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High-speed computers as a supplement to graphical methods

11. Application of LETAGROP to calorimetric titrations

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ABSTRACT

Table 3 gives special blocks for the minimizing program LETAGROP that allow one to treat data from calorimetric titrations in systems with several interacting equilibria. From the amounts of heat evolved during the various steps of a calorimetric titration, "best" ΔH values for a number of reactions involving two or three components are calculated. With the program, called LETAGROP KALLE equilibrium constants and analytical corrections may also be adjusted.

Introduction

Calorimetric data for reactions in solution are conveniently obtained by the method of calorimetric titration. With this method a large number of experimental points can be obtained in a limited time, which is especially important when complicated equilibria are studied, where as broad a concentration range as possible must be covered [1].

The experimental data obtained from a calorimetric titration are pairs of (V_T, Q) values, where Q is the measured heat effect and V_T the volume added from the buret. Let us assume we have two reagents, A and B, which form a series of complexes A_pB_q each of which has the relative molar enthalpy l_{pq} and the formation constant β_{pq}. If the equilibrium constants β_{pq} are known and also the total concentrations A and B of the reagents then one can calculate the concentrations c_{pq} of the complexes A_pB_q in each titration point. The measured heat effect Q between the additions V'_T and V''_T gives a linear relationship between the known c_{pq} and the unknown l_{pq}

$$Q = (V_0 + V'_T)\sum l_{pq}c'_{pq} - (V_0 + V''_T)\sum l_{pq}c''_{pq} + l_T(V''_T - V'_T) \qquad (1)$$

(where V_0 is the original volume of the calorimeter solution and l_T is the enthalpy excess in the buret solution; l_T is defined in equation (6) below). If one has a number of such relationships, and the c_{pq} are reliable one can determine the "best" values for l_{pq} by the standard least-square method.

However, in a real case, the c_{pq} values are not quite certain since the β_{pq} terms are not known very accurately, and there is also some uncertainty in the analysis. Even by using other methods, for instance graphical, it is often found that one can improve upon the fit of the calculated and experimental Q values by adjusting the equilibrium

constants, or introducing a small correction for analytical errors (see, e.g. [2, 3, 4]). Since such calculations are time-consuming, especially in a complicated system, there is a need for a computer method that may be used to refine not only the l_{pq} values but also the analytical composition and the equilibrium constants.

A generalized least-squares computer method will be described for treating data from calorimetric titrations. The method is based upon the principles of LETAGROP [5, 6]. With this program the computer searches for the set of unknown parameters k_i which minimizes the error square sum U, in our case defined as $U = \Sigma(Q_{calc} - Q_{exp})^2$. U is calculated for a first guessed set k_i, and for a minimum number of systematically selected sets around it. It is assumed that U is a second-degree function of the k_i (which is a better approximation, the closer one comes to the minimum), and the position of the minimum of the second-degree surface $U(k_i)$ is calculated, and used as the next approximation.

The unknown parameters when calorimetric titration data are treated are of two types: (1) the parameters l_{pq} and β_{pq} which are common to all the data and which will be called common parameters in the following; (2) group parameters which are specific for each titration ("group").

In a series of calorimetric titrations the analytical errors in the two solutions are likely to be constant within each titration ("group"), but may be different for different titrations, and so these quantities may conveniently be treated as adjustable group parameters. As such parameters we may first choose the corrections to the initial concentrations of the reagents A and B in the calorimeter and buret solutions; these corrections will be denoted δA_0, δB_0, δA_T and δB_T in the following. For each buret solution we may also introduce a correction δl_T, which accounts for possible deviations from ideal behavior in the buret solution ("heat of dilution").

Application of the LETAGROP principle to calorimetric titration data involves the calculation of U for a number of systematically selected sets of the unknown parameters. In principle it is possible to adjust both the common parameters and group parameters in the same "shot" (= calculation and minimization of U). However, the adjustment is preferably performed by shots at two levels (for disscussion see part 6 [7]). On the upper level the common parameters are varied systematically and for each set of them the group parameters, k_s, are adjusted at the lower level. By one or more shots for each separate group of data one obtains the minimum possible contribution to U from that group, and the sum gives the lowest value of U attainable with that set of the common parameters, which is carried to the higher level. After the necessary number of points $U(k_i)$ have been obtained, the position of the minimum is calculated on the upper level.

The present program for treating calorimetric data has been preceded by some earlier versions, which have been gradually changed and improved. The first version was worked out in 1961 by a group at this department (Å. Olin, S. Johansson, L. G. Sillén and R. Arnek). It was a program written in FORTRAN, and based upon the principles of LETAGROP. This first edition did not allow for the adjustment of equilibrium constants and analytical errors. At the Symposium on Thermodynamics and Thermochemistry in Lund 1963 an improved version of the program was presented [8], which allowed for the adjustment of equilibrium constants and analytical errors. This program worked fairly well in most cases. In 1964 the program was translated into ALGOL and the principles of LETAGROPVRID [9, 10] (a development of LETAGROP) were incorporated with the program.

The program to be described in this paper has all general parts in common with

the general LETAGROP program (practically full ALGOL text given in part 6, Table 1 [7]) and contains two special blocks (PUTS and UBBE) which are specific for calorimetric problems.

Background

Two or three reagents ($N_{kom}=2$ or 3) A, B, (C) form a series of complexes A_pB_q, or $A_pB_qC_r$, each of which has the relative molar enthalpy $l_{pq(r)}$ and the formation constant $\beta_{pq(r)}$. If we denote the total concentrations in a solution by capital letters A, B, C, and the concentrations of the free reagents by small letters a, b, c, then the conditions for mass balance and equilibrium give, for two components

$$A = a + \sum p\beta_{pq} a^p b^q; \quad B = b + \sum q\beta_{pq} a^p b^q; \quad c_{pq} = \beta_{pq} a^p b^q \qquad (2\,a, b, c)$$

With three reagents we have analogously

$$A = a + \sum p\beta_{pq} a^p b^q c^r; \quad B = b + \sum q\beta_{pqr} a^p b^q c^r; \quad C = c + \sum r\beta_{pqr} a^p b^q c^r; \quad c_{pqr} = \beta_{pqr} a^p b^q c^r \qquad (3\,a, b, c, d)$$

The titration starts with V_0 ml of a solution containing the total concentrations A_0, B_0, (C_0) of the N_{kom} components in the calorimeter. At a certain point we have added V_T ml of a solution with total concentrations A_T, B_T, (C_T). For the total concentration of component A in the mixture we have

$$A = A_{tot} = (A_0 V_0 + A_T V_T)/V_{tot} \qquad (4)$$

where

$$V_{tot} = V_0 + V_T \qquad (5)$$

and correspondingly for B, C.

The enthalpy excess (kj/l or kcal/l) in the calorimeter and T solution are

$$l = \sum l_{pq(r)} c_{pq(r)}; \quad l_T = (\sum l_{pq(r)} c_{pq(r)})_T + \delta l_T \qquad (6)$$

The first term in l_T is calculated assuming the same $\beta_{pq(r)}$ and $l_{pq(r)}$ in the buret solution as in the calorimeter solution; the term δl_T is a correction for possible deviations from ideal behavior in the T solution.

The heat evolved between the additions V'_T and V''_T is

$$Q_{calc} = L'_{tot} + l_T(V''_T - V'_T) - L''_{tot} = L'_{kor} - L''_{kor} \qquad (7)$$

$$L_{kor} = l(V_0 + V_T) - l_T V_T = L_{tot} - l_T V_T \qquad (8)$$

We express Q in j (cal) if V is in ml and l in kj (kcal)/l.

The experimental values are (V_T, Q) where Q is the amount of heat evolved between the next to the last and the last addition (heat evolved should really be $(-Q)$ but we use the opposite sign for convenience).

Table 1. Use of arrays for invariable quantities (*ag*, *as*, *ap*, *ak*) and adjustable parameters (*k*, *ks*) in application of LETAGROP to calorimetric data.

A″ + ″ indicates that the quantity is not given in the input but calculated by the program.

ag =
as = A_0, B_0, (C_0), A_T, B_T, (C_T), V_0, f_V
ap = V_T, Q, $+A_{tot}$, $+B_{tot}$, $(+C_{tot})$, $+f_{dil}$, $+\ln a$, $+\ln b$, $(+\ln c)$, $+c_1 \ldots c_{10}$, $+c_1' \ldots c_{10}'$
k = l_i, β_i, δQ;
ak = dum, dum, dum, (dum) for l_i
pot, *p*, *q*, (*r*) for β_i
ks = δl_T, δA_0, δA_T, δB_0, δB_T, (δC_0, δC_T)

Data for input

Table 1 indicates how the data and parameter arrays are used in the present program, Table 2 gives special instructions for the input.

In the input are given estimates of the adjustable common constants $\beta_{pq(r)}$ and $l_{pq(r)}$. The last *k*, δQ, is a possible constant error in the Q values. For each titration are given the analytical concentrations of A, B, (C) in the original and buret solutions, the original volume V_0 of the solution and f_V (= 1 in a titration with one buret). For each point in a titration the experimental values (V_T, Q) are given.

The group parameters k_s are δl_T (equation 6), and errors in the original analytical values for A_0, A_T etc.

Use of Typ and val

At present, only cases with two (*Typ* = 1) or three (*Typ* = 2) reagents are treated, but the program could easily be extended to the case of four reagents. Only one value for *fel*[*val*] is used at present in calculating U:

$$fel[1] = Q_{calc} - Q_{exp} + \delta Q \tag{9}$$

$$U = \sum fel[1]^2 \tag{10}$$

Other definitions of *fel*[*val*] and hence U could be added, if this were thought desirable.

Table 2. Input for KALLE = calorimetric version of LETAGROP.

(values with asterisk* given only for Typ = 2)

Data: *14*(Rurik), text, *9*(Rurik), *Typ*(1 or 2*), *6*(Rurik), *Ns*, 0(*Nag*), 6 (or 8*, *Nas*), 2(*Nap*), (*Np*, A_0, B_0, C_0^*, A_T, B_T, C_T^*, V_0, f_V, $(V_T, Q)_{Np})_{Ns}$,

Variable input (Dagens spaning) begins: *7*(Rurik), *Nk*(2*Nx* + 1), *Nk*(2*Nx* + 1), 3 (or 4*, *Nak*), (l_i, 0, 0, 0, 0*)$_{Nx}$, (*k*, *pot*, *p*, *q*, *r**)$_{Nx}$, d*Q*, 0, 0, 0, 0*, 5(or 7*, *Nks*), 0, 0, (all *ks*: = 0 in beginning), 0 (if no information on twist matrix is to be used),

7(Rurik), *Nk*(2*Nx* + 1), −1(Nbyk), *Nx*, (*ik*)$_{Nx}$, (removes posk protection from the $l_{pq(r)}$, which indeed are often negative. With four complexes, this line would run:
7, 9, −1, 4, 1, 2, 3, 4,)

8(Rurik), 2 (or 3*, *Nok*), *stegbyt*, *start*(ln*b*), *tol*(B/B_{tot}), *start*(ln*c*)*, *tol*(C/C_{tot})*, *start*(ln*a*), *tol*(*A*), etc.

Comment on PUTS and UBBE

Table 3 gives the text of the parts in LETAGROP that must be added for treating calorimetric data: the block PUTS, and the block UBBE for calculating U. UBBE contains the package of procedures, BDTV, which was given in full in part 8 [11], for solving equilibrium and mass balance equations ((2) or (3)).

PUTS contains a procedure Titer (N_{kom}, *trum*) (part 9, Table 1 [12]) which is used for pretreating the titration data. Titer calculates the total concentrations A_{tot}, B_{tot} etc. (equations (4) and (5)) and places them in *ap* cells, beginning with A_{tot} at *ap*[*cell* +

Table 3. PUTS and UBBE for KALLE (calorimetric version of LETAGROP). Parts of UBBE are common to programs containing "BDTV" and are given in part 8, Table 1 [11].

Procedures Titer and Titut are given in part 9, Table 1 [12].

```
PUTS:     begin
procedure Titer ... end Titer ; = part 9
          Nkom: = if Typ = 1 then 2 else 3 ;
          if Rs = 0 then begin Napa: = 23 + 2 × Nkom ; goto DATA end ;
          Titer(Nkom,2) ;
          for i: = 1 step 1 until Nkom do ap[cell + 2 + i]: = as[Rs,Nkom + i] ;
            ap[cell + 3 + Nkom]: = 0 ;
          cell: = cell + Napa ;
          for i: = 1 step 1 until Nkom do ap[cell + 2 + i]: = as[Rs,i] ; ap[cell + 3 + Nkom]: = 1 ;
          cell: = cell + Napa ; goto DATA ;
          end PUTS ;
UBBE:     if Koks ... t[1:20] ; = part 8
          real dQ, Lkor, Lold, Lq, LT, Qber, VO, VT ; integer Nq ; Boolean Nyko ;
          real array Lx[1:10] ;
          switch Apfel: = Apfel1, Apfel2;
          switch Asoks: = Asoks1, Asoks2 ;
          switch Kag: = Kag1, Kag2 ;
          switch Satsa: = Satsa1, Satsa2 ;
          switch Uttåg: = Uttåg1, Uttåg2 ;
procedure Lqber ; begin
          if Nyko then begin Titut (Nkom,2) ; Atot: = Atot + ks[Rs,2] × dil + ks[Rs,3] × (1 − dil) ;
            Btot: = Btot + ks[Rs,4] × dil + ks[Rs,5] × (1 − dil) ; Valhal(3,arum) end ;
          m: = cell + arum + Nkom ;
          for ix: = 1 step 1 until Nx do begin
            if Nyko then begin ap[m + ix]: = c[ix] ;
            if Orvar = 2 then ap[m + 10 + ix]: = c[ix] ;
            if Orvar = 3 and U > U1 then ap[m + ix]: = ap[m + 10 + ix] end
          else c[ix]: = ap[m + ix] end ;
          Lq: = 0 ; for ix: = 1 step 1 until Nx do Lq: = Lq + lx[ix] × c[ix] end Lqber ;
procedure Titut ... end Titut ; = part 9
          BDTV = procedures Betain, Dirty, Totber, Valhal ... = part 8
          U: = 0 ; if not Tage then Rs: = Rs1 ; goto Kag[Typ] ;
Nysa:     Rp: = 0 ; cell: = apcell[Rs] − Napa ;
          if Rurik = 2 then goto Satsa[Typ] ; goto Asoks[Typ] ;
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Nyp:      Rp: = Rp + 1 ; cell: = cell + Napa ;
          if Rp > Np[Rs] then begin
            if Rs2 > Rs and not Tage then begin Rs: = Rs + 1 ; goto Nysa end else begin
            if Skrikut = 1 or (Skrikut = 0 and not Tage) or (Prov and not (Tage and Skrikut < 0))
            then begin UVAR ; if Prov then
            output (61, '/') end ;
            goto UBBEUT end end ;
          goto Apfel[Typ] ;
Uber:     U: = U + fel[val]↑2 ; if Rurik = 2 then goto Uttåg[Typ] ; goto Nyp ;
Kag1: Kag2: dirt: = 0 ; dQ: = k[Nk] ; m: = entier(0.1 + 0.5 × (Nk + 1)) ; Betain(m,Nk − 1) ;
          for ix: = 1 step 1 until Nx do Lx[ix]: = k[ix] ;
          if not Tage and Orvar < 2 then begin Nq: = 0 ;
            for i: = 1 step 1 until N do begin ik: = ivar[i] ;
            if ik ≤ Nx or ik = Nk then Nq: = Nq + 1 end end ;
            if Orvar < 1 or Ri > Nq or Rj > Nq or Tage or Slusk > 0 then Nyko: = true
              else Nyko: = false ;
          arum: = Nkom + 4 ; goto Nysa ;
Satsa1: Satsa2: SATSUT ;
Asoks1: Asoks2:
          cell: = apcell[Rs] + Napa × Np[Rs] ; Lqber ;
          LT: = Lq + ks[Rs,1] ; VO: = as[Rs,2 × Nkom + 1] ;
          cell: = cell + Napa ; Lqber ; Lold: = VO × Lq ;
          cell: = apcell[Rs] − Napa ; goto Nyp ;
Apfel1: Apfel2: Lqber ; VT: = ap[cell + 1] ; Ltot: = Lq × (VO + VT) ; Lkor: = Ltot − LT × VT;
          Qber: = Lold − Lkor ; Lold: = Lkor ; fel[1]: = Qber + dQ − ap[cell + 2] ; goto Uber ;
Uttåg1: Uttåg2: output (61, '3( − 3ZD.2D)', ap[cell + 1], ap[cell + 2], fel[1]) ;
          goto Nyp end UBBE ;
FINAL:    end LETAGROP ;
```

trum + 1]. In PUTS also special sets of *ap* cells are set aside for the T solution and the original solution. In addition *ap* cells are set aside for the various $c[ix]$ and for $\ln a$, $\ln b$ etc.

UBBE contains a special procedure Titut (N_{kom}, *trum*) (part 9, Table 1) which transforms the data stored in *ap* by Titer to the quantities A_{tot}, B_{tot}, C_{tot} and f_{dil} (dilution factor $= V_0/V_{tot}$) needed by UBBE.

The UBBE block contains references to five switches: *Kag*, *Satsa*, *Asoks*, *Apfel* and *Uttåg*. *Kag* reads the common parameters k and transforms them to quantities useful for UBBE. If k are the equilibrium constants, with attached values for the power of 10 (*pot*) and numbers p, q, (and r), then procedure Betain (part 8, Table 1) reads them from the memory and transforms them to logarithms ($\ln beta$) and numerical values (*beta*).

At *Asoks* the excess enthalpy in the buret and calorimeter solution L_T and *Lold* are calculated, by means of procedures Lqber and Valhal. Valhal contains a number of subordinate procedures among them Kille(i) and Kålle and solves the equilibrium-massbalance equations ((2) or (3)) by a series of loops. Since only the total concentrations of the components are known, the concentrations of the free components and of the various complex species, are calculated from equation (2) or (3), for each composition by means of Valhal. The values for $\ln a$, $\ln b$ etc. are stored in *ap* cells for the

next application of Kålle, and also the various $c[ix]$. To avoid unnecessary repetition the $c_{pq(r)}$ are recalculated only when some $\beta_{pq(r)}$ or some correction δA_0 etc. are changed (Boolean *Nyko* = true, new constants) else *Nyko* = false, and the previous set of $c_{pq(r)}$ are taken from a store. A change in $l_{pq(r)}$ does not affect the $\beta_{pq(r)}$. When an equilibrium constant is changed by $+stek_{Ri}$ and $-stek_{Ri}$ both sets of $c_{pq(r)}$ are stored until it is decided which sign is to be used for $stek_{Ri}$.

When the concentrations $c_{pq(r)}$ have been calculated for one point, then the excess enthalpy $Lq = \Sigma lx[ix] \times c[ix]$ is calculated in procedure Lqber.

At *Apfel* the quantity Q_{ber} (calculated heat effect) is calculated for each point by means of procedures Lqber and Valhal. Finally the errors $fel[1] = Q_{\text{calc}} + \delta Q - Q_{\text{exp}}$ are calculated, the squares of which are used in the error square sum U.

At *Satsa* the headline for a new group ("sats") is printed if a complete output is asked for (Rurik = 2).

At *Uttåg* values for the experimental data (V_T, Q), and the calculated quantities $fel[1]$ are printed if Rurik = 2.

The output information from a LETAGROP calculation on calorimetric data is a "best" set of constants $l_{pq(r)}$ and $\beta_{pq(r)}$ (if varied) with their standard deviations and a set of group parameters (e.g. analytical errors) with their standard deviations. Also the standard deviation, σ_Q, in the measured quantity Q is obtained.

Applications

Examples of the application of the program LETAGROP KALLE may be found in some recent papers from this department [13–20].

When one treats data from calorimetric titrations one usually assumes that the equilibrium constants are known from independent experiments. However, sometimes there may be reason to attempt refinement of equilibrium constants from heat data. The enthalpies and equilibrium constants are then treated simultaneously as unknown parameters to be determined. Some examples are given in the papers of Arnek and Schlyter [17, 18]. One more example will be given here. Acidified chromate solutions contain the two species $HCrO_4^-$ and $Cr_2O_7^{2-}$. Using the equilibrium constants (in 3 M $NaClO_4$) $\beta_{11} = (7.76 \pm 0.35)10^5\ M^{-1}$ and $\beta_{22} = (9.6 \pm 0.9)10^{13}\ M^{-3}$ given by Sasaki [21], the ΔH values $\Delta H_{11} = (1.08 \pm 0.09)$ kcal/mol and $\Delta H_{22} = (-2.68 \pm 0.04)$ kcal/mol could be calculated from the calorimetric data of Arnek and Johansson [22]. When the ΔH and β were treated simultaneously as unknowns a minimum in U was found for the following values of the parameters:

$\Delta H_{11} = (0.9 \pm 0.3)$ kcal/mol $\qquad \Delta H_{22} = (-2.68 \pm 0.07)$ kcal/mol

$\beta_{11} = (8.3 \pm 1.2)10^5\ M^{-1} \qquad \beta_{22} = (9.2 \pm 0.6)10^{13}\ M^{-3}$

(deviations correspond to 3σ)

The equilibrium constants β_{11} and β_{22} could thus be determined independently from the calorimetric data, although less accurately than from e.g. emf measurements. The method is, however, not generally applicable but depends on the chemical systems studied. The conditions for the determination of equilibrium constants from heat data will be discussed in some detail in a forthcoming paper.

Examples of treating small analytical errors as unknown group parameters with calorimetric data using the LETAGROP method, are given in other papers [13–20].

In some cases the LETAGROP treatment can be said to have given a check of the ordinary chemical analyses. In other cases it is more reasonable to say that the computer adjustment of calorimetric titration data gave a more precise account of the composition of the solutions than did the methods of chemical analysis (see e.g. Ref. [19]).

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