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SOME SUGGESTED CALCULATION PROCEDURES AND THE VARIATION IN RESULTS OBTAINED FROM DIFFERENT CALCULATION METHODS FOR EVALUATION OF CONCENTRATION STABILITY CONSTANTS OF METAL ION COMPLEXES IN AQUEOUS SOLUTION

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CONTENTS

A INTRODUCTION

Detailed examination of values obtained for concentration stability constants of metal ion complexes existing in aqueous solution[1] show that, for many systems, the reported values measured by various workers differ markedly in magnitude. Frequently, the nature and the number of complexes reported in solution are also very different.

The usual explanation invoked to explain these discrepancies is to attribute them to the different methods, experimental conditions, techniques etc. employed in the various studies. However, one variable not usually considered to explain the discrepancies occurring in the literature is the different methods of calculation employed in the various studies.

Recently, in a series of papers Momoki et al.[2–4] have examined statistical calculations on the cadmium–thiocyanate system in considerable detail It was shown conclusively in this work that straightforward application of standard and routinely used calculation methods are not likely to give the mathematically best solutions to data The authors emphasised that complex-formation constants should be treated more carefully, both experimentally and statistically.

In the particular case of the cadmium–thiocyanate system, Momoki et al. showed that their statistical treatment of the data gave results which were not the same as those obtained by other methods of calculation This is an extremely important observation as it shows that the reported literature results for many systems could be distinct functions of the calculation method used to interpret the experimental data.

In most studies on complex ions only one routine calculation method is generally applied to any particular set of data The data obtained are measured at constant ionic strength. Nitrate or perchlorate salts are usually added to maintain the ionic strength at a fixed value and it is assumed that activity coefficients are constant for all measurements and that the electrolyte used to maintain constant ionic strength is non-complexing. As the concentration of the electrolyte used to maintain constant ionic strength is usually varied from near zero to extremely high concentrations, the activity coefficients cannot be expected to be strictly constant, nor can the complexing of nitrate or perchlorate be negligible for all data points[4,5]. Because of these inherent errors not accounted for in the commonly used methods of calculation, even if experimental data with virtually no error could ever be obtained, extremely good mathematical fits to stability constant data cannot generally be expected Consequently, the possibility arises that any particular result in the literature could be highly dependent on the calculation used. Certainly the application of only one routine method of calculation could not be anticipated to give the 'best' solution to the data except in exceptional circumstances.

In comparing literature results with their own studies on the same complexes, no attempt has been made in the past by authors to show that the solutions of all data are mathematically equal. The work of Momoki et al on the cadmium–thiocyanate system has highlighted the possibility that detailed analysis of the methods of calculation used in all studies on any particular system must play an important role in clearing up certain controversial systems and in improving the understanding of the chemistry of systems in general.

This article has been written to draw attention to this feature in an endeavour to stimulate workers in the field to consider the possibility that some apparent discrepancies in the literature on concentration stability constants could be resolved by showing that calculation methods have not given mathematically equivalent solutions

In most of the early work on complex-ion systems, manual calculation procedures, usually graphical in nature, were chosen. Recently it has been fashionable to use high-speed electronic computers and to use numerical or statistical calculation procedures, (see references 6–10 for instance), for many types of calculations on complex ions

An unfortunate tendency, in the author's view, with this current trend towards high-speed and sophisticated computational techniques, is that some chemists are using the available computer programs indiscriminantly and without understanding the real precision, accuracy or chemical significance of the results obtained. This is providing even further confusion in the literature as with the widespread availability of so many methods the possibility of 'bad' solutions being reported is ever increasing as is the difficulty of detecting that they are 'bad' solutions

Any results from any calculation procedure should be verified very carefully to see that they are both good solutions mathematically and are chemically sensible Any approximations used in the calculation should be noted carefully and it should be ascertained that the nature and means by which the experimental data were obtained do not create conditions which invalidate the calculation procedure.

A second reason for writing this review, therefore is to encourage the use of systematic approaches to calculation of stability-constant data which eliminates the possibility of 'bad' solutions being reported in the literature inadvertently or unknowingly by a worker who does not suspect his calculation method is inadequate for the system being measured.

In this work, calculations for solution of the power series function of the type

$$F_0(X) = \sum_{n=0}^{n} \beta_n C_L{}^n$$

are considered $F_0(X)$ represents an experimentally determined quantity, which is usually a function of several variables associated with the particular technique used to measure the system and β_n is the concentration stability constant of the n^{th} complex, $ML_n{}^{(x-n)+}$, which is formed when ligand, L^-, is attached to metal ion, M^{x+}

The function $F_0(X)$ or a similar function occurs in studies of complex-ion systems by potentiometric, polarographic, ion exchange, solubility, ion-selective electrode, spectrophometric and other analytical methods.

Various approaches to solving the equation are given and means of checking that the solution obtained is a good one are suggested. Two examples are chosen from the literature to show the extent of the discrepancies that can occur from use of different methods This part of the work is reported in part C of the paper

Before consideration of the calculation of $F_0(X)$, a short account is presented in section B dealing with the calculation of percentage distribution curves of the various species present in solution This type of calculation is included with this work because the type and nature of the distribution curves are used in Section C as a means of indicating whether the calculation method used to obtain the β_n values are satisfactory

B CALCULATION OF DISTRIBUTION CURVES OF SPECIES PRESENT IN SOLUTION

A distribution curve is a graphical plot of the percentage of each complex ion present in solution versus the concentration of uncomplexed ligand (see Ref. 6, for instance). Given the consecutive β_n values for each complex, then the distribution curves are simply calculated from the relationships

$$\beta_n = \frac{[ML_n{}^{(x-n)+}]}{[M^{x+}]\,[L^-]}$$

The percentage of $ML_n^{(x-n)+}$ at a particular concentration of L^-, say a, is given by

$$\% \, ML^{(x-n)+} = \frac{[ML_n^{(x-n)+}]}{[M^{x+}] + [ML^{(x-1)+}] + \ldots + [ML_n^{(n-x)+}]} \times 100$$

$$= \frac{\beta_n a^n}{1 + \beta_1 a + \ldots + \beta_n a^n} \times 100$$

These percentages can be calculated from β_n values by an arithmetic procedure. However, if a large number of species is present, the arithmetic becomes somewhat tedious and lengthy, especially when a large concentration range of L^- needs to be considered.

Such a calculation is ideally suited to computation by highspeed electronic computers. In this department, a program has been developed which can calculate the percentage of any number of complexes over any ligand concentration range[11]. The readout is designed to list numerically the percentage of each species at intervals of 0.1 logarithmic units of ligand concentration and graphically plot the distribution curves.

The program uses a function of the type $1 + K_1 a(1 + K_2 a(1 + K_3 a(\ldots)))$ which is well-suited to rapid computational analysis.

In this expression, K_n is the stepwise stability constant and thus is equal to β_n/β_{n-1}.

The readout for the $BiCl_n^{(3-n)+}$ system[12] for which there are six complexes with $\log \beta_n$ values of 2.2, 3.5, 5.8, 6.75, 7.3 and 7.36, respectively at 25°C and an ionic strength of 3.0 ($\log K_n$ values = 2.2, 1.3, 3.3, 1.95, 0.5, 0.06) are shown in Fig. 1. Several other results are also available for this system[1], but the values given in Ref. 12 were chosen purely for the purposes of providing an example.

The above type of problem represents a classical use of the computer as a time and labour-saving device. An exact answer is obtained and no difficulties arise. The solution of β_n values from $F_0(X)$ functions presents a much more difficult problem.

C CALCULATION OF β_n VALUES FROM THE $F_0(X)$ FUNCTION

(i) General considerations

The function $F_0(X)$ in its most general form can be written as

$$F_0(X) = \beta_0 + \beta_1 X + \beta_2 X^2 + \ldots \, \beta_n X^n$$

For instance, in the polarographic method for determination of stability constants[13], the equation to be solved is

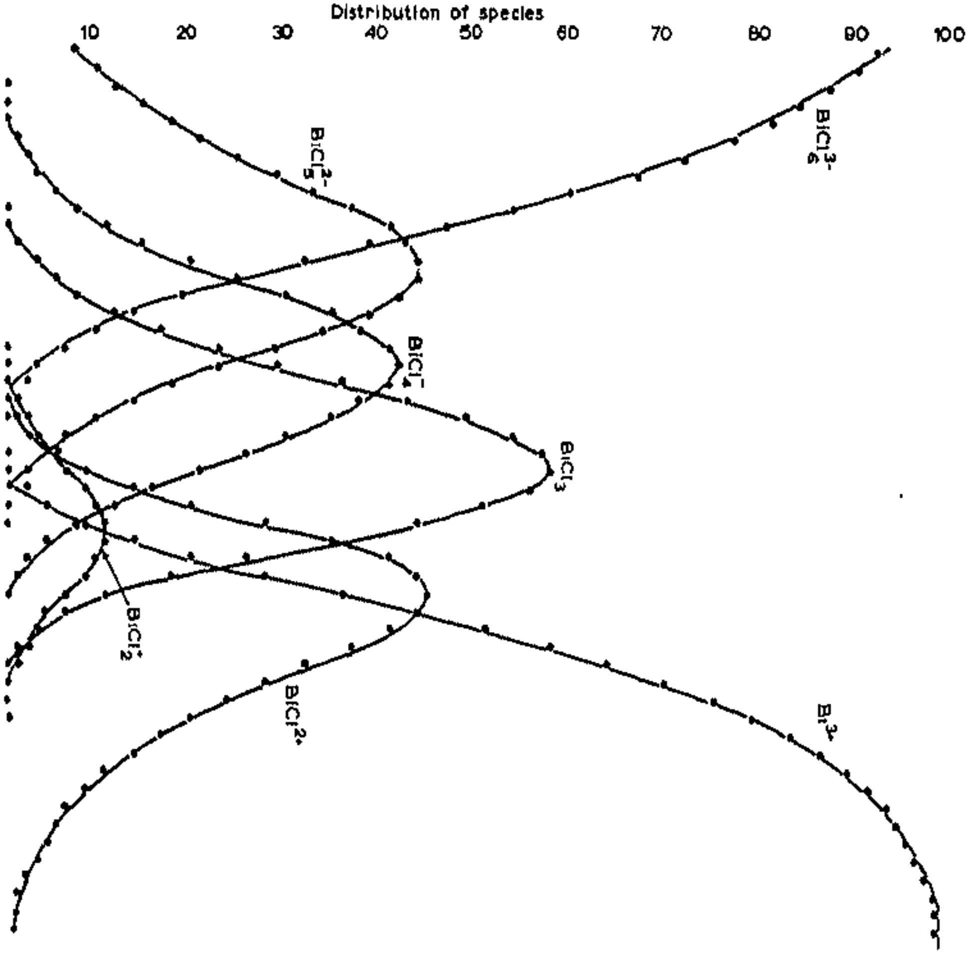
$$F_0(X) = \text{antilog} \, \{0.4343 \, (nF/RT) [(E_{1/2})_f - (E_{1/2})_c] + \log I_f/I_c\}$$

$$= 1 + \beta_1 C_L + \beta_2 C_L^2 + \ldots \, \beta_n C_L^n,$$

where the subscripts f and c refer to the free ion and complexed ion respectively. Other symbols are those used conventionally. This equation and others have been modified some-

Ranges of existence of complexes shown as a function of free ligand concentration expressed as exponents i.e. pL = −log [L]
Bismuth(III), chloride system

Successive log *K* values = 2.20 1.30 2.30 0.95 0.55 0.06



```
          MOLE PERCENTAGES
 M  ML1 ML2 ML3 ML4 ML5 ML6   pL
 0   0   0   0   0   8  92-1.0
 0   0   0   0   0  10  90-0.9
 0   0   0   0   1  12  87-0.8
 0   0   0   0   1  15  84-0.7
 0   0   0   0   1  18  81-0.6
 0   0   0   0   2  21  77-0.5
 0   0   0   0   3  25  72-0.4
 0   0   0   0   4  29  67-0.3
 0   0   0   0   6  33  60-0.2
 0   0   0   1   8  37  54-0.1
 0   0   0   1  11  41  47-0.0
 0   0   0   2  15  43  39 0.1
 0   0   0   4  20  44  32 0.2
 0   0   0   6  25  44  25 0.3
 0   0   0   8  30  42  19 0.4
 0   0   0  12  35  39  14 0.5
 0   0   0  17  38  34  10 0.6
 0   0   1  23  41  29   7 0.7
 0   0   1  29  42  23   4 0.8
 0   1   1  36  41  18   3 0.9
 0   1   2  43  38  14   2 1.0
 0   2   3  49  35  10   1 1.1
 0   3   4  54  30   7   0 1.2
 1   6   6  57  26   5   0 1.3
 1   9   7  58  21   3   0 1.4
 3  14   9  56  16   2   0 1.5
 5  20  10  51  12   1   0 1.6
 9  28  11  44   8   1   0 1.7
14  35  11  39   5   0   0 1.8
20  41  10  26   3   0   0 1.9
28  44   9  18   2   0   0 2.0
36  45   7  11   1   0   0 2.1
44  44   5   7   0   0   0 2.2
51  41   4   4   0   0   0 2.3
58  37   3   2   0   0   0 2.4
64  32   2   1   0   0   0 2.5
70  28   1   1   0   0   0 2.6
75  24   1   0   0   0   0 2.7
79  20   1   0   0   0   0 2.8
83  17   0   0   0   0   0 2.9
86  14   0   0   0   0   0 3.0
89  11   0   0   0   0   0 3.1
91   9   0   0   0   0   0 3.2
93   7   0   0   0   0   0 3.3
94   6   0   0   0   0   0 3.4
95   5   0   0   0   0   0 3.5
96   4   0   0   0   0   0 3.6
97   3   0   0   0   0   0 3.7
98   2   0   0   0   0   0 3.8
98   2   0   0   0   0   0 3.9
98   2   0   0   0   0   0 4.0
```

Fig. 1. Readout of computational analysis for the percentage distribution of various species present in the bismuth (III)–chloride system.

what to allow for mixed ligand complex formation[14] and inclusion of other equilibria[15]. In these modifications, the power series in X is more complicated, but still retains the same general form of the above equation.

Only slight variation to the above is an equation of the type

$$F_0(X) = A + B\beta_1 X + C\beta_2 X^2 + \ldots + Z\beta_n X^n;$$

where $A, B, C \ldots Z$, are constants. For instance, in a potentiometric method with an ion-selective electrode[12] the equation

$$F_0(X) = \beta_1 C_L + 2\beta_2 C_L{}^2 + \ldots + n\beta_n C_L{}^n$$

needs to be solved.

In this work, major consideration will be given to the $F_0(X) = \sum_n \beta_n C_L{}^n$ power series, however, related functions can be solved using the same procedure

To calculate β_n values, certain features and difficulties should be kept in mind

(*a*) It is useful to assess the error of $F_0(X)$ functions This is not particularly easy Often the magnitude of the error changes with C_L This can be seen to be so with the polarographic method described previously In this case $F_0(X)$ is calculated in the main from a parameter $(E_{1/2})_f - (E_{1/2})_c{}'$ or $\Delta E_{1/2}$ Individual $E_{1/2}$ values would be measured with the same precision, thus the relative error in $\Delta E_{1/2}$, $\delta(\Delta E_{1/2})/\Delta E_{1/2}$ must decrease as $\Delta E_{1/2}$ increases, i e as C_L increases, because $\delta(\Delta E_{1/2})$ is a constant. This feature should theoretically be included in calculations.

(*b*) Data collected are obtained at constant ionic strength and it is assumed that the activity coefficients, which are incorporated into the β_n values, remain constant for all values of C_L. If studies are made over wide concentration ranges of C_L, the validity of the approximation is questionable and may need to be considered in deciding if the calculated values are satisfactory

(*c*) In the main, $F_0(X)$ functions are analysed from less than twenty data points Statistically, the calculation method of up to six β_n values from this number of data points is not particularly accurate, and inherent errors in the calculation method as well as those from other sources must be reasonably large, even if the experimental data themselves are highly reproducible

(ii) Graphical methods

The simplest and probably least complicated methods for calculation of β_n values are graphical in nature. Two approaches are given below. The first is exceedingly simple, and could well be used initially on any set of data to gain an impression of the chemistry of the metal-complex system. The second method, first used by Leden[17], is quite reliable and can be used for most systems.

Consider the function

$$F_0(X) = \beta_0 + \beta_1 C_L + \beta_2 C_L{}^2 + \ldots \beta_n C_L{}^n$$

Examination of distribution curves of species present in solution shows that frequently over a certain range of C_L, virtually only one species is present and other complexes can be neglected. For these C_L values $F_0(X)$, as above, can be described to a good approximation by the expression

$$F_0(X) = \beta_n C_L{}^n$$

Taking the logarithm of both sides gives

$$\log F_0(X) = \log \beta_n + n \log C_L$$

Thus a graphical plot of $\log F_0(X)$ versus $\log C_L$ should give a straight line of slope n and intercept $\log \beta_n$. The plot therefore enables the calculation of the complex present, n, and its stability constant β_n.

Furthermore, if the β_n values for the consecutive stability constants of a particular system are quite different, then the log plot of $F_0(X)$ will consist of a series of straight lines, one straight line for each complex (see Fig. 2) and all the β_n values can be calculated from the appropriate straight lines. If a curved log plot is obtained, then more than one complex must be present for the particular C_L values used (see Fig. 2), and the method cannot be used to evaluate β_n.

An example of this calculation method is given for the indium(III)–chloride system[18], in Table 1 and Fig. 3. Three straight line sections are clearly seen The slopes of 1, 2 and 3 respectively correspond to the complexes $InCl^{2+}$, $InCl_2{}^+$ and $InCl_3$.

The graphical method of Leden[17] is considerably more sophisticated than the previous simple method and allows consecutive formation constants to be calculated even when β_n values are similar in magnitude

The approach is as follows. Rearrangement of the $F_0(X)$ functions gives $F_1(X)$ where

$$F_1(X) = (F_0(X) - \beta_0)/C_L = \beta_1 + \beta_2 C_L + \ldots + \beta_n C_L{}^{n-1}$$

A graphical plot of $F_0(X)$ versus C_L has an intercept at $C_L = 0$, of β_0 which is unity A graphical plot of $F_1(X)$ versus C_L, extrapolated to $C_L = 0$, will have an intercept of β_1 and this provides the basis for the calculation of β_n values A plot of

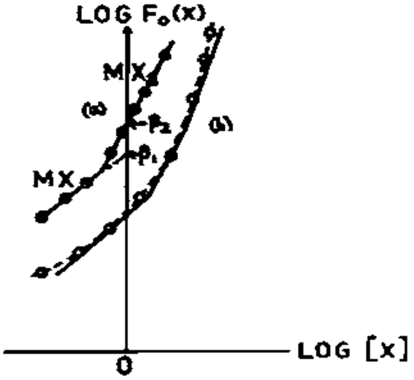


Fig. 2 Simple graphical method Plot of $\log F_0(X)$ versus log of ligand concentration, $\log [X]$ (a) Ideal case, two complexes MX and MX_2 with very different β_n values. Slopes of straight line sections are 1.0 and 2 0 respectively, (b) Curved plot (broken line), β_n values cannot be calculated because β_n values are similar. Tangents (solid lines) can be used to estimate complexes present.

TABLE 1

Data of Bond and Waugh[18] for the indium (III)–chloride system

$[Cl^-](M)$	$\log [Cl^-]$	$F_0(X)$	$\log F_0(X)$
0 004	− 2 398	$1\ 766 \times 10$	1 247
0 008	− 2 097	$4\ 581 \times 10$	1 661
0 020	− 1 699	$1\ 640 \times 10^2$	2 215
0 040	− 1 398	$4\ 065 \times 10^2$	2 609
0 080	− 1 097	$1\ 959 \times 10^3$	3 292
0 160	− 0 796	$8\ 912 \times 10^3$	3 950
0 280	− 0 553	$2\ 748 \times 10^4$	4 439
0 400	− 0 398	$9\ 727 \times 10^4$	4 988
0 600	− 0 222	$4\ 093 \times 10^5$	5 612
1 200	0 079	$2\ 691 \times 10^6$	6.430
2 000	0 301	$1\ 380 \times 10^7$	7 140

$F_2(X) = (F_1(X) - \beta_1)/C_L$ versus C_L, gives the intercept β_2. Finally a plot of $F_n(X) = (F_{n-1}(X) - \beta_{n-1})/C_L$ versus C_L allows calculation of β_n.

As a consequence of the nature of the $F_n(X)$ functions graphical plots of $F_0(X)$ to $F_{n-2}(X)$ will be curved. The plot of $F_{n-1}(X)$ must be a straight line of slope β_n and intercept β_{n-1}. A straight line parallel to the C_L axis should be observed for the $F_n(X)$ plot. The constant value of $F_n(X)$ is equal to β_n These considerations allow for the determination of the number of complexes present.

The graphical methods of Leden can be used conveniently to comply with the chemistry of the system. Extrapolation for β_1 can be weighted judiciously towards $F_1(X)$ values obtained at low C_L values, and β_n can be calculated by weighting the results from high C_L values. Such a weighted procedure means β_n values are calculated from concentrations of C_L where the complex $ML_n^{(x-n)+}$ is present in significant concentrations

Many other graphical methods are available and Ref 6 can be consulted for a summary of these

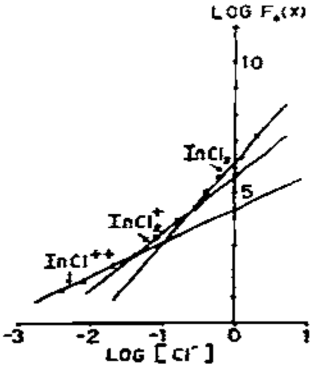


Fig 3 Simple graphical method as applied to the indium (III)–chloride system

(iii) Statistical methods

Many papers have appeared in the literature in the last twenty years dealing with new and modified methods of calculating stability constants of complexes (e g Refs 2–4, 6–10, 19–29). These are virtually all statistical in nature and are based on the 'least-square' theory. Most of these methods are ideally suited for computational analysis and this has been achieved in many cases

Most statistical methods have certain limitations and restrictions for their use and it is a lack of knowledge of these which has sometimes led to their misuse in the past For example, many of the methods assume all data to be of equal reliability, whereas frequently this is not the case, as mentioned previously.

The most important commonly occuring restriction which can easily be overlooked if the treatment if not rigorous is that most statistical methods are only valid when all complexes are present in significant concentrations over the range of C_L for which $F_0(X)$ data are calculated. For instance, if β_4 is extremely high, and the complex $ML_4^{(x-4)+}$ is present at the (95–100)% level for all C_L values measured, the function $F_0(X)$ could adequately be represented by the expression $F_0(X) = \beta_4 C_L^4$. A statistical least-squares fit as $F_0(X) = \beta_0 + \beta_1 C_L + \beta_2 C_L^2 + \beta_3 C_L^3 + \beta_4 C_L^4$ could be achieved; however the values of β_0 to β_3 in this case would have no real chemical significance as these complexes are making no real contribution to the $F_0(X)$ function Similarly one particular complex may only be present in significant concentrations over half the C_L range, however its β_n value is statistically calculated from all C_L values and data are not weighted in accordance with this fact.

Another source of potential error, in someways related to the above, which can occur in statistical analysis of data is the report of β_n values when $\beta_n < \beta_{n-1}$ Over a wide range of C_L, systematic errors in data such as non-constancy of activity coefficients at constant ionic strength or other experimental factors could cause a systematic error in the $F_0(X)$ function. This systematic form of error can exhibit itself in the mathematical analysis as a weak last complex for example. This error arises most readily from the approach of simply fitting least-squares to data, obtaining a mathematically very correct solution, but without considering the chemistry of the system

As there are so many statictical least-square methods it is not possible to consider them all in detail in this paper. The approach used to show the variations which can occur with different calculation methods is to take two representative systems from the literature and apply several graphical, statistical and computational calculation methods to each

The first system is for lead (II)–chloride These data[24] represent an ideal case for analysis and all calculation methods are in reasonable agreement as to the number and stability of the complexes

The second system, for tin (II)–fluoride, is much more difficult to calculate and widely different results can be obtained This system is used to illustrate difficulties which can occur in calculation and to show how apparent discrepancies in the literature could have arisen solely from the use of different calculation methods.

TABLE 2

Analysis of data of Kivalo and Rastas[24] for lead (II)–chloride complexes by Leden's and logarithmic graphical methods

$[Cl^-]$ (M)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	log $[Cl^-]$	log $F_0(X)$	log $[F_0(X)-1]$
0.0	1.00						
0.2	4.84	19.2	26.0	35.0	−0.699	0.685	0.584
0.4	11.44	26.1	30.0	27.5	−0.398	1.058	1.019
0.6	21.76	34.6	34.3	25.6	−0.222	1.338	1.317
0.8	40.36	49.2	44.0	31.3	−0.097	1.606	1.595
1.0	62.00	61.0	47.0	28.0	0.000	1.792	1.785
1.2	90.52	74.6	50.1	25.8	0.079	1.957	1.952
1.4	135.8	96.3	58.8	28.4	0.146	2.133	2.130
1.6	186.8	116.1	63.8	28.0	0.204	2.271	2.269
1.8	250.7	138.7	69.3	27.9	0.255	2.399	2.398

Values of $F_0(X)$ were calculated from their $F(t)$ functions, where $F(t)$ is $F_1(X)$ expressed in terms of the notation of this work.

(iv) The lead(II)–chloride system

Kivalo and Rastas[24] have measured the lead(II)–chloride complex ion system polarographically. The data obtained are given in Table 2, and the equation to be solved is

$$F_0(X) = 1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2 + \ldots + \beta_n [Cl^-]^n$$

(a) Graphical

Table 2 and Fig. 4 show the data and plot of log $F_0(X)$ versus log$[Cl^-]$ which is suggested as a useful starting point in any calculation method. The plot is curved, indicating two or more complexes are present in significant concentration over the range of

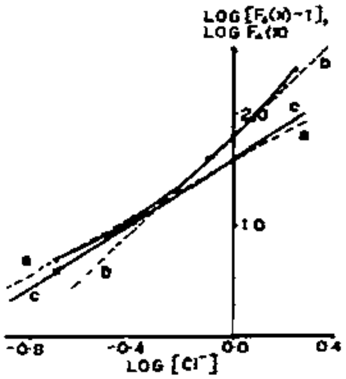


Fig 4. Analysis of the lead (II)–chloride system by the simple graphical method. (a) Slope of low chloride concentrations (broken line) = 1.3; (b) slope of medium chloride concentrations (broken line) = 2.0, (c) slope of low chloride concentrations for log $[F_0(X) - 1]$ plot. 0, refer to log $F_0(X)$ values, X, refer to log $[F_0(X) - 1]$ values.

chloride (0 2 — 1 8 *M*) for which data was obtained The limiting slope at low concentrations (Fig. 4) is 1.3 — 1.4, indicating $PbCl^+$ and $PbCl_2$ to be present at low chloride concentration At medium chloride concentrations the data fit a straight line of slope 2.0, with departure to higher slopes at the highest chloride concentrations The conclusion to be reached from this plot is that $PbCl_2$ is the major complex present, with $PbCl^+$ and $PbCl_3{}^-$ being present in significant amounts. In view of the curved plot, the β values must be similar in magnitude.

Examination of the function to be solved shows that it can be rearranged in the form

$$F_0(X) - 1 = \beta_1 [Cl^-] + \beta_2 [Cl^-]^2 + \quad \beta_n [Cl^-]^n$$

and a plot of log $[F_0(X) - 1]$ versus log $[Cl^-]$ would in general be preferable to that of log $F_0(X)$ for this function because unless β_1 is large, then $1 > \sum_{n=1}^{n} \beta_n [Cl^-]^n$ at low chloride. The value of log $[F_0(X) - 1]$, however is similar to that for log $F_0(X)$ as seen from Table 2 and shown in Fig 4, except for the lowest chloride levels, as would be expected.

Table 2 and Fig. 5 show the Leden type of calculation method. The curved $F_0(X)$ and $F_1(X)$ plots, the linear $F_2(X)$ plot and the constant $F_3(X)$ value are consistent with three complexes being present, $PbCl^+$, $PbCl_2$ and $PbCl_3{}^-$ The intercepts of these plots give values of β_1 ($PbCl^+$) = 14 ± 1, β_2 ($PbCl_2$) = 19 ± 2, and β_3 ($PbCl_3{}^-$) = 28 ± 2

These data provide an exceptionally good fit to the theoretically predicted shape of the curves and results would appear to be quite reliable. Table 3 shows a comparison of calculated and experimental $F_0(X)$ values using the above β values. This type of comparison is suggested as a simple check which can be applied to test the reliability of data.

One major problem with the graphical method is the rather arbitrary estimation of error. The errors in the above β values were calculated as the limits to which reasonable extrapolations could be achieved in this author's opinion, and so they must contain some personal bias. The extrapolation procedure to evaluate β_n similarly contains personal bias. In the above example, because of the exceptionally good fit of the data, these

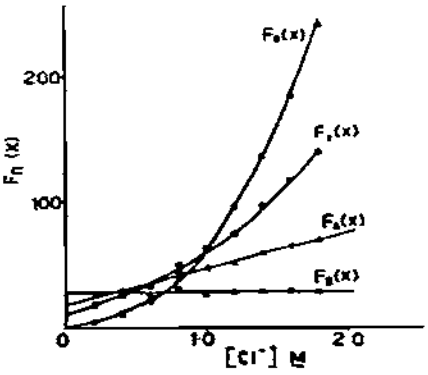


Fig. 5. Analysis of the $F_n(X)$ functions by the graphical method of Leden for the lead(II)–chloride system. ●, $F_0(X)$; ○, $F_1(X)$; X, $F_2(X)$, ■, $F_3(X)$

TABLE 3

Comparison of experimental and calculated $F_0(X)$ functions for the lead(II)–chloride system with β_n values obtained graphically by Leden's method.

$F_0(X)$	
Experimental	Calculated
4.84	4.78
11.44	11.43
21.76	22.29
40.36	38.70
62.00	62.00
90.52	93.54
135.8	134.7
186.8	186.7
250.7	251.1

problems of personal bias are not large although for many systems they can be. Kivalo and Rastas[24], with a few additional experimental points and using the graphical extrapolation procedure obtained $\beta_1 = 15.2$, $\beta_2 = 14.0$ and $\beta_3 = 30.6$ which demonstrates the magnitude of the variation of results which can be obtained by different workers even when using the same calculation procedure.

(b) Statistical analysis

In view of the mathematically good fit of the data to the graphical treatment over the whole range of ligand concentration, the system would appear to be ideal for a least-square analysis, using the assumption that all data are of equal reliability and without judicious weighting of data. The distribution curve (Fig. 6) indicates that all species are present in significant concentrations over the ligand range studied. This is a useful criterion for the successful application of a straightforward least-square or statistical analysis

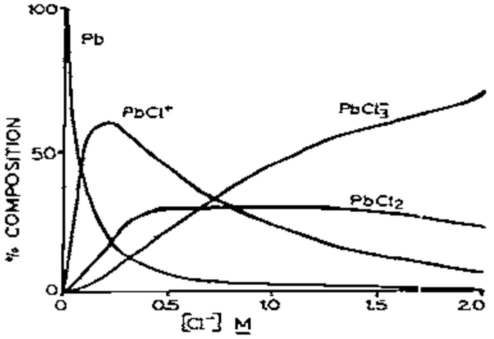


Fig 6. Percentage distribution of various species present in the lead(II)–chloride system.

TABLE 4

Comparison of calculated and experimental values of $F_0(X)$ for the lead(II)–chloride system as contained in readout of Marquardt's[30] computational analysis of the system

	$F_0(X)$		
$[Cl^-]$	Experimental	Calculated	Difference
0.2	4.84	4.94	−0.10
0.4	11.44	11.60	−0.16
0.6	21.76	22.37	−0.61
0.8	40.36	38.64	1.72
1.0	62.00	61.79	0.21
1.2	90.52	93.21	−2.69
1.4	135.8	134.30	1.50
1.6	186.8	186.44	0.36
1.8	250.7	251.02	−0.32

Use of the least-square method of Kivalo and Rastas[24] and either of the methods of Kamalkar[25] gives values of $\beta_1 = 14.4 \pm 1.8$, $\beta_2 = 18.2 \pm 4.1$ and $\beta_3 = 28.3 \pm 2.0$, for these data.

(c) Computational analysis

Marquardt[30] has developed a calculation procedure for fitting data to polynomial functions such as those considered in this work, which has been designed for computational analysis. The data of Kivalo and Rastas were used with this calculation method using an IBM 7044 computer. Values of $\beta_1 = 15.2$, $\beta_2 = 16.6$ and $\beta_3 = 28.9$ were obtained. The readout of this method also gives a comparison of calculated and experimental values as reproduced in Table 4. This table provides a useful check on the reliability of the cal-

TABLE 5

Comparison of β_n values obtained for the lead(II)–chloride system by different methods of calculation

Method	β_1	β_2	β_3
Leden's graphical method[17]	14	19	28
Kivalo and Rastas (graphical)[24]	15.2	14.0	30.6
Statistical, least squares[24,25]	14.4	18.2	28.3
Computational analysis[30]	15.2	16.6	28.9

TABLE 6

Comparison of calculated and experimental $F_0\,(X)$ values by different calculation procedure with the lead(II)–chloride system

Method	$\left\|\sum\left(\frac{F_0\,(X)_{\mathrm{expt}} - F_0\,(X)_{\mathrm{calc}}}{F_0\,(X)_{\mathrm{expt}}}\right)\right\|\frac{100}{n'}$ %	$\frac{1}{n'-1}\times\sqrt{\left\{\sum\left(\frac{F_0\,(X)_{\mathrm{expt}} - F_0\,(X)_{\mathrm{calc}}}{F_0\,(X)_{\mathrm{expt}}}\right)100\right\}^2}$ %
Leden's graphical method[17]	1.36	0.75
Kivalo and Rastas (graphical)[24]	1.75	0.91
Statistical, least squares[24,25]	1.28	0.73
Computational analysis[30]	1.69	0.81

culation method over the entire ligand concentration range. For this particular system agreement between calculated and experimental values is satisfactory for all concentrations of chloride and the β_n values should be reliable.

(d) Comparison of results from the different calculation methods

Table 5 summarises the various results obtained for β_n as calculated by the different methods. With the lead(II)–chloride system it can be seen that there is a small but significant difference in results which stems solely from variations in the calculation method.

(e) Reliability of the calculation methods

Table 4 shows the difference between calculated and experimental $F_0\,(X)$ functions using the β_n values calculated by computational analysis. For convenience and as a means of comparison with other calculation methods the reliability of each method has been evaluated in two ways in terms of this difference, namely,

$$\left|\sum\left(\frac{[F_0\,(X)]_{\mathrm{calc}} - [F_0\,(X)]_{\mathrm{expt}}}{[F_0\,(X)]_{\mathrm{expt}}}\right)\right|\frac{100}{n'}\ \%$$

and

$$\frac{1}{n'-1}\times\sqrt{\left\{\sum\left(\frac{[F_0\,(X)]_{\mathrm{calc}} - [F_0\,(X)]_{\mathrm{expt}}}{[F_0\,(X)]_{\mathrm{expt}}}\right)100\right\}^2}\quad\%$$

where n' is the number of data points.

Table 6 summarises the errors obtained for the different methods of calculation expressed as above. For this particular system, the least-square method[24] gave the 'best overall fit' to the experimental data. However, the errors for the other methods are not substantially different and since only nine experimental points were used no valid rationalisation as to which set of β_n values is the most reliable can be made.

(v) The tin(II)–fluoride system

The tin(II)–fluoride complex-ion system has been studied potentiometrically with the tin (amalgam) and fluoride ion activity electrodes[31]. Three fluoride complexes of tin(II), SnF^+, SnF_2 and SnF_3^-, are reported with β_n values of 1.80×10^6, 5.79×10^8 and 1.77×10^9 respectively at 25°C and an ionic strength of 0.85.

The potentiometric equation to be solved is

$$F_0(X) = \text{antilog}\,(0.4343(nF/RT)\Delta E) = 1 + \beta_1[F^-] + \beta_2[F^-]^2 + \beta_3[F^-]^3$$

where ΔE is the change in potential of the tin (amalgam) electrode due to fluoride complexation.

Table 7 gives the data of Hall and Slater[31] obtained at 25°C, which they used to calculate the stability constants by a 'standard regression analysis', fitting the least-mean-squares curve to the data with the aid of a 60K IBM 1620 computer system.

TABLE 7

Data of Hall and Slater[31] for the tin(II)–fluoride system and the $F_n(X)$ functions for the Leden calculation method: $F_0(X) = 1/a_0$ from data in reference 31.

ΔE(mV)	$[F^-]$ (M)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$
0	0.000	1.000			
9.2	1.5×10^{-5}	2.045	6.96×10^4		
17.3	7.4×10^{-5}	3.846	3.85×10^4	1.15×10^8	
28.4	1.65×10^{-4}	9.091	4.90×10^4	1.15×10^8	
40.0	2.9×10^{-4}	2.242×10	7.39×10^4	1.51×10^8	
52.3	4.5×10^{-4}	5.848×10	1.28×10^5	2.17×10^8	
62.7	9.5×10^{-4}	1.318×10^2	1.38×10^5	1.13×10^8	
76.1	1.5×10^{-3}	3.717×10^2	2.47×10^5	1.45×10^8	
88.3	2.3×10^{-3}	9.524×10^2	4.14×10^5	1.67×10^8	
99.6	3.8×10^{-3}	2.320×10^3	6.12×10^5	1.53×10^8	
112.2	4.9×10^{-3}	6.173×10^3	1.26×10^6	2.51×10^8	2.1×10^{10}
122.7	7.2×10^{-3}	1.379×10^4	1.92×10^6	2.63×10^8	1.6×10^{10}
131.9	8.8×10^{-3}	2.825×10^4	3.21×10^6	3.61×10^8	2.4×10^{10}
138.3	1.07×10^{-2}	4.673×10^4	4.37×10^6	4.06×10^8	2.4×10^{10}
144.0	1.30×10^{-2}	7.246×10^4	5.57×10^6	4.26×10^8	2.1×10^{10}
149.5	1.60×10^{-2}	1.122×10^5	7.00×10^6	4.36×10^8	1.8×10^{10}

Calculation of β_n values of a system such as this is not straightforward and several difficulties arise. Vastly different values of β_n can be obtained by different calculations as will be shown in this section of the paper.

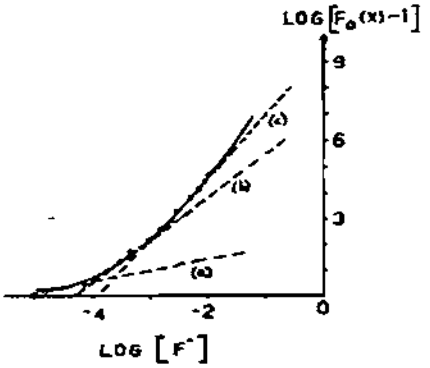


Fig. 7. Plot of log $[F_0(X) - 1]$ versus log $[F^-]$ for the tin(II)–fluoride system. (a), (b) and (c) are tangents (broken lines) to the curved plot.

A plot of log $(F_0(X) - 1)$ versus log $[F^-]$, shown in Fig. 7 from data tabulated in Table 7 reveals several of the problems. For the two lowest fluoride concentrations a straight line with slope of approximately 0.6 (line a) can be drawn. For the next five highest fluoride concentrations a straight line of slope 1.7 (line b) can be drawn. Finally for the eight highest fluoride concentrations a slope (line c) of about 2.2 can be obtained as shown in Fig. 7.

From this plot it would appear that the complex SnF_2 is predominant over most of the fluoride concentration range. At low fluoride levels there is evidence for SnF^+, and at the higher values there appears to be a higher-order complex, probably SnF_3^-.

These plots suggest that all species are not present at significant concentrations over the whole concentration range of fluoride. Simply fitting a least-squares fit over the whole range of data, therefore, would be not expected to give the most reliable result and a weighted calculation procedure could be necessary. For instance, allowance can be made for the fact that at low fluoride levels no significant concentration of SnF_3^- is present whilst at higher fluoride concentrations SnF^+ probably does not exist. Many different approaches to weighting the data are possible and this is where such a widespread variety of β_n values can be obtained with different calculation procedures. Weighted graphical and computational procedures on this system are shown which give markedly different β_n values to those tabulated in the literature by Hall and Slater and show the caution with which one should treat reported values, until the reliability of the calculation has been assessed.

The graphical calculation of Leden can easily be adapted to comply with the necessity of a weighted type of calculation. Figures 8 and 9 and Table 7 show this procedure. β_1 (SnF^+) is calculated by computation of $F_1(X)$ for the low fluoride concentrations, where SnF^+ is present in significant concentrations. The first six data points of $F_1(X)$ can be seen to approximate a straight line of intercept $\beta_1 = 3 \times 10^4$. The second to ninth data points of the $F_2(X)$ function are approximately constant with a value of β_2 (SnF_2) $= 1.5 \times 10^8$ being obtained. Thus the nine lowest fluoride concentrations can, in fact, be fitted quite satisfactorily to a quadratic equation

$$F_0(X) = 1 + \beta_1 [F^-] + \beta_2 [F^-]^2$$

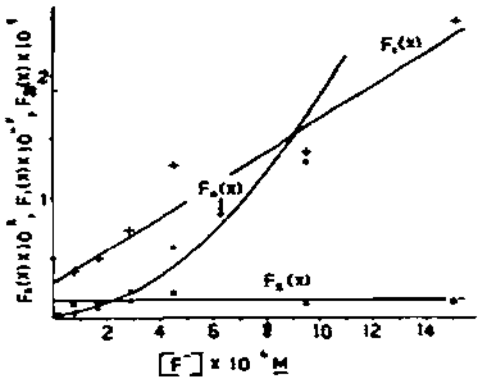


Fig 8 Analysis of the F_n (X) functions by the graphical method of Leden for low fluoride concentrations of the tin(II)—fluoride system ●, F_0 (X); +, F_1 (X), ○, F_2 (X)

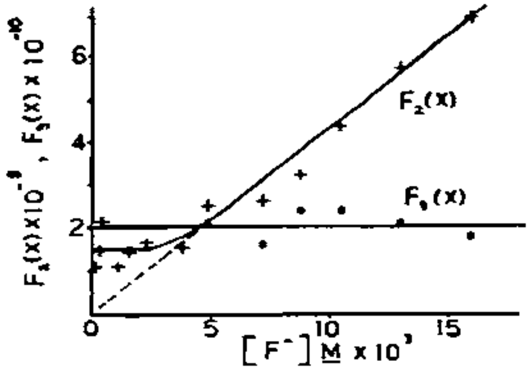


Fig. 9 Analysis of the F_2 (X) and F_3 (X) functions by the graphical method of Leden for the highest fluoride concentrations of the tin(II)—fluoride system +, F_2 (X), ●, F_3 (X)

and β_1 and β_2 values calculated from these data. It is assumed that no data relevant to higher-order complexes are contained over this concentration range

From Table 7 F_2 (X) can be seen to increase for fluoride concentrations above 4.9×10^{-3} M, i e. the six highest fluoride concentrations For this concentration range the presence of a higher-order complex becomes evident From the last six data points F_3 (X) is constant, giving a β_3 (SnF_3^-) value of 2×10^{10}

Comparison of β_n values obtained graphically and those of Hall and Slater reported in the literature, as shown in Table 8, illustrate how fundamentally important it is to take note of the method of calculation when assessing the reliability of any reported β_n values

Little detail of the calculation method used by Hall and Slater is given in their work They report the method as "a standard regression analysis was performed and the least-mean-squares cubic curve was fitted to the curves" It would appear however, that they have treated each data point equally and fitted a computational least-square analysis

Comparison of F_0 (X) calculated and experimental values for the two sets of results (Table 9), shows that the graphical results obtained with judicious weighting of data

TABLE 8

Comparison of β_n values by different calculation procedures for the tin(II)–fluoride system

Method	β_1	β_2	β_3
Computational analysis (Hall and Slater[31])	$1\ 80 \times 10^6$	$5\ 79 \times 10^8$	1.77×10^9
Leden's graphical method[17] (this work)	$3\ 0 \times 10^4$	$1\ 5 \times 10^8$	$2\ 0 \times 10^{10}$
Computational analysis Marquardt's method[30] (this work)	$-1\ 38 \times 10^6$	$5\ 22 \times 10^8$	$3\ 51 \times 10^8$
Weighted use of Marquardt's computational method[30] (this work)	$3\ 96 \times 10^4$	$1\ 51 \times 10^8$	1.89×10^{10}

provides a considerably better fit, especially at the lower fluoride concentrations as could be anticipated

If a computational statistical method of analysis is to provide answers consistent with those obtained graphically, then a weighted calculation procedure is also necessary

With Marquardt's computational procedure[30], use of all fifteen data points, and fitting a cubic equation provide chemically non-sensible results as a negative β_1 value is obtained Table 8 gives the β_n values of this method Obviously they are unacceptable but again this result illustrates the widespread magnitude of results obtained by different calculation methods

Using the knowledge obtained from the graphical method, a refined Marquardt calculation method is possible. The fit of a quadratic equation to the first nine data points gives $\beta_1 = 3.96 \times 10^4$ and $\beta_2 = 1.51 \times 10^8$ as shown in Table 9.

Finally, the function

$$F_0(X) = 1 + 3\ 96 \times 10^4\ [F^-] + 1\ 51 \times 10^8\ [F^-]^2 + \beta_3\ [F^-]^3$$

was solved for β_3 using the last six data points and then with all fifteen data points. β_3 values of $1\ 89(45) \times 10^{10}$ and $1\ 89(43) \times 10^{10}$ were obtained respectively

Table 9 shows the fit of these data calculated by a combination of graphical details provided from Leden's calculation method and computational analysis. The results can be seen to be satisfactory

Table 9, however, can also be used to draw an extremely important conclusion Despite the fact that the comparison of experimental and calculated $F_0(X)$ functions has been satisfactory, it is not particularly impressive in the mathematical sense This is a typical feature of much data in the literature because often it is not possible to obtain a mathematically unique solution. As pointed out in the introduction, even if no sources of experimental error were present, variations in activity coefficients and complexation of perchlorate or nitrate used to maintain constant ionic strength would prohibit in many

TABLE 9

Comparison of experimental and calculated $F_0(X)$ values from the various calculation methods used for evaluation of the tin(II)–fluoride system

$[F^-]$ (M)	$F_0(X)$ Experimental	$F_0(X)$ calculated from graphically obtained β_n values	$F_0(X)$ calculated from β_n values obtained by Marquardt's computational method			$F_0(X)$ calculated from Hall and Slaters' β_n values
			A	B	C	
1.5×10^{-5}	2.045	1.487	1.628		1.628	2.843×10
7.4×10^{-5}	3.846	3.445	4.759		4.766	1.374×10^2
1.65×10^{-4}	9.091	1.013×10	1.165×10		1.174×10	3.138×10^2
2.9×10^{-4}	2.242×10	2.280×10	2.520×10		2.566×10	5.717×10^2
4.5×10^{-4}	5.848×10	4.670×10	4.944×10		5.116×10	9.284×10^2
9.5×10^{-4}	1.317×10^2	1.820×10^2	1.751×10^2		1.913×10^2	2.351×10^3
1.5×10^{-3}	3.717×10^2	4.510×10^2	4.007×10^2		4.645×10^2	4.010×10^3
2.3×10^{-3}	9.524×10^2	1.107×10^3	8.921×10^2		1.122×10^3	7.225×10^3
3.8×10^{-3}	2.320×10^3	3.378×10^3	2.344×10^3		3.374×10^3	1.530×10^4
4.9×10^{-3}	6.173×10^3	6.102×10^3		6.054×10^3	6.054×10^3	2.293×10^4
7.2×10^{-3}	1.379×10^4	1.546×10^4		1.519×10^4	1.519×10^4	4.364×10^4
8.8×10^{-3}	2.825×10^4	2.551×10^4		2.497×10^4	2.497×10^4	6.189×10^4
1.07×10^{-2}	4.673×10^4	4.200×10^4		4.094×10^4	4.094×10^4	8.773×10^4
1.30×10^{-2}	7.246×10^4	6.968×10^4		6.769×10^4	6.769×10^4	1.251×10^5
1.60×10^{-2}	1.122×10^5	1.208×10^5		1.169×10^5	1.169×10^5	1.843×10^5

A, fitting a quadratic equation to first nine data points B, fitting a cubic equation to last six data points C, applied to all fifteen data points cases any possibility of obtaining an exact fit to the data. In the calculations it is assumed that the data fit an equation $F_0(X) = \sum_{n=0}^{n} \beta_n C_L{}^n$. In the presence of complexation of the electrolyte used to maintain constant ionic strength[5], variations in activity coefficients, alterations introduced by measurement of the system and a wide variety of other reasons for departure from ideality, the exact $F_0(X)$ is considerably more complex than the above $F_0(X)$ function. A high degree of correlation between experimental and calculated $F_0(X)$ is not generally expected The fact that an inexact solution is often obtained probably provides the fundamental pathway for the wide spread of results to be obtained with different calculations. Each method employs a different approach to obtain an approximate solution to the $F_0(X)$ data Consequently, the chances of finding in the literature an example where the same system has been studied on several occasions and the methods of calculation have given mathematically equivalent solutions is remote for all but the simplest systems The possibility that much of the discrepancy between two or more studies results from the non-equivalence of the calculations is correspondingly high.

Table 8 shows the variation possible from the published result on the tin(II)—fluoride system Extraordinary differences are observed. Variations are much greater than normally attributed to slight differences in temperature, ionic strength etc when an explanation of discrepancies of two studies is being looked for They are also greater than often could be attributable to different techniques of measurement on the one system. Obviously many other mathematical procedures could have been used on the data of Hall and Slater for the tin(II)—fluoride system and many other calculated values of β_n could be obtained, but the methods given should suffice to show how dependent the published β_n values are on the method of calculation and the need for careful checking of any published values before comparisons are made with other studies

Recently, Bond and Taylor[32] have also measured the tin(II)—fluoride system. A different method of measurement was used, polarographic instead of potentiometric, and a slightly different ionic strength, 1 0 compared with 0 85. Results obtained in the polarographic study were β_1 (SnF^+) = 10^4, β_2 (SnF_2) = 7×10^6, β_3 ($SnF_3{}^-$) = 2.7×10^9

These results are significantly different from the published results of Hall and Slater, and a comparison of the two sets of results can be made as follows. Experimentally, the two methods are not equivalent and both sets of measurements contain approximations in calculating their respective $F_0(X)$ functions Variations in β_n values from experimental non-equivalences as well as from slight differences in ionic strength can therefore be expected, but these should not be great

The calculation procedure for the data of Hall and Slater has been checked and the fit of data to the $F_0(X)$ plot has been shown to be extremely difficult Widespread variations are possible from the published β_n values. The data of Bond and Taylor are also extremely difficult to fit mathematically with a high degree of correlation between calculated and experimental $F_0(X)$ functions. Bond and Taylor describe their β_1 value of 10^4 to be only an approximation because of the high curvature obtained in the Leden-type graphical extrapolation procedure. On the surface the published values of β_1 (10^4 compared with 1.80×10^6) would appear to be in considerable disagreement. Table 8, however, shows that with various calculation methods β_1 values in the range 3×10^4 to the published 1.80×10^6 can be obtained with Hall and Slater's data. As Bond and Taylor's

β_1 value was only considered approximate by the authors, it can be seen that the apparent disagreement of published β_1 values of approximately two powers of ten can be accounted for by careful consideration of the two methods of calculation. The published β_3 values (2.7×10^9 compared with 1.77×10^9) are in excellent agreement Table 8 shows values in the range of 10^8 to 10^{10} which can be obtained by different calculations with Hall and Slater's data so that agreement of β_3 in both studies can be accepted. Published β_2 values (7×10^6 compared with 5.79×10^8) are apparently in considerable disagreement. Table 8 shows that different calculations with Hall and Slater's data can give answers in the range $1 \times 10^8 - 6 \times 10^8$ and the value does not depend markedly on the method. The value of Bond and Taylor's β_2 is, however, subject to considerable variation depending on the method of calculation. In the use of the Leden graphical method the authors calculated their β_2 value by strongly weighting the data towards the seven lowest concentrations of fluoride The data from higher fluoride concentrations are consistent with a considerably higher β_2 value as can be seen by examination of Fig. 4 of Ref. 32 In fact, a computer least-squares check of all data points gave a β_2 value of $4\ 74 \times 10^7$ compared with $6\ 30 \times 10^6$ using only the first seven fluoride concentrations. It can be shown that with Bond and Taylor's data use of a β_2 value of the order of 5×10^7 in fact gives calculated versus experimental F_0 (X) correlations which are quite as acceptable as the published value of 7×10^6. Use of the higher β_2 value would have meant the β_3 value has to be lowered fractionally from the reported value of 2.7×10^9 to about 2×10^9 but it can be seen that β_2 discrepancies apparently of the order of two powers of ten are again virtually insignificant after a detailed study of the calculation of both sets of data

Rather than simply accepting published values and assuming experimental discrepancies account for the apparent differences, this example shows the need for seeing if the major difference can be explained in terms of the calculation procedures to solve the data. Probably many so-called controversial systems could be unravelled in this manner as the author believes the method of calculation has not been given anywhere near the attention it deserves in comparing literature values

(vi) The possibility of obtaining a non-unique solution

In previous discussion it has been pointed out that a high degree of precision in solving the F_0 (X) function is not always possible because of inherent assumptions normally involved in studies of concentration stability constants, such as the constancy of ionic strength and possible complexing of the electrolyte used to maintain constant ionic strength.

In view of this feature it would not be surprising to find examples where the solution to a particular set of data is not unique, even after proceeding with a logical calculation procedure such as that suggested in this manuscript The F_0 (X) data are obtained over only a limited range of ligand concentration and it is therefore reasonable to expect that more than one polynomial will be fitted to the data with almost equal acceptability, and within the bounds of chemical credibility. The restriction placed upon β_n values, that they should be positive, obviously limits the number of chemically acceptable solutions that can be obtained, but it may for instance be possible to solve an equation by say either a quadratic or cubic equation with positive coefficients or β_n values. In such cases, resort has to be made to the chemical intuition of the worker which is mathematically not very satisfying but is unfortunately sometimes necessary. The compensation to this may be that deciding which solution is the "best" can provide a stimulating and intriguing problem.

Some preliminary data obtained polarographically on the lead(II)–sulphate system[33] are given in Table 10. The temperature was 25°C and an ionic strength of 3.0 was maintained by sodium perchlorate. The graphical method of Leden can be best used to illustrate the possibility of obtaining at least two solutions. Examination of the $F_1(X)$ function drawn in Fig. 10 shows that a straight line or curve could be drawn depending on how it is decided to weight the data. Excluding the last data point at 1 M Na_2SO_4, a straight line can be drawn through the remainder of data points, all points falling within the limit of experimental error. The data point obtained at 1 M Na_2SO_4 is measured in an ionic environment of pure sodium sulphate, as with the 1:2 electrolyte, no additional sodium perchlorate is needed to maintain the ionic strength at 3.0. All other data points were measured in the presence of considerable concentrations of sodium perchlorate and the ionic environment can be considered sufficiently different for the last data point to attach (with reason) less weight to this point and draw a straight line $F_1(X)$ plot. From the author's experience, the data point obtained in the absence (or data points obtained in small concentrations) of the electrolyte used to obtain constant ionic strength can often be apparently anomalous and inconsistent with the remainder of the data and are to be treated with caution. This could be the case with this system.

TABLE 10

Polarographic data and calculated values of the $F_n(X)$ functions for graphical analysis of the lead(II)–sulphate system

$[SO_4^{2-}]$ (M)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_2(X)$*	$F_3(X)$*
0.00	1.000				
0.05	1.646	12.92		58.4	
0.10	2.507	15.07	101	50.7	127
0.20	5.464	22.32	86.6	61.6	118
0.30	11.27	34.23	97.4	80.8	143
0.50	28.49	54.98	100	90.0	104
0.75	54.39	71.19	88.3	81.6	
1.00	191.9	180.9		171	133

* Three complexes assumed.

However, the possibility always exists with data of the nature obtained with this system, that a higher complex is in fact becoming important at the high concentrations of sulphate. Accepting the last data point as being of equal validity with the rest than an alternative and curved $F_1(X)^\star$ plot can be drawn as in Fig. 10. The straight line plot of $F_1(X)$ gives $\beta_1 = 5 \pm 2$, and the curved $F_1(X)^\star$ plot a β_1 value of 10 ± 2. The $F_2(X)$ plot (Fig. 10) then gives $\beta_2 = 96 \pm 4$ and indicates that the complex $Pb(SO_4)_2$ is the highest order complex. The $F_2(X)^\star$ plot (Fig. 10) would give $\beta_2^\star = 38 \pm 8$, however, a further

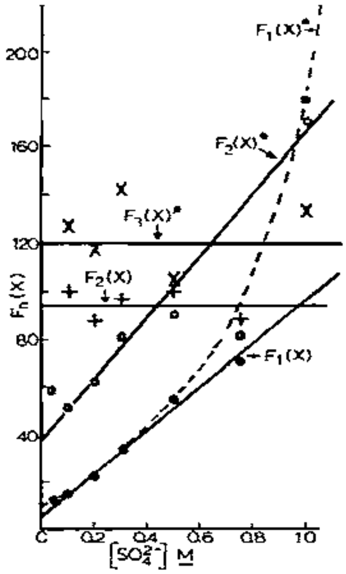


Fig. 10. Analysis of the $F_n(X)$ functions for the lead(II)–sulphate system by the graphical method of Leden ●, $F_1(X)$, +, $F_2(X)$, o, $F_2(X)^*$, x, $F_3(X)^*$.

complex is indicated from this plot with $\beta_3^* = 120 \pm 10$ being obtained from the $F_3(X)^*$ plot as in Fig. 10 Obviously for this plot the data point at 0 75 *M* does not fit the data but all other points do.

Thus the $F_0(X)$ data have been fitted in two polynomials

$$F_0(X) = 1 + 5\,[SO_4^{2-}] + 96\,[SO_4^{2-}]^2$$

and

$$F_0(X) = 1 + 10\,[SO_4^{2-}] + 38\,[SO_4^{2-}]^2 + 120\,[SO_4^{2-}]^3$$

TABLE 11

Comparison of calculated and experimental $F_0(X)$ values for the lead(II)–sulphate system

$[SO_4^{2-}]$(*M*)	$F_0(X)$		
	Exptl.	Calcd. [a]	Calcd. [b]
0 00	1 000	1 000	1 000
0 05	1.646	1.490	1 610
0.10	2.507	2 460	2 500
0 20	5 467	5 840	5 480
0 30	11 27	11 14	10 66
0 50	28 49	27 50	30 50
0 75	54 39	58.75	80.27
1.00	181.9		169 0

[a] From $F_0(X) = 1 + 5\,[SO_4^{2-}] + 96\,[SO_4^{2-}]^2$.
[b] From $F_0(X) = 1 + 10\,[SO_4^{2-}] + 38\,[SO_4^{2-}]^2 + 120\,[SO_4^{2-}]^3$.

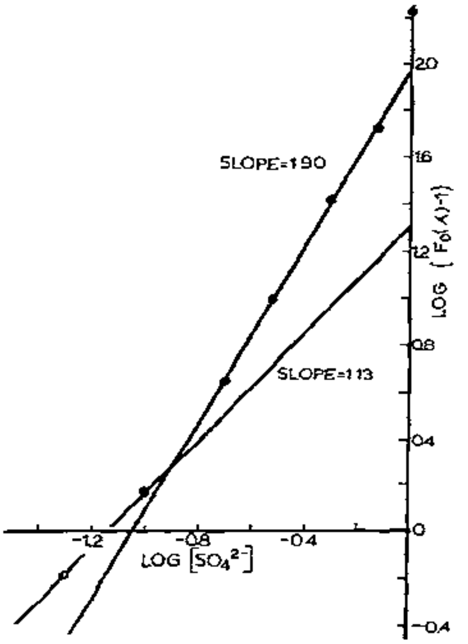


Fig 11. Plot of log $\{F_0(X) - 1\}$ versus log $[SO_4{}^{2-}]$ for the lead(II)–sulphate system

Table 11 shows a comparison of calculated and experimental $F_0(X)$ values For all except the last two data points, both solutions are entirely acceptable. The second last data point (0 75 M Na_2SO_4) does not provide a good fit to $F_0(X)^*$ nor the last data point (1.0 M Na_2SO_4) to $F_0(X)$. As there is a reason for weighting the data against the last data point, but not the second last, the quadratic $F_0(X)$ solution seems more acceptable. Furthermore the plot of log $(F_0(X) - 1)$ versus log $[SO_4{}^{2-}]$ shown in Fig 11 gives a limiting slope of 1.13 from the first two data points which is consistent with the major complex being Pb SO_4 at low sulphate concentrations. The remainder of the data up to 0.75 M give a straight line of slope 1.90 which indicates $[Pb(SO_4)_2]^{2-}$ is the major complex and no evidence for the presence of any higher complexes is provided by this plot The intercept of this plot at log $[SO_4{}^{2-}] = 0$ gives $\beta_2 = 96$ for the complex $[Pb(SO_4)_2]^{2-}$ which is in excellent agreement with the quadratic polynomial given previously. The log–log plot if it is accepted that this is a useful guide in solving complex ion systems, indicates clearly that a higher order complex could not be justified as it would be a result obtained from a one-point analysis at 1.0 M Na_2SO_4 and shows at least the practicality of starting the calculation with a plot of this type to gain some insight into the chemistry of the system.

The point needs to be made, however, that had no data been available in the 0.5 to 0.75 M concentration range of Na_2SO_4, and only the range 0.05 to 0.5 M had been covered with even say considerably more data points than given with the results in Table 10, either the quadratic or cubic polynomials would have been mathematically and chemically acceptable solutions, and the log–log plot, although used by this author as a guide, could not be said to exclude the possibility of the existence of three lead(II)–sulphate complexes. Thus the possibility of obtaining a non-unique solution always exists and needs to be considered in comparing two sets of different results. For instance, if another study were to report three sulphate complexes of lead(II) then it would need extremely careful checking to ensure that the data, compared to that given in this work, were or were not usually exclusive. It would be quite possible, that they are not, and an apparent discrepancy in the literature could be explained in terms of the calculation method of the data and/or chemical intuition of what is the best solution used by the workers.

The possibility of a non-unique solution probably becomes greater as the system becomes more complex. The bismuth(III)–chloride system has been studied on many occasions[34–43] using many techniques and conditions, and up to six complexes have been postulated. This system is probably one of the most studied and many of the results are summarised in Refs. 39–42

This system can be used to demonstrate many of the intrigues which can accompany calculation procedures on a system. Ahrland and Grenthe[34] studied this system, however, an error was incurred[35] In reporting the error of a power of ten in β_5 and β_6 the authors stated

"... It is gratifying however that the new curve, presented in the Fig. 1 (see their Fig. in Ref. 3) fits much better than the previous one to the experimental values of $\bar{n}$ ... In spite of their considerable random error, these values are therefore on the whole much more reliable than was once believed."

It can be appreciated from this statement that even with an error of a power of 10 in two β_n values the fit to the data was originally considered acceptable, presumably because the authors realised that solutions with a high degree of correlation between calculated and experimental values cannot be expected to be obtained in any case, as has been shown in this work

The potentiometric data of Ahrland and Grenthe were solved using the function under consideration in this work:

$$F_0(X) = \sum_{n=0}^{6} \beta_n \, [\mathrm{Cl}^-]^n$$

Fig 1 actually shows a distribution curve for one of the sets of data by Mironov et al. Although the distribution curve calculated from other sets of data would be different it can be seen that some of the complexes exist only in significant concentrations over small concentration ranges. Furthermore, only if data were collected over an extremely wide range of chloride concentration would the solution of the equation by the above function be completely adequate Ahrland and Grenthe, realising that data at sufficiently low concentration of chloride for significant formation of BiCl^{2+} could not be obtained, solved the equation with $\beta_1 = 0$ and obtained β_1 from solubility measurements where lower chloride concentrations could be used.

This, however, is an unusual although entirely sensible approach, and most workers, despite having used only a limited concentration range of chloride, have assumed all complexes exist up to the maximum complex and consequently solved the $F_0(X)$ function or a similar function in accordance with this belief However, in view of the nature of the distribution curves such as Fig. 1, which are obtained for this system and the not particularly high correlation found between calculated and experimental $F_0(X)$ values, it would not be surprising to find that the solution of the $F_0(X)$ function is not unique For instance, it would appear possible to solve the function in some studies (within the limit of experimental error) with various values of β_n equal to 0 This possibility arises when, after solving the $F_0(X)$ function, a distribution curve of the type in Fig. 1 is obtained in which it can be seen that a complex, say $BiCl_2^+$, is not the major species at any chloride concentration. In such a case, it is often possible to show that any value of β_2 less than some particular value, including the calculated β_2 value, and including 0, does not alter the calculated $F_0(X)$ function significantly and that a value of 0 is completely acceptable. That is, the value of β obtained is just a feature of the calculation method which assumes all complexes up to the maximum one exist, but it has no real significance If a value of 0 is reported this does not of course imply that the complex does not exist, but rather that relative to other complexes it is not present in significant concentrations at any concentration of ligand

In solubility studies by Haight et al[43], over the range 0 4 to 4 0 M in chloride, the authors concluded that $BiCl_4^-$ and $BiCl_6^{3-}$ are the only species present in solution, i e. their data could be solved with a value of $\beta_5 = 0$. They showed that " if one considers the possibility that not all possible $BiCl_n^{(3-n)+}$ complexes are found, one can fit Ahrland and Grenthes' potentiometric data with the equation

$$F_0(X) = 1 + \beta_2 [Cl^-]^2 + \beta_4 [Cl^-]^4 + \beta_6 [Cl^-]^6$$"

From results given in this work it is considered quite reasonable that the solution of any particular set of data may not be unique and undoubtedly several chemically and mathematically reasonable solutions to Ahrland and Grenthes' data can be made as indicated by the work of Haight et al[43] Apparent discrepancies between two studies are therefore explained by the non-uniqueness of data. Consideration of the data from other studies also revealed that other solutions for the bismuth(III)—chloride system are by no means unique. In fact if one used one's imagination it proved to be quite extraordinary as to the number of solutions that could be obtained to the various sets of data for the bismuth(III)—chloride system and in some ways it is surprising that agreement of results is as good as it is. Probably this has arisen because, in the main, data have in fact been solved assuming the presence of all complexes up to the maximum one and few possible variations to this have been considered. Data on the bismuth(III)—chloride system show, however, that the published solution to a set of data need not necessarily be unique or unambiguous and that if the results of two studies are in apparent disagreement then it may be worthwhile adopting the approach of Haight et al. and examing the possibility of recalculating the published data and seeing if another solution is possible, rather than simply and naively assuming that discrepancies arise because of differences in medium and method of measurement.

D. A SUGGESTED GENERAL METHOD FOR CALCULATION OF STABILITY CONSTANTS

It is apparent from the above work that a wide variety of results for β_n values can be obtained by use of different calculations. No particular method, unfortunately, is universally applicable to all systems and a great deal of discretion and prudence has to be employed in the choice and use of a method for each set of measurements on every complex-ion system studied if it is to be ensured that a reliable result has been obtained.

For example, it was observed in this work that the lead(II)–chloride system could be solved almost equally well by several calculation methods For tin(II)–fluoride, however, the same methods had to be modified drastically to obtain sensible solutions Unsatisfactory results could therefore easily have been reported for this system and undoubtedly have been with other systems of comparable or even greater complexity.

To eliminate the danger of randomly selecting a particular calculation method, feeding the data into it and reporting the results, whilst oblivious to some hidden pitfall in the calculation procedure as applied to the particular system being studied, a general procedure for the calculation of β_n values such as that used in this work and outlined below can be undertaken.

(*i*) Graphical plot of log $F_0(X)$ versus log [ligand] This provides some initial insight into the chemistry of the complex-ion system

(*ii*) A more sophisticated graphical procedure such as that of Leden This provides a set of β_n values and may reveal the type of statistical analysis which could lead to a successful solution as in (*iii*)

(*iii*) A statistical analysis with the aid of a computer. This provides a second set of β_n values which are not subject to personal bias of the worker as are the values obtained by the graphical extrapolation system of Leden

(*iv*) Compare calculated and experimental $F_0(X)$ functions to check for best set of β_n values of those calculated and to show that β_n values chosen for publication in the literature adequately describe the data for all experimental measurements

E. CONCLUSION

It seems apparent that considerable attention needs to be made in assessing the reliability of concentration stability constants reported in the literature with respect to the method of calculation used. Currently an extraordinarily large variaty of calculation procedures is available each with different approximations, limitations and subtleties. Application of various calculation procedures to the same set of data can be shown to give rise to a wide variety of calculated β_n values. The variations are of such magnitude that they could readily explain apparent discrepancies in the literature between two studies.

It would appear important, therefore, that authors give detailed accounts of their methods of calculation when reporting stability constants and carefully assess the reliability of the method they have used to check that the answers they obtained are good ones A useful check in this respect is suggested to be a comparison of experimental and calculated values for each data point. This should reveal any weaknesses in the calculation for any particular range of experimental values and ensure that the data have been adequately described by the reported β_n values. The reported values should, of course, also be checked to establish that they are chemically sensible.

Finally, it should be evident that no one particular calculation method for β_n values can be applied to every system encountered and a choice of the 'best' method has to be made in every case This is not an easy or obvious decision. However, the general procedure outlined in this work of commencing with a simple graphical method to understand the basic chemistry of the system, then proceeding to a more refined calculation procedure involving judicious graphical weighting of data or use of computational and statistical methods should eventually lead to a satisfactory solution

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