

Least Squares Computer Calculations of Equilibrium Constants from Solvent Extraction Data*

JAN RYDBERG** and JAMES C. SULLIVAN

Chemistry Division, Argonne National Laboratory, Lemont, Illinois, U.S.A.

The principle of weighted least squares was used for calculating equilibrium constants from solvent extraction data. Two different programs for digital electronic computers were developed, depending on the type of complexes investigated. With these programs, the equilibrium constants in the systems Th(IV)-acetylacetonone-benzene-0.01 M NaClO₄, and Zr(IV)-F⁻ (and -HSO₄⁻)-thenoyltrifluoroacetone-benzene-2.0 M HClO₄, were calculated. The results are discussed and compared with the equilibrium constants originally computed by graphical methods.

The methods used for calculation of equilibrium constants from solvent extraction data have been generally graphical in nature (*e.g.* Connick and McVey¹, Rydberg^{2,3}, Dyrssen and Sillén⁴, and Irving, Rossotti and Williams⁵) These methods do not give an objective measure of precision of the constants and may lead to the calculation of more parameters than are justified by the data. A more accurate procedure is to treat the data according to the principle of least squares which leads to the best values and maximum number of parameters together with their standard deviations.

The application of high speed digital computers to least squares calculations of complexity constants has been outlined in a recent paper (Sullivan, Rydberg and Miller⁶). In that study, solvent extraction was discussed only briefly. The purpose of the present paper is to give a fuller account of the application of these methods to solvent extraction data.

SOLVENT EXTRACTION EQUATIONS

Here we shall consider only the case when mononuclear complexes are formed between a metal ion Mⁿ⁺ and negatively charged anions A⁻ and B^{s-},

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** On leave of absence from the University of Stockholm, and the Research Institute of National Defense, Stockholm, Sweden.

and where only uncharged complexes MA_vB_p , where $v = (v-ps)/r$, are extracted into the organic solvent. If Q is the partition ratio of all species of M between the organic and aqueous phase, Q can be expressed in terms of concentrations of the free ligands, $[A^{r-}]$ and $[B^{s-}]$, as

$$Q = \frac{\sum_0^{P'} \lambda_{vp} \beta_{vp} [A^{r-}]^v [B^{s-}]^p}{\sum_{n=0}^N \sum_{p=1}^P \beta_{np} [A^{r-}]^n [B^{s-}]^p} \quad (1)$$

where

$$\lambda_{vp} = \frac{[MA_vB_p]_{\text{org}}}{[MA_vB_p]_{\text{aq}}} \quad (2)$$

and

$$\beta_{np} = \frac{[MA_nB_p]}{[M][A]^n[B]^p} \quad (3)$$

In eqn. 1, $P' \leq P$. For simplicity, charges are here omitted, and index "org" refers to the organic phase, while index "aq" or no index refers to the aqueous phase. Brackets indicate concentrations, and it is understood that the equations refer only to experimental conditions, where the activity factors of all species may reasonably be assumed constant; *cf.* Refs.^{7,8}

Few solvent extraction studies of the formation of mixed complexes MA_nB_p have been carried out.^{3,5} Instead the purpose has generally been to study the formation of complexes either with an inorganic or with an organic ligand, *cf.* *e.g.* Ref.⁹ The conditions are therefore usually chosen so that no mixed complexes are formed, and so that only species of one of the ligands (say A) are extracted into the organic solvent. Under these circumstances eqn. 1 can be reduced to

$$Q = \frac{\lambda_v \beta_v [A]^v}{1 + \sum_1^N \beta_n [A]^n + \sum_1^P \beta_p [B]^p} \quad (4)$$

It is always possible to test if eqn. 1 or 4 is valid, *i.e.* if mixed or only simple complexes are formed, by running experiments at various $[A]$ for constant values of $[B]$; *cf.* Ref.¹⁰

Here we shall consider only the cases of eqn. 4 when complexes with one type of ligand can be neglected compared to complexes with the other kind of ligand, *i.e.* when $\sum \beta_n [A]^n$ is either much greater or much smaller than $\sum \beta_p [B]^p$. The experimental conditions can usually be chosen to fit these mathematical conditions. For example, if complexes with an organic ligand A are being studied, B is chosen to be ClO_4^- which is known to have a negligible tendency to form complexes. Or if, for example, an inorganic ligand B is being studied, which does not form extractable complexes with M, the conditions are chosen so that in the absence of B the partition curve $\log Q$ versus

$\log [A]$ has the slope v , which means that complexes with A in the aqueous phase can be neglected, *i.e.* $\sum \beta_n [A]^n \ll 1$.

Thus eqn. 4 can be written (choosing $r = 1$),

$$\text{for } \sum \beta_p [B]^p \ll 1, \quad \frac{[A]^v}{Q} = \frac{1}{\lambda_v \beta_v} \sum_0^N \beta_n [A]^n \quad (5a)$$

Introducing the abbreviations $x = [A]$, $y = 1/Q$, and $a_n = \beta_n / \lambda_v \beta_v$, eqn. 5a can be written

$$y \cdot x^N = \sum_0^N a_n x^n \quad (6a)$$

Similarly, eqn. 4 can be written ($r = s = 1$),

$$\text{for } \sum \beta_n [A]^n \ll 1, \quad \frac{[A]^v}{Q} = \frac{1}{\lambda_v \beta_v} \sum_0^P \beta_p [B]^p \quad (5b)$$

Introducing the abbreviations $x = [B]$, $z = [A]^v/Q$ and $a_p = \beta_p / \lambda_v \beta_v$, eqn. 5b can be written

$$z = \sum_0^P a_p x^p \quad (6b)$$

We shall for simplicity refer to eqns 5a and 5b as to the equations representing investigations on "extractable" and "non-extractable" complexes, respectively.

Eqns. 6a and 6b are solved by the methods of weighted least squares as outlined in a previous paper⁶. The equations for the "non-extractable" complexes will be further discussed in a later section.

THE WEIGHT OF THE DATA

The weight ω_i for an individual observation i of unit weight is (*cf.*, *e.g.*, Ref.¹³)

$$\omega_i = 1/\sigma_i^2 \quad (7)$$

where here a measure of the variance σ_i^2 is to be obtained from a consideration of the errors σ_i encountered in the experimental work. If the weight of all points is changed by multiplying the variances by a constant factor, this does not change the values of the computed parameters nor their standard deviations (*i.e.* $a_n \pm \sigma_{a_n}$, where σ_{a_n} is computed by external consistency), but changes the value of S_{\min} , where

$$S_{\min} = \sum \omega_i V_i^2 \quad (8)$$

V_i is the difference between the measured value of the function and that calculated with the best set of parameters at that point. S_{\min} has the same statistical distribution as χ^2 (see, *e.g.*, Deming¹³ or Fisher¹⁴) with k degrees of freedom; as the weight is defined above, we can put $S_{\min} = \chi^2$. Here, k is the number of observations (L) minus the number of parameters minus 1,

i.e. $k = L - N - 1$. When the mathematical model (here eqn. 5) and the weights are consistent with the experimental data, the mean value of χ^2/k will be equal to 1, with a range of ± 0.5 at the 70 % probability level (*cf.* Ref.¹⁴).

TYPES OF ERRORS IN SOLVENT EXTRACTION

We will obtain estimates of the weights by considering the random errors encountered in the experimental work. It is assumed that systematic errors are minimized by appropriate methods.

Only three measures of random errors will be considered, namely errors in Q caused by errors in the counting when radiometric methods are used, errors in Q caused by the measuring technique when other methods are used, and errors in Q caused by errors in the determination of the free ligand concentration.

Errors in Q due to radiometric counting, $\sigma_Q(I)$. In radiometric measurements, the partition ratio Q is determined from the specific radioactivities (*i.e.*, counts per min, cpm, for a fixed amount of sample) of the organic and aqueous phases, I_{org} and I_{aq} , respectively; *i.e.*, $Q = I_{\text{org}}/I_{\text{aq}}$, provided the measuring conditions are equal for the samples from both phases. The corresponding standard deviations σ_{org} and σ_{aq} are obtained from the number of counts measured; if the time of measurement is t , $\sigma = \sqrt{I/t}$ (*cf.*, *e.g.*, Ref.¹¹). Thus we can define

$$\sigma_Q(I) = Q \sqrt{\left(\frac{\sigma_{\text{org}}}{I_{\text{org}}}\right)^2 + \left(\frac{\sigma_{\text{aq}}}{I_{\text{aq}}}\right)^2} \quad (9)$$

Constant percentage error in Q , $\sigma_Q(\%)$. When Q is not directly calculated from radioactivity measurements or when the analyses are carried out in so many different steps that it becomes hard to separate the individual errors involved, the error may be estimated from the spread of Q values at constant ligand concentration. This error will be given in P % of the Q value; thus the percentage standard error is

$$\sigma_Q(\%) = PQ \quad (10)$$

Error in Q caused by error in the ligand concentration, $\sigma_Q(A)$ and $\sigma_Q(B)$. The equations for the least squares treatment were developed on the basis that $[A]$ and $[B]$ were free of error^{6,12}. However, this is not always the case, though these errors can often be neglected compared to the error in the Q measurement. In order to make possible an approximate test of the influence of an error in the free ligand concentration, this error has to be attributed to Q as the present computer program is set up. It is possible to do so, if $Q([A])$ and $([B])$ are known. At the present, we shall only consider the influence of an error σ_A in $[A]$.

A graphical function $Q([A])$ is obtained from the smooth line through the points of a $\log Q$ plot against $\log [A]$. It has been shown² that this line can be represented by

$$\frac{d \log Q}{d \log [A]} = \nu - \bar{n} \quad (11)$$

where \bar{n} is the mean ligand number. This equation may be rearranged to give

$$d Q = 2.303 Q (\nu - \bar{n}) d \log[A] \quad (12)$$

If the standard deviation in $\log [A]$ is called $\sigma_{\log A}$, this equation can also be written

$$\sigma_Q(A) \approx 2.3 Q (\nu - \bar{n}) \sigma_{\log A} \quad (13)$$

provided σ_A is small compared to $[A]$.*

Generally (in practice) $\sigma_Q(A)$ is $\gg \sigma_Q(B)$. When the error in $[B]$ has to be computed, equations similar to those above can be derived for $\sigma_Q(B)$.

COMPUTER PROCEDURE

Two computers of the Applied Mathematics Division of this laboratory were used: the IBM 704 and the GEORGE. While the 704 program was only designed for the so-called "extractable complexes" where $\nu = N$ (eqn. 6a), the GEORGE program is set up to handle both "extractable complexes" and "non-extractable complexes" because of the simpler mathematical form of eqn. 6b. The input and output data of these programs are given in Table 1. Both computers use a floating point decimal system.

When the 704 program is used for non-radiometric data, $I_{aq} \pm \sigma_{aq}$ is replaced by $1 \pm \sigma_Q/Q$, and $I_{org} \pm \sigma_{org}$ is replaced by $Q \pm 0$.

The programs are so arranged that when negative parameter values are obtained, they are automatically omitted and the least squares computations are rerun without them; however, the computations yielding the negative parameters are always printed out.

The time at the 704 is about 20 seconds for feeding in the program and data cards and carrying out the computations for a regular program, while the printing out may take from less than a minute to several minutes depending on the length of the problem (number of repetitive runs). The GEORGE program, which uses punched tape, is slightly slower than the 704 program.

INVESTIGATION OF AN EXTRACTABLE COMPLEX **

As an example of the use of the least squares procedure on equations 5a and 6a, the Th(IV)-acetylaceton-benzene-0.01 M NaClO₄ system (Rydberg²) was chosen (see Fig. 1).

Selection of errors. The procedure used in the experimental paper gives directly I_{org} and I_{aq} . The standard deviations σ_{org} and σ_{aq} are given for some of the measurements; the rest could be obtained from unpublished primary data. From these standard deviations, $\sigma_Q(I)$ can be calculated accord-

* The logarithmic error $\sigma_{\log K}$ of a constant $K \pm \sigma_K$ is equal to $\sigma_K/2.303K$ only for small values of σ_K/K ; e.g. for $\sigma_K/K = 0.067$, the error in the computed $\sigma_{\log K}$ is 3 %; cf. e. g. Ref.¹³

** See definition p. 2059, and eqns 5a and 6a.

Table 1. Input and output data of the IBM 704 and GEORGE programs.

IBM 704, program 495/CHM 104: Equation $x^N I_{\text{aq}}/I_{\text{org}} = \sum_0^N a_n x^n$.	
Input	Output
$I_{\text{aq}} \pm \sigma_{\text{aq}}$ $I_{\text{org}} \pm \sigma_{\text{org}}$ x (free ligand concentration, $10^0 > x > 10^{-10}$) N (≤ 8) L (number of experimental points) Θ_n (indicating a_n parameters to be omitted) c_1 and c_2 (integer values between 1 and 10 for $c_1 < c_2$)	x (given x , and $10^{-c_1} \geq x \geq 10^{-c_2}$) $I_{\text{aq}}/I_{\text{org}} = y$ $a_n \pm \sigma_{a_n}$ \bar{y} (y computed with given equation and a_n values above) $\sigma_{\bar{y}}$ χ^2/k
GEORGE, program S-3-128: Equation $z = \sum_0^P a_p x^p$	
Input	Output
z (or z' or z'' according to eqn. 18) ω_x (or corresponding ω_x' and ω_x'') x (free ligand concentration) P (≤ 10) Θ_n (parameters to be omitted) L (number of experimental points)	$\sum_0^{2P} \omega_i x_i^p = W$, and W^{-1} $\sum_0^P a_p x^p$ a_n and σ_{a_n} $S_{\text{min}} = \sum_0^P \omega_i (a_p x_i^p - z_i)^2$

ing to eqn. 9 (this is not necessary to do in practice when the program is run on the 704 computer; see Table 1).

A constant percentage error was also tested. From the spread of points with approximately identical x_i values (see Fig. 1), a standard deviation of ± 0.046 log units was estimated. This corresponds approximately to a 10 % error in Q . Thus according to eqn. 10, $\sigma_Q(\%) = 0.10Q$.

The $[A]$ values are calculated from rather accurately known data, except for the pH value; the pH error was assumed ² to be ± 0.02 . Because all error

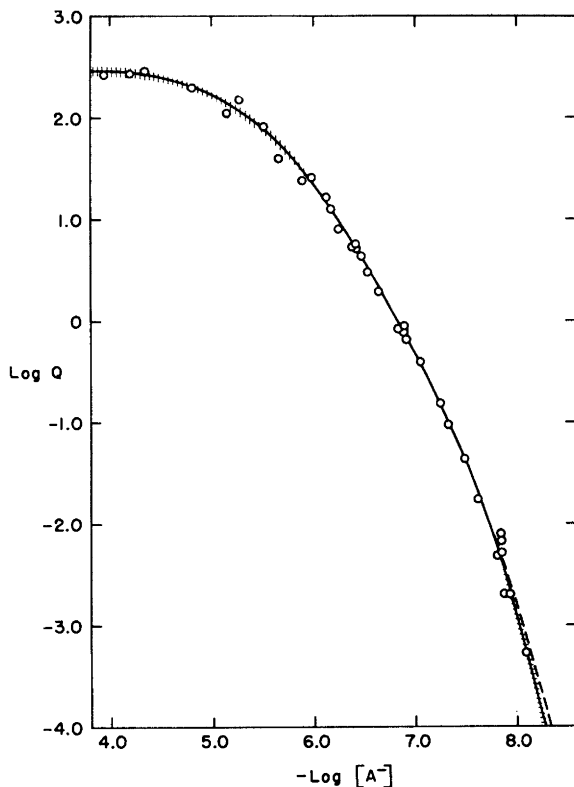


Fig. 1. The Th(IV)-acetylaceton-benzene-0.01 M NaClO₄ system. Log Q as a function of $-\log[A^-]$ computed with parameters obtained for a $\sigma_Q(I,A)$ error (solid line) and a $\sigma_Q(\%)$ error (broken line). The shaded area indicates the precision of the computed curve.

in $[A]$ can be attributed to this pH error, we can write $\sigma_{\log A} = \sigma_{pH} = 0.02$. Introducing this into eqn. 13 gives

$$\sigma_Q(A) \approx 0.5 Q (\nu - \bar{n}) \quad (14)$$

The value $\nu - \bar{n}$ is obtained from eqn. 11.

It shall be assumed that $\sigma_Q(A)$ occurs only in combination with the usually much larger $\sigma_Q(I)$. The combined standard deviation in Q is then

$$\sigma_Q(I,A) = \sqrt{(\sigma_Q(I))^2 + (\sigma_Q(A))^2} \quad (15)$$

These standard deviations will be used below to assign weights to the data.

Results of the χ^2 test. When the data were run on the IBM 704 computer, the a_1 values obtained were negative and had standard deviations around or in excess of 100%. Since negative parameters are of no significance as the equations are derived in this paper, a_1 had to be discarded. Only four para-

Table 2. Computation of χ^2/k for various kinds of errors and various weighing factors in the thorium acetylacetonate system; the left part contains σ_Q (I,A) errors and the right part σ_Q (%) errors.

σ_Q (I)	0.5	1.0	2.0	3.0	4.0	1 σ_Q (%) = est. 10 % error	
σ_Q (A)	χ^2/k	χ^2/k	χ^2/k	χ^2/k	χ^2/k	σ_Q (%)	χ^2/k
0	22.4	5.73	1.43	0.62	0.36	0.5	20.6
0.125	17.9	5.32	1.40	0.63	0.36	1.0	5.14
0.25	12.2	4.82	1.33	0.61	0.35	1.5	2.28
0.50	6.84	3.03	1.12	0.56	0.33	2.0	1.28
0.75	4.61	2.19	0.91	0.50	0.31	2.5	0.82
1.00	3.46	1.69	0.76	0.44	0.28	3.0	0.57

eters (a_0, a_2, a_3 and a_4) were therefore considered in the following. We shall thus assume that eqn. 6a with these four parameters is the correct mathematical model for our experimental data.

The χ^2/k values obtained in the various runs are given in Table 2. The table reveals that the σ_Q (I) value of 1 assumed on the basis of the number of radioactivity counts is too small (*i.e.* χ^2/k is too big, 5.73). The weight should rather correspond to 2 or 3 times σ_Q (I) (*i.e.* $\omega_i = 1/(2 \text{ or } 3 \text{ times } \sigma_Q(\text{I})^2$), somewhat depending on the correct size of σ_Q (A); a consistent combination is found for 2'' σ_Q (I)'' and 0.75'' σ_Q (A)'' . These values seem also reasonable from an examination of the original paper; while the pH error may be slightly overestimated, probably the I_{org} and I_{aq} values involve some other errors than the counting errors only; *cf.* Ref.¹

From Table 2 it is also seen that, if a constant percentage error was justified, it should have been 2.5'' σ_Q (%)'' rather than 1'' σ_Q (%)'' , where 1 σ_Q (%) corresponds to an estimated 10 % error in Q . This can be interpreted as an average 25 % error in the primary Q values, corresponding to ± 0.11 log units. A reinspection of the points in Fig. 1 does not make such a poor precision in Q improbable.

The equilibrium constants. The parameter values obtained for the various kinds of errors and with different weighing factors are given in Table 3. It is indicated in the table that the parameters and their precisions are unchanged if the errors (here σ_Q (I) and σ_Q (%)) are multiplied by a constant weighing factor. However, there is no constant factor relating the various σ_Q (I,A) errors to each other (see eqn. 15); therefore $a_n \pm \sigma_{a_n}$ varies with these errors, though within a rather limited range. The overlapping of the a_n values illustrates that this is an illconditioned system.

The parameters obtained for the 2'' σ_Q (I)''—0.75'' σ_Q (A)'' combination are given in Table 4, together with the equilibrium constants calculated from the relations

$$k_n = a_n/a_{n-1} \quad (16)$$

and

$$\lambda_n = 1/a_n \quad (17)$$

Table 3. Parameter values ($a_0 10^{29}$, $a_2 10^{13}$, $a_3 10^7$ and $a_4 10^2$) and χ^2/k (within parenthesis) obtained for the thorium-acetylacetonate system when various kinds of standard deviations are multiplied by a constant weighing factor. The upper group corresponds to a counting error only, and the lower group to a percentage error only (parameter values independent of weighing factor), while the twelve central groups represent mixed counting and ligand errors (eqn 15).

$\sigma_Q(I) \backslash \sigma_Q(A)$	0.5	1.0	2.0	4.0
0	0.510 ± 0.098 0.181 ± 0.006 0.252 ± 0.022 0.344 ± 0.060 (1.43 for $2'' \sigma_Q(I)''$)			
0.125	0.500 ± 0.095 0.181 ± 0.007 0.253 ± 0.022 0.346 ± 0.053 (17.9)	0.508 ± 0.096 0.181 ± 0.007 0.253 ± 0.022 0.345 ± 0.057 (5.32)	0.509 ± 0.097 0.181 ± 0.006 0.253 ± 0.022 0.344 ± 0.059 (1.40)	0.509 ± 0.098 0.181 ± 0.006 0.252 ± 0.022 0.344 ± 0.060 (0.36)
0.50	0.418 ± 0.092 0.183 ± 0.009 0.250 ± 0.024 0.347 ± 0.038 (6.84)	0.474 ± 0.093 0.181 ± 0.008 0.252 ± 0.023 0.347 ± 0.045 (3.03)	0.500 ± 0.095 0.181 ± 0.007 0.253 ± 0.022 0.346 ± 0.053 (1.12)	0.507 ± 0.097 0.181 ± 0.007 0.252 ± 0.022 0.345 ± 0.058 (0.33)
1.0	0.366 ± 0.093 0.187 ± 0.011 0.240 ± 0.025 0.342 ± 0.034 (3.46)	0.417 ± 0.092 0.183 ± 0.009 0.249 ± 0.024 0.347 ± 0.037 (1.69)	0.474 ± 0.092 0.181 ± 0.008 0.253 ± 0.023 0.347 ± 0.045 (0.76)	0.500 ± 0.095 0.181 ± 0.007 0.253 ± 0.022 0.346 ± 0.053 (0.28)
$\sigma_Q(\%)$	0.366 ± 0.070 0.189 ± 0.018 0.259 ± 0.045 0.330 ± 0.047 (1.28 for 20 % error)			

Table 4 also contains the primary constants β_n and ψ_n given in the original paper, where $\psi = \beta_{4-n}/\beta_4$.

The least squares method shows that the experimental data are not accurate enough to provide two separate equilibrium constants k_1 and k_2 , which dominate in the lowest Q region. Thus it is not possible from the experimental data to prove the existence of the first complex, MA^{3+} , while the results support the presence of all the other complexes (MA_2^{2+} , MA_3^+ and MA_4). The computations of separate k_1 and k_2 values in the original paper has been somewhat biased, because of the reasonable chemical assumption that all stepwise complexes should exist. The k_1 and k_2 values of the ligand number and limiting value methods are therefore given within parenthesis in Table 4.

Table 4. Parameters and equilibrium constants for the thorium acetylacetonate system.

Least square method		Ligand number method ¹		Limiting value method ²	
Primary parameters	Equilibrium constants	Primary parameters	Equilibrium constants	Primary parameters	Equilibrium constants
$a_0 10^{20} = 4.89 \pm 0.93$	$\log k_1 k_2 = 15.57 \pm 0.08$	$\beta_1 10^{-8} = 1.42$	$(\log k_1 = 8.15)$	$\psi_1 10^5 = 1.0 \pm 0.1$	$(\log k_1 = 7.82 \pm 0.16)$
$a_2 10^{14} = 1.81 \pm 0.07$	$\log k_3 = 6.15 \pm 0.04$	$\beta_2 10^{-15} = 3.80$	$(\log k_2 = 7.43)$	$\psi_2 10^{12} = 5.4 \pm 0.3$	$(\log k_2 = 7.73 \pm 0.09)$
$a_3 10^8 = 2.53 \pm 0.22$	$\log k_4 = 5.14 \pm 0.07$	$\beta_3 10^{-21} = 9.83$	$\log k_3 = 6.41$	$\psi_3 10^{19} = 1.0 \pm 0.2$	$\log k_3 = 6.27 \pm 0.05$
$a_4 10^3 = 3.41 \pm 0.45$	$\log \lambda_4^* = 2.48 \pm 0.06$	$\beta_4 10^{-28} = 8.70$	$\log k_4 = 4.95$	$\psi_4 10^{27} = 1.5 \pm 0.5$	$\log k_4 = 5.00 \pm 0.04$
		$\lambda_4 = 330 \pm 30$	$\log \lambda_4 = 2.52 \pm 0.04$	$\lambda_4 = 330 \pm 30$	$\log \lambda_4 = 2.52 \pm 0.04$

* The λ_4 value is corrected in the same manner as in ref.² because of the measuring technique.

From Table 4 it is seen that if only the numerical values of the constants are considered (e.g. comparing $\log k_1 k_2$ of the least squares method with the $\log k_1 + \log k_2$ given with the other methods), the values of the different methods agree well.

Fig. 1 shows the primary data and two curves passing through the points. The solid curve is computed with parameters obtained with the $\sigma_Q(I,A)$ error, and the dashed curve is computed with the parameters of the $\sigma_Q(\%)$ error (parameters found in Table 3). The shaded band indicates the standard deviations in the computed Q values due to the σ_{a_n} error. Approximately the same precision is obtained with the computations based on the $\sigma_Q(\%)$ error, as expected from the approximately identical σ_{a_n}/a_n values (see Table 3) for the two kinds of errors.

INVESTIGATION OF NON-EXTRACTABLE COMPLEXES *

The complex formation between Zr(IV) and F^- and HSO_4^- in 2 M H^+ are chosen as examples (Connick and McVey¹) of investigations of inorganic systems, i.e. where $\Sigma \beta_n [A]^n \ll 1$ in eqn. 4.

Development of suitable equations. In this case eqns 5b and 6b are valid, because complexes formed between Zr(IV) and ligands other than F^- and HSO_4^- in the aqueous phase are neglected¹. The organic phase (benzene) is supposed to contain only the organic ligand thenoyltrifluoroacetone (HTTA), and its extractable $Zr(TTA)_4$ complex. It can be found that at constant hydrogen ion concentration, $[TTA^-] = \text{const.}$ $[HTTA]_{\text{org.}}$. Eqn. 5b can be written

$$z' = \left(\frac{[HTTA]^4}{Q} \right)_{[H]} = \frac{1}{Q'} = \frac{1}{Q_0} \sum_{p=0}^P \beta_p [B]^p, \quad (18a)$$

where $[B] = [F^-]$ or $[HSO_4^-]$. Q' is sometimes called the normalized distribution ratio. Since $\beta_0 = 1$, it follows that at $[B] = 0$, $Q' = Q_0$, i.e. Q_0 is the normalized distribution ratio in the absence of any complexing inorganic ligand. Eqn. 18a can easily be rearranged to

$$z'' = \frac{Q_0 - Q'}{Q' [B]} = \beta_1 + \beta_2 [B] + \beta_3 [B]^2 + \dots \quad (18b)$$

which shall be used below in the F^- case.

Preparing the data for the computer; selection of errors. Eqns 18a and 18b can be solved by the least squares method using the GEORGE program. The parameters computed for z' will be $a_p = \beta_p / Q_0$, and for the z'' data $a_p = \beta_{p+1}$ for $0 \leq p \leq P$. In both cases it is assumed that only z contains errors. If the standard deviations corresponding to z' and z'' are called σ' and σ'' , it can readily be shown that

* See definition p. 2059, and eqns 5b and 6b.

$$\sigma' = P/Q' \quad (19a)$$

$$\sigma'' = \sqrt{2} \left(\frac{PQ'_0}{Q' x} \right) \quad (19b)$$

where P is the percentage error in Q' and Q'_0 (assumed to be identical). With these standard deviations the weights are computed according to eqn. 7 for known P values.

The standard deviations in Q can be estimated from the experimental data to be about 4.2 % (using the 5 points on the line in Fig. 1 and in Table 1 of Ref.¹). Thus we have $P = 0.042$.

Results on the Zr(IV)-HSO₄⁻-system. This system was tested according to eqns 18a and 19a. For $P > 3$, the higher parameters turned out negative or with standard errors over 100 %; thus it could be established that only three complexes between Zr(IV) and HSO₄⁻ had to be considered.

Using the primary data and the equations to compute Q' from them (eqn. 17 in Ref.¹)* four positive parameters were obtained, from which the three constants β_1 , β_2 and β_3 were calculated. With the 4.2 % standard deviation, χ^2/k is 1.00, demonstrating consistency with the estimates from the primary data.

The equilibrium constants k_1 , k_2 and k_3 are given in Table 5, together with Connick and McVey's original results. The agreement is found to be quite good.

Results on the Zr(IV)-F⁻-system. This system was investigated using eqns 18b and 19b. (The Q'_0 value was taken from Table III in Ref.¹) With the data run on GEORGE, three positive parameters β_1 , β_2 and β_3 were obtain-

* There seems to be some inconsistency between the primary data and E'_0 in Table III of Ref.¹

Table 5. Equilibrium constants and their precision for the Zr(IV)-HSO₄⁻ and -F⁻ complexes investigated by extraction of the Zr(TTA)₄ complex into benzene¹. Constant ionic media: 2 M HClO₄ at 25°C.

Ligand	Equilibrium constants			Reference
	k_1	k_2	k_3	
HSO ₄ ⁻	460	53 ± 4 *	1 ± 1 * -0.5	Connick and McVey
»	431 ± 30 ***	54 ± 7 ***	0.83 ± 0.43 ***	This work
F ⁻	(6.3 ± 0.6) 10 ⁵ **	(2.1 ± 0.2) 10 ⁴ ***	(6.7 ± 2.0) 10 ² **	Connick and McVey
»	(6.30 ± 0.52) 10 ⁵	(1.94 ± 0.22) 10 ⁴	(7.5 ± 1.1) 10 ²	This work

* Standard deviation in k_2 is estimated¹ to 8 %, and in k_3 to plus or minus a factor of 2

** Standard deviations in k_1 and k_2 is estimated to 10 %, and in k_3 to 30 %.¹

*** Computed with E_c^0 from E_c , γ and (HK)_b according to eqn. 17 in Ref.¹

ed. In order to obtain $\chi^2/k = 1.00$, the standard deviation in Q' and Q'_0 has to be 6.3 %. Thus, in this case, the original estimate of 4.2 % was somewhat too small.

The equilibrium constants are given in Table 5; they are seen to agree well with those given in the original paper. Particularly impressive is the good graphical estimates of standard deviations in the equilibrium constants made by the original authors.

Using the equilibrium constants computed with the least squares methods, Q' can be calculated as a function of the free ligand concentration, and the curves thus obtained may be compared with the corresponding curves in the original paper. The curves for both the F^- and HSO_4^- systems were found to coincide over the investigated range with the curves given in the original paper.

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REFERENCES

1. Connick, R. E. and McVey, W. H. *J. Am. Chem. Soc.* **71** (1949) 3182.
2. Rydberg, J. *Acta Chem. Scand.* **4** (1950) 1503.
3. Rydberg, J. *Arkiv Kemi* **8** (1955) 101, 113; *Rec. trav. chim.* **75** (1955) 207.
4. Dyrssen, D. and Sillén, L. G. *Acta Chem. Scand.* **7** (1953) 663.
5. Irving, H., Rossotti, F. J. C. and Williams, R. J. P. *J. Chem. Soc.* **1955** 1906.
6. Sullivan, J. C., Rydberg, J. and Miller, W. *Acta Chem. Scand.* **13** (1959) 2023.
7. Glueckauf, E., McKay, H. A. C. and Mathieson, A. R. *Trans. Faraday Soc.* **47** (1951) 437.
8. McKay, H. A. C. *Trans. Faraday Soc.* **48** (1952) 1103.
9. Morrison, G. H. and Freiser, H. *Solvent Extraction in Analytical Chemistry*, J. Wiley and Sons, New York 1957.
10. Sullivan, J. C. and Hindman, J. C. *J. Am. Chem. Soc.* **76** (1954) 5931.
11. Friedlander, G. and Kennedy, T. W. *Nuclear and Radiochemistry*, J. Wiley and Sons, New York 1955.
12. Rydberg, J. *Acta Chem. Scand.* **14** (1960). *In print.*
13. Deming, W. E. *Statistical Adjustment of Data*, J. Wiley and Sons, New York 1948.
14. Fisher, R. A. *Statistical Methods for Research Workers*, Oliver & Boyd, Edinburg 1954 (12th Edition).

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