

Graphical Methods for Determining Equilibrium Constants

I. Systems of Mononuclear Complexes

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A new graphical method for computing successive stability constants from experimental values of the degree of formation of the system is described. The method is particularly useful for systems in which more than two complexes coexist. Other methods of calculating stability constants are reviewed critically. The stability constants of the cadmium cyanide system are calculated from Leden's experimental data by a number of the methods, and the advantages of the present treatment over existing methods are discussed.

Numerous experimental studies of equilibria in solution have been made in the last fifteen years, and some of the methods used to calculate the stability constants have been reviewed recently by Sullivan and Hindman¹. A new method of calculating these constants is outlined in this paper, and its relationship to existing methods is described.

The overall, stoichiometric stability constant of the mononuclear species, ML_n , ($0 \leq n \leq N$) formed from a central group, M, and n ligands, L, is defined by

$$\beta_n = [ML_n]/[M][L]^n \quad (1)$$

where charges are omitted for clarity. The total, analytical concentrations of the central group, C_M , and of the ligand, C_L are given by

$$C_M = \sum_{n=0}^{n=N} \beta_n [M] [L]^n \quad (2)$$

and

$$C_L = [L] + \sum_{n=1}^{n=N} n\beta_n [M] [L]^n \quad (3)$$

The degree of formation of the system, or ligand number, \bar{n} , may be defined as the average number of ligands combined with each central group². Thus

$$\bar{n} = (C_L - [L])/C_M \quad (4)$$

The degree of formation of a given complex, ML_c , is given by

$$\alpha_c = [ML_c]/C_M \quad (5)$$

Then it follows³ that

$$\bar{n} = \sum_{n=1}^{n=N} n\beta_n [\text{L}]^n / \sum_{n=0}^{n=N} \beta_n [\text{L}]^n \quad (6)$$

or

$$\sum_{n=0}^{n=N} (\bar{n}-n)\beta_n [\text{L}]^n = 0 \quad (6a)$$

and

$$\alpha_c = \beta_c [\text{L}]^c / \sum_{n=0}^{n=N} \beta_n [\text{L}]^n \quad (7)$$

Whence

$$\frac{d \log \alpha_c}{d \log [\text{L}]} = (\bar{n}-c) \quad (8)$$

If the activity coefficients of all species are held constant, (*e. g.* by the use of a salt background, in which gross changes in the composition of the ionic medium are avoided, *cf.* Ref.⁴), the terms β_n refer to stoichiometric stability constants. In any experiment, the total concentrations, C_M and C_L , of metal and ligand will be known and, in principle, the determination of at least N values of the concentration of one of the species is sufficient for the computation of the stability constants. Methods for obtaining values of the stability constants from sets of data $[\text{M}]$, $[\text{L}]$; α_c , $[\text{L}]$; and \bar{n} , $[\text{L}]$ are discussed below.

In order to test for the possible presence of polynuclear complexes, measurements should be obtained at a number of values of C_M . If \bar{n} or α_c is a function of both $[\text{L}]$ and C_M , at least one polynuclear complex, M_pL_q ($p > 1$), is present, and the stability constants cannot be obtained by the methods described in this paper, unless the data can be extrapolated to low concentrations of metal at which polynuclear species can be neglected^{5,6}. Other methods for computing stability constants of mononuclear complexes from data obtained in the presence of polynuclear complexes are treated elsewhere^{7,8}. If no polynuclear complexes are formed, \bar{n} and α_c are functions of $[\text{L}]$ only, and are independent of C_M (*cf.* equations 6 and 7). In this case, the values of the stability constants β_n , may conveniently be calculated from the data \bar{n} , $[\text{L}]$ as follows.

PROPOSED GRAPHICAL TREATMENT OF THE DATA \bar{n} , $[\text{L}]$

As C_M and C_L are known, the value of \bar{n} can be calculated from equation (4) if the concentration of free ligand, $[\text{L}]$, is measured experimentally. Rearrangement of equation (6a) gives

$$\frac{\bar{n}}{(1-\bar{n})[\text{L}]} = \beta_1 + \beta_2 \frac{2-\bar{n}}{1-\bar{n}} [\text{L}] + \sum_{n=3}^{n=N} \frac{n-\bar{n}}{1-\bar{n}} \beta_n [\text{L}]^{n-1} \quad (9a)$$

Thus the plot of $\bar{n}/(1-\bar{n})[\text{L}]$ against $(2-\bar{n})[\text{L}]/(1-\bar{n})$ tends to a straight line of intercept β_1 and of slope β_2 , as $[\text{L}] \rightarrow 0$. An accurate value of any constant, β_i , may be obtained by using a generalisation of equation (9a). Dividing equation (6a) by $(t-\bar{n})[\text{L}]$ (where $0 < t < N$), and rearranging

$$\sum_{n=0}^{n=t-1} \left(\frac{\bar{n}-n}{t-\bar{n}} \right) \beta_n [\text{L}]^{n-t} = \beta_t + \sum_{n=t+1}^{n=N} \left(\frac{n-\bar{n}}{t-\bar{n}} \right) \beta_n [\text{L}]^{n-t} \quad (9)$$

If values of $\beta_1, \beta_2, \dots, \beta_{t-1}$, have previously been calculated, the left-hand side of equation (9) is known. A plot of this term against $(t+1-\bar{n})[\text{L}]/(t-\bar{n})$ then gives β_t as the intercept (and an approximate value of β_{t+1} as the limiting slope as $[\text{L}] \rightarrow 0$).

When $t = N-1$, equation (9) becomes

$$\sum_{n=0}^{n=N-2} \left(\frac{\bar{n}-n}{N-1-\bar{n}} \right) \beta_n [L]^{n-N+1} = \beta_{N-1} + \beta_N \left(\frac{n-\bar{n}}{N-1-\bar{n}} \right) [L] \quad (9b)$$

so that a plot of the left-hand side of equation (9b) against $(n-\bar{n})[L]/(N-1-\bar{n})$ will be a straight line of intercept β_{N-1} and of slope β_N . Now any errors in the values of $\beta_1 \dots \beta_{t-1}$ will accumulate in the value of β_t . An alternative rearrangement of equation (6a) gives

$$\begin{aligned} \left(\frac{N-\bar{n}}{N-1-\bar{n}} \right) [L] &= \frac{\beta_{N-1}}{\beta_N} + \frac{\beta_{N-2}}{\beta_N} \left(\frac{\bar{n}-N+2}{N-1-\bar{n}} \right) [L]^{-1} \\ &+ \sum_{n=0}^{n=N-3} \left(\frac{\bar{n}-n}{N-1-\bar{n}} \right) \frac{\beta_n}{\beta_N} [L]^{n-N+1} \end{aligned} \quad (10)$$

Thus the plot of $(N-\bar{n})[L]/(N-1-\bar{n})$ against $(\bar{n}-N+2)/(N-1-\bar{n})[L]$ will have an intercept of β_{N-1}/β_N , and a limiting slope of β_{N-2}/β_N , as $[L]^{-1} \rightarrow 0$. All the ratios β_i/β_N (where $\beta_0/\beta_N = 1/\beta_N$) may be found in an analogous way, and equation (10) may be used to check the values of the stability constants obtained from equation (9).

The application of this method to the determination of the stability constants of the cadmium cyanide system, and its advantages over other methods, are discussed below. (See p. 1174 and Figs. 1a, 1b and 1c).

Special cases of the present treatment

(a) Only one complex formed.

If $N = 1$, equation (9) reduces to

$$\frac{\bar{n}}{1-\bar{n}} = \beta_1 [L] \quad (11)$$

$$\text{or} \quad \log \frac{\bar{n}}{1-\bar{n}} = \log \beta_1 + \log [L] \quad (11a)$$

Equation (11a) is familiar as Henderson's or Hasselbalch's equation^{10,11}, and has been widely used for the determination of the dissociation constants of monobasic acids. It is also useful for determining constants from \bar{n} , [L] data obtained over a very limited range, *e. g.* if very strong or very weak complexes are formed, or if precipitation occurs at low values of \bar{n} .

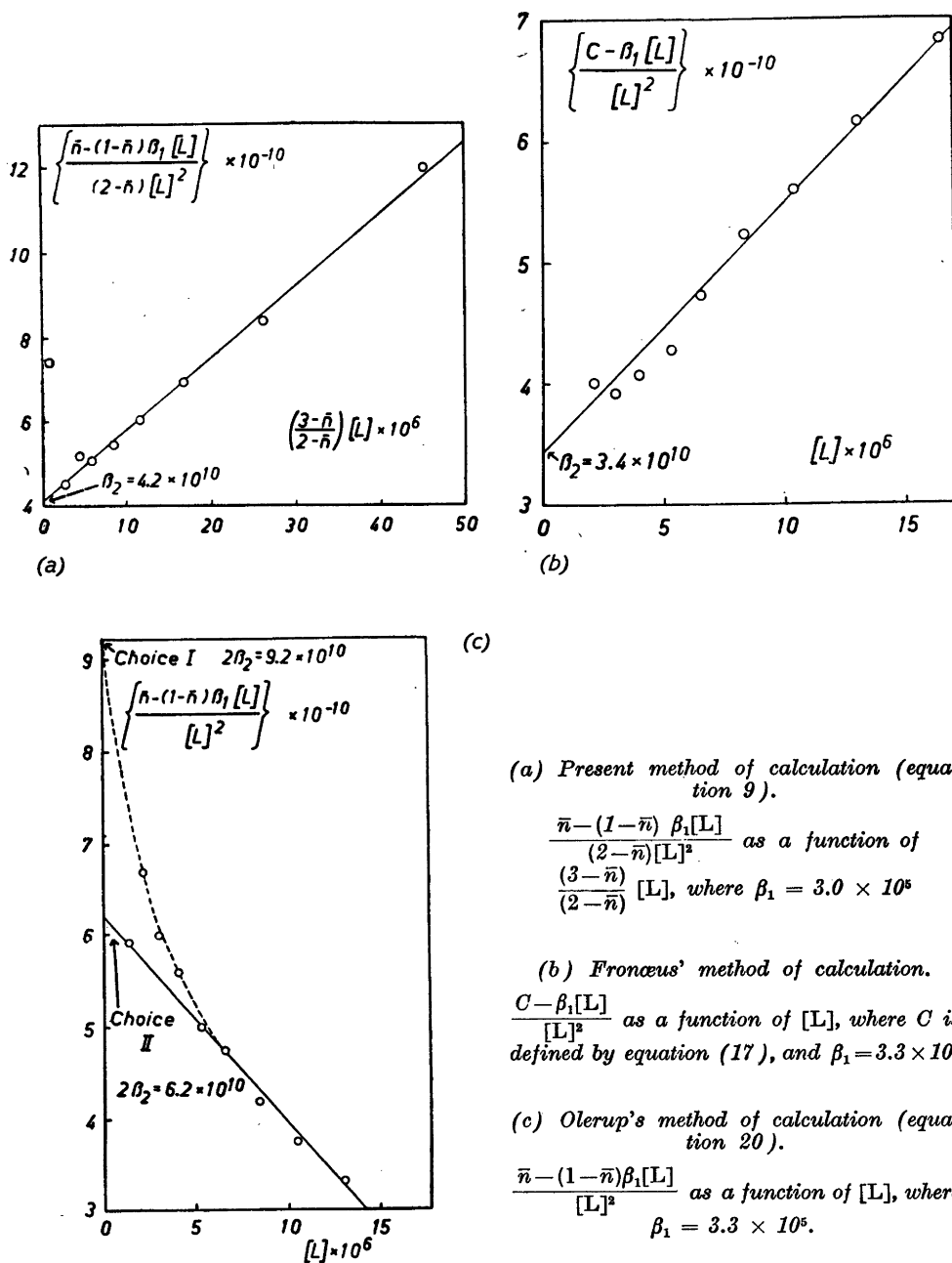
(b) Only two complexes formed.

When $N = 2$, $t = 1$, and equation (9) reduces to the linear form derived previously¹³

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_1 + \beta_2 \frac{(2-\bar{n})[L]}{(1-\bar{n})} \quad (12)$$

Alternative rearrangement gives an equation which is equivalent to that used earlier by Speakman¹⁴ for the determination of the dissociation constants of dibasic acids.

$$\frac{1}{\beta_2} + \frac{(\bar{n}-1)[L]}{\bar{n}} \frac{\beta_1}{\beta_2} = \frac{(2-\bar{n})[L]^2}{\bar{n}} \quad (12a)$$



(a) Present method of calculation (equation 9).

$$\frac{\bar{n} - (1 - \bar{n}) \beta_1 [L]}{(2 - \bar{n}) [L]^2}$$

as a function of $\frac{(3 - \bar{n})}{(2 - \bar{n})} [L]$, where $\beta_1 = 3.0 \times 10^5$

(b) Froncous' method of calculation.

$$\frac{C - \beta_1 [L]}{[L]^2}$$

as a function of $[L]$, where C is defined by equation (17), and $\beta_1 = 3.3 \times 10^5$

(c) Olerup's method of calculation (equation 20).

$$\frac{\bar{n} - (1 - \bar{n}) \beta_1 [L]}{[L]^2}$$

as a function of $[L]$, where $\beta_1 = 3.3 \times 10^5$.

Fig. 1. Determination of β_2 for the cadmium cyanide system by extrapolation to zero concentration of free cyanide ion.

OTHER GRAPHICAL METHODS FOR COMPUTING STABILITY CONSTANTS

A number of other authors have given methods for obtaining stability constants by extrapolation of certain functions to zero free ligand concentration. In each case, a polynomial in $[L]$ or $[L]^{-1}$, the coefficients of which are the required β_n , is set up using the experimental data. The graphical extrapolations reduce the polynomial to N linear equations. This general method has also been used to obtain specific rate constants for an exchange reaction⁹.

I. Data $[M]$, $[L]$

If the concentration of free metal, $[M]$, is determined, the value of $[L]$ may be obtained from the relationship

$$C_L \sim [L] \quad (13)$$

and by successive approximations^{3,16}. Alternatively, Hedström has shown⁷ that

$$\log \frac{[L]}{C_L} = \left[\int_0^{C_M} \left(\frac{\partial \log [M]/C_M}{\partial C_L} \right)_{C_M} dC_M \right]_{C_L} \quad (13a)$$

The data $[M]$, $[L]$ may be expressed as a simple polynomial in $[L]$, for which the coefficients are the stability constants. Thus Leden's function^{15,16}

$$A = (C_M - [M])/[M][L] = \beta_1 + \beta_2[L] \dots = \sum_{n=1}^{n=N} \beta_n [L]^{n-1} = \frac{g}{[L]} \quad (14a)$$

where g is the summation, $\sum_{n=1}^{n=N} \beta_n [L]^n$. The value of β_1 is obtained as the intercept of the plot of A against $[L]$. Similarly, the plot of $(A - \beta_1)/[L]$ against $[L]$ gives an intercept of β_2 . In general,

$$F_t = \frac{A - \sum_{n=1}^{n=t-1} \beta_n [L]^{n-1}}{[L]^{t-1}} = \beta_t + \sum_{n=t+1}^{n=N} \beta_n [L]^{n-t} \quad (14)$$

so that, if values of $\beta_1 \dots \beta_{t-1}$ have been calculated, the term F_t is known. β_t may then be obtained as the intercept of the plot of F_t against $[L]$.

Olerup¹⁷ defines a function

$$B = C_M/[M] = 1 + \beta_1 [L] \dots = \sum_{n=0}^{n=N} \beta_n [L]^n = 1 + g \quad (15)$$

Thus Olerup's method of obtaining β_1 as the intercept of the plot of $(B-1)/[L]$ against $[L]$ is identical to that of Leden.

If required, values of \bar{n} can be calculated from the data $[M]$, $[L]$ (see below), but Leden's treatment clearly provides a more direct method for computing stability constants from the experimental measurements.

II. Data $[ML_c]$, $[L]$

In cases where the concentration of one of the complexes, $[ML_c]$, is measured, values of $[L]$ may again have to be obtained by successive approximations. Values of α_c may be calculated using equation (5). The ligand number, \bar{n} , may

then be obtained as the slope of the curve $\log \alpha_c$, ($p[L]$) (see equation (8)), and used to calculate the stability constants by one of the methods described in this paper.

Alternatively, rearrangement of equation (7) gives

$$\frac{[L]^c}{\alpha_c} = \frac{1}{\beta_c} + \frac{\beta_1}{\beta_c} [L] \dots = \sum_{n=0}^{n=N} \frac{\beta_n}{\beta_c} [L]^n = \frac{1+g}{\beta_c} \quad (16)$$

so that the value of $1/\beta_c$ may be obtained as the intercept of the plot of $[L]^c/\alpha_c$ against $[L]$, and values of the ratios β_1/β_c , β_2/β_c may be obtained by successive extrapolations. A modified form of equation (16) has been used to compute stability constants from partition data¹⁸, from which the product of α_c and a partition coefficient is obtained. When the concentration of free metal is measured, $\alpha_c = \alpha_0$, and equation (16) reduces to (15).

III. Data, \bar{n} , $[L]$

When $[L]$ is measured, \bar{n} may be calculated directly from equation (4).

(a) *Fronæus' Method*. The value of the summation, g may be obtained from the experimental data by graphical integration. Thus, Fronæus' function, C , is given by^{5,6}

$$C = \exp. \int_0^{[L]} \frac{\bar{n}}{[L]} d[L] = \exp. \int_0^{[L]} \bar{n} d \ln [L] = \sum_{n=0}^{n=N} \beta_n [L]^n = 1 + g \quad (17)$$

The value of the residual integral may be estimated if it is assumed that only the first complex, ML , exists in appreciable concentrations at very low values of $[L]$. Then

$$\lim_{[L] \rightarrow 0} \int_0^{[L]} \frac{\bar{n}}{[L]} d [L] = \frac{1}{(1-\bar{n})} \quad (18)$$

As the function C is identical to that obtained by Olerup¹⁷ (B , equation (15)) from measurements of the concentration of free metal, values of the constants $\beta_1 \dots \beta_N$ may be obtained by successive extrapolation, as described above. The constants may also be calculated in an analogous way using the function

$$\frac{g}{[L]^N} = \beta_N + \beta_{N-1} [L]^{-1} \dots = \sum_{n=1}^{n=N} \beta_n [L]^{n-N} \quad (19)$$

which is a polynomial in $[L]^{-1}$. It is advisable to use equation (19) to check the values of the higher constants which, when calculated from equation (17) reflect any errors in the lower constants. Fronæus' method may also be used to calculate the concentration of free metal ions from measurements of the free ligand concentration, *cf.* eqns. (15) and (17).

(b) *Olerup's Method*. Equation (6a) may be rearranged^{17,19} to

$$D = \frac{\bar{n}}{[L]} = (1-\bar{n}) \beta_1 + (2-\bar{n}) \beta_2 [L] \dots = \sum_{n=1}^{n=N} (n-\bar{n}) \beta_n [L]^{n-1} \quad (20a)$$

and β_1 obtained from the intercept of the plot D , ($[L]$). Similarly, the term $2\beta_2$ may be obtained as the intercept of the plot of $D - (1 - \bar{n}) \beta_1/[L]$ against $[L]$. In general

$$F'_t = \frac{D - \sum_{n=1}^{n=t-1} (n - \bar{n}) \beta_n [L]^{n-1}}{[L]^{t-1}} \\ = (t - \bar{n}) \beta_t + \sum_{n=t+1}^{n=N} (n - \bar{n}) \beta_n [L]^{n-t} \quad (20)$$

If values of $\beta_1 \dots \beta_{t-1}$ have been calculated, the term F'_t is known, and $t \beta_t$ may, in principle, be found as the intercept of the plot F'_t , ($[L]$). Unfortunately, since the coefficient of the required β_t is a variable, $(t - \bar{n})$, the plots tend to be markedly curved, even at low values of $[L]$, and accurate extrapolation to zero free ligand concentration may be difficult (see Fig. 1c). The method has, however, been successfully used to determine the first one or two constants for systems in which weak complex formation occurs^{17,19,20}.

(c) *The present method.* The treatment described on p. 1167 has the advantage of avoiding the graphical integration which is necessary in Fronæus' method; thus no preliminary smoothing of the data is required. Compared with Olerup's method, the treatment has the further advantage that the coefficient of β_t is a constant (*cf.* equation (9)). The functions to be extrapolated are therefore much less curved, and more accurate values of the stability constants may be obtained. In common with other methods for calculating accurate values of stability constants, the present method is somewhat laborious, and requires a large number of experimental points, well spaced over the range $0 < \bar{n} < N$, and preferably of high precision.

OTHER METHODS FOR COMPUTING STABILITY CONSTANTS

It has been seen that polynomial equations in $[L]$, of the type (9), (14) and (20), can be solved for values of the stability constants by several closely-related limiting graphical methods, which reduce the polynomial to N linear functions. A number of other methods, which have also been used for computing stability constants, will be discussed.

(a) *Solution of simultaneous equations.* Some workers have obtained values of $\beta_1 \dots \beta_N$ by solving N simultaneous equations of the type (6a)^{18,21,27}. Ideally, if $m > N$ corresponding values of \bar{n} and $[L]$, or $[M]$ and $[L]$, were available, $m!/N!$ ($m - N$)! sets of equations should be solved in order to use all the data, and the computation would be very tedious. The equations would probably be inconsistent on account of experimental errors and equations formed from neighbouring points might be ill-conditioned. The problem of choosing the 'best' set of constants would then arise^{13,27}.

(b) *Successive approximations.* Stability constants are often obtained from equation (6a) by successive approximations. J. Bjerrum³ transformed (6a) to an equation of the type

$$\frac{\beta_t}{\beta_{t+1}} = \frac{1}{[L]_{\bar{n}=t-\frac{1}{2}}} \cdot \frac{\sum_{n=0}^{n=t-1} (1+2n) [L]^{-n} \beta_n^{-1}}{\sum_{n=0}^{n=N-t} (1+2n) [L]^n \beta_{n+t} \beta_t^{-1}} \quad (21)$$

or

$$\frac{\beta_t}{\beta_{t+1}} \sim \frac{1}{[L]_{\bar{n}=t-\frac{1}{2}}} \quad (21a)$$

where t is again an integer such that $0 < t < N$. Approximate values of the ratios β_i/β_{i+1} may be obtained from equation (21a), and refined by successive approximations, using equation (21). If two or more species in a system of complexes are of comparable stability, this method becomes very laborious (*cf.* Ref.²²). A further disadvantage is that only N sets of experimental data \bar{n} , $[L]$ are used. The use of simplifications of equations (21) and (21a) for the special case where $N = 2$ has been discussed elsewhere¹³.

Scatchard²³ has recently combined features of Bjerrum's treatment and of the extrapolation method in an attempt to reduce the number of successive approximations required. As $[L] \rightarrow 0$ or ∞ , the function

$$Q = \frac{\bar{n}}{(N - \bar{n}) [L]}$$

has limiting values of β_1/N and $N\beta_N/\beta_{N-1}$, respectively. Moreover, approximate values of the ratios β_2/β_1 , and β_{N-1}/β_{N-2} may be obtained from the limiting values of $d \ln Q / d \bar{n}$, as $\bar{n} \rightarrow 0$ and N . These values are then refined by successive approximations.

(c) *Curve-fitting.* Values of the stability constants may also be obtained by comparing experimental formation curves, \bar{n} , ($p[L]$), with curves calculated from equation (6), using different values of β_n . This approach, which will be discussed elsewhere by Sillén²⁴ is particularly useful for systems in which only one complex is formed ($N=1$) and the shape of the formation curve is unique. The value of β_1 is then obtained from the position of the curve on the $p[L]$ axis, using equation (11a). The method has previously been successfully applied to the determination of dissociation constants of organic acids²⁵.

If two complexes are formed, the position of the curve is determined by the value of β_2 , while the shape depends on the ratio β_1^2/β_2 . Accurate evaluation of stability constants for systems of this type would therefore require formation curves calculated for a large number of values of this ratio. The difficulty may be overcome by using a set of theoretical curves in which some property, P , of the formation curve (*e.g.* $P = d \bar{n} / d p[L]$ or $(\bar{n}_1 - \bar{n}_2) / (p[L]_1 - p[L]_2)$) is plotted against a function of β_1^2/β_2 for several values of \bar{n} , *cf.* Ref.¹³. Values of β_1^2/β_2 , corresponding to the experimental values of P , may then be obtained from the appropriate theoretical curves, and the mean taken. The value of β_1 is obtained by combining this value with the value of β_2 obtained from the position of the curve on the $p[L]$ axis.

On account of the very large number of curves that would be required, it is impracticable to obtain accurate values of the stability constants if more than two complexes are formed, unless the constants are very widely separated. Approximate values may, however, be calculated if certain assumptions are made about the term $R_n = \beta_n^2 / \beta_{n-1} \beta_{n+1}$. (Here R_n is the ratio K_n / K_{n+1} , where $K_n = [ML_n] / [ML_{n-1}][L]$). J. Bjerrum³ proposed a method assuming that the addition of ligands was statistical, *i. e.* that $R_n = f(n, N)$. Dyrssen and Sillén²⁶ assumed that R_n is a constant, and described systems in terms of two parameters

$$a = \frac{1}{N} \log \beta_N$$

$$\text{and } b = \log \beta_n - \frac{1}{2} \log \beta_{n-1} \beta_{n+1} = \frac{1}{2} (\log K_n - \log K_{n+1})$$

The value of b may be obtained by comparing the shape of the experimental $\log \alpha_c$, ($p[L]$) curve with theoretical curves calculated for given values of b , and that of a found from the position of the curve on the $p[L]$ axis. This method is particularly useful for obtaining approximate constants from partition equilibria, for which data of the highest accuracy cannot be obtained, but the treatment is only exact if not more than two complexes are formed. Further examples of this type of approach will be discussed elsewhere²⁸.

CALCULATION OF THE STABILITY CONSTANTS FOR THE CADMIUM CYANIDE SYSTEM

As an illustration of the present method, and of some of the methods reviewed above, stability constants were calculated from Leden's data for the cadmium cyanide system¹⁶. Leden measured the concentration of free cadmium, and calculated values of \bar{n} by means of equation (8). The stability constants obtained are given in Table 1.

Table 1. Stability constants of the cadmium cyanide system in a 3 M sodium perchlorate medium at 25° C.

Data	Method	$10^{-5}\beta_1$	$10^{-10}\beta_2$	$10^{-15}\beta_3$	$10^{-18}\beta_4$	Ref.
[M], [L]	Leden	3.0	4.0	1.6	6.0	Leden ¹⁶
	Dyrssen & Sillén	~3.2	~3.2	~1.0	~10	This work
\bar{n} , [L]	Bjerrum	3.5	4.0	1.8	7.0	Leden ¹⁶
	Olerup: choice I	3.3	4.6	1.1	40	This work
	" II		3.1	2.7	1.3	" "
	Fronæus	3.3	3.4	1.8	5.8	" "
	Present method	3.0	4.2	1.5	5.7	" "

Some examples of the graphical extrapolations are shown in Fig. 1. The present method (Fig. 1a) and that of Fronæus (Fig. 1b) give good linear extrapolations, but the curved function (Fig. 1c) given by Olerup's method was so difficult to extrapolate that two possible values of β_2 are given. Moreover, the extrapolation of F'_2 (equation (20)), following choice II throws most weight on points in the region $\bar{n} < 1.9$. Similarly, the value of β_4 , following choice I, is obtained mainly from data corresponding to $\bar{n} < 2.24$. It appears to be necessary to select arbitrarily suitable ranges of values of \bar{n} for each extrapolation in order to use Olerup's method effectively, *cf.* Ref.²⁰.

The validity of the sets of constants calculated by the different methods was tested by substitution of these values into equation (6). Values of \bar{n}_{calc} corresponding to given values of [L] were then calculated and compared with the appropriate experimental values, \bar{n}_{expt} . Representative values of

$$\Delta\bar{n} = \bar{n}_{\text{expt}} - \bar{n}_{\text{calc}}$$

are given in Table 2.

Table 2. Comparison of experimental and calculated formation functions for the cadmium cyanide system.

	p[L]	5.857	5.519	5.077	4.782	4.265	3.907	3.248
	\bar{n}_{expt}	0.393	0.778	1.52	2.06	2.75	3.08	3.68
Method					Δn			
Leden ^a		-0.003	-0.009	0.01	0.00	0.03	0.06	-0.04
Dyrssen & Sillén		0.014	0.064	0.13	0.12	-0.13	-0.29	-0.15
Olerup, choice I		0.023	0.016	0.00	0.007	0.51	0.62	0.26
II		0.001	-0.017	0.06	0.12	0.04	-0.11	-0.49
Fronæus		0.002	-0.026	-0.07	0.00	0.05	0.06	-0.06
Present method		0.000	-0.004	0.00	-0.04	0.00	0.04	-0.02

^a The value of Δn has been calculated from Leden's preferred set of constants, obtained by combination of the values calculated by Leden's and Bjerrum's methods, and given in Table 1.

It is seen that the present method, and those of Leden and Fronæus, yield values of the stability constants in very good agreement with the experimental data. Much larger discrepancies are found with Olerup's method, doubtless on account of the difficulty in extrapolation. The constants obtained by means of Dyrssen and Sillén's 'two parameter' method cannot be expected to agree well with the experimental data, as the ratio K_n/K_{n+1} is not a constant for the cadmium cyanide system, although $K_1/K_2 \sim K_2/K_3$.

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