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## Adjustment for systematic experimental errors and other "group parameters" in LETAGROP. Applications to potentiometric titrations

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ABSTRACT

In equilibrium analysis one adjusts the common parameters (equilibrium constants etc.) of a chemical model to get a good fit with experimental data. One should however also attempt to adjust possible systematic errors, such as analytical errors and errors in $E_0$ values. Examples are given of how this can be done. Table 1 gives special blocks for the case of precision emf titrations with 2–4 components, to be used together with the LETAGROP main program (parts 6, 7).

Equilibrium analysis is often made by means of "titrations", changing the composition of a solution by additions from a buret, or by electrolysis, and measuring the emf after each change. A titration for equilibrium analysis is a precision method with the aim of measuring precisely and explaining quantitatively each single point in a curve $E(V_T)$, whereas analytical titrations mainly aim at finding one or more equivalence points. The similarity of the experimental arrangement, and the word "titration" have sometimes made chemists underestimate the amount of information obtainable from emf titrations.

Table 1 in the present paper gives special blocks to be inserted in the general minimizing LETAGROP program (parts 6 and 7) when it is to be used for finding the "best" values for equilibrium constants for complex formation from the primary data of a potentiometric titration where $E$ measures the free concentration of one of the reagents, A($H^+$) or B. The equations for mass balance and equilibrium conditions are solved by means of the procedure package BDTV described in part 8.

The primary data are: the total concentrations of the reagents in the original and added solutions, the estimated $E_0$ value, the added volume $V_T$ and the measured emf $E$. If all the other primary data were correct, one could either decide to trust the $V_T$ and minimize the sum of $(E_{calc} - E_{exp})^2$, or one could trust the $E$ and minimize the error square sum for $V_T$ or some related quantity such as the analytical proton excess $H$.

In either case, assuming various sets of species one could apply the LETAGROP principle to find a "best" set of species and equilibrium constants. This approach as a rule leads to systematic deviations, small or large, even with the set that gives the "best" fit. The explanation is that systematic errors are present: in the estimated $E_0$, in the analytical concentrations assumed, and because of the presence of impurities.

So, it seems natural to use here one advantage of the LETAGROP approach namely that one can easily—together with common parameters $k[ik]$ like equilibrium constants—adjust "group parameters", called $k_s[Rs, ik]$, which may be different for different groups of data. For instance, in a series of emf titrations, the $E_0$ for the cell used, and the analytical errors in the two solutions used, 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.

Before we discuss the choice of group parameters we shall first comment on some other matters.

## Some useful procedures

*Titer and Titut*

The program contains, in PUTS, a single procedure, Titer ($N_{kom}$, *trum*) which may be used for pretreating various kinds of titration data provided they are given and stored in a standardized form.

UBBE contains a special procedure Titut ($N_{kom}$, *trum*), which transforms the data stored in *ap* by Titer to the quantities $A_{tot}$, $B_{tot}$, $C_{tot}$, $L_{tot}$ and $f_{dil}$ needed by UBBE.

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

$$A = A_{tot} = (A_0 V_0 + A_T V_T)/V_{tot} \tag{1}$$

and correspondingly for B, C etc. In an ordinary buret titration, $V_{tot} = V_0 + V_T$. Now we wish to use the same procedure also for the case of a coulometric titration. We may then as $V_T$ use the number $\nu$ of added microfaradays. If, for instance, $A = H^+$, we give the concentration $A_T = 0.001$, if protons are added, and $A_T = -0.001$ if protons are removed by electrolysis. (Correspondingly if $Ag^+$, $Cd^{2+}$, $e^-$ etc. are added or removed by the electrolysis.) In this way, (1) gives the right number of mmols of the reagents in the mixture. On the other hand, the total volume $V_{tot}$ remains practically constant during the electrolysis. This is taken care of by using the equation

$$V_{tot} = V_0 + V_T f_v \tag{2}$$

where $f_v$ (*vfak* in the program) is = 1 in a titration with one buret, and 0 in a titration with a coulometer. If, to take another example, equal volumes $V_T$ are added from two different burets, one may set $f_v = 2$ to get the right $V_{tot}$ from (2). To get the right result from (1), the concentration $A_T$ etc should then be given as the sum of the concentrations in the two buret solutions.

Titer requires that the "*as*" (the data specific for one group of experiments = titration) are given in the following order:

$$A_0, B_0, .. A_T, B_T .. V_0, f_v, ...$$

*Table 1.* PUTS and UBBE for emf titration problems ("ETITR").

Parts of UBBE are common to all programs with "BDTV" and are given in part 8, Table 1.

```
PUTS:     begin
procedure Titer(Nkom,trum) ; integer Nkom, trum ; begin
          real V0, V00, vfak, VT, Vtot ; real array AT, A0V0, mola[1:5] ;
          V00: = V0: = as[Rs,2 × Nkom + 1] ; vfak: = as[Rs,2 × Nkom + 2] ;
          for i: = 1 step 1 until Nkom do begin  AT[i]: = as[Rs,Nkom + i] ;
                mola[i]: = A0V0[i]: = V0 × as[Rs,i] end ;
          cell: = apcell[Rs] ;
          for Rp: = 1 step 1 until Np[Rs] do begin VT: = ap[cell + 1] ;
            if VT < 0 then goto Byt ;
            Vtot: = V0 + VT × vfak ; ap[cell + trum + Nkom + 1]: = V00/Vtot ;
            for i: = 1 step 1 until Nkom do begin mola[i]: = A0V0[i] + VT × AT[i] ; ap[cell +
                trum + i]: = mola[i]/Vtot end ;
            goto Slut ;
Byt:        j: = 1 ; m: = 0 ;
            for i: = 1 step 1 until Nkom + 1 do begin
              if j + 1 > Nap then begin j: = 0 ; m: = m + 1 end ;
              j: = j + 1 ; w: = ap[cell + m × Napa + j] ; ap[cell + m × Nap + j]: = w ;
              if i = Nkom + 1 then vfak: = w else AT[i]: = w end ;
            if m > 0 then begin
              for j: = 1 step 1 until Np[Rs] − Rp − 1 do for i: = 1 step 1 until Nap do ap[cell + j ×
                  Napa + i]: = ap[cell + (j + m) × Napa + i] ;
              Np[Rs]: = Np[Rs] − m − 1 ; Rp: = Rp − 1 ;
              for i: = 1 step 1 until Nkom do A0V0[i]: = mola[i] ; V0: = Vtot end ;
Slut:       cell: = cell + Napa end end Titer ;
          if Rs = 0 then begin Nkom: = entier(0.5 × (Nas − 2 + 0.05)) ;
            Napa: = if Typ = 3 then 4 + 2 × Nkom else 3 + 2 × Nkom ;
            arum: = if Typ = 3 then 5 + Nkom else 4 + Nkom ;
            goto DATA end ;
          if Typ = 3 then Titer(Nkom,3) else Titer(Nkom,2) ;
          if Typ = 2 then begin m: = apcell[Rs] + arum − Napa ;
            for Rp: = 1 step 1 until Np[Rs] do begin m: = m + Napa ; ap[m]: = − 16 end end ;
          goto DATA end PUTS ;

UBBE:     if Koks and not Tage and not Rakt then goto SÄRK; comment not for SPEFO ;
          begin real ..... declarations for BDTV = part 8
          real Abun, Bfak, dA, dA0,dAT, dZ, E0B, EB, EBfak, eta, ZAB, ZAC ; integer Ne ;
          BDTV = procedures Betain, Dirty, Totber, Valhal ..... = part 8
procedure Bure ; lnb: = (EB − E0B − Ej)/EBfak ;
procedure Ejber ; begin Hfri: = exp(lna) ; Ej: = jac × Hfri + Kwjalk/Hfri end ;
procedure Hure ; begin Ej: = 0 ;
Hoppe:    lnh: = (E − E0 − Ej)/Efak ; Hfri: = exp(lnh) ;  Ej: =  jac × Hfri + Kwjalk/Hfri  ;
          Eber: = E0 + Efak × lnh + Ej ;
          if abs(E − Eber) > 0.002 then goto Hoppe end Hure ;
procedure Titut(Nkom,trum) ; integer Nkom, trum ; begin m: = cell + trum ;
          if ap[cell + 1] < 0 then begin
            if Rurik = 2 then begin output(61, '/B 'BYTE AV AT'') ;
              for i: = 1 step 1 until Nkom + 1 do output(61,'2B, − ZD.5D', ap[cell + 1 + i]) end ;
            Rp: = Rp − 1 ; goto Nyp end ;
          Atot: = ap[m + 1] ; if Nkom > 1 then Btot: = ap[m + 2] ;
          if Nkom > 2 then Ctot: = ap[m + 3] ; if Nkom > 3 then Ltot: = ap[m + 4] ;
          dil: = ap[m + Nkom + 1] end Titut ;
procedure Zeta ; begin Abun: = Atot−exp(lna) ;
          ZAB: = if Btot > 0 then Abun/Btot else 0 ;
          ZAC: = if Ctot > 0 and Nkom > 2 then Abun/Ctot else 0 ;
          eta: = if Btot > 0 then loge × (ln(Btot) − lnb) else 0 end Zeta ;
          switch Apfel: = Apfel1,Apfel2,Apfel3 ;
          switch Asoks: = Asoks1,Asoks2,Asoks3 ;
```

```
            switch Kag: = Kag1,Kag2,Kag3 ;
            switch Satsa: = Satsa1,Satsa2,Satsa3 ;
            switch Uttåg: = Uttåg1,Uttåg2,Uttåg3 ;
            U: = 0 ; ..... goto Nyp ; = part 8
Kag1: Kag2: Kag3:
            temp: = ag[1] ; Efak: = RoF × (temp + 273.15) ;
            if Typ = 2 or Typ = 3 then EBfak: = Efak/ag[2] ;
            jac: = k[1] ; KHX: = k[3] ; Betain(4,Nk) ; Kwjalk: = k[2] × beta[1] ; dirt: = 1 ; goto
                  Nysa ;
Satsa1:     SATSUT ; output(61, '//4B'V'5B'EA(MV)'B'ATOT(MM)'B'LOGA'2B'Z A/B'2B'Z A/
                  C'2B'ETA'5B'DA'5B'DA/B'3B'DA/C'3B'DEA'') ;
            goto Asoks[Typ] ;
Satsa2:     SATSUT ; output(61, '//4B'V'5B'EB(MV)'B'ATOT(MM)'B'LOGA'2B'Z A/B'2B'Z
                  A/C'2B'ETA'5B'DB'5B'DEB'') ;
            goto Asoks [Typ] ;
Satsa3:     SATSUT ; output(61, '//4B'V'5B'EA(MV)'B'EB(MV)'B'ATOT(MM)'2B'LOGA'4B'Z
                  A/B'3B'Z A/C'3B'ETA'6B'DA'5B'DEA'4B'DB'5B'DEB'') ;
            goto Asoks[Typ] ;
Asoks1:     Asoks2: Asoks3:
            E0: = ks[Rs,1] ; E0B: = ks[Rs,2] ; dA0: = ks[Rs,3] ; dAT: = ks[Rs,4] ; dA: = ks[Rs,5] ;
            cHX: = ks[Rs,6] ; cHXall: = ks[Rs,7] ; Bfak: = 1 + ks[Rs,8] ;
            goto Nyp ;
Apfel1:     E: = ap[cell + 2] ; Titut(Nkom,2) ;
            Atot: = Atot + dA0 × dil + dAT × (1 − dil) + dA ; Btot: = Btot × Bfak ;
            if val = 4 then Valhal(3,arum)
              else begin Hure ; lna: = lnh ; Valhal(2,arum) end ;
            if val < 4 or Rurik = 2 then begin x: = lna ; Totber(p) ; Dirty ;
              fel[1]: = 1000 × (y − Atot) ;
              fel[2]: = if Btot > 0 then fel[1]/Btot else 0 ;
              fel[3]: = if Nkom > 2 and Ctot > 0 then fel[1]/Ctot else 0 end ;
            if val = 4 or Rurik = 2 then begin
              Ejber ; y: = E0 + Efak × lna + Ej ; fel[4]: = y − E end ;
            goto Uber ;
Apfel2:     EB: = ap[cell + 2] ; Titut(Nkom,2) ;
            Atot: = Atot + dA0 × dil + dAT × (1 − dil) + dA ; Btot: = Btot × Bfak ;
            if val = 1 then begin lna: = ap[cell + arum] ; Ejber ; Bure ; Valhal(1,arum) end
              else Valhal(3,arum) ;
            if val = 1 or Rurik = 2 then begin x: = lnb ; Totber(q) ;
              fel[1]: = 1000 × (y − Btot) end ;
            if val = 2 or Rurik = 2 then begin Ejber ; y: = E0B + EBfak × lnb + Ej ;
              fel[2]: = y − EB end ;
            goto Uber ;
Apfel3:     E: = ap[cell + 2] ; EB: = ap[cell + 3] ; Titut(Nkom,3) ;
            Atot: = Atot + dA0 × dil + dAT × (1 − dil) + dA ; Btot: = Btot × Bfak ;
            if val < 3 or val = 5 then begin Hure; lna: = lnh end ;
            if val < 5 then begin if val > 2 then lna: = ap[cell + arum] ;
              Ejber ; Bure ;
              if val < 3 then Valhal(0,arum) else Valhal(1,arum) end ;
            if val = 5 then Valhal(2,arum) ;
            if val = 6 then Valhal(3,arum) ;
            if val = 1 or Rurik = 2 then begin x: = lna ; Totber(p) ; Dirty ;
              fel[1]: = 1000 × (y − Atot) end ;
            if val = 2 or val = 4 or Rurik = 2 then begin x: = lnb ; Totber(q) ;
              fel[2]: = fel[4]: = 1000 × (y − Btot) end ;
            if val = 3 or Rurik = 2 then begin Ejber ; y: = E0 + Efak × lna + Ej ;
              fel[3]: = y − E end ;
            if val = 5 or val = 6 or Rurik = 2 then begin Ejber ; y: = E0B + EBfak × lnb + Ej ;
              fel[5]: = fel[6]: = y − EB end ;
            goto Uber ;
Uttåg1:     Zeta ; output(61, '/B, − ZD.3D, − 3ZD.2D, − 2ZD.2D, 4( − ZD.3D), 4( − 2ZD.2D)',
              ap[cell + 1], E,1000 × Atot, loge × lna, ZAB,ZAC,eta,fel[1],fel[2],fel[3],fel[4]) ;
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```
          goto Nyp ;
Uttåg2:   Zeta ; output(61, '/B, -ZD.3D, -3ZD.2D, -2ZD.2D, 4(-ZD.3D), 2(-2ZD.2D)',
          ap[cell + 1], EB, 1000 × Atot, loge × lna, ZAB,ZAC, eta, fel[1], fel[2]) ;
          goto Nyp ;
Uttåg3:   Zeta ; output(61, '/B, -ZD.3D, 3(-3ZD.2D), 4(-ZD.4D), 4(-2ZD.2D)', ap[cell + 1],
            E, EB, 1000 × Atot, log e × lna, ZAB, ZAC, eta, fel[1],fel[3],fel[2],fel[5]) ;
          goto Nyp
          end UBBE ;
FINAL:    end LETAGROP ;
```

(If there is only one reagent, the *as* values then begin $A_0$, $A_T$, $V_0$, $f_v$.) Moreover, the first data value given for each point, and placed in *ap*[*cell* + 1] should be $V_T$. The procedure Titer uses (1) and (2) to calculate the total concentrations $A_{tot}$, $B_{tot}$ etc. and places them in *ap* cells, beginning with $A_{tot}$ at *ap*[*cell* + *trum* + 1]. For the organisation of the *ap*, see also the comments on BDTV in part 8.

The computer also calculates a "dilution factor" (*dil* in the program)

$$f_{dil} = V_0 / V_{tot} \tag{3}$$

which may be useful for some applications, and stores it in an *ap* cell immediately after the total concentrations $A_{tot}$ etc.

Sometimes it is practical to change the buret solution—or to reverse the direction of the coulometric current—in the course of a titration. This implies a set of new values for $A_T$, $B_T$ etc, which are given to procedure Titer in the form of one or more "false data points", starting with a negative number in the place of $V_T$ (which otherwise has to be positive). After this one gives the new total concentrations $A_T$ etc. of the components, followed by $f_v$ and, if necessary, one or two dummies to give a number of values corresponding to an integral number of data points. At the point of buret change, $V_T$ starts again from zero. This can be repeated many times during a titration. At any rate, in $f_{dil}$ (3), $V_0$ is the original volume (*VOO* in the program).

For instance, in a case with three components, $N_{kom} = 3$ and $N_{ap} = 2$, a change of the buret solution is given as follows

$$/ -1,\ A_T,\ /\ B_T,\ C_T,\ /\ f_v,\ 0(\text{dummy}),\ /$$

thus by three false data points. The number of data points to be read, $N_p[Rs]$ is then obtained by adding three units to the actual number of experimental points for each change of buret solution. The true number of experimental points, which is needed for the calculation of standard deviations etc. is calculated by Titer, and the data are shifted to give economy of space in packing the *ap*.

*Bure, Hure and Ejber*

Another useful procedure in UBBE is Hure ("*h* ur *E*" = *h* from *E*) which calculates the hydrogen ion concentration $[H^+] = h$ from measurements of $E$ in a cell, with a glass, quinhydrone or hydrogen electrode:

$$E = E_0 + f_E \ln h + j_{ac} h + K_w j_{alk} h^{-1} \tag{4}$$

where the factor $f_E$ (*Efak* in the program) is

$$f_E = (R/F)\,T = 0.086167\ (273.15 + t) \tag{5}$$

Hure contains a short loop for solving (4). The factor $f_E$ is calculated in the beginning of UBBE, using the ratio $R/F$ (*RoF*) given in the first line of LETAGROP. The temperature ($t$ degrees Celsius) is given with the input as *ag*[1] in the cases considered.

Bure and Ejber are used for calculating $\ln b$ from an emf $E_B$ measured with an electrode sensitive to $b = [B]$

$$E_B = E_{0B} + f_{EB} \ln b + E_j \tag{6}$$

$$f_{EB} = f_E / n_e \tag{7}$$

$$E_j = j_{ac} h + K_w j_{alk} h^{-1} \tag{8}$$

The number $n_e$ is given in the input as *ag*[2].

## Chemical systems

Usually but not necessarily, A is $H^+$, and we may apply the present program to data on $H^+ - B$ complexing where B is any base or acid.

It is often convenient to define B so that some complexes have negative $p$ values. For example, in hydroxo complexing, the products may be written as $(H^+)_{-2}\,(Fe^{3+})_2$ for $Fe_2(OH)_2^{4+}$. The ion $OH^-$ may be treated as the $(-1,0)$ complex, with the formation constant $\beta_{-1,0} = K_w$.

For each point we measure $E$ with an electrode sensitive to $H^+$, and the emf of the cell is given by equation (4). The second term is the Nernst term, the third and fourth are liquid junction emfs for acidic and alkaline solutions; if the solvent is an ionic medium we may usually consider $E_j$ to be linear with $h$ or $[OH^-]$.

If some other reagent than $H^+$ is used as A, say, $Cl^-$ measured by an AgCl, Ag electrode, one must define $j_{ac}$, $j_{alk}$ $(=0)$ and the sign of $E$ so that (4) holds with $a$ instead of $h$.

Another application is measurements of some metal ion concentration ($B = Ag^+$, $Cd^{2+}$, $In^{3+}$ etc.) by means of a metal a amalgam electrode which obeys (6).

The program can also be used for *redox titrations* in which case the electron $e^-$ is counted as one component, usually B since A must be reserved for $H^+$. C is then one oxidation state, and L the ligand studied. It may often be convenient to use a positive or negative number of electrons, as the formal component B: "$\bar{e}^+$", "$\bar{e}_2^{2+}$" or "$e_2^{2-}$". One must remember two things: 1) the total concentration of B must never become negative, 2) the equations are solved somewhat more rapidly if all species contain either one B or none. E.g. one may have

$(Fe^{2+} = C,\ "\bar{e}^+" = B,\ Fe^{3+} = BC)$ or $(Fe^{3+} = C,\ e^- = B,\ Fe^{2+} = BC)$;
$(H^+ = A,\ UO_2^{2+} = C,\ e_2^{2-} = B,\ U^{4+} = A_4BC)$ or $(H^+ = A,\ U^{4+} = C,\ \bar{e}_2^{2+} = B,\ UO_2^{2+} = A_{-4}BC)$ or even $(H^+ = A,\ e^- = B,\ UO_2^{2+} = C,\ U^{4+} = A_4B_2C)$.

In the equation for $E_B$ (6, 7) $n_e$ is simply the charge of the B chosen: $-1$ for $e^-$, $+2$ for $\bar{e}_2^{2+}$ etc.

The activity scale for B must be defined so that the formal activity $b$ is always negligibly small in the mass balance equations. E.g. one may keep the formation constant of $Fe^{3+}$ ($Fe^{2+} + \bar{e}^+ \rightleftharpoons Fe^{3+}$) constant at $10^{10}$, to keep the formal $[\bar{e}^+]$ low. The value for $E_0(\bar{e}^+)$ will then come out as $e^0(Fe^{2+}, Fe^{2+}/Pt) + 10 \times 59.16 - e_{ref}$ taking $e^0$ and $e_{ref}$ on the hydrogen scale.

*Use of Typ and val*

The control number *Typ* is used as follows. $Typ=1$ if only $E_A$ is known, $Typ=2$ if only $E_B$ is known, and $Typ=3$ if both $E_A$ and $E_B$ are known. PUTS finds out the number of components, *Nkom*, by using $Nas=2+2\times Nkom$; it may be 2, 3, or 4 in the present program.

The following table gives a survey of the present uses of Typ and Val.

| *Typ* | *val* | known besides *C L* | *BA* | *fel*[*val*] | not used |
|---|---|---|---|---|---|
| 1 | 1–3 | *a B* | 2 | $\Delta A$ | |
| | 4 | $H=A\ B$ | 3 | $\Delta \ln a$ | |
| 2 | 1 | *A b* | 1 | $\Delta B$ | |
| | 2 | *A B* | 3 | $\Delta \ln b$ | |
| 3 | 1 | *a b* | 0 | $\Delta A$ | (*B*) |
| | 2 | | | $\Delta B$ | (*A*) |
| | 3 | $H=A\ b$ | 1 | $\Delta \ln a$ | (*B*) |
| | 4 | | | $\Delta B$ | (*a*) |
| | 5 | *a B* | 2 | $\Delta \ln b$ | (*A*) |
| | 6 | *A B* | 3 | $\Delta \ln b$ | (*a*) |

The third column names the quantities that are assumed to be known exactly in the calculation, the fourth gives the parameter *BA* for Valhal (part 8) and the fifth gives the error *fel*[*val*] to be used in the calculation of the error square sum *U*.

$$U=\sum(y_{calc}-y_{exp})^2=\sum(fel[val])^2 \tag{9}$$

For $Typ=1$, *fel*[2] and *fel*[3] are equal to *fel*[1] divided by *B* or *C*. When the "*fel*" is given as $\Delta \ln a$ or $\Delta \ln b$, the proportional quantities $\Delta E$ or $\Delta E_B$ are really used. With two emfs, for each *val* some part of the experimental information is not being used as indicated by the last column.

We shall take as example, studies of $H^+-B$ complexing using a $H^+$-sensitive electrode.

The experiment is carried out as a potentiometric titration, and from the analytical data for each point, procedure Titer may calculate the total concentrations $A_{tot}$ and $B_{tot}$, for which the material balance requires

$$A_{tot}=H_{tot}=h+BZ=h+\sum p\beta_{pq}h^pb^q \tag{10}$$

$$B_{tot}=B=b+\sum q\beta_{pq}h^pb^q \tag{11}$$

*Val=1.* We assume that *E* is correct, calculate *h* from (4) with procedure Hure and $H_{calc}$ by solving *b* from (11) with procedure Valhal and inserting into (10):

$$fel[1]=H_{calc}-H_{tot} \tag{12}$$

*Val=2.* We assume that *E* is correct and proceed as before but minimize the error square sum for $Z=(H-h)/B$

$$fel[2]=(H_{calc}-H_{tot})/B_{tot} \tag{13}$$

*Val* = *4*. We assume $H_{tot}$ and $B_{tot}$ to be correct, and calculate $h$ from (10) and (11) by means of Valhal. Inserting this value for $h$ into (4) gives $E_{calc}$ and

$$fel[4] = E_{calc} - E_{exp} \tag{14}$$

*Use of arrays for various Typ values*

*ag* : *temp*, *Ne* (if $E_B$ is given)
*as* : $A_0 B_0 A_T B_T V_0 f_v$, if *Nkom* = 2
$A_0 B_0 C_0 A_T B_T C_T V_0 f_v$, if *Nkom* = 3
$A_0 B_0 C_0 L_0 A_T B_T C_T L_T f_v$, if *Nkom* = 4
*ap* : $V_T E + A + B(+C+L) + f_{dil} + \ln a + \ln b\ (+\ln c + \ln l)$, if *Typ* = 1
$V_T E_B + A + B(+C+L) + f_{dil} + \ln a + \ln b(+\ln c + \ln l)$, if *Typ* = 2
$V_T E\ E_B + A + B(+C+L) + f_{dil} + \ln a + \ln b(+\ln c + \ln l)$, if *Typ* = 3
$k$ : $k_1 = j_{ac}$, $k_2 = j_{alk}$, $k_3 = K_{HX}$, $k_4 = K_w$, $k_{ik>4} = \beta$
*ak* : *pot*, *p*, *q*, (*r*, *t*,)
*ks* : $E_0\ E_{B0}\ dA_0\ dA_T\ dA\ c_{HX}\ c_{HXall}$, $1 - f_B$

As usual, a "+" means that the value is not given in the input but is calculated by the program.

## Choice of group parameters

One learns by experience to keep constant those parameters that have little or no influence on the data. For instance, one should not try to adjust $j_{ac}$ or $j_{alk}$ if the corresponding $E_j$ is negligible in the range of the experiments, nor should one adjust $K_w$ if one has few or no data in the region where $[OH^-]$ becomes noticeable. Otherwise, there will be a tendency to compensate small deviations of other kinds (experimental errors, or deficiencies in the model) by giving these parameters quite unrealistic values, moreover with large standard deviations.

*$E_0$ values*

The value for $E_0$ is often determined by independent experiments, before or after the main titration, or both. Even with the best electrode system, $E_0$ varies a little from week to week or even from day to day. In particular, if a glass electrode system is moved from one vessel to another, there may be a small change in the $E_0$. The agreement of the $E_0$ values obtained in a single titration is in general considerably better than that between $E_0$ values in different titrations. Hence, it is advisable to determine $E_0$ in the course of the same experiment, if possible both before and after the main titration, and without changing the cell.

These measurements are then conveniently treated as parts of the same titration, with $E_0$ treated as an adjustable group parameter.

In a titration of $H_3PO_4$, to take a specific example, the value for $E_0$ is intimately linked with $j_{ac}$ and the formation constant of $H_3PO_4$ since, in the dilute solutions one is studying, one will always have mixtures of $H^+$, $H_3PO_4$ and $H_2PO_4^-$. For this and other relatively strong acids one would prefer to adjust $E_0$ (and possibly also $j$) at the same time as the equilibrium constants.

For every group, the cells *ks*[*Rs*, 1] and *ks*[*Rs*, 2] are reserved for the values for $E_{0A}$ (short, $E_0$) and $E_{0B}$.

*Analytical errors*

Random errors in reading the $V_T$ (or $v$ in coulometer titrations) or $E$, will not affect the "best" values for the parameters; such variations come out as standard deviations in the statistical treatment. However, if there is an error in the original analytical value for $H_0$, $H_T$, $B_0$ or $B_T$, or in $V_0$ this will persist throughout the titration and hence be a systematic error. To deal with such errors, one can treat them as group parameters $k_s$.

Of course none of these values is known exactly, so, to be strict, each contains a systematic error. However, one cannot doubt all analytical data at once but must assume at least some of them to be correct. The reason is simple. Suppose that we have assumed a certain set of analytical concentrations $H_0$, $B_0$ etc. and then found a minimum value $U'$ for a certain set of the parameters $\beta_{pq}$ and $E_0$. Now, suppose that we multiply all concentrations by an arbitrary constant factor $f$, say, by 1.37, or by 1000, which means simply that we change the concentration unit. If we make the corresponding change in the parameters, multiplying $\beta_{pq}$ by $f^{-(p+q-1)}$, multiplying $j$ by $f^{-1}$ and subtracting $RT \ln f/F$ from $E_0$, then we would get exactly the same calculated $E$ values. Let us assume $Typ = 1$.

If $U$ is defined by the deviation in $E$ ($val = 4$, eqn 14), then there would be an infinity of sets of values for the analytical concentrations that would give the same $U'$, corresponding to a level valley bottom in multidimensional space. As one can easily see, the same would be true also for $val = 2$ (eqn 13) since $fel[2]$ is not affected by a change in $f$. For $val = 1$ (eqn 12), on the other hand, the deviation would be proportional to $f$. Hence, one could make $U$ arbitrarily small by passing to larger concentration units: kM, MM etc. Everyone would agree, however, that this would be no real improvement of the fit.

In our program we have introduced the possibility of treating the following types of analytical errors:

(1) An error in the determination of $B$, the total concentration of B. Since the original solution and the buret solution are usually made from the same stock solution, it seems reasonable to assume that $B_0$ and $B_T$ are wrong by the same factor which we shall call $f_B$, $Bfak = 1 + ks[Rs, 8]$ in the program, and which would be 1.00 in case of no error. Hence we shall set

$$B_{tot} = B_{anal}\, f_B \tag{15}$$

(2) The measured $H$ in the B, C, or L stock solution may be in error. It may be hard to determine the excess $H^+$ in, say, a solution of a metal salt, or of $H_3PO_4$, with a better accuracy than can be obtained by the mathematical analysis of emf titration data, and the exact value for $H$ is then best determined by computer adjustment. This adjustment was treated as a constant correction to $Z$, $\delta Z$ in the Z + ETA program (part 8). In the present ETITR program, $ks[Rs, 5] = \delta A$ allows a constant correction to $A(H)$ in all solutions, which may be justified if $B$, $C$, or $L$ is kept constant in each group.

(3) In the original solution, $H_0$ may be in error, and corrected by a term $\delta H_0$. One may instead adjust $H_T$, but as experiments are usually performed, $H_0$ is more likely to be slightly in error. If additions are made from a buret, one usually has the acid in the buret and the original solution is alkaline (with a slightly more uncertain $H$ value). If the addition is made coulometrically, one would usually assume that the coulometer is more precise than one's analytical determinations. So, one would assume

that the concentration of the acid in the buret, or the readings of the coulometer, are correct and let this fix the concentration scale.

We may hence express the total $H^+(A)$ excess as follows

$$H_{tot} = H_{anal} + f_{dil}\,\delta H_0 + (1 - f_{dil})\,\delta H_T + \delta H \tag{16}$$

At most one of these corrections can be adjusted at a time, and which one chooses depends on how one judges the experimental situation. In coulometric work they are usually equivalent since in each titration the volume does not change, $f_{dil} = 1$ and $B =$ constant. In other cases, there may be good reasons to prefer one or the other type of correction.

*"Dirt acid"*

Even if one tries to purify the reagents, one can never keep the concentration of impurities exactly at zero. We shall assume that the most important impurity is a "dirt acid", HX, and we shall treat its acidity constant $K_{HX}$ as a general parameter. This means that we hope at least to have the same predominating dirt in all solutions studied. The concentration of the dirt acid, $c_{HX}$, however, we must treat as a group parameter since it may be different in different solutions. We often assume that the dirt goes with the original solution $S_0$, in which $c_{HX} = ks[Rs, 6]$. In a coulometric titration, this must be so, since there are no other solutions. In a buret titration, $S_0$ is usually more alkaline, and hence more likely to be contaminated. We may also assume the same dirt concentration in $S_0$ and T, $c_{HXall} = ks[Rs, 7]$.

If one thinks one knows what is the most important "dirt acid", then $K_{HX}$ is known and need not be adjusted. Otherwise one should adjust both $K_{HX}$ and the $c_{HX}$. From the equilibrium data one will then get the following expression for $H$

$$H_{equil} = h + \Sigma p c_{pq} - K_{HX} c_{HX} f_{dil}/(h + K_{HX}) \tag{17}$$

We have assumed here that the "dirt" is a monobasic acid, but procedure Dirty allows also for a dibasic acid like $H_2CO_3$.

## Input

The input is easy to deduce from the general rules (part 6), knowing what the *as*, *ap* etc. are. We give first the general expressions and then a specific example with three components, $A = H^+$, measuring (and trusting) $E_A$ and $E_B$, and minimizing $U = \Sigma(A_{calc} - A_{exp})^2$, hence $Typ = 3$, $val = 1$; B is a 2+ cation.

*General:*

Constant input (data): 14(*Rurik*), text, 9(*Rurik*), *Typ*, 6(*Rurik*), *Ns*, *Nag*(1 if $Typ = 1$, else 2), *Nas*($2 + 2 \times Nkom$), *Nap*(2 for $Typ = 1$ or 2, 3 for $Typ = 3$), *temp*, $n_e$ (for $Typ = 2$ or 3), (*Np*, $A_0$, $B_0$, ($C_0$, $L_0$), $A_T$, $B_T$, ($C_T$, $L_T$,) $V_0$, $f_V$, ($V_T$, *E* (not for $Typ = 2$), $E_B$ (not for $Typ = 1$))$_{Np}$)$_{Ns}$.

A change of buret solution in the course of a titration (inside a group) is indicated by inserting, at the right place among the *ap*, ($-1$, $A'_T$, $B'_T$, ($C'_T$, $L'_T$) $f'_V$). If necessary, one or two zeros are added to make the number of data correspond to $n = 2$ or 3 "false experimental points". This $n$ is included in the *Np* first given and is later subtracted in the program.

Variable input (dagens spaning) begins: *7(Rurik)*, $Nk(4+Nx)$, $Nk(4+Nx)$, $Nak$ $(1+Nkom)$, $j_{ac}$, $(0)_{Nak\ times}$, $j_{alk}$, $(0)_{Nak\ times}$, $K_{HX}$, $(0)_{Nak\ times}$, 1.0 (for instance), $-14$, $-1$, $(0)_{Nkom-1\ times}$ $(=K_w)$, $(k, pot, p, q, (r, t))_{Nx}$, 8(*Nks*), 0, 1, 2, $(E_{0B})_{Ns}$ (all *ks:* $=0$ except $ks_2 = E_{0B}$), 0(*skin*),*

*7* (*Rurik*), *Nk*, $-1, 2, 1, 2$, removes posk protection for $k_1$ and $k_2$

*8*(*Rurik*), *Nok*(*=Nkom*), *stegbyt*, *start*(lnb), *tol*($B/B_{tot}$), (*start*(lnc), *tol*($C/C_{tot}$), *start*(lnl), *tol*($L/L_{tot}$)), *start*(lna), *tol*(*A*), *18*(*Rurik*), *val*.

*Specific example:*

Data: *9*(*Rurik*), 3(*Typ*), *6*(*Rurik*), *Ns*, 2(*Nag*), 8(*Nas*), 3(*Nap*), 25(*temp*), 2($n_e$), (*Np*, $A_0$, $B_0$, $C_0$, $A_T$, $B_T$, $C_T$, $V_0$, $f_V$, ($V_T$, *E*, $E_B$,)$_{Np}$)$_{Ns}$.

A change of buret solution is indicated by inserting $(-1, A'_T, B'_T, C'_T, f'_V, 0(\text{dum}))$, which is counted as 2 false experimental points.

Dagens spaning begins: e.g. *7*(*Rurik*), $4+Nx$, $4+Nx$, 4(*Nak*), $-17(j_{ac})$, 0, 0, 0, 0, $10(j_{alk})$, 0, 0, 0, 0, $2.3_{10}-6(K_{HX})$, 0, 0, 0, 0, 5.8, $-15$, $-1$, 0, $0(K_w)$, $(k, pot, p, q, r)_{Nx}$, 8(*Nks*), 0, 2, 1, 2, $(E_0, E_{0B})_{Ns}$, 0(*skin*),
*7*(*Rurik*), $Nk(4+Nx)$, $-1$(*Nbyk*), 2, 1, 2,
*8*(*Rurik*), 3(*Nok*), *stegbyt*, *start*(lnb), *tol*($B/B_{tot}$), *start*(lnc), *tol*($C/C_{tot}$), *start*(lna), *tol*(*A*), *18*(*Rurik*), 1(*val*),

In the following *Rurik*$=$*11*, *19* (or *3* or *20*), *12*, *5*, *2*, *13*, *15* etc. are used according to the general rules.

## Discussion

In several published and forthcoming papers from this and other departments, the LETAGROP method has been used for adjusting analytical parameters. Of course, this method like all others must be used with judgment, and the comparison with the analytical data may give three types of result:

(1) Agreement, but higher precision. In many cases one may reasonably say that such a computer adjustment of emf titration data gives a more precise account of the composition of the solutions than do the standard methods of chemical analysis. So one should speak rather of increasing the precision than of detecting "errors" in the analyses.

(2) Agreement, but lower precision. This type of behavior is exemplified by the experiments of Baldwin and Wiese (1968) who titrated periodate with acid, and found that $f_B$ did not influence the error square sum very much since a change in $f_B$ was balanced by a change in the equilibrium constant, and both came out with a large standard deviation. The conclusion in this and similar cases is that the results of ordinary chemical analyses should be accepted since they allow a more precise determination of the total concentration of B than do the emf data.

(3) Incompatible results. When one assumes a certain chemical model, the "best" agreement may be obtained if one assumes analytical errors that are larger than one can reasonably expect, or which show an unlikely systematic drift. Such was the case for some of the models tried for thorium hydrolysis (Hietanen and Sillén 1968), and then it seems reasonable rather to look for a better model than to accept the analytical errors deduced.

The simpler the system studied, the easier will it be to distinguish between devia-

* This is an example only. In other cases, say, $ks_1$ or both $ks_1$ and $ks_2$ may be given.

tions that stem from the model and those that come from systematic errors. In systems with polynuclear complexes, one must always be aware of the risk that systematic errors might cause effects that are quite similar to those of a new species (see e.g. Burkov, Lilič and Sillén 1965). In systems where one can reasonably expect all species to be known, such as the equilibria of phosphate ions and protons, one might find it worthwhile to test models with various types of systematic errors, and see what sort of agreement one can obtain. As computers become more available, and computer time becomes cheaper, we think in the future such a test for systematic errors should be part of the routine of equilibrium analysis.

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