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High-speed Computers as a Supplement to Graphical Methods

12. Application of LETAGROP to Data for Liquid-liquid Distribution Equilibria

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Special blocks are given in Table 3 which can be used together with the general minimizing LETAGROP program to analyze data for solvent-solvent distribution equilibria.

The program, called DISTR, calculates from data for the distribution of a component B between two phases, the "best" values of the constant for the formation of a set of complexes with two, three, or four components. Illustrations are given on the application of the program to several types of distribution data.

Analysis of solvent extraction data with a high-speed computer was first reported by Rydberg *et al.*[1–3], who applied a program based on a weighted least-squares technique. With their program Rydberg *et al.* searched for the set of values of unknown parameters a_1, a_2, $\cdots a_n$, which will minimize the error-square sum: $S = \sum_{i=1}^{I} w_i (\sum_{0}^{N} a_n x_i^n - y_i)^2$, where w is a weight factor, y_i a measured quantity and x_i quantities assumed to be known. These authors thus assumed that an explicit linear relationship can be written between the function y and the required parameters a_n, in the form of a polynomial $y = \sum_{0}^{N} a_n x^n$. It is true that in many solvent extraction systems the data can be arranged in such a way as to give an explicit linear relationship with a function y. However, this may not always be the case.

In this laboratory a general minimizing program, called LETAGROP, has been developed by Sillén and coworkers. The program orders the computer to calculate the best values of a set of unknown parameters K_1, $K_2 \cdots K_N$ by minimizing the square-sum:

$$U = \sum_{1}^{N} w\,(y_{\text{calc}} - y_{\text{exp}})^2$$

In the expression for U, w represents a weight-factor, y_{exp} a known measured quantity and y_{calc} a quantity calculated from a derived functional rela-

tionship $y=f(K_i, a_j)$ $i=1, 2,\cdots N$; $j=1, 2,\cdots M$ where a_j are quantities assumed to be known from the experimental data. The LETAGROP-program consists of a main part, common to all problems and special parts (PUTS, UBBE), which are specific for the problem in question, *e.g.* EMF data,[8] spectrophotometric data.[9] The application of Letagrop-analysis to distribution data has been reported previously.[10–12] However, most of the special parts used in connection with the main program were usually written to analyze some particular type of distribution data. For instance, a separate Puts and Ubbe were written in the treatment of the system HDBP-TBP-hexane/0.10 M H_2SO_4 (*cf.* Ref. 12a) and another type of Puts and Ubbe for the system U(VI)-HDBP-TBP-hexane/0.10 M H_2SO_4 (*cf.* Ref. 12b). The present work describes the special blocks (Table 3) to be inserted in the new version of the LETAGROP-program (parts 6, 7, and 8). The program, called DISTR, has a more general application for different types of distribution data, and may be used for the computer-analysis of solvent extraction system with two, three, or four components.

BACKGROUND AND ASSUMPTIONS

We consider a chemical model in a two-phase system, consisting of phase **1** (*e.g.* an organic solvent) and phase **0** (*e.g.* an aqueous solution), with the reaction components A, B, C, and L which are in minor quantities compared with those of the phase-solvents. The distribution of one of these reaction components, *e.g.* the reaction component B, between phase **1** and phase **0** is studied as a function of the total concentrations of A, B, C, and L. The distribution ratio D for B between the two phases, given as $D=[B]_1/[B]_0$, may be determined experimentally by the measurement of $[B]_1$ and $[B]_0$ (or the ratio $[B]_1/[B]_0$) using chemical methods, *e.g.* spectrometric or potentiometric analysis, or more conveniently in case B can be labelled with some radioactive isotope (*e.g.* with the α-emitter ^{233}U in the study of uranium distribution; with ^{32}P-labelled $(RO)_2POOH$ in the study of the distribution of dialkylphosphoric acid). In the latter case the distribution ratio D can thus be determined radiometrically as the ratio of the amount of radioactive disintegrations (*e.g.* cpm/unit volume sample) of equivalent samples of phase **1** and phase **0**. Correction to D should be made for the different absorption (in β-counting) or quenching (in liquid scintillation counting) in the two liquids (factor λ) and for the dead-time of the counter (factor τ). The corrected distribution ratio can be written as:

$$D=[B]_1/[B]_0=\lambda(I_1+\tau I_1^2)/(I_0+\tau I_0^2) \quad (1)$$

We now assume that the component B may form a number of complexes $A_pB_qC_rL_t$ with the components A, C, and L in the two phases. The distribution ratio D may now be related to the concentrations of the B-containing species as follows:

$$D_{calc}=(\sum_{i=1}^{Nk} q_i[A_{p_i}B_{q_i}C_{r_i}L_{t_i}]_1)/(\sum_{i=1}^{Nk} q_i[A_{p_i}B_{q_i}C_{r_i}L_{t_i}]_0)=$$

$$(\sum_{i=1}^{Nk} q_i\beta_i^1[A]^{p_i}[B]^{q_i}[C]^{r_i}[L]^{t_i})/(\sum_{i=1}^{Nk} q_i\beta_i^0[A]^{p_i}[B]^{q_i}[C]^{r_i}[L]^{t_i}) \quad (2)$$

In the LETAGROP-program the computer may now be ordered to find the best values of $\beta_{p1r}{}^1$ and $\beta_{p1r}{}^0$ which, for instance, will minimize the error-square sum:

$$U = \sum_{1}^{Np} (\log D_{calc} - \log D_{exp})^2$$

The component A in the complex $A_pB_qC_rL_t$ is usually H^+ and its activity (or equilibrium concentration $[H^+]$) is assumed to be known. For the other components B, C, and L we know only their *total concentrations*, which will be given in the unit *moles per liter of phase* **0**, even in the case where they are initially in phase **1**.

In this program each species is characterized by the coefficients p, q, r and t (if there are so many components), which may assume positive, zero or negative values and also by a number f_i (called "fas[i]" in the program) which can have the value 0 or 1, depending on whether the species exists in phase **0** or in phase **1**. If a certain molecule may exist in both phases, it is counted as two separate species, one in each phase, and is characterized as the species (p,q,r,t,**0**) in phase **0** and as the species (p,q,r,t,**1**) in phase **1**.

In order to make the program more general, we allow the reaction components to exist as such in either phase, and even to have a negligible concentration. Consequently, even the reaction components B, C, and L must be listed among the Nk complexes after *Rurik* = **7**, with formation constant $K = 1$, the coefficient equal to 1 for the component considered and zero for the other components along with the appropriate value for the phase-number f_i.

The concentration of the ith species $A_{p_i}B_{q_i}C_{r_i}L_{t_i}$ may be written as $[A_{p_i}B_{q_i}C_{r_i}L_{t_i}] = c_i = \beta_i a^{p_i} b^{q_i} c^{r_i} l^{t_i}$, and the following mass balance equations are valid for the components B, C, and L:

$$B = [B]_{tot} = [B]_0 + V[B]_1 = \sum_{i=1}^{Nk} q_i c_i V^{f_i} \tag{4}$$

$$C = [C]_{tot} = [C]_0 + V[C]_1 = \sum_{i=1}^{Nk} r_i c_i V^{f_i} \tag{5}$$

$$L = [L]_{tot} = [L]_0 + V[L]_1 = \sum_{i=1}^{Nk} t_i c_i V^{f_i} \tag{6}$$

V is here the volume ratio of phase **1** to phase **0** which is assumed to be known for each experimental point.

Moreover we have the following relationships for B, C, and L:

$$[B]_0 = \sum_{i=1}^{Nk} (1-f_i) q_i c_i; \quad [B]_1 = \sum_{i=1}^{Nk} f_i q_i c_i \tag{7}$$

$$[C]_0 = \sum_{i=1}^{Nk} (1-f_i) r_i c_i; \quad [C]_1 = \sum_{i=1}^{Nk} f_i r_i c_i \tag{8}$$

$$[L]_0 = \sum_{i=1}^{Nk} (1-f_i) t_i c_i; \quad [L]_1 = \sum_{i=1}^{Nk} f_i t_i c_i \tag{9}$$

The reader must excuse that c is used (without subscript) for the free concentration of the component C, and also (with subscript) to denote concentrations of any species. In the program, for convenience $c[ix]$ often stands for $c_i V^{f_i}$. As defined earlier the phase-number f_i has either the value equal zero or 1.

Given the values of the equilibrium constants β_i, log a, $[B]_{tot}$, $[C]_{tot}$, and $[L]_{tot}$, we can solve the unknown ln b, ln c, and ln l from (4), (5), and (6) by the set of procedures BDTV given in Ref. 7. Using the given values of β_i and the calculated values of ln a, ln b, ln c, and ln l, D_{calc} may be calculated using eqn. (2).

In the program $D_{calc}(=D_{ber})$ is calculated from (7):

$$D_{calc} = \frac{[B]_1}{[B]_0} = \frac{\sum_{i=1}^{Nk} f_i q_i c_i}{\sum_{i=1}^{Nk} (1-f_i) q_i c_i} \tag{10}$$

A few examples of two-phase chemical systems are given below. When a constant ionic medium is used, its ions sometimes take part in the complex formation but usually they may be left out in the equilibrium analysis.

Reaction species				Complex species	
A	B	C	L	phase **0** (aqueous)	phase **1** (org)
H^+	M^{n+}	TBP	X^-	A, B, L, $A_pB_qC_{r(=0)}L_t$ *e.g.* (0,1,0,1,0) $=MX_{(n-1)+}$	C, $A_pB_qC_rL_t$ (0,1,2,*n*,1) = $MX_n(TBP)_2$
H^+	M^{n+}	org anion C^-		A, B, C, $A_pB_qC_r$ *e.g.* (0,1,*x*,0) $=MC_{x+(n-x)}$	$A_pB_qC_r$ (*m* − *n*,1,*m*,1) = $MC_n(HC)_{m-n}$
H^+	HDBP	TBP		A, B, $A_pB_qC_{r(=0)}$ *e.g.* (0,1,0,0) = HDBP (−1,1,0,0) = DBP^-	C, $A_pB_qC_r$ (0,1,1,1) = HDBP.TBP
H^+	UO_2^{2+}	HDBP	TBP	A, B, C, $A_pB_qC_rL_{t(=0)}$ *e.g.* (−2,2,0,0,0) = $(UO_2)_2(OH)_2^{2+}$	L, $A_pB_qC_rL_t$ (−2,1,4,1,1) = $UO_2(DBP)_2(HDBP)_2TBP$

DATA FOR INPUT

Table 1 shows how the data and parameter arrays are defined in the present program for different values of the control number *Typ*. In Table 2 the special input data used in the DISTR program for *Typ* = **1**, **2**, **3**, and **4** are given. The use of the other *Rurik* values, *e.g.* **3** for giving steps, **5** for "shot", **2** for output, *etc.* is the same as for other LETAGROP programs (*cf.* Ref. 6). Note, however, that *Tage* or *Koks* (*Rurik* = **19** or **20**) may not be used since no group parameter *ks* is given. For the definition of the symbols given in Tables 1 and 2, *cf.* Refs. 4, 7.

Table 1. Use of arrays for experimentally known quantities (*ag*,*as*,*ap*,*ak*) which are not varied during the calculation and adjustable parameters (*k*,*ks*) in application of DISTR to liquid-liquid distribution data. The "+" before an *as* or *ap* means that the value is not given in the input but calculated in PUTS or UBBE.

Typ = **1** or **2**

ag = λ (-1 if λ is given as *ap*), τ;
as = V, $+\ln V$
ap = log*a*, *B*tot, *C*tot, (*L*tot),[a] I_0, I_1, (λ) (if $ag[1] = -1$), $+D_{exp}$, +ln*a*, +ln*b*, +ln*c*, (+ln*l*) [a]
k = β
ak = *pot*, *p*, *q*, *r*, (*t*),[a] *fas*
ks = none

Typ = **3** or **4**

ag = none
as = none
ap = log*a*, *B*tot, *C*tot, (*L*tot),[b] *V*, D_{exp}, +ln*a*, +ln*b*, +ln*c*, (+ln*l*),[b] $+\ln V$
k = β
ak = *pot*, *p*, *q*, *r*, (*t*),[b] *fas*
ks = none

[a] Additional data for *Typ* = **2**.
[b] Additional data for *Typ* = **4**.

Table 2. Input for DISTR = LETAGROP version of liquid-liquid distribution equilibria.

Typ = **1** or **2**

Data: **14**(*Rurik*), text, **9**(*Rurik*), *Typ*(**1** or **2**), **6**(*Rurik*), *Ns*, 2(*Nag*), **1**(*Nas*), (5 or 6[a] (*Nap*), λ) or (6 or 7[a](*Nap*), -1, if λ is given as *ap*), τ, (*Np*, *V*, (log*a*, *B*tot, *C*tot, *L*tot[a], I_0, I_1, (λ, if given as *ap*))$_{Np}$)$_{Ns}$
Day order follows (see below)

Typ = **3** or **4**

Data: **14**(*Rurik*), text, **9**(*Rurik*), *Typ*(**3** or **4**), **6**(*Rurik*), *Ns*, 0(*Nag*), 0(*Nas*), 5 or 6[b](*Nap*), (*Np*, (log*a*, *B*tot, *C*tot, *L*tot,[b] *V*, D_{exp})$_{Np}$)$_{Ns}$
Day order follows (see below)

The day order ("dagens spaning") may begin as follows:

7(*Rurik*), *Nk*, *Nk*, *Nak*(5 or 6[a,b]), (*k*, *pot*, *p*, *q*, *r*, *t* [a,b], *fas*)$_N$, 0,0, (all *ks*: = 0), 0 (if no information on twist matrix is given), **8**(*Rurik*), 2 or 3 [a,b] (*Nok*), *stegbyt*, *start*(ln*b*), *tol* (*B*/*B*tot), *start*(ln*c*), *tol*(*C*/*C*tot), *start*(ln*l*),[a,b] *tol*(*L*/*L*tot),[a,b] *etc.*

[a] Additional data for *Typ* = **2**.
[b] Additional data for *Typ* = **4**.

During a "shot" the value of D_{ber} calculated from (10) may become undefined if the formation constants for all species in any of the two phases are varied and happen to be given the value zero or some values which make the expression for $[B]_1$ or $[B]_0$ assume negligibly small values. This inconvenience may be easily avoided by inserting among the *Nk* complexes after *Rurik* = **7**, an imaginary complex (0,1,0,0 *,**1**) or (0,1,0,0*,**0**) with some negligibly small formation constant (*e.g.* $\beta = 10^{-30}$). This will thus only give a negligible contribution to the value of the calculated D_{ber} but still prevent it becoming undefined.

* Only for *Typ* = **2** and **4**.

*Table 3.** PUTS and UBBE for liquid-liquid distribution problems ("DISTR"). Parts of UBBE are common to all programs with "BDTV" and are given in part 8, Table 1 (*cf.* Ref. 7).

```
PUTS:       begin real D, i0, i1, lambda, lna, lnV, tau;
            switch Puts:=Puts1, Puts2, Puts3, Puts4; goto Puts[Typ];
Puts1:Puts2:
            if Rs=0 then begin Napa:=if Typ=1 then 10 else 12; arum:=if Typ=1
            then 8 else 9;
            Fas2:=true; goto DATA end;
            cell:=apcell[Rs]; w:=ag[1]; tau:=ag[2]; if w>0 then lambda:=w;
            as[Rs,2]:=ln(as[Rs,1]);
            for Rp:=1 step 1 until Np[Rs] do begin
            m:=if w>0 then cell+Nap-1 else cell+Nap-2;
            i0:=ap[m]; i1:=ap[m+1];
            if w<0 then lambda:=ap[m+2] else ap[m+2]:=lambda;
            lna:=ap[cell+arum]:=ln10×ap[cell+1];
            D:=lambda×(i1+tau×i1×i1)/(i0+tau×i0×i0);
            ap[cell+arum-1]:=D; cell:=cell+Napa end;
            goto DATA;
Puts3:Puts4:
            if Rs=0 then begin Napa:=if Typ=3 then 9 else 11; arum:=if Typ=3
            then 6 else 7; Fas2:=true; goto DATA end; cell:=apcell[Rs];
            for Rp:=1 step 1 until Np[Rs] do begin
            lnV:=ap[cell+arum+Typ]:=ln(ap[cell+Typ+1]);
            lna:=ap[cell+arum]:=ln10×ap[cell+1];
            cell:=cell+Napa 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
            real D, Dexp, lambda;
            switch Apfel:=Apfel1, Apfel2, Apfel3, Apfel4;
            switch Asoks:=Asoks1, Asoks2, Asoks3, Asoks4;
            switch Kag:=Kag1, Kag2, Kag3, Kag4;
            switch Satsa:=Satsa1, Satsa2, Satsa3, Satsa4;
            switch Uttag:=Uttag1, Uttag2, Uttag3, Uttag4;
procedure   Dber; begin real B0, B1; B0:=B1:=0;
            for ix:=1 step 1 until Nx do begin w:=q[ix]×c[ix]; B0:=B0+
            (1-fas[ix])×w; B1:=B1+fas[ix]×w end;
            D:=if B0>0 then B1/B0 else exp(100) end Dber;
            BDTV=procedures Betain, Dirty, Totber, Valhal
            - - - - - -
            U:=0 ..... goto Nyp;
Kag1:Kag2:Kag3:Kag4:
            dirt:=0; Betain(1,Nk); goto Nysa;
Satsa1:     SATSUT;
            output (61, '/2B 'LOGH' 7B 'BTOT' 9B 'CTOT' 9B 'IAQ' 6B 'IORG' 4B
            'LAMBDA' 2B 'LOGDEXP' 3B 'LOGB' 4B 'LOGC' 2B 'LOG(DB/DX)'
            1B 'DEXP/DBER-1'');
            goto Asoks1;
Satsa2:     SATSUT;
            output (61, '/2B 'LOGH' 7B 'BTOT' 9B 'CTOT' 9B 'LTOT' 6B 'IAQ' 6B
            'IORG' 2B 'LAMBDA' 2B 'LOGDEXP' 3B 'LOGB' 5B 'LOGC' 5B
            'LOGL' 2B 'LG(DB/DX)' 1B 'DX/DB-1'');
            goto Asoks2;
```

* A Fortran version of the DISTR program which has been made with the cooperation of Mr. Roland Ekelund is also available and may be obtained on request.

Table 3. Continued.

```
Satsa3:          SATSUT;
                 output (61, '/2B 'LOGH' 7B 'BTOT' 9B 'CTOT' 9B 'V1/V0' 4B 'DEXP'
                 3B 'LOGDEXP' 1B 'LG(DB/DX)' 1B 'DX/DB-1' 1B 'DB/DX-1");
                 goto Asoks3;
Satsa4:          SATSUT;
                 output (61, '/2B 'LOGH' 7B 'BTOT' 9B 'CTOT' 9B 'LTOT' 9B 'V1/V0'
                 4B 'DEXP' 2B 'LOGDEXP' 2B 'LG(DB/DX)' 1B 'DX/DB-1' 1B
                 'DB/DX-1");
                 goto Asoks4;
Asoks1:Asoks2: Asoks3: Asoks4:
                 if Typ<3 then lnV:=as[Rs, 2]; goto Nyp;
Apfel1:          Btot:=ap[cell+2]; Ctot:=ap[cell+3]; Dexp:=ap[cell+arum-1];
                 lna:=ap[cell+arum]; Valhal(2, arum); goto Felber;
Apfel2:          Ltot:=ap[cell+4]; goto Apfel1;
Apfel3:          lnV:=ap[cell+arum+Typ]; goto Apfel1;
Apfel4:          Ltot:=ap[cell+4]; goto Apfel3;
Uttåg1:          lambda:=if ag[1]>0 then ag[1] else ap[cell+6]; output(61, '/-2ZD.4D,
                 2(-ZD.4D10-2ZD), 2(-6ZD.D), -D.4D, 3(-2ZD.4D), 2(-ZD.4D)',
                 for i:=1 step 1 until 5 do ap[cell+i], lambda, loge×ln(Dexp), loge×lnb,
                 loge×lnc, fel[1], fel[2]);
                 goto Nyp;
Uttåg2:          lambda:=if ag[1]>0 then ag[1] else ap[cell+7];
                 output(61, '/-2ZD.4D, 3(-D.4D10-2ZD), 2(-5ZD.D), -D.4D,
                 4(-2ZD.4D), 2(-ZD.4D)',
                 for i:=1 step 1 until 6 do ap[cell+i], lambda, loge×ln(Dexp), loge×lnb,
                 loge×lnc, loge×lnl, fel[1], fel[2]);
                 goto Nyp;
Uttåg3:          output(61, '(-ZD.4D), 2(-ZD.4D10-2ZD), -3ZD.4D, 5(-2ZD.4D)',
                 for i:=1 step 1 until 5 do ap[cell+i], loge×ln(Dexp), fel[1], fel[2]), fel[3]);
                 goto Nyp;
Uttåg4:          output(61, '(-ZD.4D), 3(-ZD.4D10-2ZD), -3ZD.4D, 5(-2ZD.4D)',
                 for i:=1 step 1 until 6 do ap[cell+i], loge×ln(Dexp), fel[1], fel[2]), fel[3]);
                 goto Nyp;
Felber:          Dber; fel[1]:=loge×ln(D/Dexp); fel[2]:=Dexp/D-1; fel[3]:=D/Dexp-1;
                 goto Uber end UBBE;
FINAL:           end LETAGROP;
```

In the present program (Table 3) the activity of component A, here in the form of $\log[H^+]$ in most cases, is supposed to be known. In the case with two or three components where only the total concentration of each is known, and the $B_qC_rL_t$ complexes formed do not contain the reaction species A, we may treat A as a dummy and set $p_i = 0$ for all species and, *e.g.*, $\log a = 0$ for all points. If B is a trace component, (as is the case when some carrier-free radioactive isotope of B is used as tracer in the experiment, and thus may be assumed to form only mononuclear B-species), any low value for $[B]_{tot}$ (*e.g.* $[B]_{tot} = 10^{-10}$ M) will suffice as input data.

Use of *Typ* and *val*

In the present form of the program we may analyze 4 different types of data (*Typ* = **1**, **2**, **3**, or **4**), depending on the kind of distribution data available for analysis. The error-square sum to be minimized: $U = \sum_{1}^{Np} wfel[val]^2$ may in

the present program be defined in three ways, depending on the value chosen for *val*:

$$fel[1] = \log D_{calc} - \log D_{exp}$$
$$fel[2] = (D_{exp} D_{calc}^{-1}) - 1$$
$$fel[3] = (D_{calc} D_{exp}^{-1}) - 1$$

If the distribution ratio D is measured by chemical methods, *e.g.* spectrometric analysis, we may either use $Typ = 3$ or 4 and insert the experimental values of D directly as input data, or we may also use $Typ = 1$ or 2 by setting $\lambda = 1$, $\tau = 0$ and insert the measured total concentrations $[B]_0$ and $[B]_1$ instead of I_0 and I_1. Note that it is always the distribution of component B between phases 1 and 0 which is measured.

In the present program the weight-factor w, in the expression for the minimized error-square sum U, is given the value equal to 1, *i.e.* no distinction is made between the possible differences in accuracy of the experimental points treated. It is obvious, however, that if it is found desirable to give other appropriate values for w, this may easily be done by a small change in the program.

The three possible errors *fel*[1], *fel*[2], and *fel*[3] to be chosen which are available in the present work, will as a general rule lead to approximately the same values for the set of β_i at its corresponding U_{min}. Table 4 summarizes

Table 4. Comparison of equilibrium constants [a] log β_{p1r} for the formation of $(H^+)_p Hf(TOPO)_r$ species in the system Hf(IV) – 0.50 M H_2SO_4-TOPO-hexane (*cf.* Ref. 13) which minimize the error-square sum $U = \sum_1^{21} fel[i]^2$.

Minimized error *fel*[*i*]	(*p*,1,*r*) log β_{p1r} (org)	U_{min}	$\sigma(y)$
$Fel[1] = \log D_{calc} - \log D_{exp}$ (*val* = 1)	(0,1,1) 0.23 ± 0.12; (0,1,2) 2.61, max. = 2.84; (0,1,3) 5.20 ± 0.06;	0.030	0.041
$Fel[2] = D_{exp} D_{calc}^{-1} - 1$ (*val* = 2)	(0,1,1) 0.24 ± 0.12; (0,1,2) 2.61, max. = 2.83; (0,1,3) 5.21 ± 0.06	0.148	0.091
$Fel[3] = D_{calc} D_{exp}^{-1} - 1$ (*val* = 3)	(0,1,1) 0.23 ± 0.12; (0,1,2) 2.62, max. = 2.84; (0,1,3) 5.19 ± 0.06;	0.165	0.096

[a] The limits of β_{01r} $(= [Hf(IV)(TOPO)_r]_{org} [Hf^{4+}]^{-1} [TOPO]_{org}^{-r})$ given correspond to log $(\beta \pm 3\,\sigma(\beta))$ and if $\beta(\sigma) > 0.2\,\beta$, the maximum value $\log(\beta + 3\sigma(\beta))$ is given.

as an example of the use of *fel*[*val*], the values of β_{p1r} for the formation of the species $(H^+)_p Hf(TOPO)_r$ in the system Hf(IV) – 0.50 M H_2SO_4/TOPO-hexane (see Ref. 13), which minimized *fel*[1], *fel*[2], and *fel*[3] (*cf.* also Ref. 15, Table 17). Choosing *val* = 2 or 3 may in some cases give a more rapid convergence to U_{min} than when using *val* = 1. However, in case the value of $D_{exp} D_{calc}^{-1} \ll 1$ (or $D_{calc} D_{exp}^{-1} \ll 1$ for *val* = 3) for some of the experimental points treated, this would make the error-square sum U become rather insensitive to small variations of the β_i which are adjusted during a "shot".

TWO NUMERICAL ILLUSTRATIONS ON THE APPLICATION OF THE DISTR PROGRAM

1. *Chemical system:* Di-(2ethylhexyl)phosphate (HDEHP)-tributylphosphate (TBP)-toluene/0.10 M (Na,H)ClO_4 (*cf.* Ref. 14).

Primary data:

log a = log [H^+] was varied during the experiment and given for each point;
Btot = [HDEHP]$_{tot}$ was varied during the experiment and given for each point;
Ctot = [TBP]$_{tot}$ was varied during the experiment and given for each point;
$I_0 (= I_{aq})$ and $I_1 (= I_{org}) = \beta$-activity of P-32 labelled HDEHP in the aqueous and organic phase in cpm for equal volumes of samples and given for each point.

Input:
14(*Rurik*),
DISTRIBUTION STUDIES HDEHP-TBP-TOLUENE/0.10 M (Na,H)ClO_4
9(*Rurik*), **1**(*Typ*),
6(*Rurik*), 2(*Ns*), 2(*Nag*), 1(*Nas*), 5(*Nap*),
0.95($ag_1 = \lambda$), $1.67_{10} - 8(ag_2 = \tau)$,
40(*Np*), 1.0($as_1 = V$),
−3.9146(log a), 0.9262(Btot), 0(Ctot), 181.2(I_0), 10321(I_1),
– – – – – – *etc.* (40 experimental points)
50(*Np*), 1.0($as_1 = V$),
−4.0284(log a), 0.5790(Btot), 0.1998(Ctot), 222.3(I_0), 13559(I_1),
– – – – – – *etc.* (50 experimental points)
"*Dagens spaning*" (= Day order)
7(*Rurik*), 7(*Nk*), 7(*Nk*), 5(*Nak*),

(K)	(*pot*)	$(H)_p$	$(HA)_q$	$(TBP)_r$	(*fas*)$_t$	
1,	0,	0,	1,	0,	0,	HA(aq)
1,	0,	0,	0,	1,	1,	TBP(org)
3.39189	−1,	−1,	1,	0,	0,	A^-(aq)
7.98185,	12,	0,	2,	0,	0,	H_2A_2(aq)
6.16129,	4,	0,	1,	0,	1,	HA(org)
4.80017,	14,	0,	2,	0,	1,	H_2A_2(org)
5.92941,	6,	0,	1,	1,	1,	HAB(org)

0(*Nks*), 0(*Nks*), 0(*skin*),
8(*Rurik*), 2(*Nok*), 0.2(*stegbyt*), −2(*start*(ln b)), $1_{10} - 6$(*tol*(B/Btot)), −1 (*start*(ln c)), $1_{10} - 6$(*tol*(C/Ctot)),
11(*Rurik*), 1(*Rs*1), 1(*Rs*1),
3(*Rurik*), 4(*N*), 3($ivar_3$), 0.4(w), 4($ivar_4$), 0.2(w), 5($ivar_5$), 0.2(w), 6($ivar_6$), 0.2(w),
5(*Rurik*), (*etc.*)
11(*Rurik*), 2(*Rs*2), 2(*Rs*2),
3(*Rurik*), 1(*N*), 7($ivar_7$), 0.2(w),

5(*Rurik*), (*etc.*)
13(*Rurik*), **11**(*Rurik*), 1(*Rs*1), 2(*Rs*2),
2(*Rurik*), **−1**(stop calculation),

Result of calculations:

DISTRIBUTION STUDIES HDEHP-TBP-TOLUENE/0.10 M (Na,H)ClO_4
– – – – – – – *etc.* – – – – – – –
RURIK = 13
K(IK) =

K 1 =	1.00000 + 000	DARR = −1.000 + 000	AK = 0	0 0 1 1
K 2 =	1.00000 + 000	DARR = −1.000 + 000	AK = 0	0 1 0 0
K 3 =	3.39446 − 001	DARR = 1.278 − 002	AK = 0	−1 1 0 0
K 4 =	7.99797 + 000	DARR = 6.075 − 001	AK = 12	0 2 0 0
K 5 =	6.15735 + 000	DARR = 4.108 − 001	AK = 4	0 1 0 1
K 6 =	4.80868 + 000	DARR = 3.325 − 001	AK = 14	0 2 0 1
K 7 =	6.21149 + 000	DARR = 1.460 − 001	AK = 6	0 1 1 1

RURIK = 11
SATS 1 − 2
RURIK = 2

UTTAG
SATS 1
AS = 1.000000
KS =

LOGH	BTOT	CTOT	IAQ	IORG	LAMBDA	LOGDEXP
−3.9145	9.2620 − 001	0.000 + 000	181.2	10321	0.9500	1.7334
LOGB	LOGC	LOG(DB/DX)		DEXP/DBER − 1		
−7.5122	−7.3830	0.0441		−0.0966		

– – – – – – – *etc.* (40 experimental points)
SATS 2
AS = 1.000000
KS =

LOGH	BTOT	CTOT	IAQ	IORG	LAMBDA	LOGDEXP
−4.0284	5.7900 − 001	1.9980 − 001	222.3	13559	0.9500	1.7631
LOGB	LOGC	LOG(DB/DX)		DEXP/DBER − 1		
−7.6242	−0.7592	0.0330		−0.0732		

– – – – – – – *etc.* (50 experimental points)

Comments: (a) In this set of data the 1st group (Sats 1) consists of data with $C_{tot} = [TBP]_{tot} = 0$ and the second group (Sats 2) of data with values of *B*tot and *C*tot not equal to zero. As can be seen from the "dagens spaning" used, the data of the 1st group were used for the analysis of the $(H^+)_p(HA)_q$ species, where the equilibrium constants β_{pq0} were adjusted until the error-square sum $U = \sum_1^{40} (\log D_{calc} - \log D_{exp})^2$ was minimized. These values of the equilibrium constants β_{pq0} found were then kept constant during the analysis of the 2nd group of the data, in which only the constant for the formation of HAB(org) ($= \beta_{011}$) was varied to minimize *U* for $Np = 50$ points.

b) The starting values for β_{pqr} given after *Rurik* = 7 were found from previous computer calculations.

II. *Chemical system:* Hf(IV) – 0.50 M H_2SO_4/HDBP – TOPO – hexane (*cf.* Ref. 13)
Primary data:

$\log a = \log [H^+] = -0.2647$ was kept constant during the experiment; $B\text{tot} = [\text{Hf(IV)}]_{\text{tot}} = 1_{10} - 8$ M (or any arbitrarily small value in case only mononuclear Hf-species may be assumed);
$C\text{tot} = [\text{HDBP}]_{\text{tot}}$ was varied during the experiment and given for each point;
$L\text{tot} = [\text{TOPO}]_{\text{tot}}$ was varied during the experiment and given for each point;
$I_0 (= I_{\text{aq}})$ and $I_1 (= I_{\text{org}})$ = gamma-activity of ^{181,175}Hf in the aqueous and organic phase in cpm for equal volumes of samples and given for each point;

Input:

14(Rurik),
DISTRIBUTION STUDIES HF(IV)-0.50 M H2SO4/HDBP-TOPO-HEXANE
9(*Rurik*), **2**(*Typ*),
6(*Rurik*), 4(*Ns*), 2(*Nag*), 1(*Nas*), 6(*Nap*), $1(ag_1 = \lambda)$, $0(ag_2 = \tau)$,
21(*Np*), $1.0(as_1 = V)$,
$-0.2647(\log a)$, $1_{10} - 8(B\text{tot})$, $3.4856_{10} - 4(C\text{tot})$, $1_{10} - 15(L\text{tot})$, $77100(I\text{aq})$,
$14459(I_{\text{org}})$,
– – – – – – *etc.* (21 experimental points)
21(*Np*), $1.0(as_1 = V)$,
$-0.2647(\log a)$, $1_{10} - 8(B\text{tot})$, $0(C\text{tot})$, $4.993_{10} - 4(L\text{tot})$, $136186(I_{\text{aq}})$,
$122(I_{\text{org}})$, – – – – – – *etc.* (21 experimental points)
38(*Np*), $1.0(as_1 = V)$,
$-0.2647(\log a)$, $1_{10} - 8(B\text{tot})$, $9.959_{10} - 5(C\text{tot})$, $4.993_{10} - 4(L\text{tot})$, $177233(I_{\text{aq}})$,
$470(I_{\text{org}})$,
– – – – – – *etc.* (38 experimental points)
8(*Np*), $1.0(as_1 = V)$,
$-0.2647(\log a)$, $1_{10} - 8(B\text{tot})$, $4.9875_{10} - 4(C\text{tot})$, $2.994_{10} - 5(L\text{tot})$,
$89576(I_{\text{aq}})$, $77967(I_{\text{org}})$,
– – – – – – *etc.* (8 experimental points)

Dagens spaning (Day order):
7(*Rurik*), 20(*Nk*), 20(*Nk*), 6(*Nak*),

(K)	(pot)	$(\text{H})_p$	$(\text{Hf})_q$	$(\text{HA})_r$	$(\text{TOPO})_s$	$(fas)_t$	
1,	0,	0,	1,	0,	0,	0,	Hf^{4+}(aq)
1,	0,	0,	0,	1,	0,	0,	HA(aq)
1,	0,	0,	0,	0,	1,	1,	TOPO(org)
1.253	–1,	–1,	0,	1,	0,	0,	A^-(aq)
6.5724,	–3,	0,	0,	1,	0,	1,	HA(org)
3.50438,	1,	–1,	1,	0,	0,	0,	$Hf(SO_4)^{2+}$(aq)
1.34028,	2,	–2,	1,	0,	0,	0,	$Hf(SO_4)_2$(aq)
1.96608,	2,	0,	0,	2,	0,	1,	H_2A_2(org)
7.77969,	5,	0,	0,	4,	0,	1,	H_4A_4(org)
4.98749,	2,	0,	0,	1,	1,	1,	HA.TOPO(org)

7.74789,	4,	0,	0,	2,	1,	1,	H_2A_2.TOPO(org)
2.62129,	2,	−2,	1,	0,	1,	1,	$Hf(SO_4)_2$·TOPO(org)
6.27682,	4,	−2,	1,	0,	2,	1,	$Hf(SO_4)_2$.2TOPO(org)
2.4410,	7,	−2,	1,	0,	3,	1,	$Hf(SO_4)_2$.3TOPO(org)
8.45179,	13,	−4,	1,	4,	0,	1,	HfA_4(org)
5.83936,	18,	−4,	1,	5,	0,	1,	HfA_4(HA)(org)
5.65625,	6,	−2,	1,	1,	1,	1,	$Hf(SO_4)_2$HA.TOPO(org)
3.11934,	9,	−2,	1,	1,	2,	1,	$Hf(SO_4)_2$HA.2TOPO(org)
9.61527,	10,	−2,	1,	1,	3,	1,	$Hf(SO_4)_2$HA.3TOPO(org)
1.62186,	18,	−4,	1,	4,	1,	1,	HfA_4·TOPO(org)

0(*Nks*), 0(*Nks*), 0(*skin*),
8(*Rurik*), 3(*Nok*), 0.2(*stegbyt*), −20(*start*(ln *b*)), $1_{10}-6$(*tol*(*B*/*B*tot)),
−2(*start*(ln *c*)), $1_{10}-6$(*tol*(*C*/*C*tot)), −3(*start*(ln *l*)), $1_{10}-6$(*tol*(*L*/*L*tot)),
11(*Rurik*), 1(*Rs*1), 1(*Rs*1),
3(*Rurik*), 2(*N*), 15($ivar_{15}$), 0.2(*w*), 16($ivar_{16}$), 0.2(*w*),
12(*Rurik*), −1(*skrikut*),
5(*Rurik*), (*etc.*)
11(*Rurik*), 2(*Rs*2), 2(*Rs*2),
3(*Rurik*), 3(*N*), 12($ivar_{12}$), 0.2(*w*), 13($ivar_{13}$), 0.2(*w*), 14($ivar_{14}$), 0.2(*w*),
5(*Rurik*), (*etc.*) **11** (*Rurik*), 3(*Rs*3), 4(*Rs*4),
3(*Rurik*), 4(*N*), 17($ivar_{17}$), 0.2(*w*), 18($ivar_{18}$), 0.2(*w*), 19($ivar_{19}$), 0.2(*w*),
20($ivar_{20}$), 0.2 (*w*),
5(*Rurik*), (*etc.*)
11(*Rurik*), 1(*Rs*1), 4(*Rs*4),
13(*Rurik*), **2**(*Rurik*), −**1**(stop calculation),

Results of calculation:

DISTRIBUTION STUDIES HF(IV)-0.50 M H2SO4/HDBP-TOPO-HEXANE
– – – – – – *etc.* – – – – – –
RURIK = 13
K(IK) =

K 1 = 1.00000 + 000	DARR = −1.000 + 000	AK = 0 0 1 0 0 0
K 2 = 1.00000 + 000	DARR = −1.000 + 000	AK = 0 0 0 1 0 0

– – – – – – *etc.* – – – – – –

K11 = 7.74789 + 000	DARR = −1.000 + 000	AK = 4 0 0 2 1 1
K12 = 2.61977 + 000	DARR = 2.338 − 001	AK = 2 −2 1 0 1 1
K13 = 6.30641 + 000	DARR = 1.406 + 000	AK = 4 −2 1 0 2 1
K14 = 2.44077 + 000	DARR = 1.084 − 001	AK = 7 −2 1 0 3 1
K15 = 3.11771 + 000	DARR = 1.443 + 000	AK = 14 −4 1 4 0 1
K16 = 5.48039 + 000	DARR = 7.423 − 001	AK = 18 −4 1 5 0 1
K17 = 4.58836 + 000	DARR = 2.615 + 000	AK = 6 −2 1 1 1 1
K18 = 3.53115 + 000	DARR = 1.407 + 000	AK = 9 −2 1 1 2 1
K19 = 7.94147 − 001	DARR = 9.885 − 001	AK = 11 −2 1 1 3 1
K20 = 1.55121 + 000	DARR = 1.860 − 001	AK = 18 −4 1 4 1 1

RURIK = 11
SATS 1 – 4 88 PUNKTER
RURIK = 2

UTTAG
SATS 1
AS = 1.000000
KS =

LOGH	BTOT	CTOT	LTOT	IAQ	IORG	LAMBDA
−0.2647	1.0000−008	3.4856−004	1.0000−015	77100.0	14459.0	1.0000
LOGDEXP	LOGB	LOGC	LOGL	LG(DB/DX)		DX/DB−1
−0.7269	−10.7855	−3.5847	−15.0550	−0.0280		0.0667

– – – – – – – *etc.* (21 experimental points)

SATS 2
AS = 1.000000
KS =

LOGH	BTOT	CTOT	LTOT	IAQ	IORG	LAMBDA
−0.2647	1.0000−008	0.0000+000	4.9930−004	136186.0	122.0	1.0000
LOGDEXP	LOGB	LOGC	LOGL	LG(DB/DX)		DX/DB−1
−3.0478	−10.7156	−8.6802	−3.3016	0.0369		−0.0814

– – – – – – – *etc.* (21 experimental points)

SATS 3
AS = 1.000000
KS =

LOGH	BTOT	CTOT	LTOT	IAQ	IORG	LAMBDA
−0.2647	1.0000−008	9.9590−005	4.9930−004	177233.0	470.0	1.0000
LOGDEXP	LOGB	LOGC	LOGL	LG(DB/DX)		DX/DB−1
−2.5764	−10.7164	4.1805	−3.3158	0.0310		−0.0688

– – – – – – – *etc.* (38 experimental points)

SATS 4
AS = 1.000000
KS =

LOGH	BTOT	CTOT	LTOT	IAQ	IORG	LAMBDA
−0.2647	1.0000−008	4.9875−004	2.9940−005	89576.0	77967.0	1.0000
LOGDEXP	LOGB	LOGC	LOGL	LG(DB/DX)		DX/DB−1
−0.0603	−10.9803	−3.4458	−4.5988	−0.0146		0.0343

– – – – – – – *etc.* (8 experimental points)

Comments: (a) In this set of data the 1st group (Sats 1) consists of data with $L\text{tot} = [\text{TOPO}]_{\text{tot}} = 0$ (here given as an arbitrarily small number 10^{-15} M), the second group (Sats 2) of data with $C\text{tot} = [\text{HDBP}]_{\text{tot}} = 0$, the 3rd and 4th group (Sats 3 and Sats 4) are of data with values of Ltot and Ctot not equal zero. This may explain the procedure of analysis chosen here.

(b) In this analysis we have chosen 4 reaction species: H^+, Hf^{4+}, HA(aq) and $[\text{TOPO}]_{\text{org}}$, and we assume the formation of the Hf(IV)-species $(H^+)_p(Hf)_q(HA)_r(TOPO)_s$ in the organic phase. Since $[Hf]_{\text{tot}} < 10^{-7}$ M we make the reasonable assumption that $q = 1$, *i.e.* that only mononuclear Hf-species are formed.

The values of the formation constants of $(H^+)_p(HA)_r(TOPO)_s$ and $Hf(SO_4)^{2+}$, $Hf(SO_4)_2(aq)$ have been determined previously (*cf.* Ref. 12a, 15) and were kept constant during the Letagrop analysis.

(c) The starting values for β_{p1rs} given after *Rurik* = 7 for $\beta 12$ to $\beta 20$ were found from previous computer calculations.

The numerical application of the LETAGROP-DISTR program on the two solvent extraction systems is now given only to illustrate the use and the many possibilities of the program in treating different types of distribution data. Work to apply our LETAGROP-DISTR program to other types of distribution data is still in progress and the results will be reported elsewhere.

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