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Free Metal and Free Ligand Concentrations Determined from
Titrations Using Only a pH Electrode. Partial
Derivatives in Equilibrium Studies

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Abstract

In the studies of metal complex equilibria in aqueous solutions the variation techniques presented by Osterberg, Sarkar, Kruck, and McBryde allow one to calculate free metal and free (unassociated) ligand concentrations from titration experiments using only a pH electrode. The method makes no assumptions about the associated species present in solution and is thus model-independent. We present an alternate general derivation of the expressions and attempt to clarify the technique. Although the approach described below is applicable to any number of components (metals, ligands), in a manner analogous to Hedström's treatment of two component systems, we treat the three-component system by introducing six Jacobian unit determinants for the six variables (M , L , H , $\underline{m}$, $\underline{l}$, $\underline{h}$), that is, the three total and three free concentrations of the metal, ligand, and hydrogen, respectively:

$$\begin{array}{ll} J\left(\frac{M, \ln \underline{m}, \ln \underline{h}}{\ln \underline{l}, \underline{L}, \ln \underline{H}}\right) = 1 & J\left(\frac{M, \ln \underline{m}, H}{\ln \underline{l}, \underline{L}, H}\right) = 1 \\ J\left(\frac{L, \ln \underline{l}, \ln \underline{m}}{\ln \underline{h}, H, \ln \underline{M}}\right) = 1 & J\left(\frac{L, \ln \underline{l}, M}{\ln \underline{h}, H, M}\right) = 1 \\ J\left(\frac{H, \ln \underline{h}, \ln \underline{l}}{\ln \underline{m}, M, \ln \underline{L}}\right) = 1 & J\left(\frac{H, \ln \underline{h}, L}{\ln \underline{m}, M, L}\right) = 1 \end{array}$$

These Jacobians are very useful in deriving numerous variational expressions. Using computer-generated data, we test the techniques under a variety of conditions. A useful Fortran computer program is discussed. A simple technique for

analytically evaluating implicit functions such as $(\partial \text{pH} / \partial M)_L$ or $(\partial \text{pH} / \partial L)_M$, is presented. This enables one to avoid the use of numerical methods in the least squares refinement of formation constants, thus leading to substantial reduction in the computational effort.

Introduction

Osterberg,¹ and later, Sarkar, Kruck,² and McBryde³ introduced an extremely valuable technique for evaluating the free metal and free ligand concentrations in multi-component equilibria by the use of pH titration data alone. That is, one could indirectly measure pM ($-\log[M]$, $[M]$ = free metal concentration) and pL ($[L]$ = free (unassociated) ligand concentration) values by using only a pH-electrode. The technique is an extension of earlier work of Hedström⁴ and Sillén.⁵ It is based on partial differential relations arising from the mass balance equations (*vide infra*) and requires several titrations, per reactant, performed in a special way. Surprisingly, the method is not widely known, judging by the near absence of its reported use. Sarkar and co-workers⁶⁻⁹ have experimentally applied it to rather complicated equilibria, involving the determination of as many as three different nonhydrogen reactants. The technique has been very important in our studies of the equilibria involving Th^{4+} , U^{4+} , and Pu^{4+} complexes with catechol and hydroxamate ligands, where evidence for mixed-ligand and polynuclear species is abundant.¹⁰

We feel that the past presentation of the technique (which can be called the "variation" method – especially as it applied to determining several different reactant concentrations) needs additional clarification; which is the primary purpose of this paper. Also, we wish to introduce

some general differential relations of which the above-mentioned technique is a special case. The general relations will be presented in the form of unit Jacobians of third and higher order in exactly the same form as that presented by Hedström for two component systems. A very simple method for analytically evaluating partial derivatives of implicit functions, such as $(\partial \text{pH}/\partial M)_L$ or $(\partial \text{pH}/\partial L)_M$, will be presented. Such derivatives are used by least-square refinement of equilibrium constants and in the past have been evaluated numerically rather than analytically – a process requiring considerably more computational effort. Finally, we wish to introduce some relevant aspects of a new computer program, STBLTY,¹¹ which was used for all the calculations and most of the drawings presented here.

For solutions containing one type of metal and one type of ligand as reactants, along with hydrogen and hydroxide ions, the species present in solution may be represented by equilibria of the sort

The stability constant of the j^{th} associated species is given by

$$\beta_j = \frac{C_j}{\underline{e}_{mj} \underline{e}_{lj} \underline{e}_{hj}} \quad (2)$$

where e_{kj} is the stoichiometric coefficient of the k^{th} reagent, C_j is the concentration of the j^{th} associated species, and $\underline{m}$,

$\underline{l}$, $\underline{h}$ are the free (unassociated) concentrations of metal, ligand, and hydrogen. (See Table I for a more complete definition of terms used in this presentation.) Usually only $\underline{h}$ (in addition to the total concentrations) is known from a simple pH titration. In refinement programs such as SCOGS^{12(a)} and MINIQAD^{12(b)} unknown values of pM and pL are calculated only after a model is assumed along with the corresponding β values. Thus such values of pM and pL can be model-biased. Osterberg's¹ proposal is the model-independent "variation" relation

$$\Delta pL(M_O, L_O) = pL_2 - pL_1 = \left[\int_{pH_2}^{pH_1} \left(\frac{\partial H}{\partial L} \right)_{M_O, h} dpH \right]_{L_O} \quad (3)$$

where M , L , and H are the total metal, ligand, and hydrogen concentrations. The relation states that for given values of M and L (M_O, L_O) the change in pL (from some known value pL_1 , which can be determined in a number of ways¹⁻³ as for example in Table I) corresponding to a change in pH is related to the extent the variation of L affects H . One thus needs at least two titrations where L is the only varied nonhydrogen total concentration. A plot of H versus L at constant pH ¹⁷ shows curves that are ordinarily nearly straight lines. Since the slopes $(\partial H / \partial L)$ are dependent on L , so must be ΔpL in Eq. 3, a subtle but very important point which McBryde³ notes (his Eqs. 11 and 17) but which Sarkar and Kruck² apparently

do not. However, in the description of their calculation procedure, Sarkar and Kruck propose the evaluation of the partial derivatives at the "midpoint" of a series of curves. Presumably, "midpoint" refers to the concentration of the curve nearest the mean concentration of the varied reagent.

Using a procedure that bears some resemblance to the one proposed earlier by Sillén (Eq. 49, Ref. 5), Sarkar and Kruck² extended Osterberg's relation to the calculation of any ΔpX for any general multi-component equilibria, using relations like Eq. 3 for each reactant. Thus each reactant would require a separate series of variation titrations.

In Eq. 3, any L_o within the ligand variation range may be chosen for the integration to produce pL values as a function of pH . In the series M is kept constant (M_o). However, when the variation is extended to metal components as well, the choice of M_o and L_o is no longer arbitrary only when one complete data set of pM , pL , and pH values is to be constructed. That is, in the first series, L is varied ($M = M_o$) to produce pL values with integration performed at L_o (Eq. 3). In the subsequent series, M is varied to determine pM values. In this series L must be fixed at the L_o of the first series and the integration must be performed at the same M_o value fixed in the preceding ligand series. The intersection of the two series is at (M_o, L_o) , the "common point." Since the plots of H vs M or L appear nearly linear the above qualification apparently was not appreciated. An

uncritical reader may still infer from the presentations of the variation technique that ΔpM and ΔpL are only functions of pH! We hope to show to what extent this is not true.

Analysis of the Variation Technique

How much can the results be affected if one were to disregard the "common point" requirement mentioned above? An examination of past applications⁶⁻⁹ of the technique to multi-reactant determinations suggests that perhaps the minor qualification was not always appreciated.^{8,9} In the determination of the formation constants of copper(II) diglycyl-L-histidine⁸ the "midpoint" values (M_0 , L_0) in the metal and ligand variation series are different. (We must point out that in their other applications of the technique^{6,7} it appears that the "midpoints" are also the "common points.") We proceeded to test the reported results. Figure 1 shows the calculated titration curves¹⁰ using the reported constants and conditions,¹³ which should be compared to the observed curves in the upper part of Figure 2 in Ref. 8. Two minor differences are noted. There is a clearly discernible equivalence point around pH 6.2 in the observed titration curve, which is not substantiated by the constants. Also, the calculated curves nearly coalesce at pH 11, whereas the observed curves do not.¹⁴ We could not conclude with certainty that the "common point" requirement was the source of these discrepancies.

In order to test the "common point" requirement more reliably, we next proceeded entirely with computer generated data. For our purpose, we chose to use a relatively simple system, that of copper(II) acetylacetonate, whose formation constants are reliably known.¹⁵ Table II lists the conditions of variation. Figures 2 and 3 show typical titration curves for metal and ligand variation series, respectively.

The conditions we proceeded to test involved variation of metal and ligand over a small interval about a common point, with only a slight excess of ligand over the amount of metal present (Series A). The plots of H vs M or L at constant pH were fitted quadratically to obtain the slopes (Table III). The other series (Series B) contained a very large ligand excess. The slopes were fitted both linearly and quadratically in this category. Finally we tested the effects of linearly fitting the slopes under conditions of only slight ligand excess (Series C).

Figure 4 shows the kind of "variation errors" δ in pX we observed for the above three cases. The errors were defined to be the difference between pX^O calculated in the usual model-dependent manner¹² (using mass balance constraints) assuming the model to be absolutely correct and the pX^V calculated from the variation technique: $\delta = pX^O - pX^V$. In each of the δ plots in Figure 4 we calculated slopes at the "common point" and applied the resultant ΔpX values to all other non-common-point data sets, using the appropriately

different starting values pX_1 . Figures 5 and 6 show plots of H vs M and H vs L , respectively. Table III shows a selection of $(\partial H/\partial X)$ values under a variety of conditions.

The error trends can be summarized in the following observations. There are two kinds of errors present. One kind is related to δ 's associated with the common-point curves, which should ideally have no errors. These amount to about 0.1 pX units at pH 6, under the chosen conditions. We relate these δ 's to the accumulation of systematic, principally round-off, errors in the variation method, where we used simple Simpson's integration procedure with an interval of 0.1 pH and where we used a quadratic fitting function for (H, X) slopes. The errors observed amount to a loss of approximately .002 pX units per integration interval. This should emphasize the need for extremely accurate data over a sufficiently broad region of total concentrations in order to apply the technique successfully to real systems.

The other type of errors, the dispersion about the common point curve, are more interesting. In general, they are larger than the integration errors — up to 0.6 pX units. (One may note that an error of this magnitude in pH in a buffer region such as pH 12 can cause the refinement of constants sensitive to that region to diverge.) In general, the pL errors are smaller than pM errors (compare δ curves, Figure 4c vs 4f). The higher the ligand excess, the smaller the errors (Figure 4b, e). Finally, the largest errors occur when one

linearly fits H vs X , as in Series C. Whether or not one linearly fits the curves under conditions of a large ligand excess (Series B) makes practically no difference on the errors. These observations are related to the extent curves in (H, X) plots, such as in Figures 5 and 6, deviate from linearity. The deviation becomes larger at higher pH and when the L/M ratio is small.

In summary, the need to evaluate a complex set of pX values at a common point becomes apparent from the above observations. At this point we proceed to a more general presentation of the variation technique.

General Variational Relations

For each point, the equilibrium concentrations of the species present in solution, including polynuclear and mixed ligand-hydroxy species, are defined by the three mass balance equations,

$$M(\underline{m}, \underline{l}, \underline{h}) = \underline{m} + \sum_{j=1}^N e_{mj} C_j \quad (4)$$

$$L(\underline{m}, \underline{l}, \underline{h}) = \underline{l} + \sum e_{lj} C_j \quad (5)$$

$$H(\underline{m}, \underline{l}, \underline{h}) = \underline{h} + \sum e_{hj} C_j - K'_w / \underline{h} \quad (6)$$

(j is an index over all the N associated species). The partial derivative relations deduced from these equations,

$$(\partial M / \partial \ln \underline{\ell})_{\underline{m}, \underline{h}} = (\partial L / \partial \ln \underline{m})_{\underline{\ell}, \underline{h}} = \sum e_{mj} e_{\ell j} c_j \quad (7)$$

$$(\partial M / \partial \ln \underline{h})_{\underline{m}, \underline{\ell}} = (\partial H / \partial \ln \underline{m})_{\underline{h}, \underline{\ell}} = \sum e_{mj} e_{hj} c_j \quad (8)$$

$$(\partial L / \partial \ln \underline{h})_{\underline{m}, \underline{\ell}} = (\partial H / \partial \ln \underline{\ell})_{\underline{m}, \underline{h}} = \sum e_{\ell j} e_{hj} c_j \quad (9)$$

are easily demonstrated with the aid of Eq. 2. Note that $(\partial M / \partial \underline{\ell})_{\underline{m}, \underline{h}} \neq (\partial L / \partial \underline{m})_{\underline{\ell}, \underline{h}}$, etc. By choosing as variables the logarithms of the free reactants, the Jacobian matrix (see Table I), $J \left(\frac{M, L, H}{\ln \underline{m}, \ln \underline{\ell}, \ln \underline{h}} \right)$, becomes symmetric. One consequence of this is that there exists an exact differential¹⁶ of the form $M d \ln \underline{m} + L d \ln \underline{\ell} + H d \ln \underline{h}$. Sillén's⁵ Eq. 49 deals with this in greater detail. Again any number of metal or ligand components can be treated by corresponding additional mass balance equations. In a manner proposed by Hedström⁴ for a two component system, we can convert Eqs. 7-9 into the form of unit Jacobian determinants¹⁶ as

$$J \left(\frac{M, \ln \underline{m}, \ln \underline{h}}{\ln \underline{\ell}, L, \ln \underline{h}} \right) = 1 \quad (10)$$

$$J \left(\frac{L, \ln \underline{\ell}, \ln \underline{m}}{\ln \underline{h}, H, \ln \underline{m}} \right) = 1 \quad (11)$$

$$J \left(\frac{H, \ln \underline{h}, \ln \underline{\ell}}{\ln \underline{m}, M, \ln \underline{\ell}} \right) = 1 \quad (12)$$

The explicit expression for Eq. 10 is

$$\begin{vmatrix} \left(\frac{\partial M}{\partial \ln \underline{\ell}}\right)_{L, \underline{h}} & \left(\frac{\partial M}{\partial L}\right)_{\underline{\ell}, \underline{h}} & \left(\frac{\partial M}{\partial \ln \underline{h}}\right)_{\underline{\ell}, L} \\ \left(\frac{\partial \ln \underline{m}}{\partial \ln \underline{\ell}}\right)_{L, \underline{h}} & \left(\frac{\partial \ln \underline{m}}{\partial L}\right)_{\underline{\ell}, \underline{h}} & \left(\frac{\partial \ln \underline{m}}{\partial \ln \underline{h}}\right)_{\underline{\ell}, L} \\ \left(\frac{\partial \ln \underline{h}}{\partial \ln \underline{\ell}}\right)_{L, \underline{h}} & \left(\frac{\partial \ln \underline{h}}{\partial L}\right)_{\underline{\ell}, \underline{h}} & \left(\frac{\partial \ln \underline{h}}{\partial \ln \underline{h}}\right)_{\underline{\ell}, L} \end{vmatrix} \quad (10')$$

One notes that $\underline{h}$ in (10), $\underline{m}$ in (11) and $\underline{\ell}$ in (12) are held constant. It should be apparent that Hedström's unit Jacobian is valid for any number of components, provided that no more than two components are effectively independent. Adding constant variables does not alter the determinant from unity. Thus

$$1 = J\left(\frac{X, \ln x}{\ln y, Y}\right) = J\left(\frac{X, \ln x, A}{\ln y, Y, A}\right) = J\left(\frac{X, \ln x, A, B}{\ln y, Y, A, B}\right) = \dots \quad (13)$$

where the added variables A and B are held constant. This is essentially the basis of Osterberg's application of Hedström's equation to a three component system, to obtain from the Jacobian the relation

$$\left(\frac{\partial \ln \underline{\ell}}{\partial \ln \underline{h}}\right)_{M, L} = -\left(\frac{\partial H}{\partial L}\right)_{M, \underline{h}} \quad (14)$$

which reduces to Eq. 3. Thus using (13) we can increase the number of unit Jacobians to six, which is the number of variables $(M, L, H, \ln \underline{m}, \ln \underline{\ell}, \ln \underline{h})$, both dependent and independent, which we consider in (4) - (6):

$$J\left(\frac{M, \ell n \underline{m}, H}{\ell n \underline{L}, L, H}\right) = 1 \quad (15)$$

$$J\left(\frac{L, \ell n \underline{L}, M}{\ell n \underline{h}, H, M}\right) = 1 \quad (16)$$

$$J\left(\frac{H, \ell n \underline{h}, L}{\ell n \underline{m}, M, L}\right) = 1 \quad (17)$$

The proof for (10) - (12) has its basis in the relations (7) - (9). The proof for (15) - (17) can be procured from Sillén's⁵ Eq. 49.

Hedström showed that such unit Jacobians are extremely useful in deriving new partial derivative expressions, especially of (implicit) functions such as $\underline{m}$ (M, L, H) or the like, which cannot in general be stated explicitly. To illustrate this, we shall derive the corresponding equation for ΔpM (M_0, L_0) analogous to (3). By utilizing the chain rule for Jacobians,¹⁶ (17) can be restated in terms of any three independent variables x, y, z as

$$J\left(\frac{H, \ell n \underline{h}, L}{x, y, z}\right) = J\left(\frac{\ell n \underline{m}, M, L}{x, y, z}\right) \quad (18)$$

By choosing the variables $M, L, \ell n \underline{h}$ we have

$$\begin{vmatrix} \left(\frac{\partial H}{\partial M}\right)_{L, \underline{h}} & \left(\frac{\partial H}{\partial L}\right)_{M, \underline{h}} & \left(\frac{\partial H}{\partial \ell n \underline{h}}\right)_{M, L} \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial \ell n \underline{m}}{\partial M}\right)_{L, \underline{h}} & \left(\frac{\partial \ell n \underline{m}}{\partial L}\right)_{M, \underline{h}} & \left(\frac{\partial \ell n \underline{m}}{\partial \ell n \underline{h}}\right)_{M, L} \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}$$

which reduces to

$$\left(\frac{\partial \ln m}{\partial \ln h}\right)_{M,L} = -\left(\frac{\partial H}{\partial M}\right)_{L,h} \quad (19)$$

or

$$\Delta pM (M_o, L_o) = pM_2 - pM_1 = \left[\int_{pH_2}^{pH_1} \left(\frac{\partial H}{\partial M}\right)_{L,h} dpH \right]_{M_o} \quad (20)$$

This is McBryde's³ Eq. 17. Other useful relations can be obtained similarly. For the six variables M , L , H , $\underline{m}$, $\underline{l}$, $\underline{h}$ there are twenty choices for three independent variables x , y , z . Some of these choices, when combined with the unit Jacobians (Eqs. 10 - 12, and 15 - 17), lead to redundant results. The particular choice is dictated by what one can experimentally measure. Once a useful triplet can be decided on, any one of the unit Jacobians (10) - (12), (15) - (17) can be rearranged in the form of (18). Thus equations similar to (3) and (20) can be obtained.

Applications of the Jacobian Matrix to Equilibrium Calculations

One least-squares procedure¹¹ for the refinement of formation constants β_j calls for minimization of the differences between observed pH's and those calculated from an assumed set of constants. In the normal equations, partial derivatives $(\partial pH / \partial \log \beta_j)$ are required. These can be calculated numerically but such a procedure requires a considerable

computational effort. If one recognizes that pH is also a function of the total concentrations, one can state

$$\begin{aligned}
 \left(\frac{\partial \text{pH}}{\partial \log \beta_j} \right)_{\beta_{k \neq j}} &= \left(\frac{\partial \text{pH}}{\partial M} \right)_{L,H} \left(\frac{\partial M}{\partial \log \beta_j} \right)_{\beta_{k \neq j}, L, H} \\
 &+ \left(\frac{\partial \text{pH}}{\partial L} \right)_{M,H} \left(\frac{\partial L}{\partial \log \beta_j} \right)_{\beta_{k \neq j}, M, H} \\
 &+ \left(\frac{\partial \text{pH}}{\partial H} \right)_{M,L} \left(\frac{\partial H}{\partial \log \beta_j} \right)_{\beta_{k \neq j}, M, L}
 \end{aligned} \tag{21}$$

The partial derivatives of the explicit functions on the right side of Eq. (21) are easily

evaluated. For example, $\left(\frac{\partial L}{\partial \log \beta_j} \right)_{\beta_{k \neq j}} = 2.303 e_{lj} C_j$.

The evaluation of the implicit function derivatives, $(\partial \text{pH} / \partial X)$ is less direct.

One needs to set up the Jacobian matrix $J \left(\frac{M, L, H}{\ln m, \ln l, \ln h} \right)$ (see Table I) which linearly relates dX to $d \ln x$:

$$\begin{pmatrix} dM \\ dL \\ dH \end{pmatrix} = J \begin{pmatrix} d \ln m \\ d \ln l \\ d \ln h \end{pmatrix} \tag{22}$$

This matrix is symmetric and its elements are easily evaluated, as shown in (24). In fact, this matrix is used to calculate pM and pL values by the non-variational methods.^{11,12} In the process, its inverse is computed.

It is a remarkable fact that the elements of the inverse matrix are precisely the partial derivatives of the implicit functions that we need to compute $(\partial \text{pH} / \partial \log \beta_j)$:

$$\begin{pmatrix} \left(\frac{\partial M}{\partial \ln \underline{m}}\right)_{\underline{\ell}, \underline{h}} & \left(\frac{\partial M}{\partial \ln \underline{\ell}}\right)_{\underline{m}, \underline{h}} & \left(\frac{\partial M}{\partial \ln \underline{h}}\right)_{\underline{m}, \underline{\ell}} \\ \left(\frac{\partial L}{\partial \ln \underline{m}}\right)_{\underline{\ell}, \underline{h}} & \left(\frac{\partial L}{\partial \ln \underline{\ell}}\right)_{\underline{m}, \underline{h}} & \left(\frac{\partial L}{\partial \ln \underline{h}}\right)_{\underline{m}, \underline{\ell}} \\ \left(\frac{\partial H}{\partial \ln \underline{m}}\right)_{\underline{\ell}, \underline{h}} & \left(\frac{\partial H}{\partial \ln \underline{\ell}}\right)_{\underline{m}, \underline{h}} & \left(\frac{\partial H}{\partial \ln \underline{h}}\right)_{\underline{m}, \underline{\ell}} \end{pmatrix}^{-1} \quad (23)$$

$$= \begin{pmatrix} \underline{m} + \sum_{j=1}^N e_{mj}^2 C_j & \sum e_{mj} e_{\ell j} C_j & \sum e_{mj} e_{hj} C_j \\ \sum e_{mj} e_{\ell j} C_j & \underline{\ell} + \sum e_{\ell j}^2 C_j & \sum e_{\ell j} e_{hj} C_j \\ \sum e_{mj} e_{hj} C_j & \sum e_{\ell j} e_{hj} C_j & \underline{h} + \frac{K_w}{\underline{h}} + \sum e_{hj}^2 C_j \end{pmatrix}^{-1} \quad (24)$$

$$= \begin{pmatrix} \left(\frac{\partial \ln \underline{m}}{\partial M}\right)_{L, H} & \left(\frac{\partial \ln \underline{m}}{\partial L}\right)_{M, H} & \left(\frac{\partial \ln \underline{m}}{\partial H}\right)_{M, L} \\ \left(\frac{\partial \ln \underline{\ell}}{\partial M}\right)_{L, H} & \left(\frac{\partial \ln \underline{\ell}}{\partial L}\right)_{M, H} & \left(\frac{\partial \ln \underline{\ell}}{\partial H}\right)_{M, L} \\ \left(\frac{\partial \ln \underline{h}}{\partial M}\right)_{L, H} & \left(\frac{\partial \ln \underline{h}}{\partial L}\right)_{M, H} & \left(\frac{\partial \ln \underline{h}}{\partial H}\right)_{M, L} \end{pmatrix} \quad (25)$$

That is, $\begin{pmatrix} d \ln \underline{m} \\ d \ln \underline{\ell} \\ d \ln \underline{h} \end{pmatrix} = \tilde{K} \begin{pmatrix} dM \\ dL \\ dH \end{pmatrix}$, where $\tilde{K} = \tilde{J}^{-1}$

A more general statement of Eq. 21 thus becomes

$$\left(\frac{\partial p X_i}{\partial \log \beta_j}\right)_{\beta_{k \neq j}} = - \sum_{t=1}^3 K_{it} e_{tj} C_j \quad (26)$$

This simple relationship proves to be extremely useful and is a substantial short cut in the least-squares refinement of equilibrium data.

Conclusion

The variation techniques presented by Osterberg,¹ Sarkar, Kruck,² and McBryde³ are powerful extensions of the pH titration experiment, particularly for equilibria involving polymeric species. We have presented a completely general mathematical basis for these techniques to multi-component systems. Very useful relationships involving partial derivatives were used in the process. One of the relations derived allows for the first time the use of analytical derivatives in the refinement of equilibrium constants. However, the most important task remains the acquisition of data of sufficient accuracy so that these techniques can be successfully applied.

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13. We assume Table II in Ref. 8 has a mislabeling with respect to the q values for the ligand constants. The order should be reversed.

14. The reported⁸ change in titrant volume at pH 6 is about 0.6 ml of 1.0024 M NaOH. We calculate a change of only four ligand equivalents, or only 0.029 ml. This inconsistency could be explained if the true titrant concentration were 0.05 M, rather than the reported value of 1.0024 M.
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17. The data $(H, L)_{\text{pH}}$ or $(H, M)_{\text{pH}}$ can be obtained from a series of titration curves, such as in Figures 1 to 3, in the following manner: One can overlay the curves with a uniformly spaced series of horizontal lines of constant pH. Each line intersects the titration curves of different values of L or M . The corresponding titrant values, EQV, at the points of intersection are readily converted to values of H .

Table I
Glossary of Terms

C_j	Concentration of the j th associated species: $C_j = \left[M_{e_{mj}} L_{e_{lj}} H_{e_{hj}} \right] = \beta_j \bar{m}_j^e \bar{l}_j^e \bar{h}_j^e$
e_{kj}	Stoichiometric coefficient, referring to the number of k th type of atoms in the j th associated species. For example, for the j th species $[\text{Th}(\text{cat})_2(\text{OH})]^-$, (cat = dianionic ligand) $e_{mj} = 1$, $e_{lj} = 2$, $e_{hj} = -1$. The value of e_{hj} is negative to signify a hydroxide. Positive values refer to hydrogen atoms.
H	Total hydrogen concentration, defined by $A - B + \text{NH}^+L$, where $A = [\text{HCl}]$, $B = [\text{KOH}]$ or any other monoprotic mineral acid and base.
h	Free hydrogen ion concentration, $[\text{H}^+]$.
$J \left(\frac{U, V, W}{u, v, w} \right)$	$\begin{vmatrix} (\partial U / \partial u)_{v,w} & (\partial U / \partial v)_{u,w} & (\partial U / \partial w)_{u,v} \\ (\partial V / \partial u)_{v,w} & (\partial V / \partial v)_{u,w} & (\partial V / \partial w)_{u,v} \\ (\partial W / \partial u)_{v,w} & (\partial W / \partial v)_{u,w} & (\partial W / \partial w)_{u,v} \end{vmatrix}$ Jacobian determinant of the variation of functions U, V, W with respect to the independent variables u, v, w .
$\tilde{J} \left(\frac{U, V, W}{u, v, w} \right)$	Jacobian matrix, having elements of the above determinant.
K'_w	$[\text{H}^+][\text{OH}^-]$.
L	Total concentration of the ligand, in all of its forms.
$\bar{l}$	Concentration of the unassociated (free) ligand.
$\ln \bar{h}$, $\ln \bar{l}$, $\ln \bar{m}$, $\ln \bar{x}$	Logarithm, base e , of the concentration of the unassociated (free) reactants.
M	Total concentration of the metal, in all of its forms.
$\bar{m}$	Concentration of the free metal.
N	Number of associated species under consideration.
NH	Maximum number of dissociable hydrogens on the ligand.

Table I, Glossary of Terms, continued

NH'	Number of dissociable hydrogens on the ligand, in the form it was introduced to the solution. For example, if the ligand were the acetate ion and if it were introduced as the potassium salt, then $NH = 1$ but $NH' = 0$.
pH, pL, pM, pX	Negative of the logarithm, base 10, of the free concentrations. X refers to M or L.
PM ₁	$= -\log_{10} M$ if pH_1 is sufficiently low so no metal-ligand complexation occurs.
PL ₁	$= -\log_{10} \left[\frac{L}{1 + \sum_{i=1}^{NH} \beta_i^H h^i} \right]$ if pH_1 is sufficiently low so no metal-ligand complexation occurs. Here, β_i^H refers to the cumulative proton-ligand equilibrium quotient, $[LH_i]/[L][H]^i$.
pX ^o	"True" pX values, those calculated from a correct equilibrium model.
pX ^v	pX values calculated by the model-independent variation technique.
X	General designation for M or L.
<u>x</u>	General designation for <u>m</u> or <u>l</u> .
β_j	Cumulative formation constant for the j th associated species:
	$\beta_j = C_j / \underline{m}^{e_{mj}} \underline{l}^{e_{lj}} \underline{h}^{e_{hj}},$
	referring to the equilibrium
	$e_{mj}M + e_{lj}L + e_{hj}H \rightleftharpoons M_{e_{mj}} L_{e_{lj}} H_{e_{hj}} \quad (\equiv \text{species } C_j)$
δ	$pX^o - pX^v$, the difference between the "true" pX values and those calculated by the variation technique.

Table III

Slopes

Calc. No.	$(\partial H / \partial M)_{L,h}$		
	pH 2	pH 4	pH 6
M-1	-.052	-.850	-1.798
M-2	-.053	-.813	-1.684
M-3	-.053	-.788	-1.608
M-4	-.054	-.764	-1.533
M-5	-.054	-.727	-1.419
M-6	-.304	-1.463	-1.834
M-7	-.295	-1.478	-1.936
M-8	-.286	-1.493	-2.038

Calc. No.	$(\partial H / \partial L)_{M,h}$		
	pH 2	pH 4	pH 6
L-1	.968	.875	.859
L-2	.964	.866	.865
L-3	.962	.859	.868
L-4	.959	.853	.871
L-5	.955	.843	.877
L-6	.957	.844	.826
L-7	.959	.862	.857
L-8	.961	.879	.888
L-9	.965	.914	.950
L-10	.968	.949	1.012
L-11	.972	.958	.957
L-12	.973	.960	.961
L-13	.973	.962	.964

Figure Captions

- Figure 1. Titration curves for Cu-(diglycyl-L-histidine), calculated from the constants determined by Lau, Kruck, and Sarkar.⁸ The total ligand concentration is the same in each of the three curves, while the total metal concentration is varied. EQV refers to moles of base added per mole of ligand.
- Figure 2. Calculated titration curves for copper-acetyl-acetate,¹⁵ as a function of the variation of the total metal concentration. EQV refers to moles of base added per mole of copper.
- Figure 3. Calculated titration curves for copper-acetyl-acetate,¹⁵ as a function of the variation of the total ligand concentration. EQV refers to moles of base added per mole of copper.
- Figure 4. Variation errors (see text), copper-acetyl-acetate system. The calculation conditions are identified in Table I. The dashed curves refer to the "common point" errors.

Figure 5. H vs M isohydric plots for copper-acetylacetonate. Table I identifies conditions. Table II contains selected values of $(\partial H / \partial M)_{L, \underline{h}}$.

Figure 6. H vs L isohydric plots for copper-acetylacetonate. Table I identifies conditions. Table II contains selected values of $(\partial H / \partial L)_{M, \underline{h}}$.

TITRATION CURVE

XBL 783-7785

TITRATION CURVE

CU-ACAC GUTNIKOV AND FREISER (1968) METAL VARIATION SMALL LIGAND EXCESS

XBL 783-7777

TITRATION CURVE

CU-ACAC GUTNIKOV AND FREISER (1968) LIGAND VARIATION

XBL 783-7778

XBL 783-7776

VARIATION PLOT

XBL 783-7775

4.5

VARIATION PLOT

CU-ACAC SUTNIKOV AND FREIZER (1968) VARIATION OVER LARGE LIGAND INTERVAL

XBL 783-7774

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