chemical shift among chromium, molybdenum, and tungsten. Likewise the absolute magnitude of J_{PF} is lowered by coordination and J_{PF} decreases in the order Cr, Mo, W.

Proton Nmr Spectra.—The hexasubstituted derivatives $M[P(OCH_3)_2F]_6$ and $Mo[P(OCH_3)_3]_6$ are $(AX_6)_6$ and $(AX_9)_6$ spin systems. The proton nmr spectra consist of apparent triplets as is often the case with $(AX_n)_n$ spin systems.[21-23]

As in the case of the fluorine resonance there is no important variation in the apparent coupling constants J_{POCH} or chemical shifts in the series $M[P(OCH_3)_2F]_6$ when M = Cr, Mo, W.

The proton nmr spectra of pentasubstituted derivatives are more complex, because of two types of phosphorus ligand: trans to a carbonyl group and trans to another phosphorus group. This spin system should be classified as $(AX_n)_4BY_n$. Figure 1 represents, as an example, the spectrum of $Mo(CO)[P(OCH_3)_3]_5$. There appear to be two groups of signals: a triplet (δ −3.64 ppm) and a doublet (δ −3.53 ppm) with intensities in a 4:1 ratio. Careful examination of the doublet shows that it is not pure and very weak peaks appear between the components of the doublet due to J_{AB} coupling. These second-order transitions are attributed to a J_{AB} coupling value which is of the order of $\nu_A - \nu_B$. This interpretation is confirmed by the $[(A)_4B]$ character of the observed ^{31}P nmr spectrum.[24] A similar observation has been reported

by Verkade, *et al.*, in the case of mixed-ligand complexes $M(CO)_4LL'$.[25]

Possible Evidence of a Competition between Electronic and Steric Effects.—In a recent study of phosphorus—ligand exchange on zerovalent nickel complexes Tolman has claimed that the factor governing the exchange equilibria was steric effects.[16] In a discussion he outlined that in group VI metal complexes steric requirements are more severe because six groups need to be accommodated. *A priori* one can bear in mind that Cr, Mo, and W should not have the same steric requirements: chromium is the smallest atom and steric effects should be maximum in this case. Therefore a comparison of the highest degree of substitution obtainable with the three metal carbonyls with each ligand might lead to differentiation between steric and electronic effects.

Steric effects probably explain why the ML_6 derivatives were not observed with the bulkiest ligands $CH_3P(OCH_3)_2$, $(CH_3)_2POCH_3$, and $P(CH_3)_3$, as well as why chromium, with the smallest atomic radius, did not go beyond $Cr(CO)_2[P(CH_3)_3]_4$.

On the other hand, the failure of tungsten to form $W[P(OCH_3)_3]_6$ cannot be solely a steric effect, since W is larger than Mo. Here we suggest that the degree of substitution reflects the different nature of the M–P bond. On electronic grounds we expect decreasing metal–phosphorus d_π–d_π back-bonding on descending the triad due to the more diffuse nature of the metal d orbitals.

Apparently in the trimethyl phosphite series a combination of steric and electronic effects prevents hexasubstitution for Cr and W but permits it for Mo.

(21) R. K. Harris, *Inorg. Chem.*, **5**, 701 (1966).
(22) M. Lenzi and R. Poilblanc, *C. R. Acad. Sci., Ser. C*, **263**, 674 (1966).
(23) R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 71 (1970), and references therein.
(24) R. Mathieu, M. Lenzi, and R. Poilblanc, unpublished results.

(25) F. B. Ogilvie, R. L. Kerter, G. Wulfsberg, and J. G. Verkade, *Inorg. Chem.*, **8**, 2346 (1969).

Evaluation of Spectrophotometric and Calorimetric Methods for Calculating Thermodynamic Data on Systems Involving Multiple Equilibria

By THOMAS O. MAIER[1] and RUSSELL S. DRAGO*

In this article we present the method of nonlinear least squares for the calculation of equilibrium constants and extinction coefficients from spectrophotometric data. Examples are given showing how different workers can calculate vastly different constants from the same data. These differences occur in the computation of the parameters, in interpreting the results of and misjudging the accuracy of the computation, and in collecting and using data which will not accurately determine the parameters. We report here procedures which we feel should be employed in determining parameters for these systems and in assigning reasonable error limits to the parameters.

Introduction

Spectrophotometric measurements have long been used to determine formation constants. For those situations in which the spectrum of each of the absorbing species is not known, various graphical techniques have been used to determine simultaneously the formation constants and the molar absorptivities.[2] With the popularization of high-speed computers, graph-

ical techniques for finding the best solution have been replaced by numerical search[3] or least-squares techniques.[4] We have previously described a minimum seeking routine and sharpness of fit criterion for the analysis of 1:1 adducts.[5]

(1) NSF Predoctoral Fellow.
(2) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, N. Y., 1961.

(3) D. Dyrssen, N. Ingre, and L. G. Sillén, *Acta Chem. Scand.*, **15**, 694 (1961).
(4) (a) P. J. Lingane and Z. Z. Hugus, Jr., *Inorg. Chem.*, **9**, 757 (1970); (b) G. Wada and W. Reynolds, *ibid.*, **5**, 1354 (1966).
(5) (a) N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138 (1959); (b) T. D. Epley and R. S. Drago, *ibid.*, **89**, 5770 (1967); (c) T. F. Bolles and R. S. Drago, *ibid.*, **88**, 3921 (1966).

We have recently become interested in transition metal ion systems involving both 2:1 and 1:1 adducts. Furthermore, concentration trends in fitting data to a 1:1 expression have been proposed as evidence for the existence of 2:1 complexes. It is the purpose of this article to show several pitfalls in obtaining and calculating data on these systems. We were amazed at the magnitude of the error that could be introduced by nonrigorous calculational procedures. We shall describe an approach which we feel constitutes the most rigorous solution of the problem describing criteria which adequately indicate how reliable the results are. It should be borne in mind that the result a computer gives to any problem is no better than the worst of three variables: the computer program, the accuracy of the spectrophotometric data, and the ingenuity of the experimenter in obtaining the data. In this article, we present evidence showing how each of these three variables can lead to poor results.

Theory

Our approach to the method of least-squares is essentially the same as presented by Hamilton,[6] with only a few simplifications. Therefore, the theory pointing our our simplifications will be briefly sketched. In general, there will be n experimental observations, $o_1, \ldots, o_n$, which have random errors, $e_1, \ldots, e_n$, and which depend linearly on m unknowns, $x_1, \ldots, x_m$. The n equations are then

$$o_i = a_{i1}x_1 + \ldots + a_{im}x_m + e_i \tag{1}$$

In matrix notation, this is

$$O = AX + E \tag{2}$$

It is necessary to introduce a variance–covariance matrix, M_0, which contains the variances of each error (σ_i^2) as diagonal elements and correlation of errors $(\sigma_i\sigma_j\rho_{ij})$ as off-diagonal elements. If we introduce a vector, $\hat{X}$, which is obtained from the best fit of the experimental data, we can define a vector of residuals, V, where

$$V = O - A\hat{X} \tag{3}$$

The quantity minimized, S, then is

$$S = V'M_0^{-1}V \tag{4}$$

where V' is the transpose of V. Substituting eq 3 into eq 4

$$S = V'M_0^{-1}V = (O - A\hat{X})'M_0^{-1}(O - A\hat{X})$$
$$= O'M_0^{-1}O + \hat{X}'A'M_0^{-1}A\hat{X} -$$
$$O'M_0^{-1}A\hat{X} - \hat{X}'A'M_0^{-1}O$$

Introducing the differential operator, δ, the condition for the minimum value of S is (after rearrangement)

$$\delta(S) = \delta(V'M_0^{-1}V) =$$
$$2(\delta\hat{X})'(A'M_0^{-1}X - A'M_0^{-1}O) = 0$$

Therefore

$$(A'M_0^{-1}A)\hat{X} = A'M_0^{-1}O$$

(6) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964.

or

$$\hat{X} = (A'M_0^{-1}A)^{-1}A'M_0^{-1}O \tag{5}$$

If the relative values of σ_i are known, but not the absolute values, then

$$M_0 = \sigma^2 N \tag{6}$$

where N is assumed to be a unit matrix and σ^2 the scaling factor discussed below and for ease in notation, we define P as the inverse of N

$$P = N^{-1} \tag{7}$$

An unbiased estimate of σ^2 is given by

$$\hat{\sigma}^2 = \frac{V'PV}{n - m} \tag{8}$$

(Recall the earlier definitions of n as the number of data sets and m as the number of unknowns.) An unbiased determination of the estimated moment matrix, M_x, is given by

$$\hat{M}_x = \frac{V'PV}{n - m}(A'PA)^{-1} \tag{9}$$

The marginal standard deviations of the variables X_i are found from M_x by

$$\hat{\sigma}(X_i) = \sqrt{M_{xi,i}} \tag{10}$$

and the correlation coefficient matrix is given by

$$[\rho_{ij}] = \frac{M_{xi,j}}{\hat{\sigma}(x_i)\hat{\sigma}(x_j)} \tag{11}$$

The correlation coefficient expresses the linear dependence of x_i on all the other variables. If we define

$$B = A'M_0^{-1}A \tag{12}$$

then the partial correlation coefficients are given by

$$\rho_{ij}/(k\ldots m) = \frac{-b_{ij}}{(b_{ii}b_{jj})^{1/2}} \tag{13}$$

The partial correlation coefficient expresses the linear dependence of x_i and x_j if all the other variables, $x_k, \ldots, x_m$, are held constant.

In nonlinear least-squares theory, we express the observables in a Taylor series about the point $(x_1^0, \ldots, x_m^0)$ where superscript zero represents initial guessed values and in the equations below f_i ond o_i have been used interchangeably

$$o_i = f_i(x_1^0, \ldots, x_m^0) + \frac{\partial f_i}{\partial x_1}(x_i - x_1^0) +$$
$$\frac{\partial f_i}{\partial x_m}(x_m - x_m^0) \tag{14}$$

Therefore

$$\Delta o_i = o_i - f_i(x_1^0, \ldots, x_m^0) = \sum_{j=1}^{m} \frac{\partial f_i}{\partial x_j}\Delta x_j \tag{15}$$

where $\Delta x_j = x_j - x_j^0$. If the Taylor expansion through the first derivatives only is a valid representation of o_i, the problem is linearized with

$$A = [a_{ij}] = \left[\frac{\partial f_i}{\partial x_j}\right] \tag{16a}$$

TABLE I

IRON(III)–CHLORIDE SYSTEM IN DMSO

| | Wada and Reynolds[a] | Lingane and Hugus[b] | |
	d	c	d
K_1, M^{-1}	$(5.3 \pm 0.6) \times 10^3$	$(5.5 \pm 2.6) \times 10^4$	$(6.1 \pm 2.3) \times 10^4$
K_2, M^{-2}	1.1×10^2 [e]	$(2.80 \pm 0.17) \times 10^2$	2.8×10^2 [e]
β_2, M^{-2}	$(5.7 \pm 1.2) \times 10^5$	1.5×10^7 [f]	$(1.7 \pm 0.71) \times 10^7$
$\epsilon_{Fe^{3+}}$, M^{-1} cm^{-1}	840 ± 10	840	840
$\epsilon_{FeCl^{2+}}$, M^{-1} cm^{-1}	1180 ± 16	1045 ± 9	1045 ± 7
$\epsilon_{FeCl_2^+}$, M^{-1} cm^{-1}	2350 ± 130	1960 ± 20	1950 ± 16

[a] Reference 4b. [b] Reference 4a. [c] Calculated assuming stepwise formation constants K_1 and K_2. [d] Calculated assuming overall formation constants β_1 and β_2. [e] Calculated from data presented by assuming $K_1 = \beta_2/\beta_1$. [f] Calculated from data presented by assuming $\beta_2 = K_1K_2$.

$$O = [\Delta o_i] \qquad (16b)$$

$$X = [\Delta x_j] \qquad (16c)$$

Therefore, the solutions can be calculated from eq 5.

Because the problem is nonlinear, $\partial f_i / \partial x_j$ will vary with x_j, so, in general, the solution can only be reached by iteration, each iteration giving a better estimate of $x_1^0, \ldots, x_m^0$. For the determination of equilibrium constants from spectrophotometric data, we have used as variables K_1 and K_2 and for each wavelength (λ_i), ϵ_0^λ, ϵ_1^λ, and ϵ_2^λ, where the subscripts 0, 1, and 2 refer to the free acid, free 1:1 complex, and free 2:1 complex, respectively. Equation 15 then becomes

$$\Delta o_i = \sum_i \left[\frac{\partial f_i}{\partial \epsilon_0^{\lambda i}} \Delta \epsilon_0^{\lambda i} + \frac{\partial f_i}{\partial \epsilon_1^{\lambda i}} \Delta \epsilon_1^{\lambda i} + \frac{\partial f_i}{\partial \epsilon_2^{\lambda i}} \Delta \epsilon_2^{\lambda i} \right] +$$
$$\frac{\partial f_i}{\partial K_1} \Delta K_1 + \frac{\partial f_i}{\partial K_2} \Delta K_2 \quad (17)$$

Here o_i is the absorbance for a particular solution at a particular wavelength. An equation of this type is used for each absorbance value used in the calculation. Since f_i, which is the absorbance, is $C_0\epsilon_0 + C_1\epsilon_1 + C_2\epsilon_2$, the $\partial f_i / \partial \epsilon_j^{\lambda i}$ equals the concentration of free species j. The three partial derivatives $\partial f_i / \partial \epsilon_j^{\lambda i}$ are positive for all physically meaningful values of ϵ's or K's. In the latter two terms of eq 17, it can be seen that f_i is a function of K_j. Since f_i is a complex function of K_j, the partial derivative $\partial f_i / \partial K_j$ was not explicitly evaluated but was approximated by $\Delta f_i / \Delta K_j$ with $\Delta K_j = 0.0002 K_j$. It is not possible to predict the sign of $\partial f_i / \partial K_j$ since the sign depends on the relative values of the extinction coefficients. If the extinction coefficients do not change much during all iterations, the sign of $\partial f_i / \partial K_j$ will in general not change. If none of the signs of the derivatives $\partial f_i / \partial x_j$ change during the iterations, convergence is almost always assured. Therefore, if the initial guess of the parameters is reasonably close, no derivatives change sign and convergence occurs. If, however, the initial guess is not close (particularly the guess of the extinction coefficients), $\partial f_i / \partial K_j$ may have the wrong sign, and the iterations will iterate *away* from the correct solutions. This is usually not too hard to detect, because our experience shows that the "solution" in this case is a set of parameters which give the same calculated absorbances for all base concentrations at each wavelength. If this case arises, we have found it easiest to hold the initial (guessed) values of K_1 and K_2 constant and use the least-squares program to obtain the best esimates of the extinction coefficients. Using these values as input parameters, hold K_2 constant and use the least-squared program to find the best estimates of the extinction

coefficients and K_1. Then, use these calculated values as imput parameters and allow all parameters to vary. This method appears to work even if the initial guessed values of the constants differ from the actual final calculated values by a factor of 10^2.

Lingane and Hugus,[4a] who reported a similar analysis, have found that, in general, the errors, e_1, are dominated by spectrophotometric errors and not by concentration errors. Even when concentration errors are included, the correlation among data at two wavelengths is very small (correlation among data at one wavelength is zero) and can be neglected. Mathematically, this corresponds to setting the off-diagonal elements of matrix N (eq 6) equal to zero. We have done this, and so use the identity matrix for matrix N.

Discussion

Results are presented in Tables I and II which show

TABLE II

EQUILIBRIUM CONSTANTS AND MOLAR ABSORPTIVITIES FOR THE BIS(DIETHYLDITHIOPHOSPHINATO)NICKEL–4-PICOLINE SYSTEM

| | | | This work | | |
	a	b	c	d, e	d, f
K_1, M^{-1}	31.6	31.6	31.6	22.9	22.9
K_2, M^{-2}	215.7	215.7	215.7	45.5	45.5
ϵ_0, M^{-1} cm^{-1}		26.57	105.8	26.57	105.8
ϵ_1, M^{-1} cm^{-1}	500[c]	569.5	208.9	423.0	35.8
ϵ_2, M^{-1} cm^{-1}	22.0	59.9	6.00	28.9	2.54

[a] R. L. Carlin and D. B. Losee, *Inorg. Chem.*, **9**, 2087 (1970). Calculated with our method using the reported[a] equilibrium constants and absorbances from the reported figure at 450 mμ. [c] Calculated with our method using the reported[a] equilibrium constants and absorbances from the reported figure at 525 mμ. [d] Calculated with our method simultaneously serving data at 450 and at 525 mμ. [e] Results at 450 mμ. [f] Results at 525 mμ.

different calculated parameters from the same data for two different systems. Additional examples have been presented by Conrow, *et al.*[7] As can be seen from the numbers in those tables, vastly different parameters can be calculated by different workers using the same data. In general, errors can occur in the computation of the parameters, in interpreting the results of (and misjudging the accuracy of) the computation, and in using data which will not accurately determine the parameters.

Computation of Parameters.—It seems to have been implicitly assumed that since a computer program gives a set of formation constants and extinction coefficients,

(7) K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Amer. Chem. Soc.*, **86**, 1025 (1964).

those constants must be the constants governing the solution equilibria. This, however, is not always the case. One problem is round-off error and propagation of that error within the computer. This is particularly serious if somewhere within the calculation the computer subtracts two large, but nearly equal, numbers (as, for instance, in the inversion of the matrix in eq 5). This error is difficult to detect but can usually be avoided by using double precision for all calculations.[8] A second problem is caused by the fact that, in some systems, the shape of the function that is being minimized is not truly parabolic around the minimum but might be better described as a relatively flat surface with many small indentations in that surface. The result is that the program may fall into one of these indentations and assume that it is the real minimum without locating any of the other indentations. This error is especially common if a minimum seeking routine is used instead of the least-squares approach.

Another check is whether the difference between the measured and calculated absorbance for each solution equals the error that would be expected from the particular spectrometer.

If the acid concentration is held constant, for example, and the base concentration varied, for given values of K's and ϵ's a Calcomp plotter can construct a theoretical titration curve. This curve plots the expected absorbance for a given base concentration *vs.* the log [base]. Base concentrations are selected at regular intervals. This is comparable to making a pH plot and gives a convenient axis to represent changing base concentration. On the same plot, the measured absorbance for each experimental base concentration can be plotted, thus giving a visual estimate of the fit of the measured data and calculated constants.

If either of the above tests fails, the calculated constants must be regarded as only approximately accurate.

Accuracy of Calculated Constants.—No data will be perfectly accurate and obviously the larger the error, the less accurate the calculated values will be. In some cases, however, even small errors in the data (and, therefore, small deviation between calculated and observed absorbance) will allow large variation in the calculated constants. In the Fe^{3+}–Cl^-–DMSO system (Table I), the constants reported by Wada and Reynolds[4b] would give for the largest deviation (between calculated and experimental absorbance) 0.0042, whereas the constants given by Lingane and Hugus[4a] lead to a maximum deviation of 0.0029. The difference in errors is small, yet the reported B_1's differ by a factor of approximately 10 and the reported B_2's differ by a factor of approximately 20.

Several cases can be considered which might lead to small deviations in calculated and observed absorbances yet large variations in calculated constants.

1. $K_1 \gg K_2$.—If $K_1 \gg K_2$, there will be a region of base concentrations where only free A or free AB or free AB_2 will exist. This will usually allow one accurately to measure ϵ_0, ϵ_1, and ϵ_2 (not necessarily at the same wavelength) and measure them at wavelengths such that $\epsilon_0 \neq \epsilon_1$, $\epsilon_1 \neq \epsilon_2$, and $\epsilon_0 \neq \epsilon_2$. Therefore, the concentrations of all species will be accurately determined and the equilibrium constants calculated will be accurate

if the deviations in observed and calculated absorbances are small.

2. $K_2 \geqslant K_1$.—If $K_2 \geqslant K_1$, there will be appreciable quantities of free A, free AB, and free AB_2 at anything but the lowest and highest concentrations of base. Two cases can be considered: K_1 and K_2 are large or K_1 and K_2 are not large.

a. If K_1 and K_2 are sufficiently large such that at the highest concentration of base which can be used all A has been converted to AB_2, then ϵ_2 can be directly measured. Since ϵ_0 can always be directly measured, only ϵ_1, K_1, and K_2 are undetermined. Specifying ϵ_1 and one of the K's determines (with an absorbance and known total acid and base concentrations) the other K. However, since the absorbance due to free AB is the product of ϵ_1 and concentration of AB, the same absorbance can be calculated from a larger ϵ_1 and smaller AB concentration (which implies smaller K_1 and larger K_2) or smaller ϵ_1 and larger AB concentration (which implies larger K_1 and smaller K_2). The advantage of the least-squares approach is that it finds the best set of constants when many more data measurements are used than are necessary for the solution of the problem. In principle, this would determine the correct set of constants since any one set of constants leads to a titration curve different from the titration curve for any other set of constants. However, in the case $K_2 \geqslant K_1$, it is possible to find a series of constants such that the titration curves are almost identical. This means that even if an infinite number of absorbance measurements were made, very accurate data would be necessary to determine the correct set of constants. If a very limited number of absorbance measurements are used, even more error is possible, since those points measured may not clearly distinguish between two different sets of constants; *i.e.*, distingusishing data may be at base concentrations between the concentrations actually used (*vide infra*). Therefore, for $K_2 \geqslant K_1$ and ϵ_2 directly measured, even very accurate absorption data can result in large uncertainty in the calculated constants.

b. If K_1 and K_2 are not large, then it is not possible to convert all acid to AB_2, so ϵ_2 cannot be directly measured. In this case, there are four unknowns, ϵ_1, ϵ_2, K_1, and K_2, so all the previous arguments hold. Since there is no direct handle on the AB_2 species (since ϵ_2 is unknown), the range in values of constants which give essentially the same titration curves is much larger and the possibility of error is greater than for the previous case.

Table II contains the constants reported by Carlin and Losee[9] and the constants calculated from the same data by us. As can be seen there is a large difference in the calculated constants. This difference seems to arise from two sources. In both calculations, $K_2 \geqslant K_1$ (the 1:1 complex going to 2:1 and 0:1 going to 1:1, respectively) and the constants were not large enough to allow direct, accurate determination of ϵ_2. This is an excellent example of case 2b described above.

In order to show the wide range of values of equilibrium constants that could fit these data, K_2 was held constant and the other parameters were allowed to vary. Table III shows the results of that calculation. As can be seen, as K_2 increases, K_1 decreases, yet the

(8) I. G. Sayce, *Talanta*, **15**, 1397 (1968).

(9) R. L. Carlin and D. B. Losee, *Inorg. Chem.*, **9**, 2087 (1970).

TABLE III

COMPARISON OF THE FIT OF CALCULATED AND OBSERVED
ABSORBANCES FOR DIFFERENT VALUES OF THE
EQUILIBRIUM CONSTANTS FOR THE $Ni(dtp)_2$-4-pic SYSTEM

K_1, M^{-1}	K_2, M^{-2}	CHISQ $\times 10^{3}$ [a]	Std dev[b]	Av dev[c]
12.81	80.00	1.406	0.0133	0.0082
17.23	60.00	1.116	0.0118	0.0074
20.82	50.00	1.009	0.0112	0.0070
22.94	45.51	0.993	0.0111	0.0067
26.23	40.00	1.030	0.0113	0.0064
35.29	30.00	1.463	0.0135	0.0076

[a] Calculated from

$$CHISQ = \sum_{\substack{all \\ data \\ points}} (obsd\ absorbance - calcd\ absorbance)^2$$

[b] Calculated from: std dev = $[CHISQ/(n - m)]^{1/2}$. [c] Calculated from

$$av\ dev = \sum_{\substack{all \\ data \\ points}} |obsd\ absorbance - calcd\ absorbance|/n$$

fit parameter, CHISQ, varies only slightly. The average deviation varies from 0.0064 to 0.0082, a relatively small percentage change, when K_2 changes from 40.0 to 80.0. Although the best fit occurs when $K_2 = 45.51$, an acceptable range of K_2 is probably from 30.0 to 80.0. Increasing the accuracy of the data probably will not help much, since the difference between average deviations will still be only 0.002—about the limit of the accuracy of any spectrometer. The system, then, is such that an accurate calculation of the constants even from very accurate data is probably not possible. In this case, there is also the problem of relatively large differences between calculated and observed absorbances. With errors this large, we feel that any calculated constants must be interpreted as only approximately correct and, therefore, only give a very rough estimate of the reactivity of this nickel complex.

3. $\epsilon_{BA_i} \simeq \epsilon_{AB_{i+1}}$.—If the extinction coefficient for AB_i is very nearly the same as the extinction coefficient for AB_{i+1}, then a relatively large change in concentration of AB_i to AB_{i+1} (caused by increasing the concentration of B) will result in only a small change in absorbance. Since the change in absorbance is small, but the error in any measured absorbance is constant, the error in any measurement relative to the change in absorbance is large. This means that, even if the extinction coefficients were known, the error in the concentrations of AB_i and AB_{i+1} would be large, so the error in the equilibrium constants would be large. If the extinction coefficients are not known, the small absorbance change can then be fit (by computer) by either a relatively large ϵ_{i+1} and smaller equilibrium constant or smaller ϵ_{i+1} and larger equilibrium constant. This would seem to be one of the reasons for the wide range of values calculated for the Fe^{3+}-Cl^--DMSO system.[4] $\epsilon_{Fe^{3+}} = 840$ and $\epsilon_{FeCl^{2+}} = 1040$, so that even large concentrations of $FeCl^{2+}$ (relative to total Fe^{3+}) give only small changes in total absorbance.

The latter two cases can lead to large errors because the value of one parameter depends very much on the value of a second parameter. In general, it is difficult (or impossible) to predict how one parameter depends on another. However, with the least-squares solution

of the problem, the correlation coefficients (eq 11) and partial correlation coefficients (eq 13) give a measure of how one parameter depends on another. The absolute value of a correlation coefficient must be between 0 and 1. Physically, a value close to 0 means that an error in the calculated absorbance introduced by changing one parameter cannot be compensated for by a change in another parameter (*i.e.*, only one set of parameters will lead to any given titration curve; *vide infra*). A value close to 1 means that an error in the calculated absorbance introduced by changing one parameter can be compensated for by a change in another parameter (*i.e.*, there are many sets of parameters which will lead to essentially the same titration curve). Therefore, large correlation coefficients do indicate the possibility of large errors in the calculated parameters with only small errors in the fit of the observed and calculated data. As an example, consider the Fe^{3+}-Cl^--DMSO system.[4] The partial correlation coefficient for K_1-$\epsilon_{FeCl^{2+}}$ was -0.89, which means an increase in K_1 can be compensated for by a decrease in $\epsilon_{FeCl^{2+}}$. Lingane and Hugus reported a larger value of K_1 and a smaller value of $\epsilon_{FeCl^{2+}}$ than Wada and Reynolds. Another example is the bis(diethyldithiophosphinato)nickel ($Ni(dtp)_2$) and 4-picoline system.[9] The correlation coefficients, which were calculated from our best fit to the data, are reported in Table IV. From

TABLE IV

CORRELATION COEFFICIENTS FOR THE $Ni(dtp)_2$-4-pic SYSTEM

	$\epsilon_1^{450m\mu}$	$\epsilon_2^{450m\mu}$	K_1	K_2	$\epsilon_1^{525m\mu}$	$\epsilon_2^{525m\mu}$
$\epsilon_1^{450m\mu}$		0.19	-0.99	0.98	-0.69	0.60
$\epsilon_2^{450m\mu}$			-0.15	0.34	0.12	0.10
K_1				-0.96	0.73	-0.61
K_2					-0.60	0.59
$\epsilon_1^{525m\mu}$						-0.73

the table, it can be seen that some of the constants are very large, in particular $\rho_{\epsilon_1 K_1}$, $\rho_{\epsilon_1 K_2}$, and $\rho_{K_1 K_2}$. These high coefficients predict what was previously observed, that the constants can be varied over a wide range with only a small change in the fit of experimental and calculated parameters. Since the correlation coefficients are independent of the accuracy of the measured data (eq 11–13), the absolute value of a coefficient cannot be decreased by increasing the accuracy of measurement. Therefore, whenever there are large correlation coefficients in a calculation, the errors in the calculated parameters may be quite large even though the difference between calculated and observed absorbances is small.

Using the 29 data points and the results of Lingane and Hugus, we found that the concentration of $FeCl_2^+$ was never greater than the concentration of $FeCl^{2+}$ over the range of base concentrations studied. As a result, ϵ_2 and K_2 could not have been well determined (*vide infra*) as was reflected in the large partial correlation coefficient, -0.96. We decided to test whether additional data at base concentrations higher than those that were reported would decrease the correlation coefficients. Seventeen additional data points were calculated in which the acid concentration was held constant at 0.00015 M and the base concentration was varied from 0.007 to 1.0 M. In this region, the concentration of $FeCl_2^+$ was greater than the concentrations of Fe^{3+} or $FeCl^{2+}$. The result was that the co-
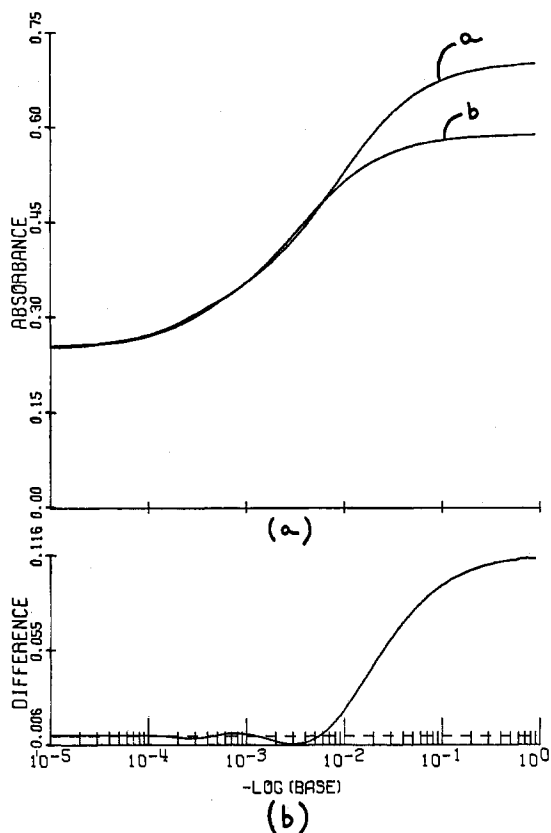
Figure 1.—(a) Theoretical titration curves based on constants reported by Wada and Reynolds[4b] (curve a) and by Ligane and Hugus[4a] (curve b). (b) Difference curve calculated from curve a minus curve b.
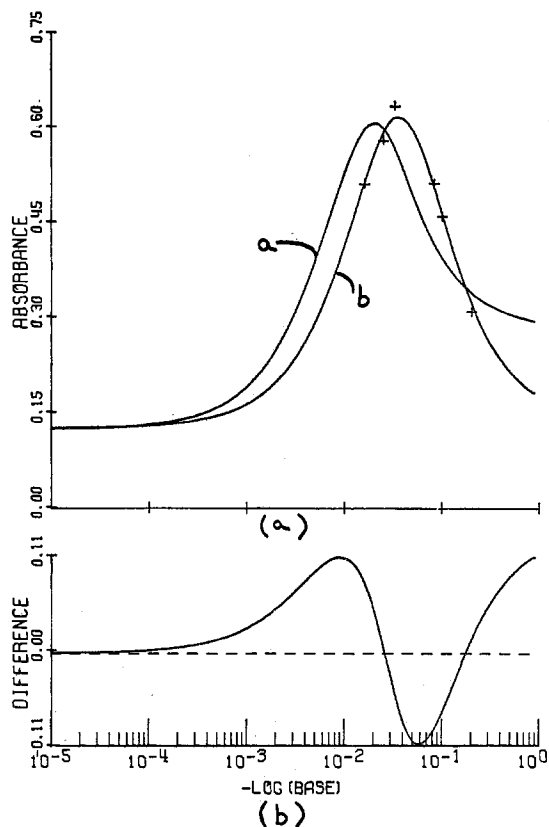

Figure 2.—(a) Theoretical titration curves based on equilibrium constants reported by Carlin and Losee[9] (curve a) and by this work (curve b). λ is 450 mμ; + indicates an experimental data point. (b) Difference curve calculated from curve a minus curve b.

efficients calculated from the 29 data points were always higher than the coefficients calculated from the 29 data points plus the 17 synthetic data points. There was only a slight difference for the coefficient of ϵ_1 with K_1 since the synthetic data did not add much information on the $FeCl^{2+}$ species. The coefficient of ϵ_2 with K_2, however, dropped to -0.67 with the addition of the synthetic data because the additional data did better define the system, particularly in regard to the $FeCl^{2+}$ species. Therefore, very large correlation coefficients may possibly be reduced by increasing the range of base concentrations used in obtaining the data for the calculation. It is probably easier to use the data one has and to calculate synthetic data to determine if the accuracy of calculated prameters could be improved by increasing the range of base concentrations used.

Data Used for Calculation of Parameters.—For the discussion of data collection, assume that the total acid concentration is always constant, so only total base concentration and wavelength at which the absorbance is measured can be varied. Since there are, in theory, an infinite number of both base concentrations and wavelengths that could be used to collect data, some selection must be made, and the accuracy of the calculated parameters will depend on this choice.

Selection of Base Concentrations.—Along with our least-squares program, we have a program which will for two given sets of ϵ's and K's, plot (using a Calcomp plotter) both theoretical titration curves and will plot

the difference in absorbance for the two data sets *vs.* log [base]. This allows for quick, visual comparison of two sets of constants and indicates at what base concentrations additional measurements should be made to distinguish which set of constants best fits the data. The results of this program (Figure 1) indicated that there is very little difference in calculated absorbance between the constants reported by Wada and Reynolds and those reported by Lingane and Hugus over the concentration range studied. However, at higher concentrations of Cl^- ion, the two sets of constants lead to theoretical titration curves which differ by 0.12 absorbance unit—more than 30 times the maximum difference observed in the concentration range studied. Obviously, even a few data points at higher Cl^- ion concentration would have differentiated between the two reported sets of constants. This shows that if a limited number of data points is to be used (as is usually done), a plot of two theoretical titration curves (one the least-squares best fit and another a least-squares best fit holding one of the equilibrium constants constant and different from the least-squares best fit by some arbitrary percentage) would indicate at what base concentrations more data should be measured.

As an example, Figures 2 and 3 show theoretical titration curves for the data of Carlin and Losee at two different wavelengths using the constants in Table II. Clearly, to distinguish further between the two sets of parameters, the absorbance should be measured at total base concentrations of 1×10^{-3} to 1×10^{-2}
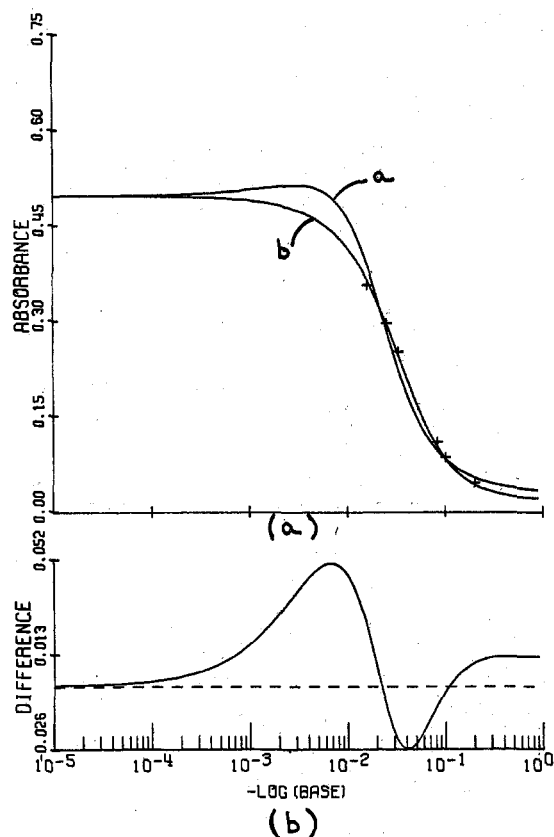
Figure 3.—(a) Theoretical titration curves based on equilibrium constants reported by Carlin and Losee[9] (curve a) and by this work (curve b). λ is 525 mμ; + indicates an experimental data point. (b) Difference curve calculated from curve a minus curve b.

and 4×10^{-2} to 7×10^{-2} M, since these are the regions of maximum difference between the two sets of parameters.

Selection of Wavelength.—In general, the more data one has, the better the accuracy of the calculated constants. One easy way to increase the number of data points is by measuring the absorbance of each solution at more than one wavelength. Since at most three new variables (ϵ_0, ϵ_1, ϵ_2) are introduced for each new wavelength used, the number of degrees of freedom is increased and the standard deviation of all calculated constants should decrease. In practice, however, the use of an increasing number of wavelengths may not increase the accuracy of the calculated constants. It has already been shown that use of wavelengths where two extinction coefficients are approximately equal will not lead to accurate values of calculated constants. Therefore, regions where there is only a small change in absorbance with large changes in base concentration should not be used.

The region with the largest absorbance change will not necessarily be the best region to use if two of the extinction coefficients are approximately equal and the other extinction coefficient (for the species leading to the large change in absorbance) is not accurately known (*i.e.*, not ϵ_0 or ϵ_2 with large K_1 and K_2). If $\epsilon_0 \gg \epsilon_1 \simeq \epsilon_2 \simeq 0$, then the concentration of free A will be accurately determined, and this wavelength will be useful but will require additional data to determine the concentrations of AB and AB$_2$. If $\epsilon_1 \gg \epsilon_0 \simeq \epsilon_2$, then ϵ_1 is not known, so the concentration of AB is not known

(only the product ϵ_1[AB] is known) and it will be difficult to determine ϵ_1, K_1, and K_2 accurately.

In general, therefore, it would be desirable to use a wavelength where ϵ_0, ϵ_1, and ϵ_2 are all different. This may necessitate using a wavelength where the absorbance change is not as great as it is at other wavelengths. In this case, we find it better to use a limited number of wavelengths. These wavelengths are chosen such that the general shape of the titration curve is different at each wavelength; *i.e.*, the relative values of ϵ_0, ϵ_1, and ϵ_2 are different at the different wavelengths. This seems to work because if the concentration of one species is not well determined at one wavelength, it might be determined at another wavelength. Therefore, the best procedure would appear to be to use data at several wavelengths, the wavelengths being picked such that the change in absorbance is large and the shape of a titration curve at each wavelength is different from the shape of a titration curve at any other wavelength. If the bands do not overlap, these difficulties are circumvented.

In summary, we recommend the use of the above procedure for calculation of extinction coefficients and equilibrium constants involving multiple equilibria. It must be borne in mind that if the correlation coefficients are large or if $K_2 > K_1$, the calculated parameters may have relatively large errors even though the calculated and observed absorbances agree very well. For these systems involving only 1:1 equilibria, the method previously reported[5] from this laboratory can be used and can give accurate results. The advantage of that method is that it is faster and requires much less computer space because it is basically a numerical search method. Briefly, that method uses an equation relating K and ϵ_1. If a value of K has been picked, ϵ_1 and consequently the absorbance can be calculated for a given set of initial concentrations. For each set of concentrations, a different curve can be calculated relating the K and ϵ_1. The curves for all of the concentration sets should intersect at the same point (or within some small region) from which the values of K and ϵ_1 are obtained. It is strongly urged that this plot be constructed in order visually to check that the intersections do occur in a small region and that the range in the values of the slopes of the lines determining these intersections is large. The function actually minimized by the computer is

$$\text{CHISQ} = \sum_n (\text{calcd absorbance} - \text{obsd absorbance})^2$$

if K is large so only a small excess of base is needed to convert all the acid to adduct. If K is small, a large excess of base is needed and the solvent properties may change with increasing concentration of base. In order not to give undue weight to data in concentrated base solution, the quantity minimized is

$$\text{CHISQ} = \sum_n \left(\frac{\text{calcd absorbance} - \text{obsd absorbance}}{\text{obsd absorbance}} \right)^2$$

It should be emphasized at this point that a series of different concentration sets could give rise to a series of parallel lines for which the observed absorbances are very nicely reproduced for the selected K. A misleading estimate of accuracy would result if the

graphical plot of K^{-1} vs. ϵ (or ΔH°) were not made. The sharpness of fit parameter could also be employed, but the graph has the advantage of showing if a given solution is clearly inconsistent with the others in the set.

Since the equation relating K and ϵ_1 is identical[5o] with an equation relating K and ΔH°, this procedure also can be used for calculating enthalpies from calorimetric data.

The Electronic Spectrum of Trinuclear Chromium(III) Acetate

By L. DUBICKI AND P. DAY*

The polarized electronic spectrum of basic chromium(III) acetate, $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 6H_2O$, is measured over the temperature range 300–4.2°K. The exchange coupling between the three chromium ions is directly observed in the 690–750-nm region where transitions originating from different ground-state spin levels are identified. Tentative assignments of the various transitions are given in terms of excited states constructed from combinations of the ligand-field states defined for the local C_{4v} sites of the individual chromium(III) ions. The intensities of the transitions to excited states derived from $^2A_2$, $^2B_1$, and $^2A_1$ are dominated by the components which originate in the lowest level of the exchange-split $^4B_1$ ground state. A highly structured band system between 365 and 330 nm is assigned to double excitation of the low-energy doublet states.

The optical consequences of exchange interactions between transition metal ions have so far been observed experimentally in two distinct classes of compounds. When such ions are doped at moderate concentrations into diamagnetic host lattices, pairs and other clusters of near-neighbor magnetic ions can occur. The spectra of exchange-coupled pairs of Mn(II) and Ni(II) ions in $KZnF_3$ have been examined by Ferguson, *et al.*[1] At the other extreme, the spectra of pure, magnetically concentrated salts such as MnF_2 have also received a lot of attention recently and have been interpreted in terms of coexcitation of spin-wave packets (magnons) and excitons.[2] From the point of view of the chemist, models of magnetic exchange involving pairs or clusters of ions are conceptually more attractive, but experiments of the type performed by Ferguson encounter the difficulty that many different types of cluster may be present in the lattice at the same time, depending on statistical and energetic considerations. Studies of exchange interactions in discrete polynuclear cluster compounds using bulk susceptibility are well advanced,[3] but no precise single-crystal work appears to have been carried out on their optical spectra. In this paper we report the polarized electronic spectrum of basic chromium(III) acetate at a number of temperatures between 77 and 4°K. This molecule is an attractive one in which to study optical effects of exchange interactions, not only because of its trimeric structure but also because of the light which its spectrum might throw on those of concentrated ruby and pure Cr_2O_3.[4]

The structure of basic chromium(III) acetate, $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 6H_2O$, has been resolved by X-ray methods.[5,6] The unit cell contains four trimeric units and the space group is $P2_12_12$. The three chromium ions, each pair bridged by two acetate ligands, lie at the apices of an equilateral triangle. The trigonally coordinated oxygen atom in the center of the triangle and the terminal water molecules complete the octahedral coordination at each metal ion (Figure 1).

The three chromium ions are antiferromagnetically coupled.[7–9] Direct Cr–Cr overlap should be very small as the Cr–Cr separation is 3.28 Å. The metal $3d_{xy}$ and $3d_{xz,yz}$ orbitals can overlap with the π orbitals of the acetate ligands, and the $2p\pi$ orbital of the trigonal oxygen atom, respectively. It is likely that the mechanism of the ground-state antiferromagnetism is principally π superexchange. Measurement of the magnetic susceptibility down to 0.5°K yields a Weiss constant of some 0.1°K, indicating that the intercluster interaction is very small.[10]

Kambe[11] has interpreted the magnetic behavior using the spin Hamiltonian $\mathcal{H} = -2J_0[S_1 \cdot S_2 + S_3 \cdot S_1] - 2(J_0 + J_1)[S_2 \cdot S_3]$ where $S_1 = S_2 = S_3 = {}^3/_2$, $J_0 = -15°K$, and $J_1 = -3.25°K$. The use of the J_1 parameter is necessary not only to obtain an improved fit between the calculated and measured magnetic susceptibility but also to ensure that the two lowest Kramers doublet states are split by several wave numbers as demanded by heat capacity measurements.[12,13] How-

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