792. *Observations on the Computation of Stability Constants by Olerup's Graphical Procedure.*

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Many methods have been proposed for calculating values of the formation constants K_1 and K_2 of the species ML and ML_2 present in mixtures of metal complexes ML_j ($j = 0$—N) from data relating the degree of formation, $\bar{n}$, to the free-ligand concentration [L]. It is now pointed out that the method which depends on the (extrapolated) initial slope and intercept of a graph of $\bar{n}/[L]$ against [L] must be used with discretion since $\bar{n}/[L]$ is not necessarily a strictly monotonic and decreasing function of [L]. The condition for one or more extrema in such plots, and their significance in diagnosing abnormalities in the relative magnitudes of successive stability constants, are discussed and illustrated by examples for systems in which the maximum co-ordination number $N = 2$, 3, and 4.

AMONG the many methods proposed for computing values of successive stability constants of metal complexes (defined by $\beta_n = [ML_n]/[M][L]^n$) from experimental data relating the degree of formation, $\bar{n}$, to the corresponding concentration, [L], of uncomplexed ligand L,[1,2] that originally suggested by Olerup [3] and later independently by Fomin and Maiorova [4] has often been commended [5] and used.[6] In this procedure the quotient $\bar{n}/[L]$ is plotted against [L] and the graph is extrapolated to [L] $= 0$. Since the variables are related by eqn. (1)

$$f([L]) = \bar{n}/[L] = \frac{\beta_1 + 2\beta_2[L] + 3\beta_3[L]^2 + \ldots}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \ldots}$$

$$= \sum_{j=1}^{N} (j\beta_j[L]^{j-1}) \Big/ \sum_{j=1}^{N} (1 + \beta_j[L]^j) \qquad (1)$$

we have $\lim_{[L]\to 0} (\bar{n}/[L]) = \beta_1$, and $\lim_{[L]\to 0} \partial(\bar{n}/[L])/\partial[L] = 2\beta_2 - \beta_1^2$, so that the intercept gives a value for β_1 directly and the slope a value for β_2.

Equation (1) can be rewritten in the equivalent form:

$$\bar{n}/[L] = \beta_1 + 2\beta_2[L] + \ldots + N\beta_N[L]^{N-1}$$
$$-\bar{n}(\beta_1 + \beta_2[L] + \ldots + \beta_N[L]^{N-1}); \qquad (1a)$$

and Olerup (ref. 3, pp. 10, 79) actually preferred to plot $\bar{n}/[L]$ against $\bar{n}$ and to obtain β_1 as the interpcept when $\bar{n} = 0$. Such graphs are less strongly curved than those of $\bar{n}/[L]$ against [L] and more suitable for linear extrapolation. Since $\partial(\bar{n}/[L])/\partial\bar{n} = \partial(\bar{n}/[L])/\partial[L] \div \partial\bar{n}/\partial[L]$, and $\partial\bar{n}/\partial[L]$ must always be positive, it follows that the conditions for extrema in graphs of $\bar{n}/[L]$ against [L], discussed later in this paper, apply equally to plots of $\bar{n}/[L]$ against $\bar{n}$.

All published graphs show $\bar{n}/[L]$ as a monotonic and decreasing function of [L] (cf. Fig. 1, curve *a*) and no one appears hitherto to have considered the possibility of any different behaviour. However, when data for the system ferrous iron–1,10-phenanthroline [7] were plotted in this way the graph showed a pronounced maximum and values of $\bar{n}/[L]$ decreased

[1] Sullivan and Hindman, *J. Amer. Chem. Soc.*, 1952, **74**, 6091; Rossotti and Rossotti, *Acta Chem. Scand.*, 1955, **9**, 1166; " The Determination of Stability Constants," McGraw-Hill Book Co. Inc., New York, 1961, and refs. therein; Sullivan, Rydberg, and Miller, *Acta Chem. Scand.*, 1959, **13**, 2023, and refs. therein.
[2] Irving and Rossotti, *J.*, 1953, 3397.
[3] Olerup, Thesis, " Järnkloridernas komplexitet," Lindstedts Universitets-Bokhandel, Lund, 1944.
[4] Fomin and Maiorova, *Zhur. neorg. Khim.*, 1956, **1**, 1703.
[5] Hearon and Gilbert, *J. Amer. Chem. Soc.*, 1955, **77**, 2594.
[6] Choppin and Chopoorian, *J. Inorg. Nuclear Chem.*, 1961, **22**, 97.
[7] Irving and Mellor, *J.*, 1962, in the press.

as [L] approached zero (cf. Fig. 3). Similar behaviour characterised data for the system ferrous iron–2,2'-bipyridyl; but no such anomalies occurred on plotting data for complexes of any of the other bivalent transition metals with either of these ligands.[7] Plots of data for certain other systems reported in the literature provide additional examples of this anomaly (Fig. 1, curves b and c).

Consideration of the properties of f([L]) shows that this behaviour should have been anticipated and that the " anomalous " behaviour may be of diagnostic value in revealing the relative magnitudes of successive stability constants. Since the limiting value of $\bar{n}$ is N, the maximum effective co-ordination number (Bjerrum's characteristic co-ordination number [8]), it follows from eqn. (1) that the graph of $\bar{n}/[L]$ against [L] must approach the [L] axis asymptotically from above as [L] $\longrightarrow \infty$. Likewise, from the expansion of $\bar{n}/[L]$ as a polynomial in [L],

$$\bar{n}/[L] = \beta_1 + (2\beta_2 - \beta_1{}^2)[L] + (3\beta_3 - 3\beta_1\beta_2 + \beta_1{}^3)[L]^2 + \ldots, \qquad (2)$$

it is clear that the graph must start from the initial intercept of β_1 when [L] = 0 and possess an initial slope of $(2\beta_2 - \beta_1{}^2)$.

If $2\beta_2 > \beta_1{}^2$, this initial slope will be positive and the graph of f(L) must pass through a maximum. Since $\beta_n = K_1 K_2 \ldots K_n$ (where $K_n = [ML_n]/[ML_{n-1}][L]$), this condition is equivalent to $2K_2 > K_1$ or $\log K_2 + 0.3 > \log K_1$. Whenever $2K_2 > K_1$ a maximum must occur, irrespective of the value of N. There may, however, be any odd number of extrema
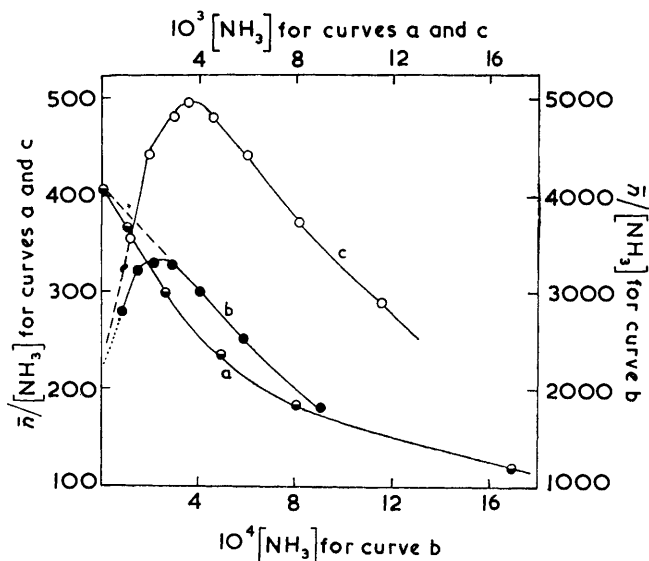

FIG. 1. Plots of ($\bar{n}/[NH_3]$) against [NH$_3$] for complexes of ammonia with (a) cadmium, (b) silver, and (c) zinc. Data from Bjerrum (ref. 9).

consistent with the effective degree of the numerator of the derived function $\partial(\bar{n}[L])/\partial[L]$. Conversely, if $2K_2 < K_1$, the initial and the final slope of the graph of f(L) will both be negative: there may now be either no extremum or an even number of extrema consistent with the degree of the derived function. Particular cases will now be discussed.

The Case where $N = 2$.—By differentiation of eqn. (1) and by setting $\partial(\bar{n}/[L])/\partial[L] = 0$ we arrive at the following condition for an extremum:

$$(2\beta_2 - \beta_1{}^2) - 2\beta_1\beta_2[L] - 2\beta_2{}^2[L]^2 = 0$$

whence $\qquad\qquad [L]_* = \{-\beta_1 + \sqrt{(4\beta_2 - \beta_1{}^2)}\}/2\beta_2. \qquad (3)$

[8] Bjerrum, *Chem. Rev.*, 1950, **46**, 381.

The subscript asterisk is used here and subsequently to distinguish a value of one of the parameters at an extremum. Clearly, no extremum can occur unless $-\beta_1 + \sqrt{(4\beta_2 - \beta_1{}^2)}$ is positive, *i.e.*, unless $2\beta_2 > \beta_1{}^2$. As a general rule, successive stability constants decrease regularly in the sense $K_1 > K_2 > K_3 \ldots$ and the difference between $\log K_n$ and $\log K_{n+1}$ is often quite large. A classical example of an exception to this generalisation is provided by Bjerrum's measurements with silver ammines.[9] His data for the system Ag^+-NH_3 at $30°$ in 2M-ammonium nitrate are plotted in Fig. 1 (curve b). The maximum is clearly visible. Extrapolation of a line through the last two points (Fig. 1, dotted line) yields the value $\log K_1 = 3.40$ from the intercept, and the value $\log K_2 = 3.43$ can be computed from the measured slope of 7.26×10^6. The best values computable by making use of all the data for this system in a weighted least-squares treatment (Sullivan *et al.*[2]) are $\log K_1 = 3.181 \pm 0.008$ and $\log K_2 = 3.848 \pm 0.008$. Had one been influenced by the common experience and expectation that $\bar{n}/[L]$ increases monotonically as $[L]$ approaches zero it is not inconceivable that an inexperienced worker might have rejected at least two of the three lowest points on the grounds that they were especially liable to experimental error. The erroneous extrapolation (Fig. 1, curve b, broken line) would then have led to the values $\log K_1 = 3.61$ from the intercept and $\log K_2 = 3.24$ from the measured slope of -2.71×10^6, values which are seriously in error absolutely and indicate the wrong relative magnitudes of K_1 and K_2.

Although a value for β_2 can be calculated from the limiting slope of the graph of $\bar{n}/[L]$ against $[L]$ (or $\bar{n}$) as mentioned above, it is preferable and usual to obtain this by the graphical extrapolation of a new function. Olerup's procedure [3] differs from that of Fomin and Maiorova [4] at this point. Olerup plots the function

$$N_2(\bar{n}) = \{(\bar{n}/[L]) - \beta_1(1 - \bar{n})\}/[L]$$
$$= (2\beta_2 + \ldots + N\beta_N[L]^{N-2})$$
$$- \bar{n}(\beta_2 + \ldots + \beta_N[L]^{N-2})$$

against $\bar{n}$, and obtains $2\beta_2$ as the intercept when $\bar{n} = 0$. An obvious discrepancy between the value of β_2 obtained in this way and the value obtained previously through eqn. (1) ought certainly to indicate a systematic error. It must, however, be emphasised that both in Olerup's method [3] and in that of Fomin and Maiorova [4] (who extrapolate the graph of the function $\{(\bar{n}/[L]) - \beta_1\}/[L]$ against $[L]$ to obtain $(2\beta_2 - \beta_1{}^2)$ as the intercept when $[L] = 0$), any error in β_1 will seriously affect the calculated value of β_2.

The position of the maximum in the graph of $f(L)$ (or more conveniently in the graph of $\bar{n}/[L]$ against pL, *i.e.*, $-\log_{10} [L]$) can in principle be used to calculate values of the relevant stability constants. Thus, from eqns. (1) and (3) we have

$$\bar{n}_* = 1 - \beta_1(4\beta_2 - \beta_1{}^2)^{-\frac{1}{2}}, \tag{4}$$

whence
$$K_1/K_2 = \beta_1{}^2/\beta_2 = 4(1 - \bar{n}_*)^2/[1 + (1 - \bar{n}_*)^2]. \tag{5}$$

From a large-scale plot of Bjerrum's data for $\bar{n}/[NH_3]$ against $p[NH_3]$ we find $\bar{n}_*/[NH_3]_* = 3.32 \times 10^3$ and $p[NH_3]_* = 3.65$, whence $\bar{n}_* = 0.74_3$ and $[NH_3]_* = 2.24 \times 10^{-4}$. By substituting this value of $\bar{n}_*$ in eqn. (5) we obtain $K_1/K_2 = 0.22_9$, thus confirming that this is an " abnormal " system. By substituting the value of this ratio and the corresponding value for $[L]_*$ into eqn. (3) in its equivalent form

$$K_2 = \{-1 + \sqrt{(4K_2/K_1) - 1}\}/2[L]_*, \tag{3a}$$

we obtain $\log K_2 = 3.84$, whence $\log K_1 = 3.19$, values in excellent agreement with those calculated by making the fullest use of all the experimental data.[1,2]

Whenever $K_n \leqslant K_{n+1}$ the species ML_n forms only a small fraction of the equilibrium

[9] Bjerrum, " Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

mixture of step-complexes even when [L] has its optimum value. Wormser [10] has pointed out that it may be difficult to distinguish between the case where $K_n \leqslant K_{n+1}$ and where $K_n = \beta_n = 0$ (*i.e.*, when the species ML_n does not exist) unless accurate data are available. Indeed, had Bjerrum's measurements for the system Ag^+–NH_3 been only slightly less precise it would have been possible to interpret his results by assuming that $\log \beta_2 = 7 \cdot 03$ and that $K_1 = 0$ (cf. Fig. 5–18 of Rossotti and Rossotti's book [1]). Unfortunately the form of the graph of $\bar{n}/[L]$ against [L] fails to establish immediately whether or not the species ML exists in equilibrium with M and ML_2, for it follows from eqn. (3) that it will still have an extremum: the condition $\beta_1 = 0$ is only a special case of the general condition $2\beta_2 > \beta_1^2$ (see above). On the other hand, it is easily shown that the maximum will occur when

$$\log \beta_2 = 2pL_*, \text{ and } \bar{n}_* = 1. \tag{6}$$

Since graphically we are able to demonstrate that the maximum in the plot of Bjerrum's data occurs at $\bar{n}_* = 0 \cdot 74_3$ (Fig. 1) the existence of the species $Ag(NH_3)^+$ in the equilibrium mixture is established beyond doubt.
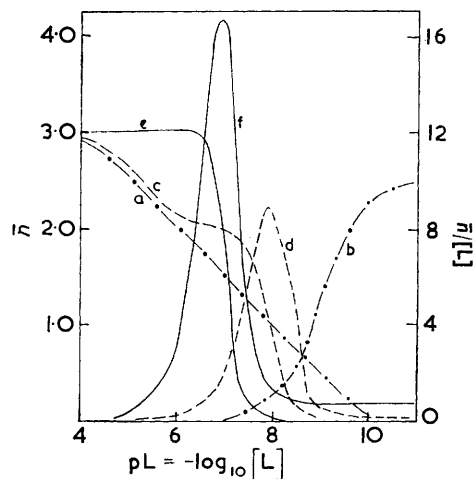
Fig. 2. Systems for which $\log \beta_3 = 21 \cdot 14$ in each case, but for which (i) $K_1 = 10^9$, $K_2 = 10^7$, $K_3 = 10^{5 \cdot 13}$ (curves a and b), (ii) $K_1 = 10^{5 \cdot 86}$, $K_2 = 10^{10 \cdot 03}$, $K_3 = 10^{5 \cdot 25}$ (curves c and d); and (iii) $K_1 = 10^{5 \cdot 86}$, $K_2 = 10^{5 \cdot 25}$, $K_3 = 10^{10 \cdot 03}$ (curves e and f).

The left-hand ordinate refers to the formation curves a, c, and e. On the right-hand side the ordinate must be multiplied by the factors 10^{-8}, 10^{-7}, and 10^{-6} for curves b, d, and f, respectively.

The Case where $N = 3$.—By differentiation of eqn. (1) the condition for an extremum can be shown to be

$$(2\beta_2 - \beta_1^2) + 2(3\beta_3 - \beta_1\beta_2)[L]_* - 2\beta_2^2[L]_*^2 - 4\beta_2\beta_3[L]_*^3 - 3\beta_3^2[L]_*^4 = 0. \tag{7}$$

Three possibilities now present themselves. (i) If $K_1 > 2K_2$, and $K_1 > 3K_3$ (*i.e.*, provided $\beta_1^2 > 2\beta_2$, and $\beta_1\beta_2 > 3\beta_3$) there can be no extremum and f(L) will be strictly monotonic and decreasing. (ii) If $K_1 < 2K_2$ there can be an odd number of extrema. Since, however, the numerator of the derivative $\partial(\bar{n}/[L])/\partial[L]$ is effectively of the fourth degree [cf. eqn. (7)], the application of Descartes's rule of signs shows that there can never be more than two real positive roots. Thus one extremum, a maximum, can occur when $K_1 < 2K_2$, irrespective of the relative values of K_1 and K_3. (iii) If $3K_3 > K_1 > 2K_2$ (*i.e.*, $3\beta_3 - \beta_1\beta_2$ is positive whereas $2\beta_2 - \beta_1^2$ is negative) there may be two extrema or none. Descartes' rule of signs does not provide a definitive answer in this case.

An example of the first possibility is illustrated in Fig. 2 for a (hypothetical) system in which $\log K_1 = 9 \cdot 0$, $\log K_2 = 7 \cdot 0$, and $\log K_3 = 5 \cdot 14$ (so that $\log \beta_2 = 16$ and $\log \beta_3 = 21 \cdot 14$). The formation curve (the plot of $\bar{n}$ against pL) shown in Fig. 2, curve a, is characteristic of a mixture of complexes with similar stability constants, and it lacks the wave-like character shown when $\log K_n/K_{n+1} \geqslant 4$. The function $\bar{n}/[L]$ for this

[10] Wormser, *Bull. Soc. chim. France*, 1954, 387.

system (not reproduced) increases monotonically as [L] decreases (or pL increases) and approaches the limiting value of $n/[L] \longrightarrow \beta_1 = 10^9$. Curve b of Fig. 2 shows the plot of $10^8 \bar{n}/[L]$ against pL for this system.

The second possibility is illustrated in Fig. 2 for a (hypothetical) system of the same overall stability in which $\log K_1 = 5{\cdot}86$, $\log K_2 = 10{\cdot}03$, and $\log K_3 = 5{\cdot}25$ (so that $\log \beta_2 = 15{\cdot}89$, and $\log \beta_3 = 21{\cdot}14$, as before). The formation curve (Fig. 2, curve c) now starts with a very steep portion (characteristic of systems in which $K_1 \leqslant K_2$) and the clear " step " at $\bar{n} = 2$ marks the gradual formation of the weaker complex ML_3. The plot of $\bar{n}/[L]$ against pL (curve d of Fig. 2) or against [L] (not reproduced) shows the predicted maximum. As the free-ligand concentration decreases below the value $pL_* = 7{\cdot}95$ at $n_* = 0{\cdot}9896$, the function $\bar{n}/[L]$ certainly decreases towards the limiting value of $\beta_1 = 10^{5{\cdot}86}$, as predicted by eqn. (2). However, any attempt to obtain a reliable value for β_1 by graphical extrapolation will fail. By calculation it can be shown that $\bar{n}$ $0{\cdot}1316$ when $pL = 8{\cdot}521$, and that $\bar{n} = 0{\cdot}0161$ when $pL = 9{\cdot}00$. Although it would be impossible to obtain reliable experimental values of $\bar{n}$ as low as or lower than this, a graph of $\bar{n}/[L]$ against [L] was drawn to include these points and extrapolated linearly to [L] = 0. The
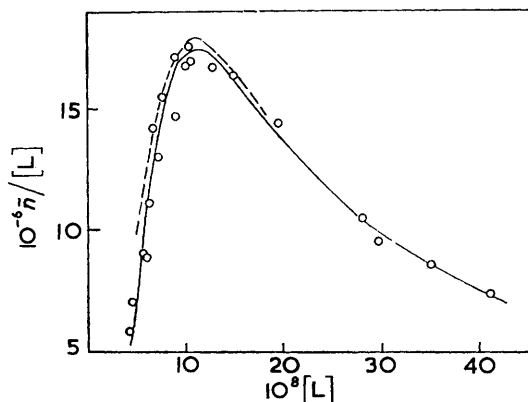

Fig. 3. Experimental data for the system iron(II)$-$1,10-phenanthroline.[7] The continuous line is calculated with the stability constants $\log \beta_1 = 5{\cdot}86$, $\log \beta_2 = 11{\cdot}11$, and $\log \beta_3 = 21{\cdot}14$. The broken line is calculated by using the values $\log \beta_1 = 5{\cdot}86$, $\log \beta_2 = 11{\cdot}11$, and $\log \beta_3 = 21{\cdot}17$.

value derived for $\beta_1 = 1{\cdot}2 \times 10^7$ ($\log \beta_1 = 7{\cdot}08$) is grossly in error. Further calculation shows that the graph of f(L) is far from linear in this neighbourhood and it would be essential to reach values of $\bar{n} \leqslant 0{\cdot}0001$ before a satisfactory extrapolation could be performed. Such values are experimentally inaccessible and Olerup's method would fail badly if applied to such a system.

The third possibility is also illustrated in Fig. 2 by experimental data for the system ferrous iron$-$1,10-phenanthroline [7] for which $\log K_1 = 5{\cdot}86$, $\log K_2 = 5{\cdot}25$, and $\log K_3 = 10{\cdot}03$ (so that $\log \beta_2 = 11{\cdot}11$ and $\log \beta_3 = 21{\cdot}14$, as before). The very steep rise in the formation curve (curve e of Fig. 2) shows the dominant influence of the stability of the 3 : 1 complex, $Fe(phenan)_3{}^{2+}$, as compared with that of the lower complexes. The plot of $\bar{n}/[L]$ against pL (curve f of Fig. 2) or against [L] (Fig. 3) shows a pronounced maximum at $[L]_* = 1{\cdot}1 \times 10^{-8}$ and $\bar{n}_* = 1{\cdot}96$. However, theory predicts two extrema (or none) for the system in which $3K_3 \gg K_1 > 2K_2$ (case (iii) above); furthermore, the function $\bar{n}/[L]$ should increase ultimately to the limiting value of $\beta_1 = 7{\cdot}244 \times 10^5$ as [L] $\longrightarrow$ 0. Calculation shows that the initial branch of the curve does decrease monotonically to a minimum value of $\bar{n}_*/[L]_* = 7{\cdot}2443 \times 10^5$ when $[L]_* = 3 \times 10^{-11}$ and $\bar{n}_* = 0{\cdot}0000217$: thereafter it increases to the maximum at $[L]_* = 1{\cdot}1 \times 10^{-8}$, as shown in Fig. 3. Obviously this first part of the curve is not experimentally accessible, and with any values of $\bar{n}$ that can be realised in practice, the plot of $\bar{n}/[L]$ against [L] will appear initially to be monotonic and increasing. Extrapolation of such a curve to [L] = 0 (cf. Fig. 3) could only lead to an erroneous value for $\log K_1$.

The position of the maximum must depend upon the values of the relevant stability constants, and the co-ordinates $\bar{n}_*/[L]_*$, and $[L]_*$, must satisfy both equations (7) and (1). If these co-ordinates can be obtained with some accuracy from experimental data (cf. Fig. 3) there will result two simultaneous equations in β_1, β_2, and β_3. If any one of these stability constants is known accurately (usually that for the overall reaction, *viz.*, β_3), those for β_1 and β_2 can be obtained. Attempts to apply this procedure to the experimental data for the iron–phenanthroline system failed, for the resulting equations proved to be ill-conditioned and the numerical parameters were extremely sensitive to small changes in the values of $\bar{n}_*$ and $[L]_*$, arising both from experimental errors and the uncertainties attaching to the graphical interpolation of the extremum. As might have been expected, the magnitude (but not especially the position) of the maximum value of $\bar{n}_*/[L]_*$ was sensitive to the value chosen for β_3, while being relatively insensitive to those selected for β_1 and β_2. This is illustrated in Fig. 3.

In such systems as those illustrated in Fig. 3 it is often possible to represent the experimental data fairly well in terms of only one constant, β_3. The existence of a 1 : 1 complex $Fe(phenan)^{2+}$ in solution can, however, be established experimentally under conditions where the highest complex is not present in dominant concentration, and a value of β_1 can be obtained under these conditions. The formation curve plotted in terms of the two constants, β_1 and β_3, agrees still better with the experimental results. The problem arises whether it is possible to demonstrate the coexistence of the intermediate species $Fe(phenan)_2^{2+}$ or whether it is legitimate to place $\beta_2 = 0$. The condition for extrema under these conditions follows from eqn. (7) in the form

$$\beta_1^2 - 6\beta_3[L]_* + 3\beta_3^2[L]_*^4 = 0, \tag{7a}$$

which can have at most two real roots. As in the case (iii) above, there can be two extrema or none, and a plot of f(L) which takes the form shown in Fig. 3 (in which the minimum near $[L] = 0$ does not appear) whether or not $\beta_2 = 0$. However, since eqn. (7a) and

$$\bar{n}_* = (\beta_1[L]_* + 3\beta_3[L]_*^3)/(1 + \beta_1[L]_* + \beta_3[L]_*^3) \tag{8}$$

eqn. (8) must be satisfied simultaneously we have, for the co-ordinates of an extremum:

$$(\bar{n}_* - 3)\beta_1^2 - 9(\bar{n}_* - 2)\beta_3[L]_* - 3(\bar{n}_* - 1)\beta_1\beta_3[L]_*^2 = 0. \tag{9}$$

If eqn. (8) is satisfied by the experimental values of $\bar{n}_*$ and $[L]_*$ and the chosen values of β_1 and β_3, this could be taken as showing that the species ML_2 was of negligible importance to the equilibrium. Alternatively, by assuming the experimental value for β_3 a value for β_1 could be calculated from eqn. (9) (on the assumption that $\beta_2 = 0$), and the formation curve could be calculated on the basis of these two constants alone for comparison with the experimental data. In the last issue the " fit " of various possible formation curves must be assessed objectively by standard statistical procedures. When this is done it may frequently be found that the precision of the experimental data is not great enough to yield an unambiguous result, and the decision to retain a non-zero value for any particular step-constant may well rest on the intuitive feeling that the particular intermediate species must play some part, if only a very subordinate one, in the sequential equilibria.

The Case where $N = 4$.—By differentiation of eqn. (1) we obtain as a condition for an extremum:

$$(2\beta_2 - \beta_1) + 2(3\beta_3 - \beta_1\beta_2)[L]_* - 2(\beta_2^2 - 6\beta_4)[L]_*^2$$
$$-4(\beta_2\beta_3 - \beta_1\beta_4)[L]_*^3 - (2\beta_2\beta_4 + 3\beta_3^2)[L]_*^4 - 6\beta_3\beta_4[L]_*^5 - 4\beta_4^2[L]_*^6 = 0. \tag{9}$$

If $K_1 > 2K_2 > 3K_3 > 4K_4$ there can be no extremum. If $K_1 < 2K_2$ there can be an odd number of extrema (1, 3, or 5), but the last possibility is excluded by the degree of the

derivative. Discussion of the many other possibilities would follow on the lines indicated under $N = 2$ or 3.

Curve a of Fig. 1 presents Bjerrum's data [9] for the system $Cd^{2+}-NH_3$. This is a " normal " system and extrapolation to $[L] = 0$ gives $\log K_1 = 2\cdot64$ in good agreement with Bjerrum's value of $2\cdot65$. On the other hand, the corresponding graph for the system $Zn^{2+}-NH_3$ (Fig. 1, curve c) starts with a positive slope and displays a definite maximum at $[NH_3]_* = 4 \times 10^{-3}M$, confirming the anomalous sequence of stability constants, *viz.*, $K_1 = 10^{2\cdot37} < 2K_2 = 10^{2\cdot74} < 3K_3 = 10^{2\cdot98} > 4K_4 = 10^{2\cdot75}$.

From the foregoing we may conclude that no reliance can be placed on a value for β_1 obtained from the intercept of the graph of $\bar{n}/[L]$ against $[L]$ unless the initial slope is negative, and not even then if the whole function is not strictly monotonic and decreasing. On the other hand, the occurrence of one or more extrema is a definite proof of an " abnormal " sequence of stability constants and in favourable cases may be used to confirm the relative magnitudes of such constants obtained by other methods of computation and even to establish whether a particular species participitates in the step equilibria.

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