Studies on the Extraction of Metal Complexes

V. Two-parameter Equations for a Complex-formation System and their Application to the Two-phase Distribution of Metal Complexes

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In recent years much work has been done on the extraction on metal ions (M) from aqueous solutions with an organic solvent and a complex-forming group (A). In mathematical calculations on such processes, the standard approach has been to assume that the organic phase contains only the uncharged complex MA_N, and the aqueous phase only the uncomplexed metal ion M. This assumption leads to the very simple equation (7) below.

Rydberg [1] found that this simple equation certainly did not hold true for the thorium-acetylacetonate system studied very carefully by him (M = Th^{4+}, A = Aa^- = $(CH_3COCHCOCH_3)^-$, N = 4). The experimental data could be explained only by considering the formation in the aqueous phase of all the complexes, MA, MA_2, MA_3, and MA_4. The same conclusion has been reached for a number of other systems studied by our team.

In the special system studied by Rydberg, the accuracy of the data allowed the determination of five constants: the distribution constant λ_4 for MA_4, and the complexity products $\varkappa_1$, $\varkappa_2$, $\varkappa_3$, and $\varkappa_4$ for the formation of all the complexes MA_n. In other cases, however, the data may be too few or of too low accuracy to allow the determination of so many independent constants.

The present paper gives an approximation that has already proved useful for describing a number of systems where the data are accurate enough to rule out the simple equation (7) but not to determine all equilibrium constants independently.

GENERAL EQUATIONS

Let M be the metal ion and A the (negatively charged) ligand. (We shall for simplicity leave out the signs for charge.) We assume that a series of mononuclear complexes MA_n are formed. MA_N is the uncharged complex and MA_S the saturated complex; e.g. with $M = Th^{4+}$ and $A = X^-$, a uninegative ion, MA_N would be ThX_4, and MA_S might be ThX_6^{2-}. Polynuclear complexes and hydroxo complexes are neglected.

The equilibrium constants for the stepwise formation of the complexes are

$$k_n = \frac{[MA_n]}{[MA_{n-1}][A]} \tag{1}$$

Here, as in the following, brackets denote the concentration in the *aqueous* phase, unless the index "org" is added to indicate the organic solvent phase. We assume that, by the use of a constant ionic medium, the activity factors are kept constant so that concentrations can be used instead of activities in the law of mass action.

The complexity products $\varkappa_n$ are defined as

$$\varkappa_n = \frac{[MA_n]}{[M][A]^n} = k_1 k_2 \ldots \ldots k_n \tag{2}$$

For reasons of symmetry we shall introduce

$$\varkappa_0 = 1 \tag{2a}$$

The total concentration of M in the aqueous phase will be

$$[M]_{total} = [M] + \sum_1^S [MA_n] = [M]\left(1 + \sum_1^S \varkappa_n[A]^n\right) = [M]\sum_0^S \varkappa_n[A]^n \tag{3}$$

The organic phase, we assume, can dissolve M only in the form of the uncharged complex MA_N. The distribution constant of this complex is

$$\lambda_N = \frac{[MA_N]_{org}}{[MA_N]} \tag{4}$$

The quantity directly observed in the experiments is usually the (variable) net distribution ratio.

$$q = \frac{[M]_{total, \; org}}{[M]_{total, \; aq}} = \frac{[MA_N]_{org}}{[M]_{total}} \tag{5}$$

The data are conveniently recorded by plotting $\log q$ versus $\log$ [A]. It follows from the equations (2), (3), (4), and (5):

$$\log q = \log \lambda_N + \log \varkappa_N + N \log [A] - \log \sum_0^S \varkappa_n [A]^n \tag{6}$$

The curve $\log q$ versus $\log$ [A] will have 2 asymptotes, namely

$$[A] \to 0; \ \log q = \log \lambda_N + \log \varkappa_N + N \log [A] \tag{7}$$

$$[A] \to \infty; \ \log q = \log \lambda_N + \log \varkappa_N - \log \varkappa_S - (S-N) \log [A] \tag{8}$$

Equation (7) implies that in the aqueous phase M is present chiefly as uncomplexed M. This equation has been used repeatedly in literature. However, in many systems studied by our team it has been of little use even as an approximation.

Equation (8) implies that in the aqueous phase M exists practically only in the form of the saturated complex MA_S, which may be either identical with the uncharged MA_N $(S = N)$ or negative $(S > N)$. From the slope of the asymptote, $(S-N)$ can thus be obtained.

TWO-PARAMETER EQUATIONS FOR A COMPLEX SYSTEM

We shall now suggest a two-parameter approximation for the formation of the consecutive complexes MA_1, MA_2 ..... MA_S. We assume that the complex formation stops at MA_S.

As one parameter we choose the quantity a defined by

$$\varkappa_S = 10^{Sa}; \ \log \varkappa_S = Sa \tag{9}$$

It may be noted that J. Bjerrum's [2] mean complexity constant k is equal to 10^a in the present paper.

The other parameter b should determine the ratios between subsequent complexity constants. At the present state of our knowledge it seems hard to predict these ratios for a new system from arguments on, say, statistical factors and electrostatic forces. We shall make the simple approximation that the ratio k_n/k_{n+1} is equal for each step. We thus have

$$\frac{k_n}{k_{n+1}} = 10^{2b} = \beta^2; \ \log k_n - \log k_{n+1} = 2b = 2 \log \beta \tag{10}$$

From (2), (9), and (10) follows (noting that the $\log k_n$ form an arithmetical series)

$$\log k_n = a + b(S + 1 - 2n) \tag{11}$$

$$\log \varkappa_n = an + bn(S-n) \tag{12}$$

We shall introduce for convenience a variable y defined by

$$y = [A] \cdot 10^a; \quad \log y = \log [A] + a \tag{13}$$

We find from (2), (10), (12), and (13)

$$[MA_n] = \varkappa_n [M][A]^n = [M] \, y^n \beta^{n(S-n)} \tag{14}$$

To visualize the meaning of the parameters a and b one may consider the diagrams I or II in Fig. 1. They are of the well-known type giving, as a function of log [A], the percentage of the total M present as a certain complex. (See the text of Fig. 1.)

A horizontal line at 50 % will cut the boundaries of the field for MA_n approximately at the points with $-\log [A] = \log k_n$ and $\log k_{n+1}$, provided b is positive and not too small. At the first point, the amounts of MA_n and MA_{n-1} are equal, in the second point $[MA_{n+1}] = [MA_n]$. The maximum fraction of MA_n is obtained very nearly at the intermediate point, $-\log [A] = \frac{1}{2} (\log k_n + \log k_{n+1})$.

The abscissa value $\log y = 0$, thus $\log [A] = -a$, will be the mid-point of the range of complex formation; thus, for an even S, the mid-point of the area for $MA_{\frac{1}{2}S}$. The spacing between the curves at the 50 % level will be approximately $2b$, provided b is positive and not too small; in the curves in Fig. 1, the parameter b is either 0.25 or 0.5, thus the pacing 0.5 or 1.0. With decreasing b, the spacing decreases but of course never becomes negative, even for negative b.

One might add that our equations are exact (and not only approximate) for the simple cases $S = 2$ or 1. For $S = 1$, of course, only one parameter is necessary.

APPLICATION TO DISTRIBUTION EQUILIBRIA

Introducing (12), (13), and (14) into (6) we find

$$\log q = \log \lambda_N + N \log y + bN(S-N) - \log \sum_0^S y^n \beta^{n(S-n)} \tag{15}$$

It follows from (13) and (15) that a change in a or λ_N will only mean a parallel shift of the curve log q versus log [A] whereas, as we shall see, a change in b will affect the shape of the curve.

We shall consider in detail three cases I, II, and III, typical complex formation curves for which have been given in Fig. 1.

In case I no negative complexes are formed; thus the saturated complex MA_S is identical with the uncharged MA_N ($S = N$).

In case II, the saturated complex is negative ($S > N$), and the uncharged MA_N is an intermediate, whose formation is not specially favored.
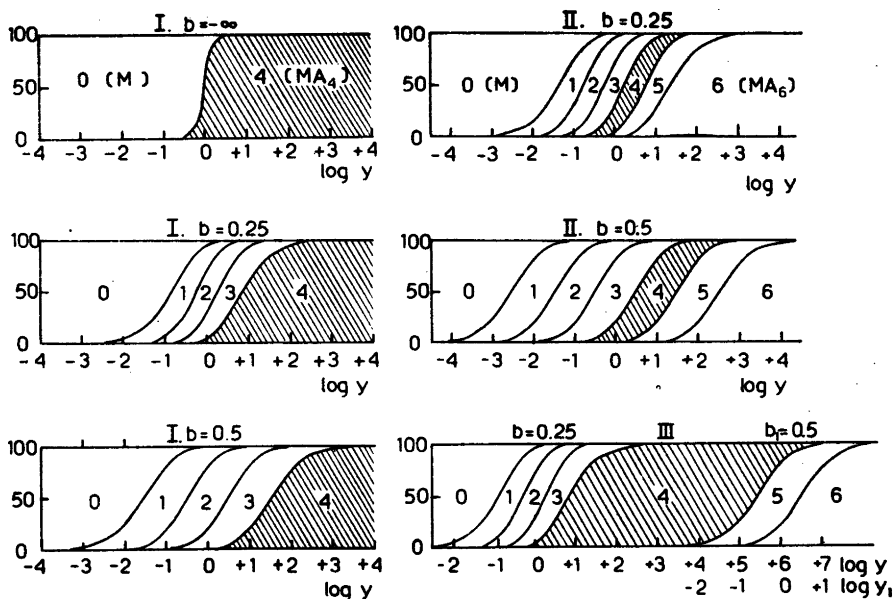
Fig. 1. Distribution of total M in the aqueous phase over the complexes MA_n, for varying log $[A]$. The abscissa is log $y = \log [A] + a$. On the ordinate axis, the distance $0-100$ represents the total amount of M present. If, for a given value of $[A]$, a vertical line is drawn at the corresponding log y, the segment of this line falling in a certain area, e.g. "2" $= MA_2$, represents the fraction of the total amount of M present as that complex. In each diagram the area for the extractible complex MA_N has been shaded. The diagrams have been calculated with the approximation proposed in the text, that the ratio between consecutive complexity constants is a constant $(= 10^{2b})$. They represent the cases I, II, III considered in the text:

   I. No negative complexes formed; the extractible complex is saturated $(N = S)$. In the diagrams $N = S = 4$, $b = -\infty$, 0.25, or 0.5.

  II. The extractible complex is intermediate in the series and not expecially favored. In the diagrams $N = 4$, $S = 6$, $R = S-N = 2$, $b = 0.25$ or 0.5.

 III. The ranges of positive and negative complexes are separated by a broad range where MA_N predominates. In the diagram: $N = 4$, $S = 6$, $R = S-N = 2$, $b = 0.25$ (for positive complexes), $b_1 = 0.5$ (for negative complexes), and $a = a_1 + 6$, thus log $y_1 = \log y - 6$.

In case III, as in case I, the complexes up to MA_N are formed in a rather narrow log y $(= \log [A] + a)$ range, with roughly equal spacing. If log y is further increased, there is first a broad range where MA_N predominates. At still higher log y values, a group of negative complexes are formed, $MA_{N+1}...MA_S$; the spacing here is not necessarily the same as for the lower complexes. In case III the formation of positive and negative complexes can be treated separately.

I. No negative complexes formed

If the complex formation stops at the uncharged complex MA_N, then we have in equations (6)—(15)

$$S = N \tag{1.1}$$

and for instance (15) gives

$$\log q = \log \lambda_N + N \log y - \log \sum_0^N y^n \beta^{n(N-n)} \tag{1.2}$$

The asymptotes will be

$$y \to 0; \log q = \log \lambda_N + N \log y = \log \lambda_N + Na + N \log [A] \tag{1.3}$$

$$y \to \infty; \log q = \log \lambda_N \tag{1.4}$$

In order to grasp how the three constants λ_N, a, and b (or β) affect the experimental curves we shall consider for a moment the special case $N = 4$. We find from (12)

$$\log \varkappa_1 = a + 3b; \log \varkappa_2 = 2a + 4b; \log \varkappa_3 = 3a + 3b; \log \varkappa_4 = 4a \tag{1.5}$$

and from (1.2)

$$\log q = \log \lambda_4 + 4 \log y - \log (1 + y \beta^3 + y^2 \beta^4 + y^3 \beta^3 + y^4) \tag{1.6}$$

or in full

$$\log q = \log \lambda_4 + 4a + 4 \log [A] - \log [1 + [A] \cdot 10^{a+3b} +$$

$$[A]^2 \cdot 10^{2a+4b} + [A]^3 \cdot 10^{3a+3b} + [A]^4 \cdot 10^{4a}] \tag{1.7}$$

In Fig. 2 we have plotted $\log q - \log \lambda_4$ as a function of $\log y = a + \log [A]$ for various values of b, namely $-\infty$, 0, 0.25, 0.50, 1, 1.50, and 2. All the curves go together at high values for $\log y$ (practically only MA_4 present in both phases, equation 1.4), and at low y (practically only M in the aqueous phase, equation 1.3). In an intermediate y range the curve family spreads out; the difference between the curves is greatest at $y = 1(\log y = 0)$. Similar families of curves would be obtained for other values of N.

Of especial interest is the curve for $b = -\infty(\beta = 0)$, which corresponds to the assumption that the only species to be considered are M, MA_N and A. This curve has been drawn thicker than the others in Fig. 2. We shall denote the q function so calculated by Q; it obeys he equation

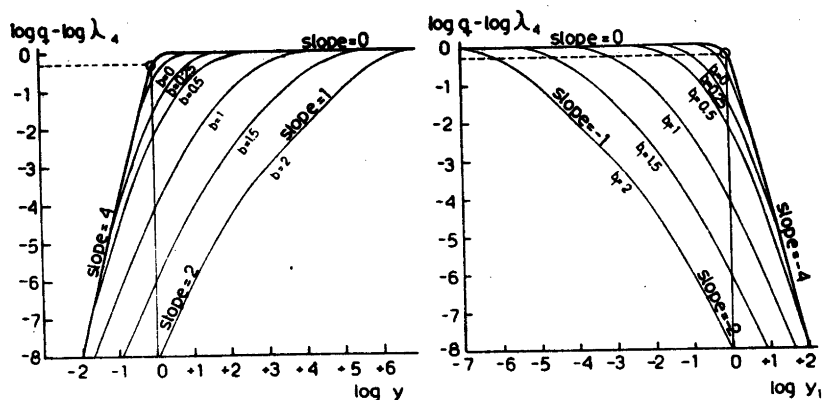$$\log Q = \log \lambda_N + N \log y - \log(1 + y^N) \tag{1.8}$$

Fig. 2. Variation of the net distribution ratio q with [A] for case I with N = 4, (case III with R = 4) and various values for the parameter b (b_1). Abscissa = log y = log [A] + a. Ordinate: log q—log λ_4; λ_4 = true distribution constant for MA_4. The thick limiting curve, which may be used as a templet, corresponds to b = — ∞, β = 0 (no intermediate complexes formed). The circles give the points for log y = 0, log [A] = — a. The diagram to the right (for the negative complexes in case III) is the mirror image of the left diagram (for positive complexes in case I).

It can easily be shown from equation (1.2) and (1.8) that the function (log Q—log q) has a maximum at y = 1. This maximum difference, which we shall call △, can be used for determining the second parameter b. We find from (1.2) and (1.8)

$$\triangle = (\log Q - \log q)_{y=1} = \log \tfrac{1}{2} \sum_{0}^{N} \beta^{n(N-n)} \tag{1.9}$$

For the N values between 1 and 6, equation (1.9) gives

$$
\begin{array}{ll}
N = 1 & \triangle = 0 \\
N = 2 & \triangle = \log (1 + \tfrac{1}{2}\beta) \\
N = 3 & \triangle = \log (1 + \beta^2) \\
N = 4 & \triangle = \log (1 + \beta^3 + \tfrac{1}{2}\beta^4) \\
N = 5 & \triangle = \log (1 + \beta^4 + \beta^6) \\
N = 6 & \triangle = \log (1 + \beta^5 + \beta^8 + \tfrac{1}{2}\beta^9)
\end{array}
\tag{1.9a}
$$

For each N, △ may be calculated as a function of β or of b = log β.

Determination of a, b, and λ_N. Suppose that measurements in a wide range of [A] are available and that we have plotted log q versus log [A]. To determine a, b, and λ_N one can prepare a templet giving, for this N value, log Q versus log y according to (1.8). The templet should have a mark at log y = 0 (y = 1),

thus at an ordinate -0.3 ($q/\lambda_4 = \frac{1}{2}$) units lower than the limiting value. This templet is moved parallel with the experimental plot, log q versus log [A], until the two extreme parts of the experimental curve coincide with the templet (cf. Fig. 5).

Then log λ_N is, of course, the limiting value for log q, and a can be read as $-$log [A] at the mark for log $y = 0$ on the templet. Finally one measures the distance $\triangle$ from the templet to the curve below the mark for log $y = 0$ and finds β or $b = \log \beta$ from (1.9).

If b is greater than 0.5, and log q values are not available over a very wide range, it may be hard to locate accurately the asymptote for low [A] by fitting a templet for $b = -\infty$ (see the lowest curves in Fig. 2). One may then prepare a series of templets with the same N and varying b values, each with a mark at log $y = 0$. The one or those that give the best fit can be used for finding the asymptote and then b and a. One may also proceed by successive approximations, preparing a number of templets around the best b value.

If b were greater than 0.75 or 1.0, the limiting slope N would not be even approached in the measurable range of q. On the other hand, λ_N and one or two of the k_n could be calculated with a good accuracy from the curve. For instance, in the lowest curve in Fig. 2, the two almost rectilinear parts of slopes 1 and 2, corresponding to the predominance of MA_{N-1} and MA_{N-2} in the aqueous phase, could be used for calculating k_N and k_{N-1}. It is then a matter of judgment whether one should use equations (11) and (12) to calculate a and b, and to predict approximate values for the other equilibrium constants. Systems with such a great spread in the complexity constants have not yet been found by our team.

II. Negative complexes; formation of MA_N not especially favored

We shall assume that, besides the positive complexes MA .... MA_{N-1} and the uncharged MA_N, a series of negative complexes up to MA_{N+R} can also be formed, and that the area for MA_N in the formation diagrams has the same spacing as those for the surrounding complexes.

In equations (9)—(15) we then have

$$S = N + R \tag{2.1}$$

Equation (15) will take the form

$$\log\ q = \log\ \lambda_N + N\ \log\ y + bRN - \log \sum_0^{N+R} y^n\ \beta^{n(N+R-n)} \tag{2.2}$$

Fig. 3. *Variation of net distribution ratio q with [A] for case II with (as in Fig. 1) N = 4, S = 6, and b = 0.25 (broken) or 0.5 (full-drawn curve). Abscissa: log y = a + log [A]. Ordinate = log q — log λ_N — bRN. Straight lines: asymptotes with slope N (chiefly M in aqueous phase) and slope — R (chiefly MA_S in aqueous phase). Points: 1) intersection of asymptotes, 2) point on curve at the abscissa of point 1, 3) maximum of curve. The line q = λ_N has been marked out for each curve.*
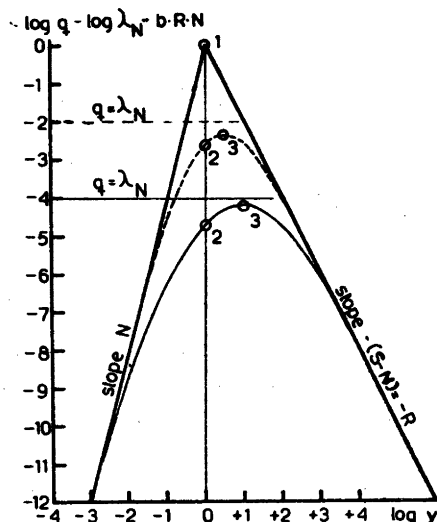
For some calculations it will prove useful to transform this equation by using the new index j

$$j = N - n \tag{2.3}$$

$$\log q = \log \lambda_N - \log \sum_{-R}^{+N} y^{-j} \beta^{j(N-R-j)} \tag{2.4}$$

The asymptotes of the log q curve will be

$$y \rightarrow 0; \log q = \log \lambda_N + bRN + N \log y \tag{2.5}$$

$$y \rightarrow \infty; \log q = \log \lambda_N + bRN - R \log y \tag{2.6}$$

Fig. 3 shows curves for a system with $N = 4$, $R = 2$, and $b = 0.25$ or 0.50.

From experimental data on a system one could thus plot log q versus log [A] and find N and $-R$ as the slopes of the asymptotes. To determine the three remaining unknowns, a, b (β), and λ_N, one may use the coordinates of three points:

1) The intersection point of the asymptotes at log $y_1 = 0$. We have here

$$\log [A]_1 = -a \tag{2.7}$$

$$\log q_1 = \log \lambda_N + bRN \tag{2.8}$$

2) The point on the curve immediately below point 1, thus with log $y_2 = 0$ has

$$\log q_2 = \log \lambda_N + bRN - \log \sum_0^{N+R} \beta^{n(N+R-n)} = \log \lambda_N - \log \sum_{-R}^{+N} \beta^{j(N-R-j)} \tag{2.9}$$

3) The maximum of the log q curve will very nearly coincide with the point

$$\log \ [A]_3 = -a + b(N-R) \tag{2.10}$$

$$\log \ q_3 = \log \lambda_N - \log \sum_{-R}^{+N} \beta^{-j^2} \tag{2.11}$$

For β values larger than 2, only two or three terms in the sum need be taken into account:

$$\log \ q_3 = \log \lambda_N - \log \ (1 + 2 \beta^{-1} + 2 \beta^{-4} + \ldots \ldots) \tag{2.11a}$$

We would thus have five equations to calculate our three unknowns; however, with actual experimental data one or two of the coordinates may be so inaccurately known as to be of little use.

In the special case $N = R$, points 2 and 3 coincide. The equations for case I are obtained by setting $R = 0$, as could be expected.

III. Negative complexes formed; broad range for uncharged complex

We shall now assume that the existence range of the uncharged complex MA_N is broader than the others and so broad that one can treat the formation of positive and negative complexes separately. Thus in one (lower) range of [A], only the positive or uncharged complexes M, MA . . . . . MA_N need be considered: in another (higher) [A] range, only the uncharged or negative complexes, MA_N, MA_{N+1} . . . . . MA_{N+R} are present in appreciable concentrations. The curve log q versus log [A] will be almost horizontal, at log $q = \log \lambda_N$, in the intermediate range where MA_N predominates (Fig. 4).

For the "positive" range one can proceed as for case I.

The formation of negative complexes by the addition of A to the core MA_N can be described by a set of complex constants k_r' and $\varkappa_r'$ defined by

$$k_r' = \frac{[MA_{N+r}]}{[MA_{N+r-1}][A]} = k_{N+r} \tag{3.1}$$

$$\varkappa_r' = \frac{[MA_{N+r}]}{[MA_N][A]^r} = k_1' k_2' \ldots \ldots k_r' = \frac{\varkappa_{N+r}}{\varkappa_N} \tag{3.2}$$

We may then, in analogy with (9) and (10), assume that these equilibria are described by two new parameters a_1 and b_1, or β_1.

$$\log \varkappa_R' = Ra_1 \tag{3.3}$$

$$\log \ k_r' - \log \ k_{r+1}' = 2b_1 = 2 \ \log \beta_1 \tag{3.4}$$

Fig. 4. Variation of net distribution ratio
q with [A] for case III with $N = 4$, $R = 2$,
$b = 0.25$, and $b_1 = 0.5$; $a = a_1 + 6$ as in
Fig. 1. Abscissa: $\log y = \log [A] + a$; (log
$y = \log y_1 + 6$). Ordinate: $\log q - \log \lambda_N$.
To the left, positive complexes predominate
in the aqueous phase, to the right negative
complexes; each part of the curve can be
treated separately by the methods given for I.
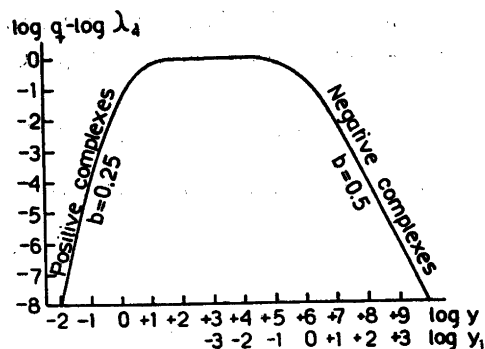
This gives, as above,

$$\log \varkappa'_r = a_1 r + b_1 r(R-r) \tag{3.5}$$

$$\log \varkappa_{N+r} = \log \varkappa_N + \log \varkappa'_r = Na + a_1 r + b_1 r(R-r) \tag{3.5a}$$

Inserting the latter into (6), and neglecting the positive ions $(n < N)$

$$\log q = \log \lambda_N - \sum_0^R \varkappa'_r [A]^r = \log \lambda_N - \log \sum_0^R y_1^r \beta_1^{r(R-r)} \tag{3.6}$$

with the variable

$$\log y_1 = \log [A] + a_1 \tag{3.7}$$

We may transform (3.6) as follows:

$$\log q = \log \lambda_N - R \log y_1 - \log \sum_0^R y_1^{-(R-r)} \beta_1^{r(R-r)} =$$

$$\log \lambda_N - R \log y_1 - \log \sum_0^R y_1^{-r} \beta_1^{r(R-r)} \tag{3.6a}$$

Equation (3.6) has the same form as (1.2) except that N is replaced by R and
$\log y$ by $-\log y_1 (= \log y_1^{-1})$. The family of $\log q$ curves (3.6) for negative
complexes with, say, $R = 3$ and various b values is then the mirror image of
the family of $\log q$ curves (1.2) for positive complexes with $N = 3$.

We may thus use the same set of templets as for positive complexes after
half a turn around the vertical axis. As master templet (for a given R) we may
use the curve with $\beta_1 = 0$.

$$\log Q = \log \lambda_N - \log (1 + y_1^R) \tag{3.8}$$

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the shape of which is the mirror image of (1.8). The maximum difference (log Q—log q) occurs at log $y_1 = 0$ ($y_1 = 1$).

$$\triangle = (\log \ Q - \log \ q)_{y_1=1} = \log \ \tfrac{1}{2} \sum_0^R \beta_1^{r(R-r)} \tag{3.9}$$

Equation (3.9) has the same form as (1.9), and can be used for finding β_1 and b_1.

APPLICATION TO THORIUM-ACETYLACETONATE COMPLEXES

It is interesting to apply this method (case I) to the Th-acetylacetone (Th—HAa) system which has been carefully studied by Rydberg [1]. From Fig. 5 we may see that the theoretical curve with $a = 6.66$ and $b = 0.45$ fits the experimental values rather well. The constants calculated in this way are given in Table 1 together with Rydberg's values. It is seen that the values of $\varkappa_4$, k_1, and k_3 are the same within reasonable limits of error: k_2 and k_4, however, deviate somewhat. The value of λ_4 is also somewhat different. A careful study of Fig. 5 shows small divergences between the two-parameter curve and the experimental values around $-\log$ [Aa] ≈ 6 and 7.7. These divergences have been accounted for by Rydberg using four parameters.

Table 1.

|	Values calculated with two parameters	Values calculated by Rydberg with four parameters
log $\varkappa_4$	26.64 ($= 4a$)	26.86
log k_1	8.01 ($= a + 3b$)	7.85 $\pm$ 0.35
log k_2	7.11 ($= a + b$)	7.73 $\pm$ 0.16
log k_3	6.21 ($= a - b$)	6.28 $\pm$ 0.08
log k_4	5.31 ($= a - 3b$)	5.00 $\pm$ 0.04
log λ_4	2.43	2.52 $\pm$ 0.04

In part VI of this series [3], our equations are applied to the thorium-oxinate and thorium-cupferrate complexes.

APPLICATION TO OTHER EXPERIMENTAL METHODS

The approximate two-parameter equations may also prove useful when complex formation equilibria are studied by other experimental methods. Starting from equation (14), it is not hard to derive the necessary equations and devise methods for obtaining a and b.

For instance it is often possible, by means of an electrode of the corresponding metal or amalgam, to measure either log [M] directly or, if the E_0

Fig. 5. Data of Rydberg[1] treated by the approximation case I. The abscissa is here — log [A] = — log y + a. Crosses = Rydberg's experimental data, full-drawn curve = values calculated with a = 6.66, b = 0.45. Broken curve (master templet): calculated with b = — ∞, a = 6.66, thus neglecting all complexes in the aqueous phase besides M and MA₄.
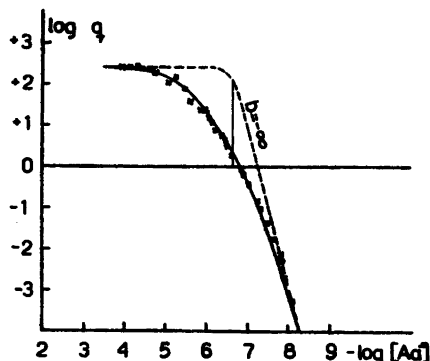
is not accurately known, log [M] + constant. From analytical data, $[M]_{total}$ is known. Now it follows from (3) and (14).

$$\log [M] - \log [M]_{total} = - \log \sum_{0}^{S} y^n \beta^{n(S-n)} \qquad (16)$$

The sum on the right of (16) is of the same form as the sums in (1.2) or (3.6). Thus, from a plot of log [M]—log $[M]_{total}$ versus log [A], the parameters, a and b can be determined using the same templet and method as for cases I and III; the templet should be turned as for the negative complexes in case III.

In this case it is immaterial whether A is charged or not. The charge of MA_S is also immaterial.

SUMMARY

As a reasonable approximation it has been assumed that the ratio of adjacent complexity constants is the same throughout a series of complexes of a metal ion M and a ligand A (eq. 10). The complex-formation equilibria can be described by two parameters, called a and b; sometimes it is convenient to use $\beta = 10^b$. The complexity products $\varkappa_n$ then follow eq. (12), and the concentration of each complex MA_n eq. (14); y is defined by eq. (13).

This approximation has proved helpful in systems where the data are not accurate enough to allow a separate determination of all the consecutive equilibrium constants. Equations are given and methods are devised for application to distribution equilibria, where one complex (the uncharged) MA_N can be extracted with an organic solvent. It is shown that the equations can also be applied to electrometric measurements of the concentration of free M.

For extraction, three cases are discussed in detail (see Fig. 1): (I) The extractible complex MA_N is identical with the saturated MA_S, (II) MA_N is

intermediate in the series, thus $S > N$, (III) the negative complexes $(n > N)$ are formed at a much higher [A] than the positive complexes $(n < N)$; in a broad intermediate range of [A], MA_N predominates. For each case it is shown how a diagram of log q versus log [A] (q = net distribution ratio) can be used for finding the parameters a and b, and the true distribution constant λ_N.

As an example (of case I), the methods are applied to Rydberg's data [1] on the thorium-acetylacetonate complexes and found to give rather good agreement.

More applications are given in a paper by Dyrssen [3].

REFERENCES

1. Rydberg, J. *Acta Chem. Scand.* **4** (1950) 1503 (= Part II).
2. Bjerrum, J. *Chem. Revs.* **46** (1950) 381.
3. Dyrssen, D. *Svensk Kem. Tidskr.* **65** (1953) 43 (= Part VI).