

59. *Complex Ions in Molten Salts: A Computer Method for the Calculation of Stability Constants from Metal-ion Concentration Data.*

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A computer method for the calculation of the stability constants of complex ions from uncomplexed metal ion-total ligand concentration data is described. It involves several cycles of a weighted least-squares curve-fitting by means of the metal-balance equation and a Newton-Raphson iteration using the ligand-balance equation. The method is illustrated by application to a typical study of complex ions in molten salts. Special features of this type of analysis are discussed.

LIST OF SYMBOLS

- C_M = total metal-ion concentration.
 C_m = the uncomplexed (but solvated) metal-ion concentrations.
 $F_o = C_M/C_m$.
 C_L = the total ligand concentrations.
 C_l = the unbound ligand concentrations.
 \bar{n} = the ligand number, defined as the average number of ligands combined with each central metal ion.
 \bar{n}_m = maximum observed value of \bar{n} .
 N = the maximum number of ligands bound per metal ion.
 C_{ML_n} = concentration of the solvated complex ML_n .
 β_n = the overall formation constant of the complex ML_n .
 k = slope of the plot of the e.m.f. of a cell against $\log_{10} C_M$ in the absence of ligand.
 E = difference between the cell e.m.f. in the presence and the absence of ligand.
 E_c = value of E calculated from the final iterated β_n and C_l values.
 ΔE = probable error in E .
 w = statistical weight of an equation.
 I = total number of sets of data.
 G = a function.
 G' = derivative of the function G .
 $C_{l,a}; C_{l,b}$ = successive best estimates for C_l .
 $F_{o,c}$ = F_o values calculated from the final iterated β_n and C_l values.
 $S_{\min.}$ = the minimum value of $\sum_1^I w(F_o - F_{o,c})^2$.
 σ_{β_n} = standard deviation of β_n .
 $W_{n,n}^{-1}$ = diagonal elements ($W_{o,o} \rightarrow W_{N,N}$) of the invert of the matrix of coefficients of β_n 's in the weighted least-squares normal equations.
 S_{F_o} = standard error of the estimate = $\sqrt{[\sum_1^I (F_{o,c} - F_o)^2]/I}$.
 σ_{E_c} = standard deviation of E_c .

THE (mainly graphical) calculation of stability constants of complex ions from various types of experimental data has recently been extensively discussed by Rossotti and Rossotti,¹ but some of the well-established graphical techniques for metal-ion concentration data have been criticised by Braunstein *et al.*² The latter authors proposed a

¹ Rossotti and Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, 1961.

² Braunstein, Blander, and Lindgren, *J. Amer. Chem. Soc.*, 1962, **84**, 1529.

graphical procedure which employed a series in the stoichiometric ligand concentrations that is an improvement because, *inter alia*, it eliminates the usual graphical successive approximation steps.

Computer methods have come into increasing favour during the last few years.³ For instance, Tobias and Hugus⁴ used a computer to analyse their metal-ion concentration data for a tin-aqueous system by a least-squares technique, and our method resembles theirs in some respects. The application⁵ is a particularly favourable one for this simplified procedure because, apart from e.m.f. changes, all other quantities needed for the computation are weighings, so that we are justified in assuming errors in the independent variable of the fitting polynomial to be negligible with regard to those in the dependent variable. It should be generally applicable to the type of data for which these assumptions can be made.

COMPUTATIONAL PROCEDURE

Before data are analysed in a computer the following points should be considered, best by graphical examination.

First, it is necessary to determine whether the data are "reasonable" with regard to chemical considerations, whether there are any "wrong" points which should be discarded, and whether systematic errors have been introduced by the techniques used. Of these matters the first two are best considered by plotting F_o against C_L (F_o may have been determined in various ways—an e.m.f. method involving an electrode of the third kind is employed here). This plot should be a smooth curve extrapolating to unity on the F_o axis. Initially, the third matter may be checked by examining the positions of the plots obtained with different total metal-ion concentrations, C_M . It is preferable to use log-log plots for this purpose. Reproducibility can be tested by examining the concordance of plots obtained in different experiments at the same C_M .

Secondly, the degree of the polynomial to be fitted to the data can be determined graphically. In the region where the log F_o -log C_L plots become straight, approximately parallel lines, $C_L \gg C_M$ and $C_l \rightarrow C_L$. Therefore in this region, $d \log F_o / d \log C_L \approx \bar{n}_m$, where $\bar{n} = (C_L - C_l) / C_M$.

A preliminary value for N can thus be estimated. This can be confirmed by a preliminary graphical analysis⁶ of the data, approximating C_l by C_L . If dinuclear complexes are assumed to be absent, the data can then be fitted with the polynomial

$$F_o = \sum_0^N \beta_n C_l^n.$$

Thus the β_n values required are those involved in the relation between F_o and C_l whereas, except in special cases, the data determined experimentally are F_o and C_L . (It would be desirable to determine the corresponding values of C_l . This, especially in molten salt solvents, is often not possible. For example, silver halides are much more soluble than in aqueous solutions.) Therefore, before the final computation of the β_n 's, it is necessary to obtain C_l values from the F_o - C_L data. For this purpose a Newton-Raphson iterative procedure⁷ involving the ligand-balance equation, in conjunction with a weighted least-squares curve-fitting technique with the metal-balance equation was employed.

Metal-balance Equation; Curve Fitting.—It is possible, in this and similar cases, to assume that possible errors in C_L , and thus in C_l , are negligible compared with those in F_o , and that possible errors in F_o are due to those in e.m.f. measurements rather than to those in C_M . This is reasonable when all quantities needed for the computation apart from the e.m.f.'s are precise

³ Sullivan, Rydberg, and Miller, *Acta Chem. Scand.*, 1959, **13**, 2023; Rydberg, *ibid.*, 1961, **15**, 1723.

⁴ Tobias and Hugus, *J. Phys. Chem.*, 1961, **65**, 2165.

⁵ Inman, *Nature*, 1962, **194**, 279.

⁶ Leden, *Z. phys. Chem.*, 1941, *A*, **188**, 160; Sullivan and Hindman, *J. Amer. Chem. Soc.*, 1952, **74**, 6091.

⁷ Whittaker and Robinson, "The Calculus of Observations," 4th edn., Blackie and Son, Glasgow, 1944, p. 84.

weighings. In addition, one of the parameters F_o involved is not a directly measured quantity subject to the usual (assumed) random experimental errors but is exponentially related to, in this case, the e.m.f. of a galvanic cell. The residual equations must thus be suitably weighted. In this case the weights are given by:

$$\frac{1}{F_o^2} \cdot \frac{k^2}{2 \cdot 303^2} \cdot \frac{1}{(\Delta E)^2}$$

In the experiments to be described there was no reason to suspect any variations in ΔE for different values of F .

The coefficients of the β_n 's in the normal simultaneous equations arising from the application of the standard weighted least-squares technique to the metal-balance equation, *i.e.*, the minimisation of the sum

$$\sum_1^I w(F_o - \sum_0^N \beta_n C_l^n)^2,$$

are therefore computed. In the first instance C_l is replaced by C_L . The preliminary β_n values are then obtained by using a "Pegasus" Autocode pivotal condensation procedure.

Ligand-balance Equation; Newton-Raphson Iteration.—Equating the total, bound and unbound ligand concentrations we obtain the equation:

$$C_L = C_l + C_m \sum_1^N n \beta_n C_l^n.$$

We now define a function

$$G = -C_L + C_l + C_m \sum_1^N n \beta_n C_l^n,$$

such that it is desired to obtain the value of C_l which makes $G = 0$. We use, as an example, the case for $N = 3$. Now

$$G' = 1 + C_m(\beta_1 + 4\beta_2 C_l + 9\beta_3 C_l^2).$$

Therefore, by the usual Newton-Raphson procedure

$$C_{l,b} = C_{l,a} - \left(\frac{-C_L + C_{l,a} + C_m(\beta_1 C_{l,a} + 2\beta_2 C_{l,a}^2 + 3\beta_3 C_{l,a}^3)}{1 + C_m(\beta_1 + 4\beta_2 C_{l,a} + 9\beta_3 C_{l,a}^2)} \right).$$

The procedure is then repeated, setting, in the equation above, $C_{l,b} = C_{l,c}$ and $C_{l,a} = C_{l,b}$, and so on to constancy in the C_l values, so as to obtain C_l values corresponding to the preliminary β_n values obtained as described above. As $C_{l,a}$ in this iteration we take C_L . Usually three iterations are needed to obtain constant C_l values corresponding to each β_n set.

The whole cycle is then repeated with the new C_l and original F_o values. Cycling is continued until successive β_n and C_l values remain constant during two or three complete cycles. Normally, about ten complete cycles were required. Probably a greater number of cycles would be required if the complexes were strong, *i.e.*, $C_l \ll C_L$ (see β_n values for system below).

The β_n and C_l values are printed out after each complete curve-fitting-Newton-Raphson cycle. In addition, after the last cycle the following parameters were calculated and printed out:

$$F_{o,c}; F_{o,c} - F_o; S_{\min.}; S_{F_o}; E_c; \sigma_{E_c}$$

(σ_{E_c} calculated by assuming, according to the χ^2 method, that

$$\sum_1^I \frac{1}{\sigma_{E_c}^2} \cdot \frac{(E - E_c)^2}{I - N} = 1.)$$

RESULTS

An example of the application of this technique to the computation of the stability constants of the chloro-complexes of cadmium in molten sodium-potassium nitrate eutectic solvent at

254° is given below. In a preliminary programme the computer calculates the values of F_o , C_L , w , C_m , and C_M required in the main computation from input values of E , h , and the balance weighings of the various solutes and the solvent melt. Also fed into the computer are the degree of the fitting polynomial, the number of cycles required, the number of pairs of data, the molecular weights of the solute nitrate and ligand, and the expected error in E , ΔE (the calculation, in this example, does not depend on the value of ΔE but it is required in the calculation of $S_{\min.}$).

The results of the final two cycles (obtained by using computed rather than graphical preliminary β_n values) are shown in Table 1.

TABLE 1.

	β_n values (molal units)		Other parameters			
	Cycle (9)	Cycle (10)	$F_{o,e}$	$F_{o,e} - F_o$	E_c (mv)	E (mv)
β_0	1.03	1.03	1.186	-0.004	4.3	4.2
β_1	86.8	86.7	1.517	+0.002	10.5	10.5
β_2	1670	1670	2.008	+0.016	17.5	17.7
β_3	16,700	16,700	2.943	+0.000	27.1	27.1
			4.482	-0.028	37.7	37.5
			7.944	-0.039	52.0	51.9
Ligand concentrations			14.74	-0.02	67.5	67.5
$10^2 C$ (mole kg. ⁻¹)			26.73	+0.23	82.5	82.7
Cycle (9)	Cycle (10)		42.95	+0.19	94.4	94.5
0.1732	0.1732		65.86	+0.22	105.1	105.2
0.5082	0.5083		98.06	-0.43	115.1	115.0
0.9399	0.9401		138.7	-1.7	123.8	123.5
1.619	1.619		200.1	+1.5	133.0	133.2
2.490	2.490					
3.902	3.902					
5.758	5.758					
7.933	7.933					
9.988	9.988					
12.13	12.13					
14.41	14.41					
16.65	16.65					
19.31	19.31					
			$S_{\min.} = +7.60$	(assuming $\Delta E = 0.2$ mv)		
			$S_{F_o} = 0.654$			
			$\sigma_{E_c} = \pm 0.17$			
			$\sigma_{\beta_0} = \pm 0.01$			
			$\sigma_{\beta_1} = \pm 1.8$			
			$\sigma_{\beta_2} = \pm 60$			
			$\sigma_{\beta_3} = \pm 350$			

σ_{β_n} is calculated, according to the χ^2 method, from $\sigma_{\beta_n}^2 = W_{n,n}^{-1} S_{\min.} / (I - N)$.

DISCUSSION

These results show the satisfactory constancy in iterated ligand concentrations C_1 and stability-constants (β_n) obtained from experimental F_o - C_L data. Equal constancy was observed with all the data analysed by this technique.

Although at the beginning of this work the preliminary β_n values were obtained graphically it was of interest to see whether this graphical stage was necessary. In some cases, including that above, through ill-conditioning of the data one or more of the preliminary β_n values, obtained by a computer analysis of the F_o - F_L data, was negative and did not agree with the corresponding value obtained graphically. This negative value was, however, rapidly eliminated during the subsequent iteration and the same final result obtained (see Table 2).

TABLE 2.

	β_0	β_1	β_2	β_3
	Preliminary β 's obtained graphically			
Preliminary	1.00	40.0	200	11,800
Final	1.03	86.7	1670	16,700
	Preliminary β 's obtained in computer			
Preliminary	+0.95	+49.2	-105	13,300
Final	1.03	86.7	1670	16,700

On the other hand, if a polynomial having a degree greater than that required to account for the complexes formed in the experiments was used to fit the data, then either a negative β_n value was obtained which was not eliminated during the iteration or the standard deviations of the β_n 's were very large.

An attempt to use the usual graphical successive approximation procedures¹ numerically in the computer was not successful and led to oscillating values of the stability constants and ligand concentrations. The reasons for this were not elucidated.

The statistical weights consist of two parts: that arising from the exponential relation between the experimental E values and the F_o values (the dependent variable of the fitting polynomial), and that arising from the precision of the E values. As a first approximation these were assumed to have been determined with the same precision, because of the physical basis of the technique and the dependence on time of the E values (the programme, however, could take into account weights due to differing precisions). Consequently, as long as the weights were proportional to $1/F_o^2$, the final iterated β_n 's and σ_{β_n} 's were the same. However, the value of $S_{\min.}$ depended on the absolute values of the weights. In the above case the value of σ_E indicates that in the calculation of the weights ΔE should have been chosen as 0.17 mv rather than 0.2 mv. If the $S_{\min.}$ value is thus corrected, $S_{\min.}/(I - N) = 1.05$, and therefore the data and weighting are statistically reasonable. The weights vary over a very wide range. The derived β_n 's thus depend very much on the low F_o values. The agreement between E and E_c over the whole range of the data thus leads to confidence in the method used to obtain the data and implies that the dependence of cell e.m.f. on metal-ion concentration is the same over the range of metal-ion concentrations corresponding to the F_o values. If no weights are used in the computation, the $F_{o,c}$ values are completely different from the initial F_o values.

At the moment, the precision of the β_n 's obtained from one set of F_o-C_L data is better than their reproducibility. In other words, the precision of the electrochemical technique is better than the reproducibility of the system. A small systematic error in the set of data used to illustrate the computational procedure in this paper is shown by the value of β_o (1.03) obtained. Graphically, the β_o value could not be distinguished from unity.

It was noticed that β_3 remains relatively constant throughout the iteration, whereas the other β_n 's vary widely. This result is expected on the basis of the series in the stoichiometric concentrations published recently.²

The programme has been generalised to allow fitting with polynomials up to any degree. However, the number of items which can be included in the cases of the higher degrees may be severely restricted by the storage capacity of the computer.

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