

Some Graphical Methods of Determining Equilibrium Constants III. A Projection Strip Method for Two-Parameter Systems

F. J. C. ROSSOTTI, HAZEL ROSSOTTI and LARS GUNNAR SILLÉN

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

Experimental data may often be represented by a single curve $y(x)$. It is sometimes possible to describe this function, either rigorously or approximately, in terms of only two parameters, p_1 and p_2 , such that the value of p_2 determines the shape of the curve $y(x)$, while the value of p_1 fixes its position on the x axis. Values of p_1 and p_2 may always be obtained by comparing the shape and position of the experimental $y(x)$ curve with theoretical $y(X)_{p_2}$ curves calculated for different values of p_2 . It is, however, more convenient to determine them by fitting the data in the form of a projection strip $(x)_y$ to the set of theoretical curves $p_2(X)_y$, where the normalised function $X = x + p_1$. This device is used to calculate equilibrium constants for a number of systems containing polynuclear hydrolysis products, and its application to systems of mononuclear complexes is indicated. The set of curves $p_2(X)_y$ is also useful for the rapid calculation of theoretical $y(x)$ curves for systems in which the values of p_1 and p_2 are known.

In studies of equilibria in a solution containing complexes formed from a central group, M, and a ligand, L, the measurements may often be explained, within the limits of experimental error, in terms of two parameters. For the special case where only the first two mononuclear complexes, ML and ML_2 , are formed, two parameters, K_1 and K_2 , suffice for a rigorous mathematical description of the system. (Here the stability constant of the species ML_n is given by $K_n = [ML_n]/[ML_{n-1}][L]$ and charges are omitted.) A number of methods for calculating K_1 and K_2 from the experimental data have been described, and are discussed critically elsewhere¹. When $N > 2$ mononuclear complexes are formed, an exact treatment requires N parameters, K_1, K_2, \dots, K_N , which may be determined experimentally if the data are sufficiently precise². However, it may not be possible to obtain more than two independent stability constants from less accurate data, *e. g.* some partition measurements, and it is often convenient to give an approximate description of systems of this type

in terms of only two parameters³. A rigid mathematical treatment of a system containing polynuclear complexes, M_qL_p ($1 < p < P$, $1 < q < Q$) requires PQ parameters, which could only be determined if a very large number of precise data were available⁴. In practice, it is seldom possible to obtain more than three or four independent constants for these systems, and in many cases the experimental data may again be satisfactorily explained in terms of only two parameters⁵⁻⁷.

A general discussion of the determination of two or more parameters by curve-fitting, successive extrapolations, or other methods is given elsewhere^{2,8}. This paper is restricted to the calculation of equilibrium constants for systems in which the experimental data are of the form $y(x)$, and which may be described in terms of only two parameters, p_1 and p_2 , where p_1 fixes the position of the $y(x)$ curve on the x axis, and p_2 determines the shape of the curve. It is always possible to determine the values of p_1 and p_2 by direct curve-fitting⁸, using the family of normalised curves $y(X)_{p_1}$, where

$$X = x + p_1 \quad (1)$$

An approximate value of p_2 may be obtained from the parameter of the calculated curve which gives the best fit, and the value of p_1 obtained from the experimental value of x corresponding to $X = 0$. The family of theoretical curves $y(X)_{p_1}$ is useful as a first approach for testing whether the experimental data are compatible with a certain hypothesis, and for recognising and correcting for systematic errors⁸.

If the experimental $y(x)$ data are found to fit in with the family of theoretical $y(X)_{p_1}$ curves, the values of p_1 and p_2 may conveniently be refined by comparing a projection strip of the experimental $y(x)$ curve with the family of curves $p_2(X)_y$. The method is used as follows.

The experimental data (yx) are plotted using the same abscissa scale as in the family of curves $p_2(X)_y$. For each value of y tabulated, the corresponding value of x , together with the experimental uncertainty in this value, is marked off on the x axis (*cf.* Fig. 1a). This projection strip (x) _{y} of the data $y(x)$ is then superimposed on the family of curves $p_2(X)_y$, parallel to the X axis, and in such a position that the best possible fit is obtained for all the values of y shown (*cf.* Fig. 1b).

The value of p_2 is then obtained as the ordinate, corresponding to the best position of the strip. The maximum limits of error in this value may be estimated from the vertical distance through which the projection strip may be moved, whilst allowing the calculated values of $(X)_y$ to remain within the experimental uncertainty. The value of p_1 is obtained as $(-x_0)$ where x_0 is read at the point of intersection of the p_2 axis ($X = 0$) with the projection strip (*cf.* eqn. 1). The maximum error in p_1 is then given by the permissible horizontal displacement of the strip. If data are only available in a very narrow range of y , a number of additional theoretical $p_1(X)_y$ curves may be calculated in this range. The value of p_2 can be found as described above, and the value of p_1 obtained by producing the projection strip to the point of intersection with the line ($X = 0$).

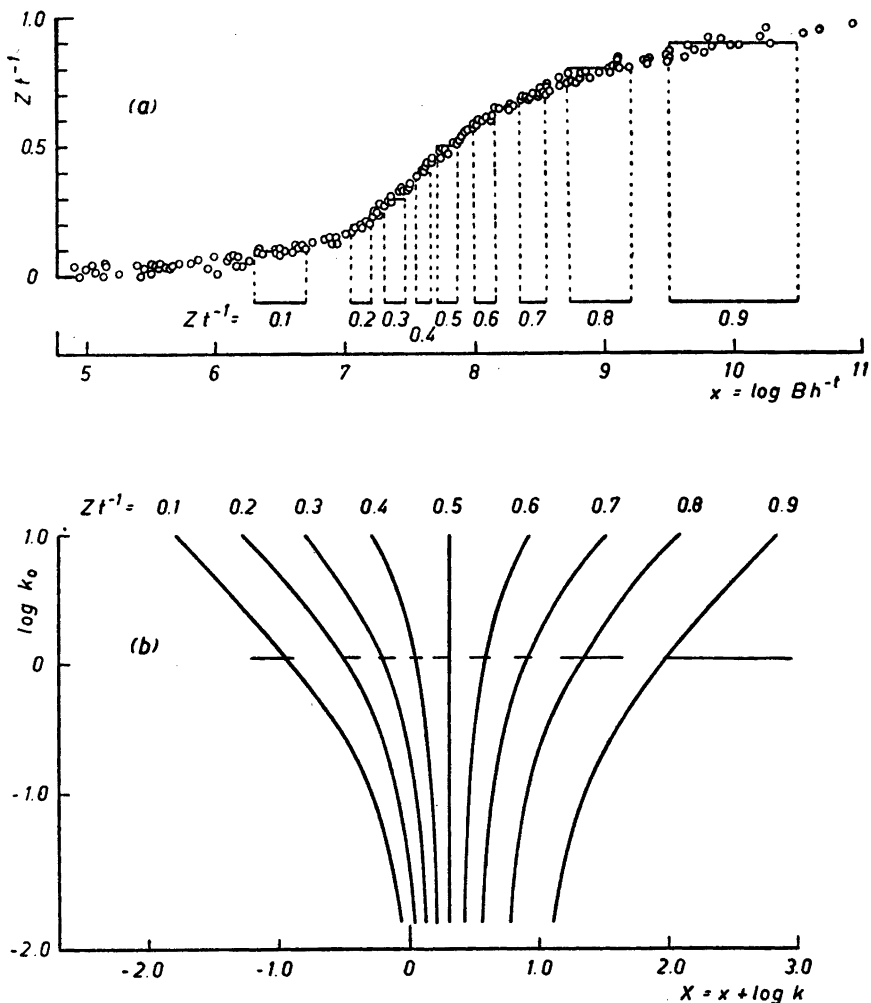


Fig. 1. The determination of the hydrolysis constants of the Th^{4+} ion in a 1.0 M perchlorate medium at 25° C. (a) Experimental curve $y = Zt^{-1}$ as a function of $x = \log Bh^{-t}$ (Hieta-nen¹²) and projection strip. Points for different total concentrations of metal are not dif-ferentiated. (b) Projection strip of the $y(x)$ curve superimposed on the family of theoretical curves $\log k_0(X)_y$, in the position corresponding to $\log k_0 = +0.06$ and $\log k = -7.53$.

When both p_1 and p_2 are known, the set of curves $p_2(X)_y$ may be used to calculate the theoretical curve $y(x)$. Values of X are obtained as the abscissae corresponding to the value of p_2 previously calculated, for a number of values of y . As p_1 is known, these values of X may then be substituted into equation (1) to give values of x .

The present method for calculating the parameters is no less accurate than those described elsewhere^{2,8}, and may be used much more rapidly, once

a preliminary check with the $y(X)_{p_2}$ curves has been made. Moreover, it may give a clearer estimate of the limits of error in the values of p_1 and p_2 obtained. Its application to the determination of equilibrium constants in systems of polynuclear hydroxyl complexes is described below. The adaptation of the treatment to other two-parameter systems is also indicated.

LIST OF SYMBOLS

B	total concentration of metal ions
b	concentration of free metal ions
H	total analytical excess concentration of hydrogen ions, assuming no hydrolysis
h	concentration of free hydrogen ions
K_n	stability constant of complex ML_n , defined by $K_n = [ML_n]/[ML_{n-1}][L]$
k	equilibrium constant, defined by $k = k_{n+1} k_n^{-1}$ (Hypothesis IIIa)
k_n	equilibrium constant, defined by $[Me((OH)_t Me)_n]/b^{n+1} h^{-t}$
k_0	equilibrium constant, defined by $k_0 = k_n k^{-n}$ (Hypothesis IIIa)
N	maximum value of n (mononuclear systems)
n	number of L groups in complex ML_n , or number of $Me(OH)_t$ "links" in "core + links" complex, $Me((OH)_t Me)_n$
\bar{n}	average value of n
P	maximum value of p
p	number of L groups in complex $M_t L_p$
p_1	parameter determining position of $y(x)$ curve on x axis
p_2	parameter determining shape of $y(x)$ curve
Q	maximum value of q
q	number of M groups in complex $M_q L_p$
t	number of hydroxyl groups per metal ion in "link", $Me(OH)_t$
$X =$	$x + \log k$
$x =$	abscissa of experimental curve
$x_{\frac{1}{2}} =$	value of x corresponding to $y = \frac{1}{2}$
$y =$	ordinate of experimental curve
Z	average number of hydroxyl groups per metal ion $= (H-h)B^{-1}$
α_s	fraction of total metal in the form $ML_s = [ML_s]/\sum_{n=0}^N [ML_n]$
$\eta =$	$\log Bb^{-1}$
$\beta_n =$	$\sum_{i=0}^n K_i$

THE CALCULATION OF EQUILIBRIUM CONSTANTS OF POLYNUCLEAR "CORE + LINKS" COMPLEXES

Previous work in this laboratory has indicated that the main products of hydrolysis of many metal ions, Me, are polynuclear "core + links" hydroxyl-complexes, of general formula $Me((OH)_t Me)_n$, where n is variable and t constant (Ref.⁹ and refs. therein). A treatment of equilibria involving complexes of this type, together with methods for obtaining the value of t has been given elsewhere^{7,10}. The equilibrium constant $k_n = [Me((OH)_t Me)_n]/[Me]^{n+1}[H]^{-t}$ for the formation of the complex $Me((OH)_t Me)_n$ may then be determined if certain

simplifying assumptions are made⁷. Potentiometric measurements for a number of systems, *e. g.*¹¹⁻¹⁴ may be explained by assuming that complexes with all positive integral values of n are formed, and that the ratio of successive equilibrium constants k_n/k_{n+1} , is constant (⁷ hypothesis IIIa). The system may then be approximately described in terms of two parameters, k and k_0 , such that

$$p_1 = \log k = \log k_{n+1} - \log k_n \quad (2)$$

and
$$p_2 = \log k_0 = \log k_n - n \log k \quad (3)$$

These parameters may readily be determined by the method described above.

Treatment of the data B , H , h

If the total concentrations of metal, B , and hydrogen, H , and the concentration of free hydrogen ions, h , are known, it is convenient to plot $Z = (H-h)B^{-1}$ as a function of $\log h$. If only "core + links" complexes are formed in appreciable amounts, the curves $Z(\log h)_B$ will be parallel, and the value of t may be determined from the spacing between them¹⁰. When $y = Z/t$ is plotted against $x = \log Bh^{-1}$, the experimental points fall on a single curve, which may often be approximately represented in terms of two parameters (*cf.* (2) and (3)). The shape of the curve is determined by the value of $\log k_0$ (parameter p_2) and its position on the x axis by the value of $\log k$ (parameter p_1).

If the experimental curve $y(x)$ is found to fit in with a set of theoretical curves, calculated for a few widely separated values of k_0 assuming hypothesis IIIa (*cf.*⁷, Fig. 2a), the value of k_0 may be calculated by one of the methods described previously⁷:

a) The shape of the experimental curve may be compared with $y(X)$ curves calculated for different values of k_0 ,

where
$$X = x + \log k \quad (4)$$

This method makes use of the whole range of experimental data, and as it has the further advantage of revealing systematic errors in y , it is a good first approach. For subsequent refining of the parameters it is somewhat time-consuming, as fresh curves will usually have to be calculated for values of k_0 not already available.

b) The value of k_0 may be calculated from corresponding values of y and x , using the equation

$$k_0 = y [1 - 10^X (1 - y)]^2 [10^X (1 - 2y)^2]^{-1} \quad (5)$$

where
$$X = \log 2 + x - x_{\frac{1}{2}} \quad (6)$$

and where $x_{\frac{1}{2}}$ is the value of x for $y = \frac{1}{2}$. If full use is to be made of the data, k_0 should be calculated for many values of y , and this method would also be rather laborious.

c) The slope of the curve $y(x)$ at the point $y = \frac{1}{2}$ is given by

$$(dy/dx)_{y=\frac{1}{2}} = \frac{1}{2} \ln 10 \cdot (1 + 2\sqrt{k_0})^{-1} \quad (7)$$

Even if the data are of the highest precision and extend to values of $y > \frac{1}{2}$, it may be difficult to measure this slope with any great accuracy. Moreover, this method only uses data in one small region of the curve, and does not indicate whether the value of k_0 so obtained gives a good description of the curve as a whole.

The value of $\log k$ has previously been calculated from the relationship⁷ obtained by combining eqns. (4) and (6)

$$\log k = \log 2 - x_{\frac{1}{2}} \quad (8)$$

but as the value of $x_{\frac{1}{2}}$ is obtained directly from the midpoint of the $y(x)$ curve, this method does not make full use of all the experimental data.

Values of k_0 may be obtained rapidly by the present method, which makes use of the set of theoretical curves $\log k_0(X)_y$. Corresponding values of $\log k_0$ and X have been calculated for different values of y , using equation (5), and are shown in Table 1 and Fig. 1b.

Table 1. The function $\log k_0(X)z^{-1}$ for hypothesis IIIa.

$\log k_0$	$(X)_{0.1}$	$(X)_{0.2}$	$(X)_{0.3}$	$(X)_{0.4}$	$(X)_{0.5}$	$(X)_{0.6}$	$(X)_{0.7}$	$(X)_{0.8}$	$(X)_{0.9}$
-2.000	-0.071	0.033	0.117	0.204	0.301	0.415	0.562	0.766	1.109
-1.699	-0.115	0.005	0.101	0.197	0.301	0.423	0.573	0.792	1.167
-1.301	-0.210	-0.048	0.070	0.182	0.301	0.438	0.608	0.843	1.256
-1.000	-0.303	-0.107	0.035	0.166	0.301	0.454	0.642	0.903	1.356
-1.699	-0.445	-0.189	-0.012	0.143	0.301	0.477	0.693	0.986	1.494
-0.301	-0.684	-0.344	-0.109	0.097	0.301	0.523	0.787	1.140	1.731
0.301	-1.166	-0.708	-0.353	-0.026	0.301	0.646	1.029	1.502	2.208
0.699	-1.529	-1.022	-0.594	-0.162	0.301	0.718	1.274	1.819	2.565
1.000	-1.812	-1.289	-0.823	-0.306	0.301	0.925	1.501	2.088	2.863

As an illustration of the method described above, values of k_0 and k have been calculated for the products of hydrolysis of the ions Th^{4+} , UO_2^{2+} and In^{3+} , and are compared with the values obtained by the original authors, *cf.* pp. 210-211.

When the values of both k_0 and k are known, the theoretical curve $y = Zt^{-1}$ as a function of $x = \log Bh^{-t}$ may be calculated rapidly with the aid of Fig. 1b. For a given value of $\log k_0$, values of X may be obtained from the curves for the values of y tabulated. As $\log k$ is also known, these values may be substituted into eqn. (4) to give values of x .

Treatment of the data B , H , b and h

If the free concentrations of both metal ions, b , and hydrogen ions, h , can be measured, the data may be plotted in the form $\eta = \log Bb^{-1}$, as a function of $\log h$. If "core + links" complexes predominate, the curves $\eta (\log h)_B$ are parallel, and the value of t may be obtained from the spacing between them¹⁰. When $y = \eta$ is plotted as a function of $x = \log Bh^{-t}$, the experimental points will therefore lie on a single curve which may approximately be described in terms of the parameters $\log k_0$ and $\log k$ (eqns. (2) and (3)).

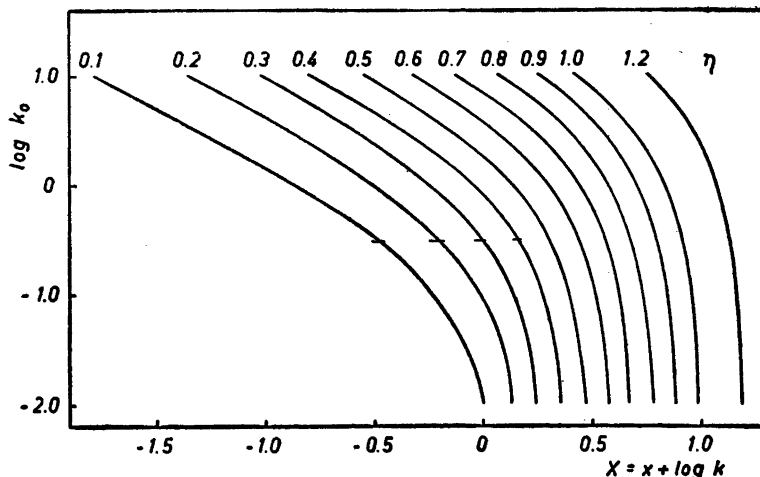


Fig. 2. The determination of the hydrolysis constants of the In^{3+} ion in a 3.0 M perchlorate medium at 25° C. Projection strip of plot of $y = \eta$ against $x = \log Bh^{-t}$ (Biedermann¹⁴) superimposed on the family of theoretical curves $\log k_0(X)\eta$ in the position corresponding to $\log k_0 = -0.50$ and $\log k = -4.70$.

The present method for determining these parameters may again be more convenient than that⁷ of calculating theoretical curves $\eta(X)$ for hypothesis IIIa to compare with the experimental data $\eta(x)$. Corresponding values of $\log k_0$ and X have been calculated for different values of η , using the equation⁷

$$X = \log \left(1 - \sqrt{\frac{k_0}{10\eta - 1 + k_0}} \right) + \eta \quad (9)$$

and are given in Table 2.

The experimental curve $\eta(\log Bh^{-t})$ is plotted using the same abscissa scale as for the curves $\log k_0(X)\eta$, and a projection strip on the x axis is prepared as before. The values of $\log k_0$ and $\log k$, together with the limits of error, are then obtained by a method exactly analogous to that described above (cf. Fig. 2). The method has been applied to the hydrolysis of the In^{3+} ion and the results are given on p. 211.

Fig. 2 may also be used to construct theoretical $\eta(x)$ curves for systems in which k_0 and k are known. From the intersection of the curves with the horizontal line at the required value of $\log k_0$, a number of corresponding values (X, y) are obtained. The corresponding values of x are given by $X = x + \log k$ (eqn. 4).

The experimental data B, H, b and h could also be plotted in the form $\eta(x - \eta)$, and curves of this type could be treated analogously by means of a set of curves $\log k_0(x - \eta)\eta$.

Table 2. The function $\log k_0(X)\eta$ for hypothesis IIIa.

$\log k_0$	$(X)_{0.1}$	$(X)_{0.2}$	$(X)_{0.3}$	$(X)_{0.4}$	$(X)_{0.5}$	$(X)_{0.6}$	$(X)_{0.7}$	$(X)_{0.8}$	$(X)_{0.9}$	$(X)_{1.0}$	$(X)_{1.3}$
-2.000	0.007	0.140	0.254	0.363	0.469	0.574	0.678	0.781	0.883	0.985	1.189
-1.699	-0.035	0.113	0.234	0.347	0.456	0.563	0.668	0.772	0.876	0.979	1.184
-1.301	-0.123	0.057	0.193	0.314	0.429	0.540	0.649	0.756	0.862	0.966	1.174
-1.000	-0.226	-0.009	0.144	0.276	0.397	0.514	0.626	0.737	0.845	0.952	1.163
-0.699	-0.368	-0.105	0.071	0.218	0.351	0.475	0.593	0.708	0.820	0.931	1.147
-0.301	-0.625	-0.293	-0.075	0.100	0.253	0.393	0.524	0.649	0.770	0.887	1.114
0.000	-0.864	-0.487	-0.234	-0.033	0.141	0.298	0.443	0.579	0.710	0.835	1.074
0.301	-1.128	-0.719	-0.438	-0.210	-0.013	0.164	0.326	0.478	0.622	0.759	1.016
0.699	-1.504	-1.008	-0.761	-0.508	-0.284	-0.081	0.107	0.282	0.448	0.605	0.897
1.000	-1.796	-1.353	-1.034	-0.767	-0.530	-0.313	-0.109	0.083	0.265	0.439	0.763

Application of the method to the hydrolysis of some metal ions

It has previously been found¹²⁻¹⁴ that the experimental Zt^{-1} ($\log Bh^{-t}$) curves for the ions Th^{4+} , UO_2^{2+} and In^{3+} , and the $\log Bb^{-1}$ ($\log Bh^{-t}$) curve for In^{3+} fitted in with the appropriate families of theoretical curves⁷, calculated assuming hypothesis IIIa. Values of $\log k_0$ and $\log k$ have now been calculated from the theoretical curves by the method described above. The limits of error quoted represent the maximum uncertainty both of individual measurements and of the validity of hypothesis IIIa. The preparation of a projection strip for a system, and the determination of the constants may be carried out in about ten minutes, once the diagrams $y(x)$ and $\eta(x)$ are available.

The Th^{4+} ion. The experimental curve¹², $y = Zt^{-1}$ as a function of $x = \log Bh^{-t}$, and the projection strip obtained from it, are shown in Fig. 1a. In Fig. 1b, the strip is superimposed on the family of curves $\log k_0(X)_y$. The best fit is obtained with the following values of the constants, which are in satisfactory agreement with those given by Hietanen¹².

Present method	$\log k_0 = +0.06 \pm 0.04$	$\log k = -7.53 \pm 0.05$
Hietanen ¹²	$\log k_0 = -0.15 \pm 0.15$	$\log k = -7.50$

The UO_2^{2+} ion. The projection strip of the experimental curve, $y = Zt^{-1}$ as a function of $x = \log Bh^{-t}$, for the hydrolysis of the uranyl ion¹³ is shown in Fig. 3a. Using Fig. 1b and eqn. (4), the following values were obtained, in good agreement with those previously calculated¹³

Present method	$\log k_0 = 0.3 \pm 0.3$	$\log k = -6.40 \pm 0.18$
Ahrland, Hietanen and Sillén ¹³	$\log k_0 = 0.3$	$\log k = -6.35 \pm 0.10$

The In^{3+} ion. The projection strip of $y = Zt^{-1}$ as a function of $x = \log Bh^{-t}$ for the hydrolysis of the In^{3+} ion¹⁴ is shown in Fig. 3b, and the constants obtained using the family of curves $\log k_0(X)_y$ are given below. As the concentration of free indium ions, b , could be measured, the constants

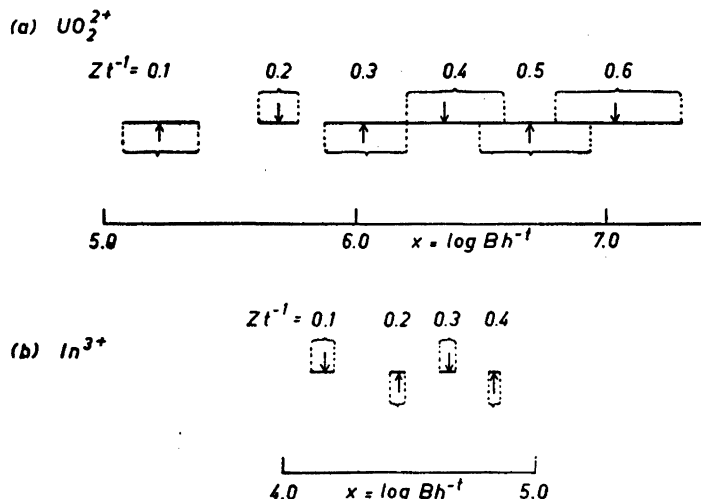


Fig. 3. Projection strips of plots of $y = Zt^{-1}$ as a function of $x = \log Bh^{-t}$ for the hydrolysis of metal ions. (a) The ion UO_2^{2+} in a 1.0 M perchlorate medium at 20° C. The experimental curve $y(x)$ is taken from Ahrlund, Hietanen and Sillén¹³. The arrows indicate the points of intersection of the family of theoretical curves $\log k_0(X)_y$ with the strip in the position corresponding to $\log k_0 = 0.3$ and $\log k = -6.40$. (b) The ion In^{3+} in a 3.0 M perchlorate medium at 25° C. The experimental $y(x)$ curve is taken from Biedermann¹⁴. The arrows indicate the points of intersection of the family of theoretical curves $\log k_0(X)_y$ with the strip in the position corresponding to $\log k_0 = -0.5$ and $\log k = -4.72$.

may also be calculated from the experimental curve $y = \eta$ as a function of $x = \log Bh^{-t}$. The projection strip of this curve is superimposed on the set of curves $\log k_0(X)_\eta$ in Fig. 2

	$\log k_0$	$\log k$
Present method $Zt^{-1}(x)$	-0.5 ± 0.1	-4.72 ± 0.04
Present method $\eta(x)$	-0.5 ± 0.1	-4.70 ± 0.05
Biedermann ¹⁴	-0.52	-4.70 ± 0.05

The constants obtained by the present method are in excellent agreement with those calculated by Biedermann¹⁴.

DISCUSSION

Comparison of the sets of curves $\log k_0(X)_{Zt^{-1}}$ and $\log k_0(X)_\eta$ shown in Figs. 1b and 2b emphasizes that the value of k_0 has a much greater influence on the shape of the former set. Thus, small uncertainties in the experimental curve $\eta(x)$ lead to much greater uncertainties in k_0 than do small uncertainties in the curve $Zt^{-1}(x)$. If h and b could be determined with equal precision, constants calculated from the curves $Zt^{-1}(x)$ would probably be more reliable than those obtained from $\eta(x)$ curves, although curves of both types are valuable for determining the nature of the species in solution. However, it is sometimes

possible to measure b with much greater accuracy than h , and in such cases the curves $Zt^{-1}(x)$ and $\eta(x)$ may be of comparable value for the determination of the constants.

The shape of the curves $\eta(x-\eta)$ is also influenced by the value of $\log k_0$ to a greater extent than the shape of the curves $\eta(x)$, but the $\eta(x-\eta)$ curves have the disadvantage that any experimental uncertainty in η appears in both the value of the ordinate and the abscissa. The curves are therefore less suitable for determining equilibrium constants than are $Zt^{-1}(x)$ and $\eta(x)$ curves, especially if the data are not of the highest precision. The present method could also be readily adapted for use with hypotheses other than IIIa provided that not more than two parameters are required to describe a system.

ADAPTATION OF THE METHOD TO OTHER TWO-PARAMETER SYSTEMS

Several other types of experimental curves $y(x)$ may also be described, either rigorously or approximately, in terms of only two parameters, p_1 and p_2 , such that p_2 determines the shape of the curve, and p_1 fixes its position on the x axis. If the curve $y(x)$ is found to fit in with the family of theoretical curves $y(X)_{p_2}$, small systematic errors may be corrected for, and approximate values of p_1 and p_2 obtained⁸. These values may be refined by superimposing a projection strip of the experimental $y(x)$ curve on the family of theoretical curves $p_2(X)_y$, as described above.

Systems of mononuclear complexes

If $N > 2$ mononuclear complexes are formed, the experimental data may be plotted in the form $y(x)$, where

$$y = \bar{n} = \frac{\sum_{n=1}^{n=N} n[\text{ML}_n]}{\sum_{n=0}^{n=N} [\text{ML}_n]} = \frac{\sum_{n=1}^{n=N} n\beta_n[\text{L}]^n}{\sum_{n=0}^{n=N} \beta_n[\text{L}]^n} \quad (10)$$

or

$$y = \log \alpha_S = \log \frac{[\text{ML}_S]}{\sum_{n=0}^{n=N} [\text{ML}_n]} = \log \frac{\beta_S[\text{L}]^S}{\sum_{n=0}^{n=N} \beta_n[\text{L}]^n} \quad (11)$$

and

$$x = \log [\text{L}] \quad (12)$$

Here $0 \leq S \leq N$ and $\beta_n = \prod_{i=1}^n K_i$. If the species ML_S is distributed between two phases, the term α_S may be obtained from partition data, provided that the value of the partition coefficient $[\text{ML}_S]_{\text{org}}/[\text{ML}_S]_{\text{aq}}$ can be determined; and if $S = 0$, α_S may be measured potentiometrically by means of an electrode which is reversible to free metal ions.

The present method can only be used if the number of parameters can be reduced to two by some assumption about the relationship between successive stability constants K_n . For example, if the ratio $K_n K_{n+1}^{-1}$ is fixed ($= k$), or a function of n ($= k \psi(n)$), the parameters p_1 and p_2 may be chosen as

$$p_1 = \frac{1}{N} \sum_{n=1}^{n=N} \log K_n = \frac{1}{N} \log \beta_N \quad (13)$$

and

$$p_2 = \frac{1}{2} \log \left\{ K_n K_{n+1}^{-1} / \psi(n) \right\} = \log \left\{ \beta_n^2 \beta_{n+1}^{-1} \beta_{n-1}^{-1} / \psi(n) \right\} \quad (14)$$

Then from eqns. (1), (12), and (13)

$$X = \log [L] + \frac{1}{N} \log \beta_N \quad (15)$$

Although it would be possible to devise equations for the "statistical" case¹⁵, where

$$\psi(n) = \frac{(N-n+1)(n+1)}{(N-n)n} \quad (16)$$

the present discussion will be limited to Dyrssen and Sillén's simpler approximation³ that $\psi(n) = 1$.

In this case

$$\log \beta_n = n p_1 + n(N-n)p_2 \quad (17)$$

and from eqns. (13) and (15)

$$\log [L] = X - p_1 \quad (18)$$

Whence

$$\log \beta_n [L]^n = n \left\{ X + p_2 (N - n) \right\} \quad (19)$$

and y may be expressed in terms of p_2 , S and N , and of the normalised variable X .

Thus

$$y = \bar{n} = \frac{\sum_{n=1}^{n=N} n 10^{n\{X+p_2(N-n)\}}}{\sum_{n=0}^{n=N} 10^{n\{X+p_2(N-n)\}}} \quad (20)$$

and

$$\log \alpha_S = S \left\{ X + p_2 (N - S) \right\} - \log \sum_{n=0}^{n=N} 10^{n\{X+p_2(N-n)\}} \quad (21)$$

Approximate values of p_1 and p_2 may be found by direct comparison of the experimental data $y(x)$ with the set of curves $\bar{n}(X)_{p_2}$ or $\log \alpha_S(X)_{p_2}$, calculated from eqns. (20) and (21) using the appropriate value of N and S . The values of p_1 and p_2 may very conveniently be refined using the projection strip method, and the set of curves $p_2(X)_{\bar{n}}$ or $p_2(X)_{\log \alpha_S}$.

If only two mononuclear complexes, ML and ML₂ are formed, the system may be rigorously defined in terms of the two parameters

$$p_1 = \frac{1}{2} \log K_1 K_2 = \frac{1}{2} \log \beta_2 \quad (13a)$$

and

$$p_2 = \frac{1}{2} \log K_1 K_2^{-1} = \log \beta_1 \beta_2^{-\frac{1}{2}} \quad (14a)$$

In eqns. (13a) and (14a) ($\frac{1}{2} \cdot 10^{p_1}$) is the spreading factor, and 10^{p_1} is the average constant, defined by J. Bjerrum¹⁵.

When $N = 2$, equation (20) reduces to

$$\bar{n} = \frac{10^{X+p_2} + 2 \cdot 10^{2X}}{1 + 10^{X+p_2} + 10^{2X}} \quad (20a)$$

If p_2 is defined alternatively as $\sqrt{K_1 K_2^{-1}}$, eqn. (20a) reduces to eqn. (14) in Part II⁸.

Accurate values of p_1 and p_2 may be determined using the projection strip method, as described above. A somewhat similar device, which makes use of the symmetrical properties of the $\bar{n}(x)$ curves for systems of this type, has been described previously¹.

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