

680. *Methods for Computing Successive Stability Constants from Experimental Formation Curves.*

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Attention is drawn to the approximations implicit in existing methods for computing, from experimental data, the successive stability constants governing the formation of complexes in step-equilibria. A new "correction term" method is described. This makes use of the symmetry properties of the formation curve for the particular case $N = 2$.

The problem of computing the "best" set of stability constants from inconsistent experimental data is shown to be soluble by a least-squares treatment after an algebraic transformation. This procedure is applicable to systems of higher complexity. The effects of improved methods of computation are illustrated by examples taken from the literature.

Note on Symbolism.—Following Bjerrum most authors have used k_n to represent the stability constant of a complex ML_n relative to ML_{n-1} . Schwarzenbach uses \bar{K}_{ML_n} . Now K is customarily used for equilibrium constants, and k for velocity constants, and to avoid confusion we shall use K_n for the above stability constant. The overall constant $[ML_n]/[M][L]^n$ (see p. 3399) has been variously designated $\bar{K}_{ML_n}^L$ (Schwarzenbach), K_n (Bjerrum), and β_n (Fronaeus and other Scandinavian authors). We prefer the last, so that the expression $\beta_n = K_1K_2K_3 \dots K_n$ in our terminology corresponds to $K_n = k_1k_2k_3 \dots k_n$ in Bjerrum's.

THE formation of a complex species ML_n from a central atom or ion M , and molecules or ions of a *ligand* L , is assumed to be governed by a series of thermodynamic equilibrium constants defined by

$$K_n^T = \{ML_n\}/\{ML_{n-1}\}\{L\} = K_n/F_n$$

where K_n is the classical (concentration) equilibrium constant, $F_n = f_{ML_{n-1}} \cdot f_L/f_{ML_n}$, and charges are omitted for the sake of generality. If L is uncharged, ML_n and ML_{n-1} carry the same ionic charge, so that, provided measurements are made in solutions of constant, and not too high, ionic strength, F_n may be set equal to unity, and the convenient approximation $K_n \cong K_n^T$ is valid. Bjerrum (*Kgl. Danske Videnskab. Selsk.*, 1946, **22**, Nr. 18) used a single average value of F_n in his studies of complexes formed by cupric and chloride ions. The same author ("Metal Ammine Formation in Aqueous Solution," P. Haase, Copenhagen, 1941) introduced the concept of the *degree of formation*, or ligand number, \bar{n} , which he defined as the average number of ligand molecules or ions per molecule of M , and showed that for all systems in which only mononuclear complexes occur, values of \bar{n} , and of $[L]$, the concentration of free ligand, are related by the equation

$$\sum_{n=0}^{n=N} (\bar{n} - n)\beta_n[L]^n = 0 \quad \dots \dots \dots (1)$$

where $\beta_n = K_1K_2 \dots K_n$, and $\beta_0 = 1$, by definition.

Experimental methods for the determination of stability constants, developed by Leden, Bjerrum, and Fronaeus, have recently been discussed by Sullivan and Hindman

(*J. Amer. Chem. Soc.*, 1952, **74**, 6091), who point out that sets of equations of the type (1) can be solved for unique, non-trivial values of K_1 , K_2 , and K_n if the determinant

$$\begin{vmatrix} (\bar{n}_1 - 1)[L_1] + \dots (\bar{n}_N - N)[L_1]^N \\ (\bar{n}_1 - 1)[L_N] + \dots (\bar{n}_N - N)[L_N]^N \end{vmatrix} \neq 0$$

This expresses the condition that N inhomogeneous equations of the type (1) are needed for the evaluation of N stability constants in systems where the highest complex has the formula ML_N . In practice, experimental data exceed these minimal requirements, and the real problem is to find those values for the constants, k_n , which will best represent all the experimental results. Two difficulties arise. (i) The substitution of experimentally determined values of \bar{n} and $[L]$ into (1) will give a set of $m > N$ equations which will probably be inconsistent owing to experimental errors. (ii) The data obtained experimentally may not be fully representative of the whole function. As a particular case, linear equations formed from neighbouring points may be ill-conditioned. The present paper deals with this problem of obtaining the best set of stability constants from experimental values of \bar{n} and $[L]$, and will be restricted to systems for which $N = 2$ and the equation

$$\bar{n} + (\bar{n} - 1)K_1[L] + (\bar{n} - 2)K_1K_2[L]^2 = 0 \quad \dots \quad (2)$$

is applicable.

The current methods for obtaining K_1 and K_2 from the formation curve are discussed below, as the limitations and assumptions underlying the calculations do not always seem to be fully appreciated. Additional methods for computing stability constants are suggested, and applied to some formation curves in the literature. The present object is to compute the best stability constants from experimental data, rather than to discuss the significance of the values so obtained, or the quality of the experimental work.

Method A. Successive Approximations.—From equation (2), we have

$$K_1 = \frac{1}{[L]} \cdot \frac{\bar{n}}{(1 - \bar{n}) + (2 - \bar{n})K_2[L]} \quad \dots \quad (3a)$$

and

$$K_2 = \frac{1}{[L]} \cdot \frac{\bar{n} + (\bar{n} - 1)K_1[L]}{(2 - \bar{n})K_1[L]} \quad \dots \quad (3b)$$

which emphasise that the calculation of K_1 depends on the value of K_2 and *vice versa*. Bjerrum (*op. cit.*, p. 37) applies these equations to the refinement by successive approximations of "temporary" constants obtained by other methods. If n experimental points determine the formation curve, there are $m(m - 1)/2$ pairs of values which could be treated in this way; but some judgment would be necessary since several combinations would yield ill-conditioned equations and the resulting values of K_1 and K_2 would have to be omitted from the general average.

Method B. Solution of Simultaneous Equations.—When $N = 2$, the required stability constants can be obtained by solving pairs of simultaneous equations derived from (2). The criticisms of Method A apply equally here.

Method C. Interpolation at Half \bar{n} Values.—From equations (3a) and (3b) we have

$$\log K_1 = pL_{1/2} + \log [2/(1 + \sqrt{1 + 12K_2/K_1})] \quad \dots \quad (4a)$$

and

$$\log K_2 = pL_{3/2} - \log [2/(1 + \sqrt{1 + 12K_2/K_1})] \quad \dots \quad (4b)$$

where pL_a represents the free ligand exponent when $\bar{n} = a$. Provided that $K_{n-1} \gg K_n$, approximately equal amounts of ML_{n-1} and ML_n will be present in solution when $\bar{n} = n - \frac{1}{2}$, and the contributions of ML_{n-2} and ML_{n+1} may be neglected. Following Bjerrum (*op. cit.*, p. 36) we may write

$$\log K_n = pL_{n-\frac{1}{2}} \quad \dots \quad (5)$$

Unless $K_1/K_2 \gg 10^{2.5}$, this very commonly used approximation can introduce considerable error (see p. 3404), and in the case where $N = 2$ it has the disadvantage of using only two points on the formation curve.

Method D. Interpolation at Various \bar{n} Values.—Rewriting equation (2) for the point ($pL_{1-a}, 1 - d$), we have

$$\log K_1 = pL_{1-a} + \log \{2(1 - d)/[d + \sqrt{d^2 + 4(1 - d^2)k_2/k_1}]\} \quad (7)$$

which reduces to

$$\log K_1 = pL_{1-a} + \log [(1 - d)/d] \quad (8a)$$

when $K_1 \gg K_2$. Similarly,

$$\log K_2 = pL_{1+a} - \log [(1 - d)/d] \quad (8b)$$

The use of these equations over the whole range of the formation curve ($0 < d < 1$) is only justified if $K_1/K_2 > 10^4$, though in this case Method D is preferable to Method C as it can be applied at several points along the formation curve, and the mean values of K_1 and K_2 obtained from the results. If $K_1/K_2 < 10^4$, calculated values of stability constants show a drift which is more pronounced the lower the value of d . Albert (*Biochem. J.*, 1950, **47**, 531) averages constants obtained in this manner. Jonassen, LeBlanc, and Rogan (*J. Amer. Chem. Soc.*, 1950, **72**, 4960) take the most probable value to be that obtained from the point where $d = \frac{1}{2}$; this is, in effect, employing Method C.

Method E. Use of the Mid-point.—(i) At the mid-point of the formation curve, where $\bar{n} = 1$

$$K_1 K_2 [L_1]^2 = 1, \text{ or } \log K_1 K_2 = 2pL_1 \quad (9)$$

The abscissa of the mid-point will therefore give a value for the overall constant β_2 whose precision is limited only by that of the experimental measurements. The common practice of evaluating individual values of K_1 and K_2 from the product $K_1 K_2$ so obtained, together with equation (5), demands a full appreciation of the implicit approximations, and does not make full use of the experimental data.

(ii) For a system in which $N = 2$, Bjerrum (*op. cit.*, p. 24) defines a spreading factor, $x = \sqrt{K_1/4K_2}$, and relates it to the mid-point slope, D , of the formation curve at the point where $\bar{n} = 1$ by the expression $D = -2.303/(1 + x)$. From the measured mid-point slope the ratio K_1/K_2 may be calculated, and individual values of K_1 and K_2 obtained from this and equation (9). This method is only applicable where K_1/K_2 lies between 10^3 and 10^{-2} (as $K_1/K_2 \rightarrow \infty, D \rightarrow 0$, and as $K_1/K_2 \rightarrow 0, D \rightarrow -2.303$) and it uses only a very small portion of the formation curve in the region of the mid-point. Significant errors may be introduced both in plotting the "best" formation curve to pass through the experimental points, and in measuring its mid-point slope.

Method F. Schwarzenbach's Graphical Method.—Schwarzenbach, Willi, and Bach (*Helv. Chim. Acta*, 1947, **30**, 1303) described a graphical method for computing the dissociation constants of dibasic acids from data obtained by potentiometric titrations; this was later applied to the computation of stability constants of metal complexes (Schwarzenbach and Ackerman, *ibid.*, 1948, **31**, 1029).

Their method can be adapted to the computation of stability constants from experimental values of \bar{n} and $[L]$ by plotting values of $A = (\bar{n} - 1)[L]/\bar{n}$ and $B = (\bar{n} - 1)/(2 - \bar{n})[L]$ as abscissæ and ordinates respectively. All lines passing through pairs of points (A, B) should intersect when extrapolated at the point ($1/K_1, K_2$). This procedure is unreliable if lengthy extrapolation is necessary and is only suited to experimental data of high precision.

General Comments.—It will have been seen that the choice of computational method depends on the ratio K_1/K_2 in the system under consideration. An approximate value of this ratio may rapidly be obtained from the mid-point slope, D , of the formation curve, without introducing the concept of the spreading factor. For systems in which $N = 2$, D is given by

$$D = -4.606/(2 + \sqrt{K_1 K_2})$$

and values of D for given K_1/K_2 ratios are given in Table 1. Thus, if Method C is to be used, K_1/K_2 must be $> 10^{2.5}$, and D must be > -0.23 . The formation curve is then wave-like. For Method D, K_1/K_2 must be $> 10^4$, and D must be > -0.04 , giving rise to a formation curve showing two very distinct steps. Method E is applicable to systems where $10^{-2} < K_1/K_2 < 10^3$, and $-2.2 < D < -0.14$. It is seen that, in the "normal" case, where

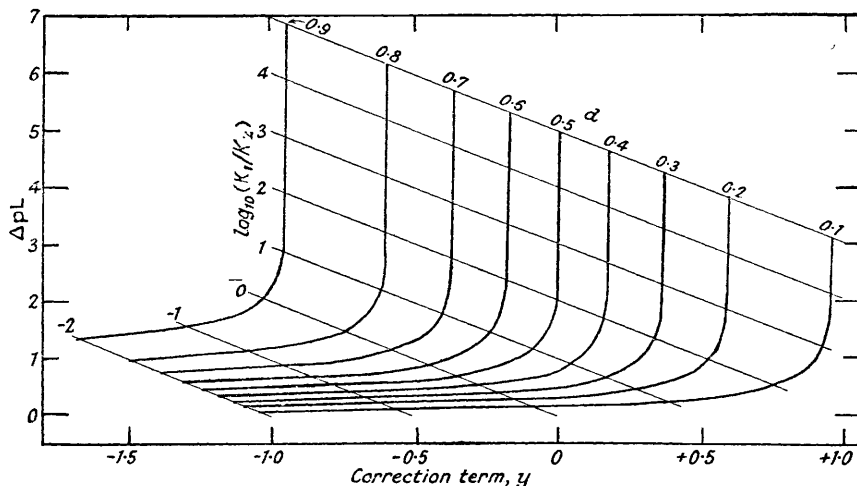
$K_1 > K_2$, $0 > D > -1.535$, while if $K_2 > K_1$ (e.g., for the complex amines of Ag^+ in water) $-1.535 > D > -2.303$.

TABLE 1. The mid-point slope, D, for systems in which $N = 2$.

$\log K_1/K_2$	5	4	3	2	1	0
D	-0.0145	-0.0451	-0.137	-0.384	-0.892	-1.535
$\log K_1/K_2$	-1	-2	-3	-4	-5	$-\infty$
D	-1.989	-2.193	-2.267	-2.292	-2.300	-2.303

Additional Methods for Computing Stability Constants.—The ideal method should minimise the subjective “smoothing” implicit in most graphical procedures and ought to employ the experimental data as fully as possible. The two new methods presented below do not fully attain this ideal, but represent a real improvement on existing ones.

FIG. 1. Correction terms.



Method G. “Correction-term” Method.—In a system where $N = 2$, the theoretical formation curve is symmetrical about its mid-point so that from (8) and (9)

$$pL_{1-d} + pL_{1+d} = 2pL_1 = \log K_1 K_2 \quad (10)$$

From (7),

$$\log K_1 = pL_{1-d} + y \quad (11a)$$

and

$$\log K_2 = pL_{1+d} - y \quad (11b)$$

where the “correction term,” y , is given by

$$y = \frac{2(1-d)}{d + \sqrt{d^2 + 4(1-d^2) \cdot K_2/K_1}} \quad (12)$$

and depends in magnitude both upon d and upon the ratio K_2/K_1 . If $K_1/K_2 > 10^4$, equation (12) reduces to $y \cong \log [(1-d)/d]$, and the correction term depends only on the value of d (Method D) and becomes zero in the special case where $d = \frac{1}{2}$ (Method C).

If pL_{1-d} and pL_{1+d} are two points on the formation curve disposed symmetrically about the mid-point, then from equations (10) and (11)

$$\Delta pL_d = pL_{1-d} - pL_{1+d} = \log(K_1/K_2) + 2y \quad (13)$$

By using equations (12) and (13), corresponding values of y and ΔpL have been calculated for nine values of d for each of a series of values of K_1/K_2 ranging from 10^5 to 10^{-2} . The relationship between y and ΔpL is shown graphically in Fig. 1, but full advantage of the method can only be taken if this is drawn on a much larger scale, for which the necessary data are given in Table 2.

The correction-term method is applied as follows to pairs of values (\bar{n} , pL) symmetrically disposed about the mid-point. Suppose the experimental values were $pL_{0.4} = 9.50$ and $pL_{1.6} = 8.00$. The value of the correction term, $y (= -0.23)$, is read off from the curve for $d = 0.6$ as abscissa corresponding to $\Delta pL = 1.50$. Thence $\log K_1 = 9.50 - 0.23 = 9.27$, and $\log K_2 = 8.00 + 0.23 = 8.23$. The process is repeated for several values of d and the mean value of the calculated stability constants is taken. In practice, it is convenient to draw the best formation curve through the experimental points and to read off values of $pL_{1 \pm d}$ for those values of d tabulated. Although this involves some "smoothing" of the experimental data, the correction-term procedure is very rapid and reliable as it takes fully into account the complicating factors introduced by the absolute magnitude of the ratio K_1/K_2 which may vitiate the application of Methods C and D. On the other hand, small changes in ΔpL correspond to large changes in y when the ratio K_1/K_2 becomes low (cf. Table 2). This is especially marked in the central part of the curve, and if $K_1 < K_2$, values calculated from d smaller than 0.5 will not be reliable.

TABLE 2. *The relationship between y and pL for several values of d.*

log K_1/K_2	$d = 0.1$		$d = 0.2$		$d = 0.3$		$d = 0.4$		$d = 0.5$	
	y	ΔpL	y	ΔpL	y	ΔpL	y	ΔpL	y	ΔpL
5.000	0.954	3.092	0.602	3.796	0.368	4.264	0.176	4.648	0.000	5.000
4.000	0.954	2.092	0.602	2.796	0.368	3.264	0.176	3.648	0.000	4.000
3.523	0.942	1.639	0.599	2.325	0.366	2.789	0.175	3.173	0.000	3.523
3.000	0.916	1.167	0.592	1.816	0.364	2.272	0.174	2.652	-0.001	3.003
2.523	0.861	0.802	0.574	1.376	0.355	1.812	0.169	2.185	-0.004	2.531
2.000	0.746	0.507	0.523	0.954	0.330	1.341	0.158	1.684	-0.012	2.025
1.523	0.593	0.336	0.430	0.663	0.273	0.976	0.120	1.283	-0.035	1.592
1.000	0.388	0.225	0.274	0.452	0.159	0.682	0.036	0.928	-0.094	1.188
0.523	0.178	0.167	0.093	0.336	0.004	0.515	-0.085	0.693	-0.196	0.916
0.000	-0.065	0.130	-0.131	0.262	-0.202	0.405	-0.278	0.556	-0.362	0.725
-0.477	-0.296	0.116	-0.354	0.231	-0.413	0.349	-0.477	0.477	-0.549	0.621
-1.000	-0.551	0.101	-0.602	0.204	-0.656	0.312	-0.715	0.430	-0.778	0.556
-1.477	-0.786	0.095	-0.835	0.193	-0.885	0.294	-0.940	0.402	-1.000	0.523
-2.000	-1.046	0.091	-1.092	0.184	-1.141	0.282	-1.193	0.287	-1.251	0.502

log K_1/K_2	$d = 0.6$		$d = 0.7$		$d = 0.8$		$d = 0.9$	
	y	ΔpL	y	ΔpL	y	ΔpL	y	ΔpL
5.000	-0.176	5.352	-0.368	5.736	-0.602	6.205	-0.954	6.908
4.000	-0.176	4.352	-0.368	4.736	-0.602	5.205	-0.954	5.908
3.523	-0.176	3.876	-0.368	4.260	-0.602	4.727	-0.954	5.431
3.000	-0.177	3.354	-0.368	3.737	-0.602	4.204	-0.954	4.909
2.523	-0.178	2.880	-0.369	3.261	-0.603	3.728	-0.954	4.432
2.000	-0.184	2.367	-0.372	2.745	-0.604	3.209	-0.955	3.910
1.523	-0.198	1.918	-0.381	2.285	-0.609	2.741	-0.957	3.437
1.000	-0.238	1.477	-0.407	1.815	-0.615	2.230	-0.964	2.928
0.523	-0.317	1.158	-0.465	1.452	-0.662	1.846	-0.980	2.482
0.000	-0.459	0.917	-0.582	1.164	-0.749	1.497	-0.032	2.064
-0.477	-0.633	0.789	-0.736	0.996	-0.879	1.281	-1.123	1.770
-1.000	-0.852	0.705	-0.944	0.887	-1.066	1.133	-1.279	1.557
-1.477	-1.069	0.661	-1.154	0.831	-1.268	1.060	-1.459	1.441
-2.000	-1.317	0.634	-1.398	0.796	-1.506	1.012	-1.680	1.359

The value of the correction term, y , may also be calculated from the exact equation

$$y = \log \frac{1-d}{d} + \log \left\{ 1 - \frac{(1+d)[L]_{1-d}}{(1-d)[L]_{1+d}} \right\} \dots \dots \dots (14)$$

which is useful in the absence of Fig. 1 if only occasional use is made of the correction-term, at d values which are not tabulated.*

Since the above treatment postulates the symmetry of the formation curve about its mid-point, it cannot be used for complex systems where $N > 2$. Lack of symmetry may, however, also appear even in some systems where $N = 2$ if polydentate ligands are involved. In the system Cu^{++} and diethylenetriamine ("dien"), \bar{n} increases slowly with $[L]$ over the range $1 < \bar{n} < 2$ and does not approach 2 asymptotically (Jonassen *et al.*, *loc. cit.*). This is explicable if the second ligand molecule is not co-ordinated through each of its nitrogen

* We are grateful to one of the Referees who pointed this out, and who also made fruitful suggestions which have been incorporated in this paper.

atoms. Ligands such as $\alpha\beta$ -diamino-carboxylate ions could chelate with metal ions in three different ways (Albert, *Biochem. J.*, 1952, **50**, 690) to give three different 1:1 complexes and six different 1:2 complexes. In these circumstances the formation curve would not be represented by equation (2). Unsymmetrical formation curves may also result if polynuclear complexes are involved. Many unsymmetrical formation curves are, however, depicted in the literature for systems where $N = 2$ and where none of these possible complications is expected. In such cases the experimental work must be regarded as suspect. It is always advisable to test an experimentally determined formation curve for symmetry about its mid-point, for, if this test fails, only limited confidence can be placed on stability constants calculated from it by any of the methods described in this paper, since they all postulate that the results may be represented accurately by equation (2).

Method H. Least-squares Treatment.—Equation (2) can be rewritten as

$$\frac{\bar{n}}{(\bar{n} - 1)[L]} = \frac{(2 - \bar{n})[L]}{(\bar{n} - 1)} \cdot K_1 K_2 - K_1 \quad \dots \quad (15)$$

which is the equation to a straight line. Since, in practice, the term $[L]$ may vary by several powers of ten, it is seldom convenient to plot $\bar{n}/(\bar{n} - 1)[L]$ against $(2 - \bar{n})[L]/(\bar{n} - 1)$ to obtain the slope, $K_1 K_2$, and the intercept, $-K_1$, of the best straight line. The constants are best evaluated by the method of "least squares" which makes use of all the experimental data and avoids subjective "smoothing" of data incidental to plotting the "best straight line." A minor disadvantage arises from the properties of the functions $\bar{n}/(\bar{n} - 1)$ and $(2 - \bar{n})/(\bar{n} - 1)$, which becomes very large in the centre of the curve ($0.95 < \bar{n} < 1.05$) and very sensitive to slight experimental errors in \bar{n} . Points in this small region are therefore best rejected in this treatment.

This method was first tested on three systems with widely different values of K_1/K_2 and as many experimental points as possible. The values of K_1 and K_2 obtained by Method H being used, values of \bar{n} corresponding to the experimental values of pL were calculated. Values of pL, $\bar{n}_{\text{expt.}}$, and $\Delta\bar{n} (= \bar{n}_{\text{expt.}} - \bar{n}_{\text{calc.}})$ are given in Tables 3, 4, and 5, together with

TABLE 3. Cu^{++} and dimethylethylenediamine ("dimen"), in water, at 25° ($K_1/K_2 \sim 10^3$) (Irving and Griffiths, *J.*, 1953, in the press).

pL ...	10.889	10.351	10.074	9.954	9.835	9.726	9.607	9.518	9.270	8.942	8.414	7.727
$\bar{n}_{\text{expt.}}$...	0.048	0.192	0.313	0.374	0.433	0.493	0.553	0.614	0.773	0.853	0.971	1.088
$\Delta\bar{n}$...	+0.011	-0.013	-0.021	-0.021	-0.016	-0.014	-0.005	-0.016	-0.046	+0.001	-0.002	-0.007
pL ...	7.311	7.163	7.025	6.907	6.799	6.701	6.593	6.486	6.271	6.009	5.672	
$\bar{n}_{\text{expt.}}$...	1.202	1.259	1.319	1.376	1.432	1.491	1.547	1.604	1.716	1.821	1.918	
$\Delta\bar{n}$...	-0.004	+0.015	+0.004	+0.029	+0.013	+0.011	+0.017	+0.020	+0.013	+0.012	-0.003	
						$\log K_1$	$\log K_2$	$\log \beta_2$	σ			
Method A						9.69	6.65	16.34	—			
Method G						9.69	6.69	16.38	—			
Method H						9.69	6.71	16.40	± 0.017			

TABLE 4. Cu^{++} and glycine in water at 25° ($K_1/K_2 \sim 10^{1.4}$) (Irving and Griffiths, unpublished).

pL	9.612	8.667	8.607	8.549	8.492	8.423	8.358	8.294	8.221	8.150
$\bar{n}_{\text{expt.}}$	0.008	0.250	0.270	0.296	0.326	0.351	0.385	0.426	0.463	0.511
$\Delta\bar{n}$	-0.005	-0.025	-0.019	-0.018	-0.019	-0.009	-0.005	-0.008	+0.001	0.000
pL	8.076	7.993	7.902	7.803	7.715	7.630	7.530	7.423	7.318	7.215
$\bar{n}_{\text{expt.}}$	0.564	0.620	0.681	0.749	0.807	0.872	0.938	1.012	1.088	1.169
$\Delta\bar{n}$	-0.003	-0.002	0.000	+0.001	+0.005	-0.001	+0.001	0.000	-0.004	-0.014
pL	7.084	6.975	6.838	6.708	6.565	6.380	6.192	5.886	5.034	
$\bar{n}_{\text{expt.}}$	1.251	1.339	1.425	1.515	1.606	1.697	1.788	1.880	1.972	
$\Delta\bar{n}$	-0.005	-0.016	-0.007	-0.009	-0.015	+0.002	-0.013	+0.002	+0.010	
						$\log K_1$	$\log K_2$	$\log \beta_2$	σ	
Method A						8.16	6.73	14.89	—	
Method G						8.13	6.78	14.91	—	
Method H						8.12	6.77	14.89	± 0.010	

TABLE 5. *Ag⁺ and ammonia in 2N-aqueous ammonium nitrate at 30°* ($K_1/K_2 \sim 10^{-6}$) (Bjerrum, *loc. cit.*, p. 132).

pL	4.051	3.816	3.656	3.523	3.385	3.232	3.030
\bar{n}_{expt}	0.247	0.495	0.741	0.988	1.230	1.477	1.711
$\Delta\bar{n}$	+0.002	-0.003	-0.002	+0.002	-0.004	-0.002	-0.006
			log K_1	log K_2	log β_2	σ	
Method A			3.20	3.83	7.03	± 0.004	
Method G			3.18	3.84	7.02	—	
Method H			3.19	3.84	7.03	± 0.004	

the standard deviation, $\sigma = [\Sigma(\Delta\bar{n})^2/\text{number of observations}]^{1/2}$. The stability constants calculated by Methods G and H are compared with those obtained by the original workers. In these three systems, it is seen that the stability constants calculated by using Method H are in very good agreement with those obtained by the original workers using Method A, and that the standard deviations of $\Delta\bar{n}$ are low. As a further test of Method H, stability constants were calculated for some systems where the workers' own method of calculation seemed suspect, or where the experimental formation curve was incomplete. The results are given in Tables 6—9.

TABLE 6. *Cd⁺⁺ and L-asparagine in water* ($K_1/K_2 \sim 10^{0.6}$) (Albert, *Biochem. J.*, 1950, 47, 531).

pL	4.75	4.40	4.10	3.80	3.62	3.45	3.30	3.16	3.05	2.92
\bar{n}_{expt}	0.10	0.20	0.40	0.57	0.74	0.93	1.11	1.26	1.42	1.56
$\Delta\bar{n}$ (Albert) ...	+0.019	+0.040	+0.008	+0.033	+0.041	+0.012	-0.033	-0.057	-0.121	-0.152
$\Delta\bar{n}$ (Method H)	-0.014	-0.017	-0.067	-0.003	-0.003	+0.006	-0.007	+0.002	-0.051	-0.067
			log K_1	log K_2	log β_2	σ				
Albert			3.87	2.90	6.77	± 0.069				
Method H			3.71	3.07	6.78	± 0.036				

The stability constants obtained by using Method H lead to much lower standard deviations of $\Delta\bar{n}$ than do those obtained by Albert, using Method D, which should only be used for systems in which $K_1/K_2 > 10^4$.

The magnitude of σ is a measure of the precision, rather than of the accuracy, of the experimental data. It is seen that the values of $\Delta\bar{n}$ obtained by using Method H are very small in the centre of the curve, but increase as d increases. This effect, which is observed with several of the systems studied, is due to the "weighting" of the central terms by the least-squares treatment. It is fortunate that the points where d is small may be determined with greater experimental precision than those where $d \rightarrow 1$.

TABLE 7. *Ni⁺⁺ and oxine, in 70% aqueous dioxan at 25°* ($K_1/K_2 \sim 10^{1.2}$) (Maley and Mellor, *Australian J. Sci. Res.*, 1949, 2, 98).

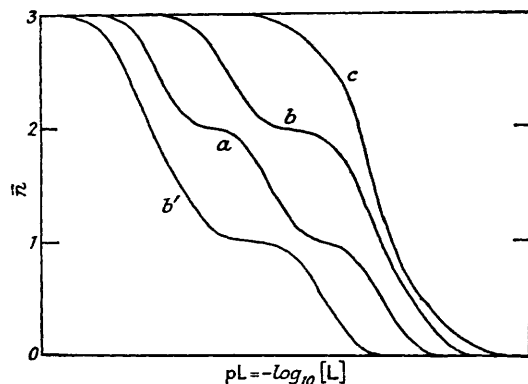
pL	11.71	11.68	11.63	11.56	11.54	11.27	11.08
\bar{n}_{expt}	0.37	0.47	0.53	0.63	0.70	0.85	1.04
$\Delta\bar{n}$ (M. and M.)	+0.128	+0.046	+0.020	-0.030	-0.084	-0.043	-0.061
$\Delta\bar{n}$ (Method H)	+0.131	+0.052	+0.014	-0.020	-0.075	-0.017	-0.021
pL	10.83	10.51	10.33	10.28	9.94	9.57	
\bar{n}_{expt}	1.20	1.42	1.48	1.53	1.80	1.91	
$\Delta\bar{n}$ (M. and M.)	-0.079	-0.070	-0.003	-0.019	-0.095	-0.055	
$\Delta\bar{n}$ (Method H.)	-0.021	+0.004	+0.080	+0.033	-0.035	-0.022	
			log K_1	log K_2	log β_2	σ	
Maley and Mellor			11.65	10.35	22.00	± 0.068	
Method H			11.64	10.47	22.11	± 0.056	

In this system the experimental points do not lie on a smooth curve, and even with Method H, a high value of $\sigma = \pm 0.056$, is obtained, indicating a low precision of the data. The constants calculated by using Method H do, however, fit the experimental curve appreciably better than do those obtained by Maley and Mellor, using Method C. It has been pointed out (p. 3400) that the use of Method C is not justified unless $K_1/K_2 > 10^{2.5}$.

Values of \bar{n} ($= 1 \pm d$) are only recorded in the two regions where $d \cong 0.5$, but it is seen that, even with such a very incomplete formation curve, Method H gives satisfactory

results, which are in good agreement with those obtained by Jonassen *et al.*, using, in effect, Method C. This would be expected in such a system, where $K_1/K_2 > 10^{2.5}$.

This system is also represented by an incomplete formation curve ($0.85 < \bar{n} < 1.75$). Johnston and Freiser used Method C to obtain K_2 , but do not indicate how K_1 was calculated. From the value they obtained, it seems possible that equation (9) was used. This illustrates the misleading results which may be obtained when Method C is applied to a formation curve where $K_1 \cong K_2$. Values of \bar{n} calculated from stability constants given by the authors differ considerably from the experimental values. Not only are the deviations large, but there is an unmistakable trend in their magnitude. On recalculation by Method H, a

FIG. 2. *Formation curves.*

satisfactory fit is obtained with $\log K_1 = 13.05$ and $\log K_2 = 13.15$, values which differ considerably in magnitude from those calculated by the authors, who, moreover, report $\log K_1 > \log K_2$. It is significant that the revised value for the overall constant β_2 is in good agreement with that previously obtained; this emphasises that calculated values of K_1 and K_2 may together satisfy equation (9), although the individual constants may both be in error.

TABLE 8. Ni^{++} and "dien," in water at 30° ($K_1/K_2 \sim 10^{2.7}$) (Jonassen *et al.*, *loc. cit.*).

pL	11.10	11.05	10.97	10.68	10.51	10.39
$\bar{n}_{\text{expt.}}$	0.376	0.406	0.443	0.582	0.639	0.689
$\Delta\bar{n}$ (Jonassen)	-0.015	-0.018	-0.011	+0.016	+0.051	+0.055
$\Delta\bar{n}$ (Method H)	-0.023	-0.033	-0.025	+0.002	+0.038	+0.047
pL	8.55	8.32	8.16	8.09	7.93	7.78
$\bar{n}_{\text{expt.}}$	1.295	1.399	1.502	1.532	1.604	1.679
$\Delta\bar{n}$ (Jonassen)	-0.019	-0.003	-0.015	-0.004	+0.014	+0.015
$\Delta\bar{n}$ (Method H)	-0.019	-0.003	-0.014	-0.004	+0.015	+0.018
			$\log K_1$	$\log K_2$	$\log \beta_2$	σ
Jonassen <i>et al.</i>			10.85	8.14	18.99	± 0.025
Method H			10.82	8.14	18.96	± 0.024

TABLE 9. Cu^{++} and oxine in 50% aqueous dioxan ($K_1/K_2 \sim 1$) (Johnston and Freiser, *J. Amer. Chem. Soc.*, 1952, **74**, 5340).

pL	13.18	13.16	13.07	13.05	12.89	12.74	12.72	12.50
$\bar{n}_{\text{expt.}}$	0.84	0.90	1.05	1.11	1.33	1.48	1.55	1.75
$\Delta\bar{n}$ (J. and F.)	+0.087	+0.048	-0.037	-0.048	-0.103	-0.109	-0.16	-0.180
$\Delta\bar{n}$ (Method H)	+0.035	+0.008	0.000	-0.014	+0.035	-0.013	-0.020	-0.018
			$\log K_1$	$\log K_2$	$\log \beta_2$	σ		
Johnston and Freiser			13.49 (calc.)	12.73	26.22	± 0.108		
Method H			13.05	13.15	26.20	± 0.021		

In view of the real possibilities of authors' failing to obtain the most satisfactory constants from their experimental data through unsatisfactory methods of computation, it is clearly desirable to state precisely the method of calculation adopted, so that even in the absence of experimental values for \bar{n} and pL it would be possible to assess the reliability

of the values given and even to estimate with the aid of Fig. 1 or Table 2 the order of magnitude of the correction which must be applied.

Systems of Higher Complexity.—There are no simple methods of calculating stability constants in systems where $N \gg 3$. If all the successive constants differ greatly in magnitude the formation curve has N distinct steps (cf. Fig. 2*a* for the case where $N = 3$) and Method C can be used. When $N = 3$ and $K_1 \sim K_2 \gg K_3$, the formation curve will show only two steps, corresponding to $0 < \bar{n} < 2$, and $2 < \bar{n} < 3$ (Fig. 2*b*). Here $\log K_3 = pL_{2\frac{1}{2}}$ (Method C) and K_1 and K_2 may be calculated by treating the lower step as a complete formation curve of a system where $N = 2$, using one of the appropriate methods described above. Fig. 2*b* represents a formation curve where $K_1 \gg K_2 \cong K_3$, which can again be treated as if it consisted of two separate portions. When the successive complexes are of similar stability the curve loses its wave-like character (Fig. 2*c*) and a set of trial constants [obtained appropriately from equation (5)] must be refined by successive approximation by using the following equation

$$\log K_{\bar{n}} = pL_{\bar{n}} + \log \left\{ \frac{t=0 \sum_{t=0}^{t=\bar{n}-1} (\bar{n}-t) \beta_t [L]^t}{t=\bar{n} \sum_{t=\bar{n}}^N \frac{(t-\bar{n}) \beta_t [L]^{t-1}}{K_n}} \right\} \quad (16)$$

The general equation (1) for a formation curve may be written in the form

$$\sum_{n=0}^{n=N} \frac{(\bar{n}-n)}{(\bar{n}-1)} \cdot [L]^{n-1} \beta_n = 0 \quad \dots \quad (17)$$

of which equation (15) is a particular case for $N = 2$. If there are m experimental values for the points (\bar{n}, pL) , substitution in (17) will give m inhomogeneous linear equations in $\beta_1, \beta_2 \dots \beta_N$. The normal equations obtained therefrom by the usual methods form a set of N simultaneous linear equations which can be solved for $\beta_1, \beta_2 \dots \beta_N$ by matrix or other methods.

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