J. Leggett, S.L. Kelly, L.R. Shine, Y.T. Wu, D. Chang and K.M. Kadish, Talanta, 30 (1983) 579.
5 R.M. Alcock, F.R. Hartley and D.E. Rogers, J. Chem. Soc., Dalton Trans., (1978) 115.
6 F. Gaizer and A. Puskás, Talanta, 28 (1981) 925.
7 F. Gaizer and A. Puskás, Talanta, 28 (1981) 565.
8 J. Lumbiarres, C. Mongay and V. Cerdá, J. Therm. Anal., 22 (1981) 275.
9 J. Lumbiarres, J.L. Cerdá and V. Cerdá, Quim. Anal., 2 (1983) 55.
10 A. Mantecón, V. Cádiz and V. Cerdá, Afinidad, 38 (1981) 137.
11 V. Cerdá, E. Casassas and F. Borrull, An. Quim., 78B (1982) 327.
12 V. Cerdá, E. Casassas and F. Borrull, Thermochim. Acta, 57 (1982) 195.