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QUANTITATIVE STUDIES IN COMPLEX CHEMISTRY

PART 1 ELECTROMETRIC METHODS

by

H. J. de BRUIN

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ABSTRACT

Methods for the determination of stability constants are considered with particular reference to the method of pH titration. Mathematical derivations proposed by several authors are discussed and rationalized by using a common symbolism. The use of acid association constants is advocated in preference to dissociation constants. The authors' current work on the beryllium/oxalate system is used to illustrate the methods.

Suggestions are made for the application of the fundamental data to problems in chemical processing and analytical chemistry.

CONTENTS

1. INTRODUCTION

The problem of separating different metals in a mixture occurs in many fields of chemistry. In order to bring about such a separation, we have to take advantage of the differences in physico-chemical behaviour of the metal compounds, in particular the relative stabilities of the various species that can be formed in solution. Thus if a ligand L is added to the solution, it will react with the metals to form one or more complexes to an extent given by the mass action constants for reactions such as:

$$y\,M^{+a} + n\,L^{-b} = M_y\,L_n{}^{ya-nb} , \qquad (1)$$

namely: $$k = \frac{(M_y\,L_n)}{(M)^y\,(L)^n} ,$$

in which the charges on the ionic species have been omitted. Once the different k values have been determined and the charges ya–nb are known a separation process can be worked out by methods such as selective precipitation, solvent extraction, ion exchange, and chromatography.

The purpose of this paper is to introduce some of the concepts and procedures used in quantitative coordination chemistry, by examining a few of the more important theoretical papers, explaining them in terms of a common system of symbols and comparing their merits. Attention is drawn to a few of the review articles on this subject*.

To indicate the complexity of the subject consider some of the actual species which can be expected in an aqueous system containing metal and ligand ions. Not only would we expect a number of anionic, neutral, or cationic species to be present as indicated in equation 1, where y and n may vary between zero and some maximum value, but also association products including metal ion hydrolysis products, partly dissociated ligand species, hydrated metal ions, and, in cases where organic solvents are present, solvated molecules as well.

Extensive use is made in this paper of the concepts first introduced by Bjerrum (1941), who realized that reactions such as those indicated in equation 1 usually proceed through a number of intermediate stages, each obeying the law of mass action. This gives rise to the now classical concepts of stepwise formation constants and $\bar{n}$, the average number of ligands per metal ion.

The symbolism used is in essence that recommended in the survey by Bjerrum, Schwarzenbach, and Sillén (1957). It is summarized in Appendix 1.

In interpretations of chemical systems through the use of stability constants, careful consideration must be given to the definition of a constant. An overall stability constant is different from an intermediate formation constant, while a concentration constant cannot be used for thermodynamic purposes.

Some of the theoretical considerations are explained by using the stabilities of beryllium oxalate complexes as illustrations. Appendix 2 is a summary of the equations for the beryllium oxalate system as derived from the general equations in the text.

The use of acid association constants is advocated in preference to dissociation constants. Not only does this lead to a uniform treatment of both complex formation and acid association, but also a comparison between acid association constants and complex formation constants is far more meaningful. In other words an acid is treated as a complex between ligand and hydrogen ions, similar to a complex between ligand and metal ions.

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* Bjerrum (1950), Irving et al. (1952, 1953), Sullivan and Hindman (1952), Rossotti and Rossotti (1955), Sillen (1956, 1958) West (1956), Stuart Tobias (1958), Oosting (1959).

2. pH TITRATIONS

2.1 General Considerations

Prior to the classical work by Bjerrum in 1941, the concentrations of different species in a solution containing metal and ligand were deduced from a knowledge of the original concentrations, the measured value of the hydrogen ion concentration, the condition of electrical neutrality, and the application of the Law of Mass Action to the various equilibria involved. It was necessary to introduce approximations because the number of unknown concentrations exceeded the number of equations (for example see Cannan and Kibrick, 1938). Bjerrum developed a concise general method, which is applicable to almost any system containing a metal ion and ligand in a homogeneous aqueous medium. The most important innovation in his treatment was the realization that complex formation is not a single process, but rather a number of overlapping stages, for each of which an equilibrium constant can be calculated. The systems with mononuclear complexes ($y = 1$ in equation 1), represented in Table 1 will be considered here.

To facilitate understanding of the general expressions, they have been applied to the beryllium/oxalate system. The equivalents of the numbered equations in the text are shown in Appendix 2; Table 1 has been extended to define the corresponding beryllium oxalate constants, and Table 2 to include the acid association constants for oxalic acid.

TABLE 1

Stepwise Complex Formation

Reaction	Stepwise formation constant	Overall complexity constant
$M + L = ML$	$k_1 = \frac{(ML)}{(M)\ (L)}$	$\beta_1 = k_1$
$ML + L = ML_2$	$k_2 = \frac{(ML_2)}{(ML)(L)}$	$\beta_2 = k_1 \cdot k_2 = \frac{(ML_2)}{(M)\ (L)^2}$
$\vdots$	$\vdots$	$\vdots$
$ML_{n-1} + L = ML_n$	$k_n = \frac{(ML_n)}{(ML_{n-1})(L)}$	$\beta_n = \prod_{o}^{n} k_n = \frac{(ML_n)}{(M)\ (L)^n}$
$\vdots$	$\vdots$	$\vdots$
$ML_{N-1} + L = ML_N$	$k_N = \frac{(ML_N)}{(ML_{N-1})(L)}$	$\beta_N = \prod_{o}^{N} k_n = \frac{(ML_N)}{(M)\ (L)^N}$
For beryllium oxalates		
$Be^{++} + Ox^{=} = BeOx$	$k_1 = \frac{(BeOx)}{(Be)\ (Ox)}$	$\beta_1 = k_1$
$BeOx + Ox^{=} = BeOx_2^{=}$	$k_2 = \frac{(BeOx_2)}{(BeOx)(Ox)}$	$\beta_2 = \frac{(BeOx_2)}{(Be)\ (Ox)^2}$

Bjerrum introduced the quantity $\bar{n}$, defined as the average number of ligands bound to a metal ion. From the known initial concentration of metal and ligand it follows that $(M)_t$ the total concentration of metal is given by:

$$(M)_t = \sum_{n=o}^{n=N} (ML_n) \tag{2}$$

and the total ligand concentration by:

$$(L)_t = \sum_{p=o}^{p=b} (H_pL) + \sum_{n=1}^{n=N} n\,(ML_n) \tag{3}$$

Thus $\bar{n}$ is defined as:

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n\,(ML_n)}{\sum_{n=o}^{n=N} (ML_n)} \tag{4}$$

Introduction of the constants in Table 1 will give:

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n\beta_n\,(L)^n}{\sum_{n=o}^{n=N} \beta_n\,(L)^n} \tag{5}$$

where $\beta_o = 1$ by convention, or

$$\sum_{n=o}^{n=N} (\bar{n}-n)\,\beta_n\,(L)^n = o \tag{6}$$

This is the well-known Bjerrum equation from which values for β can be obtained if N sets of $[\bar{n}, (L)]$ data are known. A graph of $\bar{n}$ versus some function of (L), usually $-\log(L)$, is called the formation curve.

To obtain the stability constants, β_n, several methods can be applied. As a first approximation, the values of the stepwise formation constants, k_n, can be read from the formation curve if the strengths of the bonds between the central metal ion and successive ligands are quite different, i.e. when $\log \frac{k_{n+1}}{k_n}$ is much greater than 2. In that case it can be shown from statistical considerations that when $\bar{n}=n-0.5$, $\log k_n \cong -\log(L)$. Verification can be found in most textbooks, for example Martell and Calvin (1953) chapter 3.

The solution of a set of N simultaneous equations (6) has been worked out in detail by Block and McIntyre (1953) for systems in which N = 1, 2, or 3. Commonly, more than N sets of experimental data are obtained and the graphical method of Irving and Rossotti (1953) is well suited to enabling all these data to be used to advantage. By rearrangement of equation 6 we have:

$$\frac{\bar{n}}{(1-\bar{n})(L)} = \beta_1 + \beta_2\,\frac{(2-\bar{n})}{(1-\bar{n})}(L) + \sum_{n=3}^{n=N} \frac{(n-\bar{n})}{(1-\bar{n})}\,\beta_n (L)^{n-1} \tag{7}$$

By plotting the term on the left hand side against $\frac{2-\bar{n}}{1-\bar{n}}$ (L), a curve is obtained which will become a straight line as (L) tends to zero. The slope of this line will be β_2, while the intercept on the ordinate when (L) = o will be β_1. Similarly the higher constants can be calculated from the intercepts and slopes of equations obtained by rearranging equation 7. The lines are best obtained by applying the method of least squares to the experimental data.

2.2 Acid Dissociation and Acid Association Constants

We have so far not shown how values for $\bar{n}$ and (L) can be obtained from experimental measurements. The above argument is applicable to any experimental procedure in which $\bar{n}$ and (L) can be determined and is not confined to the pH titration method.

Molecules or ions with an affinity for metal ions can usually also bind hydrogen ions. The acid dissociation constants of this form of the protonated ligand can be used to calculate (L) at any hydrogen ion concentration.

By convention the formation of metal complexes and the dissociation of acids are considered from different starting points. (An exception is found in many Russian reports, dealing with this topic, where the use of complex instability or dissociation constants is preferred). Logically there seems to be no difference between the formation of mononuclear complexes of the type ML_n, and the association of ligand and hydrogen ions to form acid molecules of the type H_bL. However, in the case of the complex, we study its association and degree of formation, whereas when dealing with acids we use concepts such as dissociation constants and degree of dissociation.

As long as the acid can provide only one proton, this distinction is artificial from a mathematical point of view. For polybasic acids the quantitative treatment of dissociation is quite different from that of the formation of a complex. Table 2 shows the differences between the conventional concepts of the dissociation of an acid and the consequences of considering an aqueous acid system from an association point of view.

As indicated in Table 2 the numbering of the constants is reversed, i.e. $K_b = 1/A_1$ and $K_1 = 1/A_b$. If we now compare Tables 1 and 2 it can be seen that any mathematical expression derived for metal complexes can be transformed to an equivalent one applicable to the calculation of acid association constants, simply by making the following substitution of symbols:

Symbols used in expressions for:

acid	complex
H	L
L	M
p	n
b	N
A	k
$\bar{A}$	β

This is shown in Table 3 which summarizes the equivalents of equations 2 to 7 when applied to the association of protons and ligands.

TABLE 2

Acid Association

Reaction	Conventional Dissociation Constants	Proposed Constants	
		Stepwise Association	Overall Association
$L^{b-} + H^+ = HL^{(b-1)-}$	$K_b = \frac{(H)(L)}{(HL)}$	$A_1 = \frac{(HL)}{(L)(H)} = \frac{1}{K_b}$	$\bar{A}_1 = A_1$
$HL^{(b-1)-} + H^+ = H_2L^{(b-2)-}$	$K_{b-1} = \frac{(H)(HL)}{(H_2L)}$	$A_2 = \frac{(H_2L)}{(HL)(H)} = \frac{1}{K_{b-1}}$	$\bar{A}_2 = \frac{(H_2L)}{(L)(H)^2} = A_1 \times A_2$
$H_{p-1}L^{(b-p+1)-} + H = H_pL^{(b-p)-}$	$K_{b-p+1} = \frac{(H)(H_{p-1}L)}{(H_pL)}$	$A_p = \frac{(H_pL)}{(H_{p-1}L)(H)} = \frac{1}{K_{b-p+1}}$	$\bar{A}_p = \frac{(H_pL)}{(L)(H)^p} = A_1 \times A_2 \times \ldots \times A_p$
$H_{b-2}L^{2-} + H^+ = H_{b-1}L^-$	$K_2 = \frac{(H)(H_{b-2}L)}{(H_{b-1}L)}$	$A_{b-1} = \frac{(H_{b-1}L)}{(H_{b-2}L)(H)} = \frac{1}{K_2}$	$\bar{A}_{b-1} = A_1 \times A_2 \times \ldots\ldots \times A_{b-1}$
$H_{b-1}L^- + H^+ = H_bL$	$K_1 = \frac{(H)(H_{b-1}L)}{(H_bL)}$	$A_b = \frac{(H_bL)}{(H_{b-1}L)(H)} = \frac{1}{K_1}$	$\bar{A}_b = \frac{(H_bL)}{(L)(H)^b}$
For Oxalic Acid			
$Ox^= + H^+ = HOx^-$	$K_2 = \frac{(H^+)(Ox^=)}{(HOx^-)}$	$A_1 = \frac{(HOx^-)}{(Ox^=)(H^+)}$	$\bar{A}_1 = A_1$
$HOx^- + H^+ = H_2Ox$	$K_1 = \frac{(H^+)(HOx^-)}{(H_2Ox)}$	$A_2 = \frac{(H_2Ox)}{(HOx^-)(H^+)}$	$\bar{A}_2 = \frac{(H_2Ox)}{(H^+)^2(Ox^=)}$

TABLE 3

Comparison Between Metal Complex Formation and Acid Association

Eq. No.	Metal Complex Formation	Acid Association
2	$(M)_t = \sum_{n=o}^{n=N} (ML_n)$	$(L)_t = \sum_{p=o}^{p=b} (H_p L)$
3	$(L)_t = \sum_{p=o}^{p=b} H_p L + \sum_{n=o}^{n=N} n(ML_n)$	$(H)_t = (H) + \sum_{p=o}^{p=b} p(H_p L)$
4	$\bar{n} = \dfrac{\sum_{n=o}^{n=N} n(ML_n)}{\sum_{n=o}^{n=N} (ML_n)}$	$\bar{p} = \dfrac{\sum_{p=o}^{p=b} p(H_p L)}{\sum_{p=o}^{p=b} (H_p L)}$
5	$n = \dfrac{\sum_{p=o}^{n=N} n \beta_n (L)^n}{\sum_{N=o}^{n=N} \beta_n (L)^n}$	$\bar{p} = \dfrac{\sum_{p=o}^{p=b} p \bar{A}_p (H)^p}{\sum_{p=o}^{p=b} \bar{A}_p (H)^p}$
6	$\sum_{n=o}^{n=N} (\bar{n}-n) \beta_n (L)^n = o$	$\sum_{p=o}^{p=b} (\bar{p}-p) \bar{A}_p (H)^p = o$
7	$\dfrac{\bar{n}}{(1-\bar{n})(L)} = \beta_1 + \beta_2 \dfrac{(2-\bar{n})(L)}{(1-\bar{n})} + \sum_{n=3}^{n=N} \beta_n \dfrac{n-\bar{n}}{1-\bar{n}} (L)^{(n-1)}$	$\dfrac{\bar{p}}{(1-\bar{p})(H)} = \bar{A}_1 + \bar{A}_2 \dfrac{2-\bar{p}}{1-\bar{p}} (H) + \sum_{p=3}^{p=b} A_p \dfrac{p-\bar{p}}{1-\bar{p}} (H)^{p-1}$

It should be noted in Table 3 that the acid equivalent of equation 3 is not quite obtained by mere conversion of symbols. This equation is only an intermediate in the derivation of expressions 5, 6, and 7. In this case the term $\sum_{p=o}^{p=b} H_pL$ must be replaced by (H) in the equivalent acid equation.

It is now possible to determine acid association constants for complexing agents according to the above method by obtaining data for $\bar{p}$ and (H) and applying equation 7. This is done by conventional titration of the acid form of the complexing agent against standard alkali in the absence of the metal.

After each addition, the concentration of base (K), is noted and the pH measured. $\bar{p}$ is then calculated from its definition:

$$\bar{p} = \frac{\text{total bound hydrogen}}{\text{total ligand}}$$

$$= \frac{(H)_t - (H) - (K)}{(L)_t}$$

$$\text{and } (H)_t = b\,(L)_t$$

Hence:

$$\bar{p} = \frac{b(L)_t - (H) - (K)}{(L)_t} \qquad (8)$$

A graph of $\bar{p}$ versus pH, the association curve, is of the same significance as the formation curve in the case of a complex.

In the following discussion the proposed acid association constants will be used. Wherever authors of original work, to be considered here, have made use of conventional dissociation concepts, the proposed association is introduced. This has brought a significant simplification in the mathematical derivation.

2.3 Formation Curves from pH Measurements

Having established a relationship between $\bar{n}$ and (L) (equations 6 or 7) and discussed the way in which acid association constants can be determined, it is now necessary to show how all these relations can be used to calculate values for $\bar{n}$ and (L) from experimental procedures.

Since a protonated ligand can be regarded as an acid in the Brønsted sense, it liberates protons in a reaction with metal ions to an extent determined by the state of equilibrium in the system:

$$M^{+a} + n\,H_bL = ML_n^{(a-nb)+} + nbH^+$$

When the complexes formed are sufficiently soluble, titration of the system of metal ion and complexing agent against standard alkali can provide the information necessary for calculating $\bar{n}$ and (L).

2.3.1 The general case

Many authors follow procedures similar to those proposed by Li, Gawron, and Bascuas (1954).

From equations 2, 3, and 4 it follows that

$$\bar{n}\,(M)_t = \sum_{n=o}^{n=N} n\,(ML_n)$$

and:

$$(L)_t = \sum_{p=o}^{p=b} H_pL + \bar{n}\,(M)_t$$

$$= (L) + \bar{A}_1(L)(H) + \bar{A}_2(L)(H)^2 + \ldots\ldots\ldots + \bar{n}(M)_t$$

By rearrangement we obtain:

$$\bar{n} = \frac{(L)_t - (L)\left\{\sum_{p=o}^{p=b} \bar{A}_p\,(H)^p\right\}}{(M)_t} \qquad (9)$$

Thus if the acid association constants $\bar{A}_p$ and the free ligand concentration are known, $\bar{n}$ can be calculated.

(L) can be obtained by considering the concentrations of free and bound protons. In the case of pH titration, standard alkali is added and a number of protons are liberated in an amount equivalent to the alkali added.

Representing the concentration of alkali titrated by (K), then the concentration of hydrogen ions which could possibly be liberated on complete dissociation of the originally protonated ligand is given by:

$$(H)_t = (H) - (OH) + (K) + \sum_{p=o}^{p=b} p(H_pL)$$

$$= b\,(L)_t$$

where the term (OH) is inserted because of the dissociation of the water, i.e.

$(OH) = \frac{K_w}{(H)}$ This term can only be significant in alkaline media. It should also be realized that (K) does not include other potassium ions, apart from alkali addition, such as those added to maintain a constant ionic strength.

Putting the summation term equal to h we have:

$$h = \sum_{p=o}^{p=b} p(H_pL) = b(L)_t - (H) + (OH) - (K) \qquad (10)$$

All the terms on the right hand side are measured and hence h can be calculated at any stage of the titration. Also:

$$h = (HL) + 2(H_2L) + 3(H_3L) + \ldots\ldots\ldots$$

$$= \bar{A}_1(L)(H) + 2\,\bar{A}_2(L)(H)^2 + 3\,\bar{A}_3(L)(H)^3 + \ldots\ldots\ldots$$

and therefore:

$$(L) = \frac{h}{\sum_{p=o}^{p=b} \bar{A}_p(H)^p} \qquad (11)$$

If the values of the association constants are known, and h can be obtained from the experimental conditions, expressed in equation 10, (L) can be calculated from equation 11.

2.3.2 A variation of Bjerrum's approach

Maley and Mellor (1949) derived an expression for $\bar{n}$ which is identical to that obtained if (11) is substituted in (9). Their expression for $\bar{n}$ in a general form using conventional symbolism (Appendix 1), becomes:

$$\bar{n} = \frac{(L)_t \left\{1 - \frac{b}{\bar{p}}\right\} - \left\{\frac{h - b\,(L)_t}{\bar{p}}\right\}}{(M)_t} \qquad (12)$$

$\bar{p}$ has the same significance as before, namely the ratios of the concentrations of protons associated with ligand and the amount of ligand not bound to metal (see equation 5), i.e.

$$\bar{p} = \frac{\sum_{p=o}^{p=b} p\bar{A}_p\,(H)^p}{\sum_{p=o}^{p=b} \bar{A}_p\,(H)^p} \qquad (13)$$

Substitution of (13) into (12) gives an expression identical to the expression given by substituting (11) into (9). However it is unfortunate that whereas application of equations 9 and 11 provide all the data necessary for the formation curve, Maley and Mellor's approach at this same stage still requires some means of estimating the free ligand concentration. They describe two methods for this, the second being similar to that suggested by Li et al. (1954). The first procedure, based on Henderson's equation, is applied to their experimental results. This method gives accurate results for monobasic acids. For polybasic acids an approximation is applied. The case of a ligand containing two replaceable hydrogen atoms will be explained and applied to the experimental results in Section 2.5.

Thus for the acid H_2L

$$A_1 = \frac{(HL)}{(H)(L)} \quad \text{and} \quad A_2 = \frac{(H_2L)}{(HL)\,(H)}$$

Let $(L)_{t,h}$ be the total ligand concentration in the complex solution which is not bound to metal ion. Then

$$(L)_{t,h} = (L)_t - \bar{n}\,(M)_t = (L) + (HL) + (H_2L)$$

or

$$(HL) = (L)_{t,h} - (L) - (H_2L)$$

$$= \{(L)_t - \bar{n}(M)_t\} \left\{1 - \frac{(L)}{(L)_{t,h}} - \frac{(H_2L)}{(L)_{t,h}}\right\}$$

This may be approximated to:

$$(HL) = \{(L)_t - \bar{n}\,(M)_t\} \left\{1 - \frac{(L)}{(L)+(HL)} - \frac{(H_2L)}{(H_2L)+(HL)}\right\} \qquad (14)$$

if the stages in the association of the acid are sufficiently distinct, i.e. if $\log \frac{A_2}{A_1} > 2$. In this case (H_2L) can be neglected in the denominator of the term $\frac{(L)}{(L)+(HL)+H_2L)}$ when (L) is significant, and under the conditions that H_2L is present in an appreciable concentration, (L) may be omitted from the denominator of the term $\frac{H_2L}{(L)+(HL)+(H_2L)}$.

Since L is the base conjugate to HL, it follows from Henderson's equation that

$$\frac{(L)}{(L)+(HL)} = \frac{\text{antilog}\,(\text{pH}-\log A_1)}{1+\text{antilog}\,(\text{pH}-\log A_1)} \qquad (15)$$

Similarly since H_2L is the completely associated acid:

$$\frac{H_2L}{(H_2L)+(HL)} = \frac{1}{1+\text{antilog}\,(\text{pH}-\log A_2)} \qquad (16)$$

These Henderson's equations can be plotted as functions of (pH–log$A$) and the values of expressions (15) and (16) read from these graphs. Alternatively these ratios can be calculated from (15) and (16), substituted into equation 14, and the value of (HL), thus obtained, introduced into the definition of A_1 (see Table 2 above). By rearrangement we obtain the following simple expression for a doubly protonated ligand:

$$(L) = \frac{(A_1 - A_2)\ \{(L)_t - \bar{n}\,(M)_t\}}{A_1\,\{1+A_1(H^+)\}\ \{1+A_2\,(H^+)\}} \qquad (17)$$

In the example mentioned in Section 2.5, the values calculated according to equation 17 are well within the experimental error.

2.3.3 The horizontal difference method

It is sometimes possible to deduce the bound ligand concentration, and hence $\bar{n}$, from the horizontal difference of two titration curves, namely the curve for a titration of complexing agent only, and one for the complexing agent in the presence of metal ion. (Calvin and Melchior, 1948; Banks and Singh, 1959) (Figure 1). However two conditions are essential:

(1) The complexing agent must be present in large excess, i.e. it must have a sufficiently large solubility. This is necessary, because the method is based on the assumption that the horizontal difference between the curves is entirely due to the hydrogen ions evolved in the complexing process:

$$M^{a+}\ \ n\,H_bL = ML_n^{(a-nb)} + nbH^+ \qquad (18)$$

This is only true if the consumption of H_bL in the above reaction does not substantially effect the total H_bL concentration. If the ratio $\frac{(L)_t}{(M)_t}$ approaches n, the hydrogen ions evolved in this process will be complementary to the dissociation of some of the associated anions of H_bL and hence one of the other methods of calculation must be used.

(2) The complex formed must be sufficiently stable. The hydrogen ions evolved in reaction (18) should give rise to a sufficiently large horizontal difference to be read with a satisfactory degree of accuracy.

Under these conditions the amount of chelate bound to metal is calculated from the stoichiometry of equation 18. This quantity expressed in concentration units, divided by the total amount of metal will give ($\bar{n}$) for any point on the titration curves.

(L) can then be calculated by any of the previous methods, once ($\bar{n}$) is known. Banks and Singh (1959), for example, use equation 9, rearranged to give:

$$(L) = \frac{(L)_t - \bar{n}\,(M)_t}{\sum_{p=o}^{p=b} \bar{A}_p\,(H)^p}$$

2.3.4 An approximation method

Albert (1950, 1952) followed a suggestion by Flood and Loras (1945) and calculated ($\bar{n}$) and (L) according to equations 9 and 11. However, he processed the results in an approximate way from equations which can be summarized in the general form:

$$k_n = \frac{\bar{n} - n + 1}{(n - \bar{n})(L)} \qquad (19)$$

The assumption is made that the concentrations of the species ML_n and ML_{n-1} are the only significant quantities to be considered, while the concentrations of the species ML_{n+1}, ML_{n+2}, ..., ML_N and ML_{n-2}, ML_{n-3}, ..., M can be neglected.

The experimental condition for this approximate method is that metal and complexing agent must be present in stoichiometric amounts, and the values of ($\bar{n}$) and (L) used in the calculations must be chosen carefully to comply with the above assumption.

Equation 19 follows readily from Bjerrum's equation, (6), which if expanded becomes:

$$\bar{n} + (\bar{n}-1)\beta_1(L) + (\bar{n}-2)\beta_2(L)^2 + \ldots (\bar{n}-n+1)\beta_{n-1}(L)^{n-1} + (\bar{n}-n)\beta_n(L)^n + \ldots.$$
$$\ldots\ldots + (\bar{n}-N)\beta_N(L)^N = 0 \qquad (20)$$

Dividing equation 20 by $(\bar{n}-n)\ \beta_n\ (L)^n$, we obtain:

$$\frac{\bar{n}}{(\bar{n}-n)\beta_n(L)^n} + \frac{(\bar{n}-1)\beta_1}{(\bar{n}-n)\beta_n(L)^{n-1}} + \ldots\ldots\ldots + \frac{(\bar{n}-n+1)\beta_{n-1}}{(\bar{n}-n)\beta_n(L)} + 1 + \ldots..$$
$$\ldots\ldots + \frac{(\bar{n}-N)\beta_N}{(\bar{n}-n)\beta_n(L)^{n-N}} = 0 \qquad (21)$$

If the concentrations (M), (ML),...., (ML_{n-2}),......, (ML_{n+1}),....., $(ML)_N$ can be neglected, equation 21 becomes:

$$\frac{\bar{n} - n + 1}{(\bar{n} - n)k_n(L)} = -1. \text{ which by rearrangement is}$$

identical with (19).

It should be noted that application of the same approximations to Irving and Rossotti's (1953) graphical method of processing [$\bar{n}$, (L)] data (equation 7), yields the same conclusion as expressed in equation 19. These approximations were also made by Schwarzenbach (1950) for the evaluation of stabilities of protonated complexes. This author points to an additional condition, namely the need for the complex formation to take place in clearly defined steps.

2.3.5 An integration method

The use of unorthodox symbolism by Hearon and Gilbert (1955) complicates the appreciation of their work. However their derivation of expressions for $\bar{n}$ and (L) (their equations 10 and 12) are identical with equations 9 and 11 above. These authors go into considerable detail about the processing of experimental data to give the best value of overall complexity constants.

The methods are based on the fact that if we put

$$g = \sum_{n=o}^{n=N} \beta_n (L)^n \qquad (22)$$

then

$$\frac{g-1}{(L)} = \beta_1 + \beta_2(L) + \beta_3(L)^2 + \ldots\ldots \qquad (23)$$

and

$$\frac{g-\beta_1(L)-1}{(L)^2} = \beta_2 + \beta_3(L) + \beta_4 \underline{(L)^2} + \ldots. \qquad (24)$$

and so on.

It can be seen that if g can be determined, graphs of the left hand sides of equations 23 and 24 versus (L), will result in values for β_1, β_2, etc. as slopes and intercepts as (L) approaches zero.

Since $(M)_t = g(M)$, g can be obtained if (M) can be measured. This is in fact the classical method proposed by Leden (1941). However it is possible to obtain g from a graph of $\bar{n}/(L)$ versus (L), because from equations 5 and 22 it follows that

$$\frac{\bar{n}}{(L)} = \frac{\partial \ln g}{\partial (L)} \qquad (25)$$

and hence

$$\ln g = \int \frac{\bar{n}}{(L)}\, d(L) \qquad (26)$$

The area under the curve $[\bar{n}/(L), (L)]$ between 0 and (L) will produce g and hence the constants β_n by means of equations 23, 24, etc.

2.4 Practical Considerations

2.4.1 Conditional stability constants

The failure to appreciate the effect of side reactions on the determination of chemical equilibrium constants has, on occasions, led to some confusion in the literature. It would be safe to state that many published values for "thermodynamic" stability constants are incorrect, and are constant only for the conditions under which they were determined.

Consider the formation of a mononuclear complex ML for which the thermodynamic stability constant is defined by:

$$k_1 = \frac{(ML)}{(M)(L)}$$

The total metal concentration $(M)_t$ is very often not (ML) + (M), and the total ligand concentration $(L)_t$ is not (ML) + (L), since both M and L may react with other components of the solution. As an example, many metals tend to form hydroxy complexes, particularly in alkaline solution, and in this case

$$(M)_t = (ML) + (M) + \left(M(OH)\right) + \left(M(OH)_2\right) + \ldots.. + \left(M(OH)_N\right)$$

and in an analogous manner,

$$(L)_t = (ML) + (L) + (HL) + (H_2L) + \ldots.. + (H_bL)$$

In practical applications of stability constant data other metals may be present to compete for the ligand, and other ligands for the metal. All these interfering side reactions have to be taken into account if the aim is to determine, from thermodynamic data, the equilibrium concentration of a particular component of the solution. This problem may be overcome to a large extent by using the concept of conditional stability constants, the term implying that the constant depends on the prevailing experimental conditions (Ringbom, 1958). A conditional constant, partly or completely expressed in terms of primed concentrations can be handled in quite the same way as an ordinary equilibrium constant. In the equilibrium case quoted above, a conditional stability constant is given by,

$$k_{M'L'} = \frac{(ML)}{(M')(L')}$$

where $(M') = (M) + \big(M(OH)\big) + \big(M(OH)_2\big) + \dots\dots + \big(M(OH)_N\big)$,

i.e. total metal uncombined with ligand,

and $(L') = (L) + (HL) + (H_2L) + \dots\dots + (H_bL)$,

i.e. total ligand uncombined with metal. (Note (L') is used here instead of $(L)_{t,h}$).

If $\alpha_M = \frac{(M')}{(M)}$ and $\alpha_L = \frac{(L')}{(L)}$ then $k_{M'L'} = \frac{k_1}{\alpha_M \alpha_L}$

The coefficients may be expressed in terms of the equilibrium constants of the interfering reactions, for example,

$$\alpha_M = 1 + \beta_1 (OH) + \beta_2 (OH)^2 + \dots\dots + \beta_n (OH)^n + \dots\dots,$$

where β_n is used in this instance as the overall stability constant for the formation of a mononuclear metal hydroxide $M(OH)_n$ and

$$\alpha_L = 1 + \bar{A}_1 (H) + \bar{A}_2 (H)^2 + \dots\dots + \bar{A}_b (H)^b$$

By means of equations of this type, diagrams may be constructed of values of α as a function of concentration of competing ion, enabling rapid calculation of a series of conditional stability constants. Often, in practice, not one but several interfering ions have to be considered. In this case the overall α coefficients α_M and α_L are equal to the sum of the individual α coefficients.

2.4.2 Polynuclear complexes

The general equation for the formation of a polynuclear complex is,

$$yM + nL = M_yL_n$$

The hydrolysis products of many metals are polynuclear, and some (for example uranium and thorium), do not appear to form mononuclear species. This effect makes the quantitative treatment of equilibrium data very difficult, since for polynuclear complexes the degree of complex formation is a function not only of the concentration of the ligand, but also of the total concentration of the metal. However, polynuclear complexes usually exist only within a narrow pH range, and only at relatively high concentrations of total metal. The presence of polynuclear complexes may be detected by observing the effect of $(M)_t$ on a graph of $\bar{n}$ versus $-\log(L)$. If only mononuclear complexes are present, variation of $(M)_t$ will not affect the curve.

The approximate metal ion concentration at the point where the mononuclear complexes begin to predominate ("mononuclear wall") may be calculated from the stability constants of the mononuclear and dinuclear complexes:

$$\beta_{n,2} = \frac{M_2(OH)_n}{(M)^2(OH)^n}$$

$$\beta_{n,1} = \frac{M(OH)_n}{(M)(OH)^n} ,$$

and the ratio of complexes:

$$\frac{M_2(OH)_n}{M(OH)_n} = (M)\,k, \text{ where}$$

$$k = \frac{\beta_{n,2}}{\beta_{n,1}}$$

If this ratio is smaller than or equal to unity, the mononuclear species will predominate, i.e.

$$(M)k \leq 1 \quad \text{or} \quad (M) \leq \frac{1}{k}$$

2.4.3 Application to beryllium oxalates

To illustrate the implications of the discussions in the previous sections, the various methods of calculation have been applied to the beryllium oxalate system, first studied by Sidgwick and Lewis (1926).

From our pH titration curves it follows that the beryllium oxalate complexes are relatively weak. They are stable below pH 4. As soon as the hydrogen–ion–activity decreases sufficiently for the beryllium aquo–ions to dissociate and form hydroxy–ions, the oxalate complexes will decompose. Thus if complications due to hydrolysis of the beryllium ion are to be avoided, calculations can only be applied to results in solutions below pH 4 (Kakihana and Sillén, 1956). In this region the free ligand concentration is relatively small. Since it is possible to calculate stabilities only within certain limits for the ligand concentration, it was necessary to work with relatively concentrated solutions. Because of these high concentrations, the use of a large excess of neutral salt, to maintain a constant ionic strength, becomes impracticable. Therefore no attempt was made to keep the ionic strength constant.

Because the time necessary for equilibrium to be reached is usually quite considerable in the case of beryllium complex formation, so–called batch titration was used. In this a number of solutions are made up containing known concentrations of the metal ion and complexing agent. Different concentrations of standard alkali are added to the solutions, and the pH is read after equilibrium has been reached. In the present case standard sodium hydroxide was added to solutions containing beryllium perchlorate, oxalic acid, and free perchloric acid. These were then made up to volume and left in a waterbath at 25 °C for at least 24 hours so that equilibrium would be reached. The pH of each solution was then measured on a Radiometer PHM3 pH meter, which had been standardized on a potassium hydrogen tartrate buffer and a mixed–phosphate buffer, made up from recrystallized analytical grade reagents using the Hitchcock and Taylor (1937) scale. The pH readings were reproducible to 0.005 pH unit.

Figure 1 shows such titrations for 0.05 molar oxalic acid. In the original of this figure the scale was five times as large, to do justice to the accuracy of the measurements. The calculations were made from the smoothed curve.

Table 4 shows the calculations involved in the determination of the acid association constants of oxalic acid using the experimental results and equation 8. The method of least squares was applied to the data in columns 4 and 5 according to equation 7. The values obtained for the association constants were $A_1 = 8.62 \times 10^3$ and $A_2 = 21.5$. This corresponds to $\log K_1 = -1.33$ and $\log K_2 = -3.94$, values which agree with those mentioned in the compilation of stability constants by Bjerrum et. al. (1957).

Figure 2 shows the formation curve for oxalic acid.

TABLE 4

Dissociation of Oxalic Acid

Total oxalate concentration 0.05 M
Added perchloric acid 0.00625 M
Total volume 50.0 ml

(NaOH)	pH	$\bar{p}$	$\frac{\bar{p}}{(1-\bar{p})(H^+)}$	$\{\frac{2-\bar{p}}{1-\bar{p}}\}$ (H^+)
0.00	1.466	1.442	$-9.537\text{x}10$	$-4.318\text{x}10^{-2}$
$0.80\text{x}10^{-2}$	1.537	1.386	$-1.236\text{x}10^{2}$	$-4.619\text{x}10^{-2}$
$1.60\text{x}10^{-2}$	1.624	1.330	$-1.696\text{x}10^{2}$	$-4.826\text{x}10^{-2}$
$2.40\text{x}10^{-2}$	1.731	1.274	$-2.502\text{x}10^{2}$	$-4.923\text{x}10^{-2}$
$3.20\text{x}10^{-2}$	1.865	1.212	$-4.188\text{x}10^{2}$	$-5.074\text{x}10^{-2}$
$4.00\text{x}10^{-2}$	2.043	1.144	$-8.773\text{x}10^{2}$	$-5.384\text{x}10^{-2}$
$4.80\text{x}10^{-2}$	2.304	1.066	$-3.252\text{x}10^{3}$	$-7.028\text{x}10^{-2}$
$5.60\text{x}10^{-2}$	2.778	0.972	$+2.023\text{x}10^{4}$	$+6.120\text{x}10^{-2}$
$6.40\text{x}10^{-2}$	3.298	0.836	$+1.013\text{x}10^{4}$	$+3.574\text{x}10^{-3}$
$7.20\text{x}10^{-2}$	3.634	0.682	$+9.232\text{x}10^{3}$	$+9.628\text{x}10^{-3}$
$8.00\text{x}10^{-2}$	3.882	0.524	$+8.391\text{x}10^{3}$	$+4.068\text{x}10^{-4}$
$8.80\text{x}10^{-2}$	4.157	0.364	$+8.217\text{x}10^{3}$	$+1.792\text{x}10^{-4}$
$9.60\text{x}10^{-2}$	4.505	0.206	$+8.300\text{x}10^{3}$	$+7.063\text{x}10^{-5}$
$10.40\text{x}10^{-2}$	5.430	0.046	$+1.298\text{x}10^{4}$	$+7.609\text{x}10^{-5}$

$A_2 = 21.5$ or $\log K_1 = -1.33$

$A_1 = 8.62\text{x}10^3$ $\log K_2 = -3.94$

TABLE 5

Formation of Beryllium Oxalate Complexes

Total oxalate concentration 0.050M
Total beryllium concentration 0.0135M
Free perchloric acid added 0.00625M
Total volume of the solution 50.0 ml

1 (NaOH)	2 pH	3 $\bar{n}$	4 (L) Eq.11	5 (L) Eq.17	6 $\frac{\bar{n}}{(1-\bar{n})(L)}$	7 $\frac{2-\bar{n}}{1-\bar{n}}(L)$	8 $\frac{\bar{n}}{1-\bar{n}}$	9 $\frac{\bar{n}-1}{2-\bar{n}}$	10 $\frac{\bar{n}}{(L)}$	11 ln g	12 g
			$4.0x10^{-5}$							0.321	1.378
			$6.0x10^{-5}$							0.464	1.593
			$8.0x10^{-5}$							0.618	1.855
0.00	1.385	0.420	$6.579x10^{-5}$	$6.553x10^{-5}$	$1.101x10^{4}$	$1.792x10^{-4}$	0.724	–	$6.384x10^{3}$		
$0.40x10^{-2}$	1.412	0.464	$7.110x10^{-5}$	$7.079x10^{-5}$	$1.218x10^{4}$	$2.037x10^{-4}$	0.866	–	$6.526x10^{3}$		
$0.80x10^{-2}$	1.443	0.493	$7.813x10^{-5}$	$7.776x10^{-5}$	$1.245x10^{4}$	$2.322x10^{-4}$	0.972	–	$6.310x10^{3}$		
$1.20x10^{-2}$	1.475	0.526	$8.586x10^{-5}$	$8.550x10^{-5}$	$1.292x10^{4}$	$2.670x10^{-4}$	1.110	–	$6.126x10^{3}$		
$1.60x10^{-2}$	1.509	0.560	$9.486x10^{-5}$	$9.444x10^{-5}$	$1.342x10^{4}$	$3.105x10^{-4}$	1.273	–	$5.903x10^{3}$		
			$1.0 x 10^{-4}$							0.722	2.058
$2.00x10^{-2}$	1.543	0.640	$1.042x10^{-4}$	$1.038x10^{-4}$	$1.464x10^{4}$	$3.673x10^{-4}$	1.525	–	$6.142x10^{3}$		
$2.40x10^{-2}$	1.583	0.639	$1.169x10^{-4}$	$1.164x10^{-4}$	$1.514x10^{4}$	$4.407x10^{-4}$	1.770	–	$5.466x10^{3}$		
$2.80x10^{-2}$	1.628	0.696	$1.319x10^{-4}$	$1.313x10^{-4}$	$1.736x10^{4}$	$5.658x10^{-4}$	2.289	–	$5.277x10^{3}$		
			$1.4 x 10^{-4}$							0.942	2.564
$3.60x10^{-2}$	1.731	0.714	$1.786x10^{-4}$	$1.779x10^{-4}$	$1.398x10^{4}$	$8.031x10^{-4}$	2.497	–	$4.000x10^{3}$		
$4.40x10^{-2}$	1.863	0.756	$2.574x10^{-4}$	$2.543x10^{-4}$	$1.141x10^{4}$	$1.317x10^{-3}$	3.098	–	$2.937x10^{3}$		
$5.20x10^{-2}$	2.022	0.842	$3.862x10^{-4}$	$3.843x10^{-4}$	$1.380x10^{4}$	$2.831x10^{-3}$	5.329	–	$2.180x10^{3}$		
			$4.0 x 10^{-4}$							1.477	4.378
$5.60x10^{-2}$	2.127	0.881	$5.016x10^{-4}$	$4.995x10^{-4}$	$1.476x10^{4}$	$4.717x10^{-3}$	7.403	–	$1.756x10^{3}$		
			$6.0 x 10^{-4}$							1.833	6.250
$6.00x10^{-2}$	2.265	0.914	$7.040x10^{-4}$	$7.007x10^{-4}$	$1.510x10^{4}$	$8.890x10^{-3}$	10.628	–	$1.298x 10^{3}$		
$6.40x10^{-2}$	2.441	0.956	$1.067x10^{-3}$	$1.062x10^{-3}$	$2.036x10^{4}$	$2.532x10^{-2}$	21.727	–	$8.960x10^{2}$		
			$1.2 x 10^{-3}$							2.471	11.82
$6.80x10^{-2}$	2.640	1.038	$1.651x10^{-3}$	$1.642x10^{-3}$	$-1.654x10^{4}$	$-4.180x10^{-2}$	–	0.040	$6.287x10^{2}$		
			$2.2 x 10^{-3}$							3.084	21.83
$7.20x10^{-2}$	2.874	1.135	$2.690x10^{-3}$	$2.675x10^{-3}$	$-3.125x10^{4}$	$-1.724x10^{-2}$	–	0.156	$4.219x10^{2}$		
$7.40x10^{-2}$	3.000	1.180	$3.463x10^{-3}$	$3.447x10^{-3}$	$-1.893x10^{3}$	$-2.033x10^{-2}$	–	0.220	$3.407x10^{2}$		
$7.60x10^{-2}$	3.120	1.231	$4.352x10^{-3}$	$4.332x10^{-3}$	$-1.225x10^{3}$	$-1.449x10^{-2}$	–	0.300	$2.829x10^{2}$		
$7.80x10^{-2}$	3.230	1.262	$5.360x10^{-3}$	$5.334x10^{-3}$	$-8.989x10^{2}$	$-1.510x10^{-2}$	–	0.355	$2.354x10^{2}$		
$8.00x10^{-2}$	3.339	1.339	$6.385x10^{-3}$	$6.356x10^{-3}$	$-6.185x10^{2}$	$-1.245x10^{-2}$	–	0.513	$2.097x10^{2}$		

Table 5 shows the relevant data for the formation of beryllium oxalate complexes, extracted from the pH titration curve. Equations 9 and 11 were used in the calculation of $\bar{n}$ and (L) in columns 3 and 4 respectively. Figure 3 indicates the formation curve of the beryllium oxalate complexes. The free ligand concentrations calculated by Maley and Mellor's method (equation 17) using the same experimental results, are shown in column 5. It can be seen that these values are well within 1 per cent. of those in column 4, which demonstrates the validity of the approximations implied in Maley and Mellor's method.

From Figure 1 it can be seen that $\bar{n}$ calculated by the horizontal difference method (Section 2.3.3) varies between 0.8 and 1.15 in the same pH region used in the previous method. This is in serious disagreement with the data in Table 5, column 3, calculated by more rigorous methods. It is due to the low stability of the complexes and the fairly strong nature of oxalic acid. Serious overlap occurs between the pH region in which complex formation takes place and the one in which oxalic acid dissociates in the absence of metal ions. Hence the method of horizontal differences cannot be applied in this particular example. The use of a large excess of oxalic acid would not solve the difficulty because beryllium oxalates are weak complexes and any horizontal differences would still be almost insignificant.

The assumptions in the approximation method of Section 2.3.4 do not hold in this particular example. The results for the monochelate, which is quite stable, are reasonably close to those obtained by previous methods of calculation, but the dichelate does not give good agreement because the concentrations of other metal species are significant. Table 5, columns 8 and 9, show the calculations involved using equation 19. In Figures 4 and 5 the graphical solutions for this equation are worked out. Although Albert did not use a graphical solution, its inclusion seems reasonable. Thus for the determination of k_1 equation 19 becomes:

$$(L) = \frac{1}{k_1}\,\frac{\bar{n}}{1-\bar{n}}$$

and for the determination of k_2:

$$(L) = \frac{1}{k_2} - \frac{\bar{n}-1}{2-\bar{n}}$$

The results for β_1 and β_2 are derived by this method are 1.87×10^4 and 1.82×10^6 respectively.

If Hearon and Gilbert's method of integrating the $[\bar{n}/(L), (L)]$ data is used instead of Irving and Rossotti's method of least squares, the results in columns 10, 11, and 12 of Table 5 are obtained. In this case $N = b = 2$ and the equivalents for equation 23 and 24 are shown in Appendix 2.

Figure 6 shows the curve of $\frac{\bar{n}}{(L)}$ versus (L). Accurate integration of the curve for small values of (L) is extremely difficult, because in this region the curve is almost asymptotic to the ordinate. Figure 7 is a graph of equation (23). The curve is almost parallel to the abscissa. An accurate determination of the slope is therefore very difficult. However a value of 2.5×10^6 is found for β_2.

We conclude that the best procedure is to calculate ($\bar{n}$) and (L) according to equations 9 and 11 followed by the Irving and Rossotti process of developing these results.

TABLE 6

Summary of Results of Calculations *

Method	k_1	k_2	$\log \beta_1$	$\log \beta_2$
2.3.1)) 2.3.2)	1.21×10^4	67.4	4.08	5.91
2.3.3	NOT APPLICABLE			
2.3.4	1.87×10^4	97.6	4.27	6.26
2.3.5	9.43×10^3	260	3.97	6.40

* Acid association constants used in these calculations are shown in **Table 4.**

3. OTHER ELECTROMETRIC METHODS

3.1 Polarography and Potentiometric Measurements

Polarography and potentiometric measurements, although not as versatile as the pH titration method for the determination of stability constants, may be useful in certain favourable cases. Other electrometric methods are less important, but have been reviewed in a general reference book on the topic (Martell and Calvin, 1953).

The study of complex metal ions by the polarographic method relies on the fact that the reduction potentials of metal ions at the dropping mercury electrode are shifted (usually to a more negative value) by complex formation. By measuring this shift as a function of the concentration of the complex-forming substance, both the formula and the dissociation constant of the complex can be determined. However, this information can only be obtained when the reduction or oxidation of the metal complex is reversible at the dropping mercury electrode (D.M.E.), a limitation which is sometimes overlooked. The reversibility of the electrode process must thus be established before attempting to draw quantitative conclusions from the experimental data. Complexes of metal ions which are non-reducible at the D.M.E. (e.g. Be and Th) cannot, of course, be investigated by polarography, and studies involving the more electronegative elements (e.g. alkaline earths) are often inconvenient for similar reasons. The polarographic method for determining stability constants is at its best when applied to the transition metals.

3.2 Determination of the Co-ordination Number

It may be deduced that the half-wave potential of a complex metal ion should shift with changing activity of the complexing agent according to:

$$\frac{\Delta E_{\frac{1}{2}}}{\Delta \log(L)} = -N \frac{0.0591}{n}$$

where $\Delta E_{\frac{1}{2}}$ is the half-wave potential shift, N is the co-ordination number, and n is the number of electrons involved in the reduction. If a graph of $\Delta E_{\frac{1}{2}}$ versus $\Delta \log(L)$ is constructed, N may be found from the slope.

The half–wave potential depends on the logarithm of the stability constant of the complex metal ion, and is more negative the greater the value of β_n, i.e. the more stable the complex. The usual (approximate) relationship used is:

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{-0.0591}{n} \log \beta_n - N \frac{0.0591}{n} \log (L),$$

in which the subscripts c and s refer to the complex and simple metal ions respectively. The overall stability constant β_n may be determined from the intercept of a graph of $(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s$ versus log (L). More refined treatments have also been developed (McMasters, 1959) and a simple and rapid method for estimating stability constants from a single half–wave potential measurement has been suggested.

Potentiometry using the mercury electrode for the determination of stability constants has recently been extensively applied by Reilley and co–workers (1956). The method consists of measuring the extent to which the exchange reaction,

$$HgL + M = Hg + ML$$

takes place at the mercury–cup indicator electrode. Stability constants for various metal complexes at 25 °C may be calculated from the measured potential E_{Hg} by,

$$E_{Hg} = E^{o}_{Hg} + 0.0296 \log \frac{(M)\,(HgL)}{(ML)\,\beta_{HgL}} + 0.0296 \log \beta_{ML}$$

The value for the standard potential of the Hg electrode (E^{o}_{Hg}) at any particular pH value is given in Latimer (1952). The total concentrations of HgL, M, and ML are held constant during each experiment, and a graph of log β_{ML} versus pH is constructed, the stability constant then being determined from the pH – independent region. The method is capable of high accuracy, since a change of one unit in log β_{ML} corresponds to a potential change of 29.6 mV.

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APPENDIX 1

SYMBOLISM USED IN THE TEXT

Molecular and Ionic Species, Concentrations

H_bL	protonated ligand, electrically neutral
$H_pL^{-(b-p)}$	partly protonated ligand
L^{-b}	free ligand, of charge –b
M^{+a}	free metal ion of charge +a
$ML_n^{+(a-nb)}$	intermediate complex
ML_N	complex with maximum number (N) of ligands
$M(OH)_n^{+(a-n)}$	hydrolysed metal ion species
$Ox^{=}$	free oxalate ion, $C_2O_4^{=}$
$BeOx_n^{-(2n-2)}$	beryllium oxalate complexes; n = o, 1, or 2

Concentrations or activities of all these species are indicated by ( ), omitting charges

(M')	concentration of metal species other than ML_n
$(M)_t$	the total metal concentration
$(L)_t$	the total ligand concentration
$(L)_{t,h}$)	the total ligand concentration, except for those species containing ligand
(L'))	bound to metal ion
$(H)_t$	total concentration of available protons
h	the concentration of protons in all species containing ligand
(K)	concentration of potassium hydroxide added to the experimental solution

Other Parameters

$\bar{n}$	average number of bound ligands per metal ion
$\bar{p}$	average number of protons per ligand
α_M	ratio of the total metal concentration in species not bound to ligand and the concentration of free metal ion
α_L	ratio of the total ligand concentration in species not bound to metal ion, and the free ligand concentration
g	a function defined by Hearon and Gilbert (1955) as

$$\sum_{n=o}^{n=N} \beta_n (L)^n$$

APPENDIX 1 (continued)

$E_{\frac{1}{2}}$	half–wave potential (subscripts c and s refer to complex and simple ion solution respectively)
$\Delta E_{\frac{1}{2}}$	shift in half–wave potential due to complexing

Constants

k_n	stepwise formation constant for the reaction $ML_{n-1} + L = ML_n$
β_n	overall complexity constant for the reaction $M + nL = ML_n$
$\prod_{0}^{n} k_n$	the product of n stepwise formation constants $k_0\, k_1\, k_2 \ldots\ldots k_n$
A_p	stepwise acid association constant for the reaction: $H_{p-1}\, L^{-(b-p+1)} + H^+ = H_pL^{-(b-p)}$
K_w	ionic product of water = (H) (OH)
K_p	acid dissociation constant for the reverse of the above reaction
$\bar{A}_p$	overall acid association constant for the reaction: $L^{-b} + pH^+ = H_pL^{-(b-p)}$

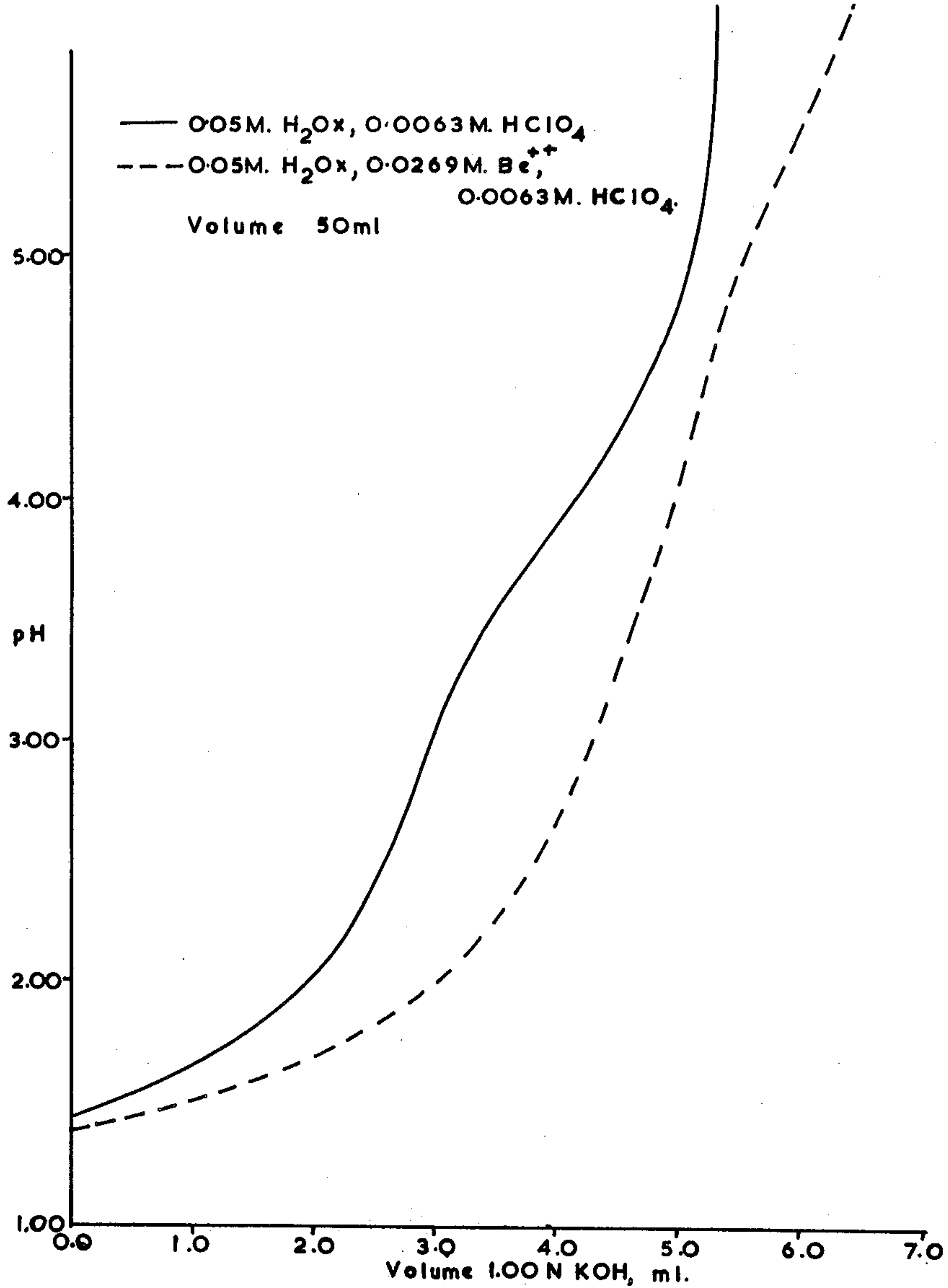

Figure 1. pH Titration of Beryllium Oxalates

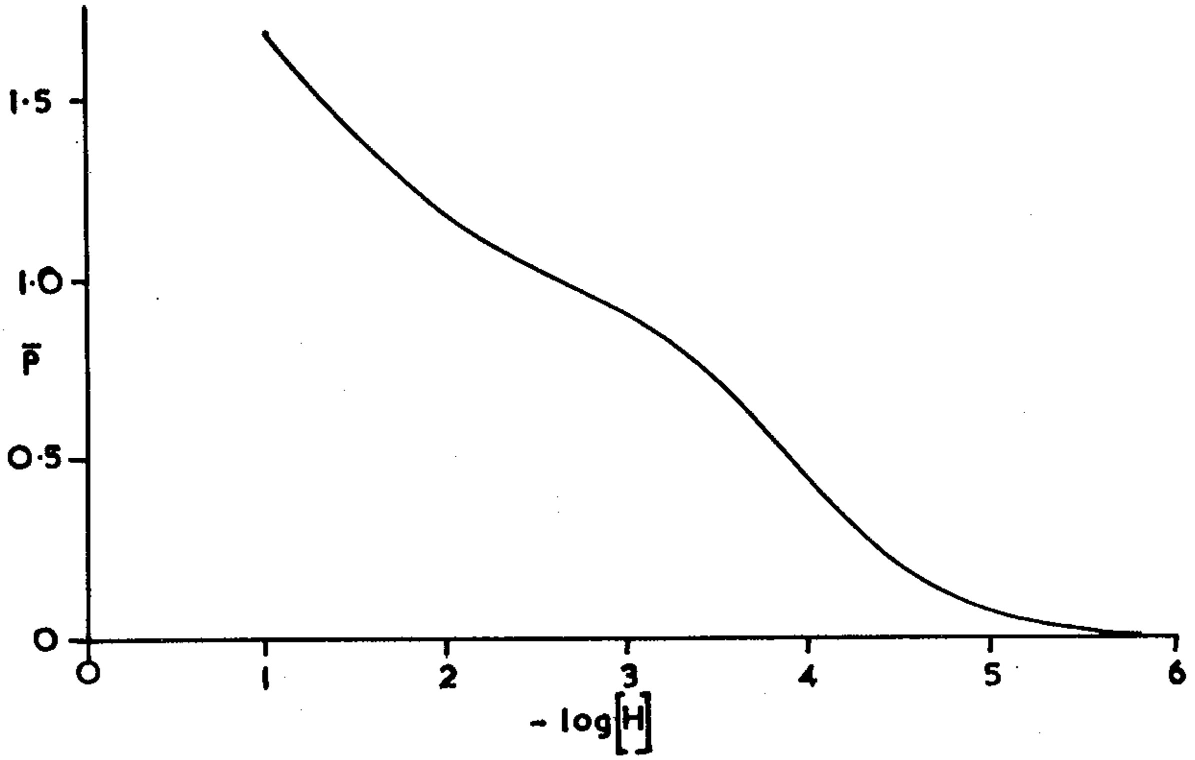

Figure 2. Association Curve of Oxalic Acid.

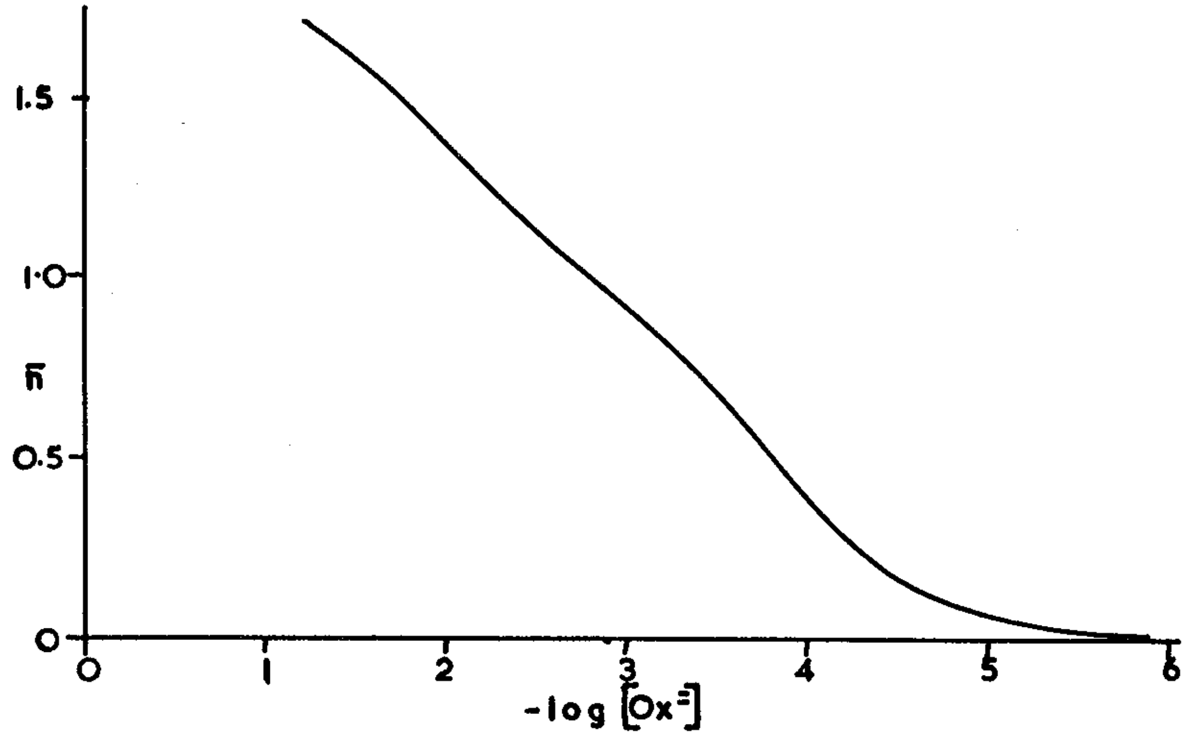

Figure 3. Formation Curve of Beryllium Oxalates.

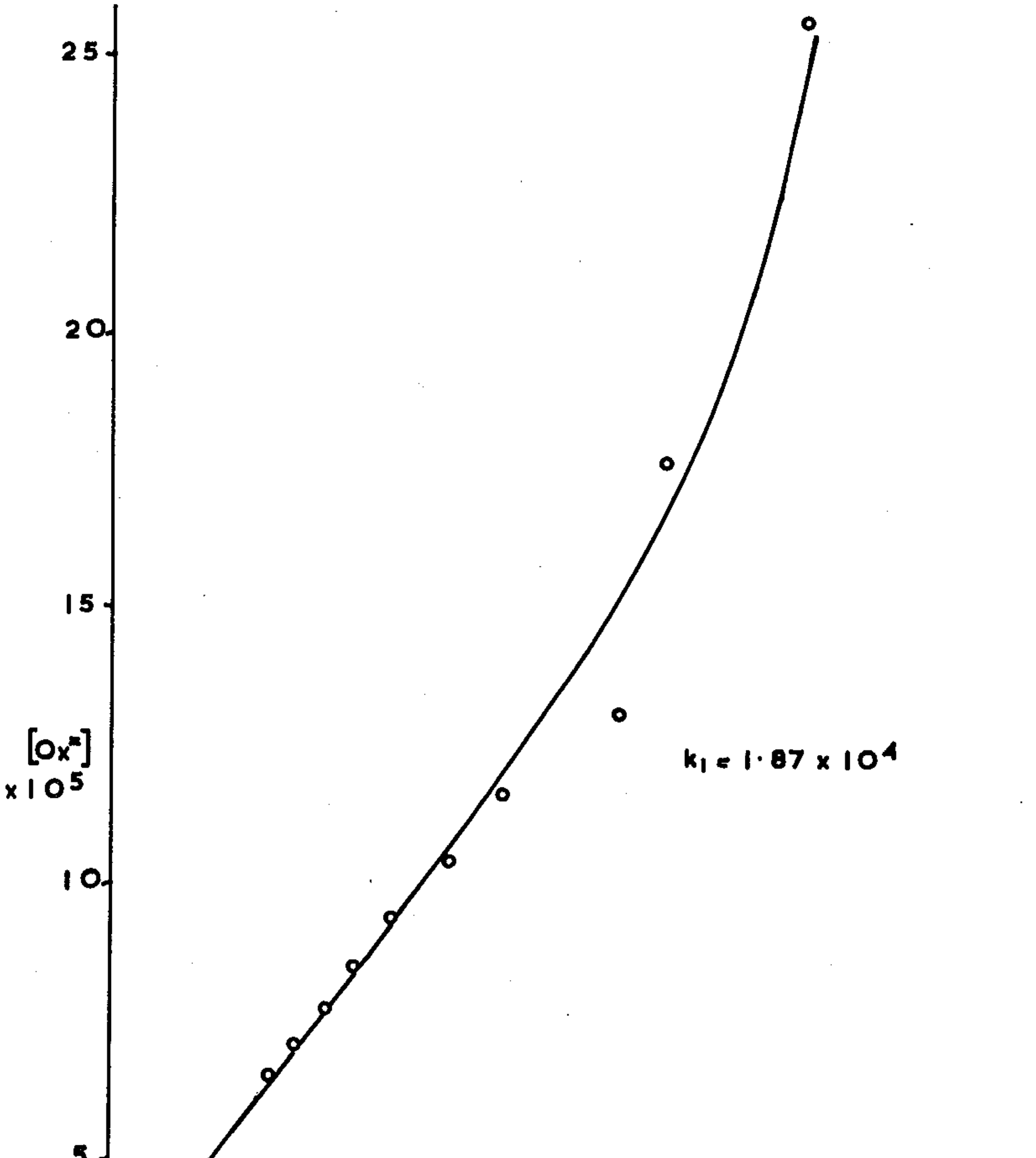

Figure 4. Albert's Approximation for k_1.

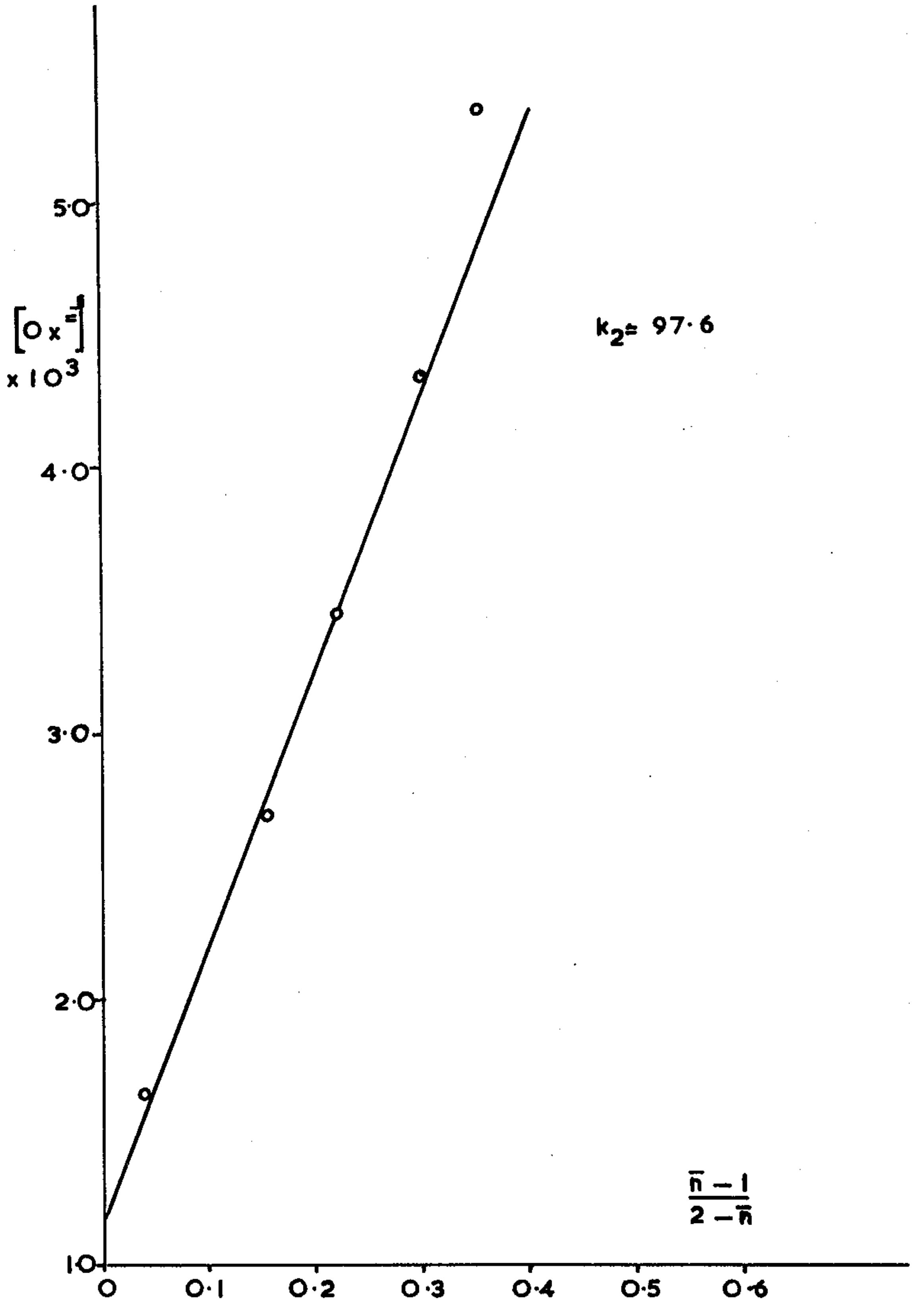

Figure 5. Albert's Approximation for k_2.

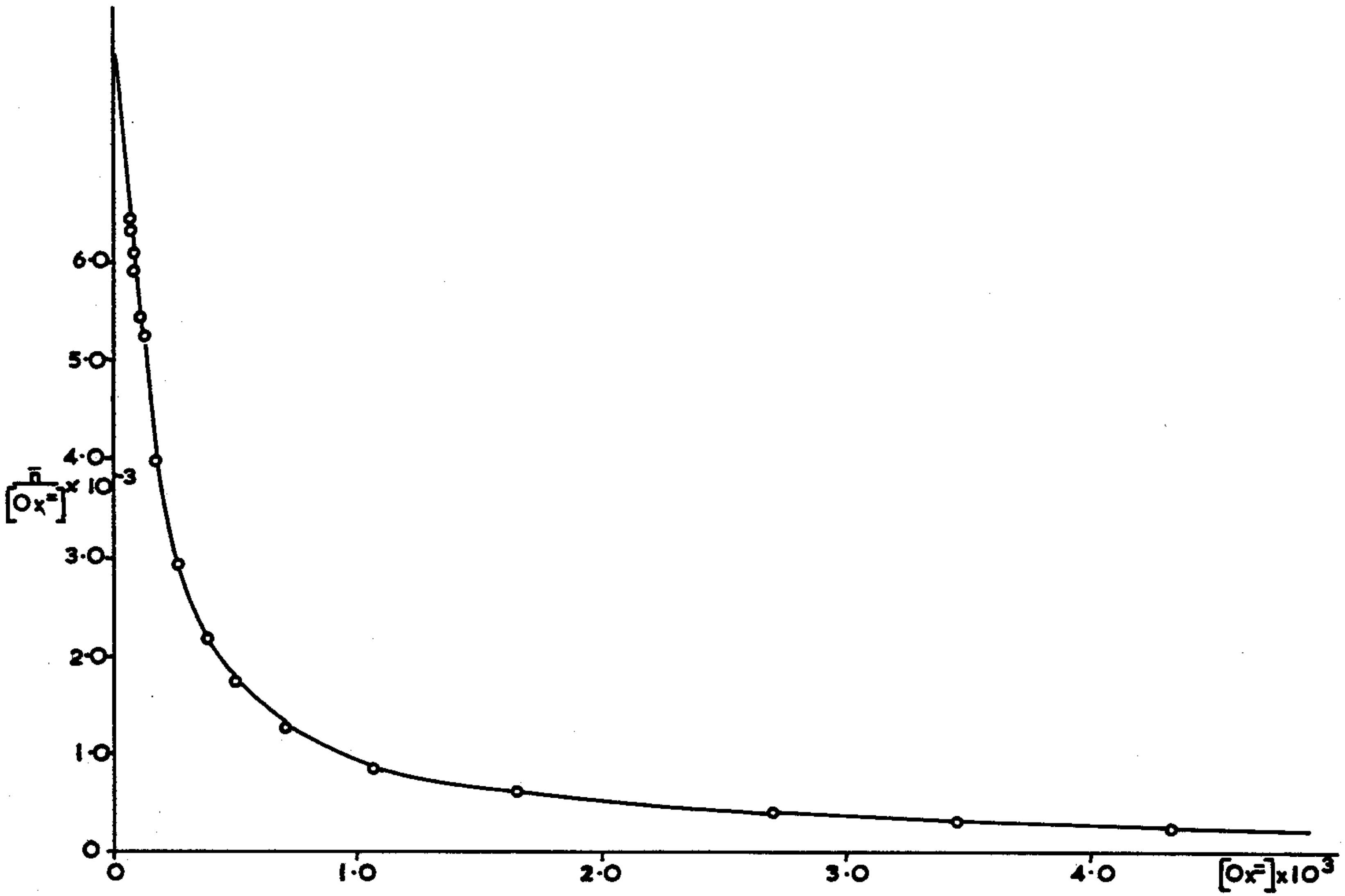

Figure 6. Graphical Integration by Hearon and Gilbert.

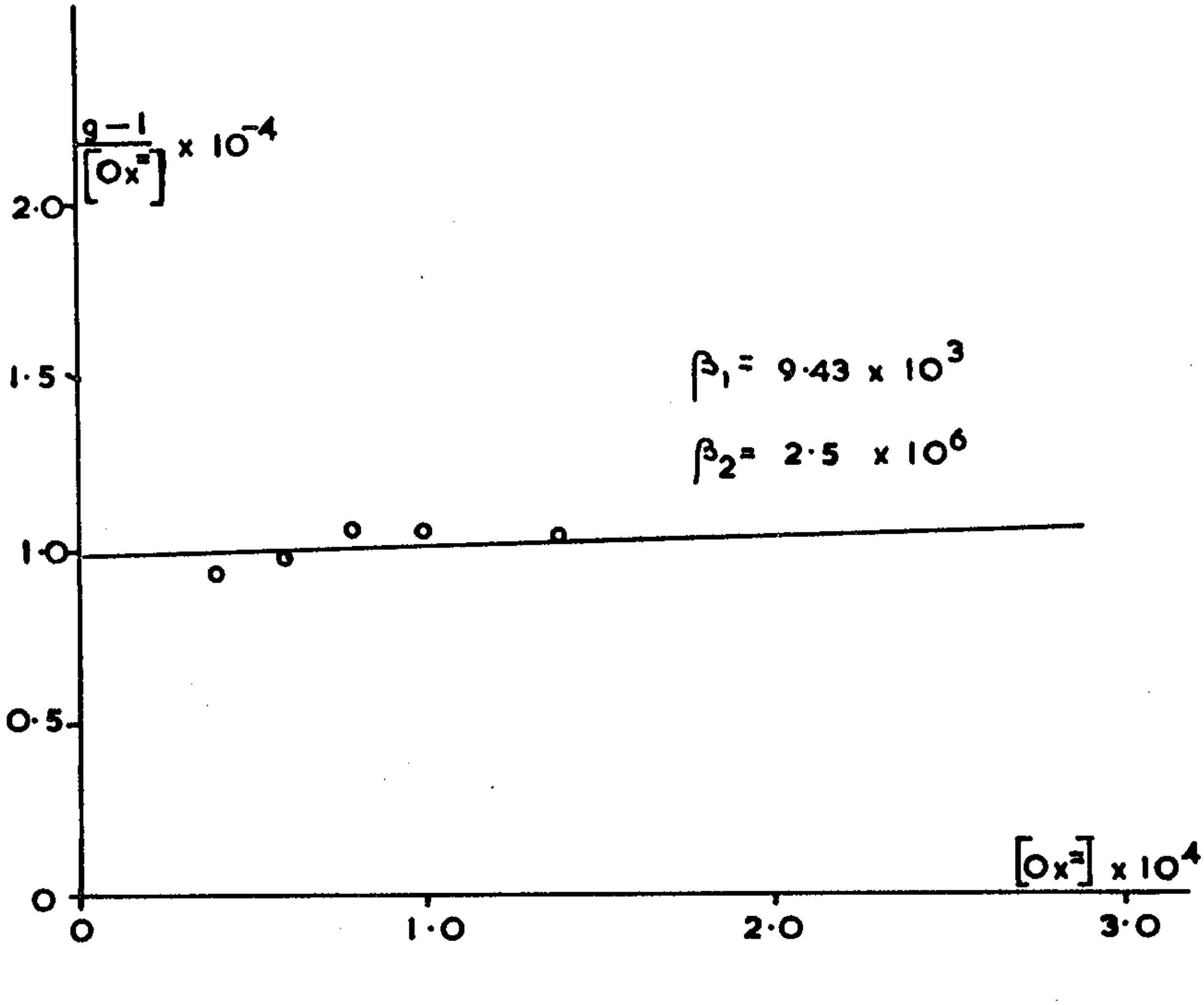

Figure 7. Leden's Function.