This would achieve considerable stabilization of this intermediate and relatively low $\Delta H^{\ddagger}$ values. Stereospecificity would be achieved by entry of the incoming nucleophile below the tetragonal plane as the ethylenediamine ligands revert to their ground-state octahedral sites.

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# Normal Equations for the Gaussian Least-Squares Refinement of Formation Constants with Simultaneous Adjustment of the Spectra of the Absorbing Species

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This paper describes the salient features in the derivation of the normal equations appropriate to the calculation of molar absorptivities and formation constants from spectrophotometric data. Since concentration errors are common to all the measurements on a solution, a nondiagonal weight matrix is required if spectrophotometric measurements are made at more than one wavelength. This matrix is approximately diagonal for spectrophotometric errors of a few thousandths of 1 absorbance unit and concentration errors of a few tenths of 1%. Even when concentration errors are more significant, accurate estimates of the parameters and of $\chi^2$, but not necessarily of the correlation coefficients, are obtained when the off-diagonal elements are neglected. Calculations on data for iron(III)–chloride complexes in DMSO are described; the constants for the stepwise formation of $FeCl^{2+}$ and $FeCl_2^+$ are $(5.5 \pm 2.6) \times 10^4$ and $280 \pm 17$ $M^{-1}$ and the molar absorptivities of these species are $1045 \pm 9$ and $1960 \pm 20$, respectively, at 400 nm.

## Introduction

Spectrophotometric measurements have long been used to determine formation constants.[1] For those situations in which the spectra of the absorbing species are not known, various graphical techniques have been developed to evaluate the formation constants and molar absorptivities simultaneously.[2,3] Numerical search techniques have been used to estimate the least-squares parameters from spectrophotometric[4] and mathematically equivalent calorimetric data.[5] Newton and Baker,[6] Hugus,[7] and Prasad and Peterson[8] have applied Gaussian least-squares procedures to spectrophotometric[6,8,9] and calorimetric data.[10] However these treatments do not take cognizance of the strong correlation among the analytical errors if measurements are made at more than one wavelength.

The present paper describes the salient features of the derivation of the normal equations appropriate to the multiwavelength problem. The correlation of the analytical errors makes this an unusual and interesting application of the Gaussian method of least squares. Data for the iron (III)–chloride system in DMSO[9] are reevaluated. Complex formation between $Cu(tfac)_2$ and pyridine in benzene solvent[11] and between Hg(II) and iodide in DMSO solvent[12] is the subject of other communications.

## The General Normal Equations

The *modus operandi* of a least-squares analysis is to estimate the error-free values associated with a series of measurements by minimizing the sum of the squares of the differences between the experimental values and "adjusted" values where each term is weighted as the reciprocal of its variance.[13] Note that one does not proceed to minimize the sum of the squares of some condition function with a weighting function calculated from propagation of error formulas. When these two approaches are equivalent, the second may be derived from the first.

In the spectrophotometric problem discussed here, we have the possibility of errors in the total metal concentration, in the total ligand concentration, and in the spectrophotometric measurement itself. Consequently, $\mathcal{S}$, the weighted sum of the squares of the

(1) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(2) S. Fronaeus, "Technique of Inorganic Chemistry," Vol. I, Interscience Publishers, New York, N. Y., 1963, p 1, and references therein.

(3) W. B. Person, *J. Am. Chem. Soc.*, **87**, 167 (1965), and references therein.

(4) K. Conrow, G. D. Johnson, and R. E. Bowen, *ibid.*, **86**, 1025 (1964).

(5) P. Paoletti, A. Vacca, and D. Arenare, *J. Phys. Chem.*, **70**, 163 (1966).

(6) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **4**, 1166 (1965).

(7) Z Z. Hugus, Jr., unpublished data.

(8) J. Prasad and N. C. Peterson, *Inorg. Chem.*, **8**, 1622 (1969).

(9) G. Wada and W. L. Reynolds, *ibid.*, **5**, 1354 (1966).

(10) M. K. Lundeen, Ph.D. Thesis, "Determination of Thermodynamic Functions for Silver–Ammonia and Scandium–Fluoride Complexes in Aqueous Solutions," University of Minnesota, 1967.

(11) H. F. Henneike and P. J. Lingane, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 172.

(12) R. J. Peterson, P. J. Lingane, and W. L. Reynolds, *Inorg. Chem.*, **9**, 680 (1970).

(13) W. E. Deming, "Statistical Adjustment of Data," John Wiley and Sons, New York, N. Y., 1948.

residuals, contains three terms, one for each experimental variable

$$\mathcal{S} = \sum_J \left\{\frac{(C_M - c_m)^2}{s^2(C_M)}\right\} + \sum_J \left\{\frac{(C_L - c_l)^2}{s^2(C_L)}\right\} + \sum_{\lambda,J} \left\{\frac{(A - a)^2}{s^2(A)}\right\} \quad (1)$$

Capital letters are used to represent experimental values and lower case letters to represent the values that would have been observed had there been no errors made in their measurement. $\lambda$ indexes the wavelengths; $J$ indexes the solutions. Therefore, $A(\lambda,J) - a(\lambda,J)$ represents, for example, the least-squares estimate of the error (residual) associated with a particular absorbance measurement at wavelength $\lambda$ on solution $J$. The factors $s^2(A)$, $s^2(C_M)$, and $s^2(C_L)$ in the denominators represent estimates of the variances of particular data and will vary from one datum to another. The estimates of the residuals, and of the parameters, will be independent of the absolute values of these variances so long as their correct relative ratios are maintained. The summations are meant to be taken over all experimental values of the absorbance and of the total metal and ligand concentrations. Thus each sum need not contain the same number of terms. In particular, there will be more spectrophotometric measurements than concentration measurements if spectrophotometric measurements are taken at more than one wavelength.

In choosing the values of $a$, $c_m$, and $c_l$ which minimize $\mathcal{S}$, it is necessary to remember that these values are interrelated by several assumptions about the system. In particular, if we assume we are dealing with a series of mononuclear complexes M, ML, ..., $ML_N$ and that Beer's law is obeyed by each absorbing species in the system, there are three types of constraints that must be satisfied.

(1) For each solution and at each wavelength, the absorbance (per unit path length) must obey Beer's law

$$H(J,\lambda) = a(c_m,c_l,\lambda) - \epsilon_L(\lambda)[l] - \epsilon_M(\lambda)[m] - \cdots - \epsilon_{ML_N}(\lambda)[m_n] \quad (2)$$
$$= a - \epsilon_L[l] - [m]\{\epsilon_M + k_1[l]\epsilon_{ML} + (k_1 \cdots k_N)[l]^N\epsilon_{ML_N}\}$$
$$= 0$$

where

$$k_i = [ml_i]/[ml_{i-1}][l] \quad (3)$$

$\epsilon_L(\lambda)$ represents the true molar absorptivity of the ligand at the wavelength $\lambda$ and the quantities in brackets represent the actual equilibrium concentrations of the various species. Later we will use upper case letters, *i.e.*, $E_L(\lambda)$, [M], ..., $[ML_N]$, to represent experimental values or initial estimates. The $k_i$ are *concentration* equilibrium quotients since the spectrophotometric measurements depend on the concentrations of the absorbing species.

(2) The total metal concentration must satisfy a mass balance equation for each solution

$$F(J) = c_m - [m] - [ml] - \cdots - [ml_N] \quad (4)$$
$$= c_m - ([m]/\rho)$$
$$= 0$$

where

$$1/\rho = 1 + k_1[l] + k_1k_2[l]^2 + \cdots + (k_1 \cdots k_N)[l] \quad (5)$$

(3) The ligand concentration must also satisfy a mass balance equation

$$G(J) = c_l - [l] - [ml] - 2[ml_2] - \cdots - N[ml_N]$$
$$= c_l - [l] - [m]\{k_1[l] + 2k_1k_2[l]^2 + \cdots + N(k_1 \cdots k_N)[l]^N\} \quad (6)$$
$$= 0$$

Estimates of the free ligand and free metal concentrations (designated [L] and [M] because they are approximate values) are obtained as the solutions to the equations

$$F_0 = C_M - ([M]/R) = 0 \quad (7)$$

$$G_0 = C_L - [L] - [M]\{K_1[L] + 2K_1K_2[L]^2 + \cdots + N(K_1 \cdots K)_N[L]^N\} = 0 \quad (8)$$

in which experimental values have been introduced for the total metal and ligand concentrations and estimates have been employed for the several equilibrium constants. $R$ is the approximate value of $\rho$ in eq 5.

The explicit form and number of mass balance equations will depend on the particular system. For example, polynuclear complexes are treated by making the appropriate changes in eq 4 and 6; acid-base equilibria are treated by introducing a third mass balance, the proton condition.

General methods for the numerical solution of simultaneous mass balance equations have been described.[14,15] Upon combining the estimates for the free ligand and free metal concentrations obtained from eq 7 and 8 with the experimental value for the absorbance and estimates for the various equilibrium constants and molar absorptivities, we can calculate the residual $H_0$.

$$H_0 = A - [L]\epsilon_L - [M]\{E_M + K_1[L]E_{ML} + \cdots + (K_1 \cdots K_N)[L]^N E_{ML_N}\} \quad (9)$$

Although $H_0$ will seldom be exactly zero because of the experimental errors in $A$, $C_L$, and $C_M$ and because of the errors in the estimates of the various equilibrium constants and molar absorptivities, it is hoped that $H_0$ will be sufficiently small that it can be represented, at least approximately, by the linear terms in a Taylor's expansion (eq 10) about the point $H$.[13] $H_A$, $H_L$, etc., represent the derivative of eq 2 with respect to $A$, L, etc.

$$H_0 \approx H_A(A - a) + H_L([L] - [l]) + H_M([M] - [m]) + \Sigma H_{E_{ML_i}}(E_{ML_i} - \epsilon_{ML_i}) + \Sigma H_{K_i}(K_i - k_i) \quad (10)$$

The approximate mass balance conditions $F_0$ and $G_0$ (which are identically zero) may be linearized in a similar fashion and these linearized equations solved for [L] − [l] and [M] − [m]. Combining these expressions with eq 10 yields $\lambda \times J$ equations of the form

$$H_0(\lambda,J) \approx (A - a) + \Sigma H_{E_{ML_i}}(E_{ML_i} - \epsilon_{ML_i}) + \alpha(C_M - c_m) + \beta(C_L - c_l) + \Sigma(H_{K_i} + \gamma_i)(K_i - k_i) \quad (11)$$

(14) Z Z. Hugus, "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 379.

(15) P. Mentone, Ph.D. Thesis, University of Minnesota, 1969.

where

$$\alpha(\lambda,J) = (H_L G_M - H_M G_L)/(F_M G_L - G_M F_L)$$
$$\beta(\lambda,J) = (H_M F_L - H_L F_M)/(F_M G_L - G_M F_L)$$
$$\gamma_i(\lambda,J) = \{H_L(G_M F_{K_i} - F_M G_{KK_i}) - H_M(G_L F_{K_i} - F_L G_{K_i})\}/(F_M G_L - G_M F_L)$$
$$= \alpha(\lambda,J)F_{K_i} + \beta(\lambda,J)G_{K_i}$$

In writing eq 11, we have made use of the fact that $F_{C_M}$, $H_A$, and $G_{C_L}$ equal 1.

We have succeeded in approximating $H_0$, whose numerical value is calculated from eq 9, in terms of a series of linear corrections to be applied to the initial estimates for the various parameters. If measurements are made at $\lambda$ wavelengths for $J$ solutions, there will be $\lambda \times J$ values of $H_0$.

$\mathcal{S}$ may be minimized subject to the $\lambda \times J$ constraints (eq 11) as illustrated by Deming.[13] If this is done, the following equations result.

$$h(\lambda,J) = \frac{(\mathrm{A} - a)}{s^2(A)} \qquad \lambda \times J \text{ equations} \qquad (12)$$

$$\sum_\lambda \{\alpha(\lambda,J)(\lambda,J)\} = \frac{(C_M - c_m)}{s^2(C_M)} \qquad J \text{ equations} \qquad (13)$$

$$\sum_\lambda \{\beta(\lambda,J)h(\lambda,J)\} = \frac{(C_L - c_l)}{s^2(C_L)} \qquad J \text{ equations} \qquad (14)$$

$$\sum_J \{h(\lambda,J)H_{E_{ML_i}} = 0 \qquad \lambda \text{ equations for each } E_{ML_i} \qquad (15)$$

$$\sum_{\lambda,J} \{h(\lambda,J)(H_{K_i} + \gamma_i(\lambda,J)\} = 0 \qquad \text{one equation for each } K_i \qquad (16)$$

The $h(\lambda,J)$ are Lagrange multipliers introduced in the minimization of $\mathcal{S}$.

Since there are more than $2J(\lambda + 1)$ equations represented by eq 11–16 and an equal number of unknowns, this approach is impractical except for very modest amounts of data.

If measurements are made at only one wavelength, the solution is simplified since values of the Lagrange multipliers can be obtained in terms of $(A - a)$, $(C_M - c_m)$, and $(C_L - c_l)$ from eq 11–14. When eq 17 and 18 are introduced into eq 15 and 16, one obtains a set of

$$h(\lambda,J) = \mathbf{W}[H_0 - \Sigma\{H_{E_{ML_i}}(E_{ML_i} - \epsilon_{ML_i})\} - \Sigma\{(H_{K_i} + \gamma_i)(K_i - k_i)\}] \qquad (17)$$

$$\mathbf{W}^{-1} = s^2(A) + \alpha^2 s^2(C_M) + \beta^2 s^2(C_L) \qquad (18)$$

normal equations which may be solved for the corrections to the molar absorptivities and equilibrium constants.

The normal equations implicit in eq 15–18 are identical with the normal equations for a series of experiments in which $H_0$ would be measured directly with $s^2(H_0) = s^2(A) + \alpha^2 s^2(C_M) + \beta^2 s^2(C_L)$. The simplifying assumptions needed to arrive at these equations—namely, that measurements are made only at one wavelength or that concentration errors are negligible—are equivalent to assuming that there is no correlation among the errors in the several values of $H_0$. This suggests that a way to mix spectrophotometric measurements at more than one wavelength is to introduce a nondiagonal variance–covariance matrix as is illustrated by Hamilton.[16]

Let us designate this variance–covariance matrix as $\mathbf{M}$. The diagonal elements will be given by eq 18. The off-diagonal elements, which are a measure of the error common to pairs of values of $H_0$, depend upon the design of the experiment. Most commonly, a pair of values of $H_0$ will only be correlated when they correspond to spectrophotometric measurements at different wavelengths on the same solution. Since concentration errors are common to both, we take the covariance between such pairs of data to be $\sqrt{\alpha_1^2 s^2 + \beta_1^2 s^2} \cdot \sqrt{\alpha_2^2 s^2 + \beta_2^2 s^2}$. Note that $\mathbf{M}$ is symmetrical and of rank $\lambda \times J$.

We require a column matrix $\mathbf{H}$ which is simply the $\lambda \times J$ values of $H_0$ and a second column matrix $\mathbf{\Delta}$ composed of the $p$ values of the corrections to the initial estimates of the parameters. Finally, we introduce a design matrix $\mathbf{A}$ whose elements are the coefficients of the terms $(K_i - k_i)$ and $(E_{ML_i} - \epsilon_{ML_i})$ in eq 11. Each column in $\mathbf{A}$ corresponds to differentiation with respect to a particular parameter and each row corresponds to the derivative evaluated for a particular solution and wavelength. $\mathbf{A}$ is composed of $\lambda \times J$ rows and $p$ columns and is not symmetrical.

The corrections to the parameters may be calculated from eq 19.[16] (Note that if $\mathbf{M}$ is diagonal, this equation is identical with the normal equations implicit in eq 11–18.) $\mathbf{A'M^{-1}A}$ is known as the matrix of the

$$(\mathbf{A'M^{-1}A})\mathbf{\Delta} = \mathbf{A'M^{-1}H} \qquad (19)$$

coefficients of the normal equations. When appropriately normalized,[17] the off-diagonal elements are partial correlation coefficients and serve to measure the direct linear dependence of one parameter on another, the other $p - 2$ parameters remaining fixed. Since the experiment is assumed to be designed so that correlations among errors in the preparation of different solutions are negligible, $\mathbf{M}$ can be partitioned into $J$ nonzero $\lambda \times \lambda$ submatrices lying along the diagonal. Consequently, the matrix of the coefficients of the normal equations

$$\mathbf{M} = \begin{bmatrix} m_1 & & & & \\ & m_2 & & 0 & \\ & & \cdot & & \\ & & & \cdot & \\ & 0 & & & \cdot \\ & & & & m_J \end{bmatrix}_{J,J}$$

can be calculated as the sum of $J$ $p \times p$ matrices where the $a_i$ are $\lambda \times p$ blocks resulting from the partitioning

$$\mathbf{A'M^{-1}A} = \sum_{i=1,J} a'_i m_i^{-1} a_i \qquad (20)$$

of $\mathbf{A}$ into a single column. In a similar fashion, $\mathbf{H}$ may be partitioned into $\lambda \times 1$ submatrices so that

$$\mathbf{A'M^{-1}H} = \sum_{i=1,J} a'_i m_i^{-1} h_i \qquad (21)$$

(16) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, Section 4.1.

(17) See ref 16, Section 5.9.

Equations 20 and 21 greatly simplify the calculations.

## Application to the Iron(III)–Chloride System in DMSO

As part of their study of isotope exchange in the iron(II)–iron(III)–chloride ion system in DMSO, Wada and Reynolds[9] determined the equilibrium constants for the formation of $FeCl^{2+}$ and $FeCl_2^+$ and the molar absorptivities of these species at 400 nm using least-squares procedures developed by Hugus;[7] their results form the left column in Table I. Twenty-nine spectrophotometric measurements are given in the original paper.[9] When these data were adjusted as described above, the solutions iterated away from the Wada and Reynolds estimates of the parameters.[18] The parameters reported here appear unique as the calculations converge to them from a range of initial estimates. Our results form the middle column in Table I. The errors indicated for the values of the parameters in Table I are the square roots of the appropriate diagonal elements in the reciprocal matrix, *i.e.*, $(\mathbf{A'M}^{-1}\mathbf{A})^{-1}$. Note: These values have not been multiplied by an internal estimate of the variance of an observation of unit weight. The values of $\chi^2$ have been normalized by division by the number of degrees of freedom. (The 1 and 99% points on the $\chi^2$ distribution lie at 44.3 and 11.5 for 25 degrees of freedom. Hence $1.77 > \chi^2/25 > 0.46$.) The values of the parameters do not change appreciably if the data are all weighted equally or are weighted by assuming a uniform error in the absorbance rather than in the transmittance.

Table I

The Iron(III)–Chloride System in DMSO[a]

| | | | |
|---|---|---|---|
| $10^{-4}k_1$ | $53 \pm 6$[b,d] | $5.5 \pm 2.6$[c] | $6.1 \pm 2.3$[d] |
| $k_2$ | ... | $280 \pm 17$ | ... |
| $10^{-7}\beta_2$ | $570 \pm 120$ | ... | $1.7 \pm 0.71$ |
| $\epsilon_{FeCl^{2+}}$ | $1180 \pm 16$ | $1045 \pm 9$ | $1045 \pm 7$ |
| $\epsilon_{FeCl_2^+}$ | $2350 \pm 130$ | $1960 \pm 20$ | $1958 \pm 16$ |
| $\chi/25$ | ... | 0.70 | 0.60 |

[a] Spectrophotometric errors assumed to be 0.001 transmittance unit. Concentration errors assumed to be 0.2%. [b] Reference 9. [c] Calculated assuming stepwise formation constants $k_1$ and $k_2$. [d] Calculated assuming overall formation constants $\beta_1$ and $\beta_2$.

The data of Wada and Reynolds had been analyzed[9] in terms of the overall formation constants $\beta_1 = k_1$ and $\beta_2 = k_1k_2$, rather than in terms of the stepwise equilibrium constants as was done here. Consequently, these calculations were repeated. (This requires only trivial modification of eq 2–9.) The results of these calculations, which form the right column in Table I, are not significantly different.

One of the more striking features of the results of calculations with both real and synthetic data is the low precision with which $k_1$ is determined. The origin for this would appear to be the similarity in the molar absorptivities of $Fe^{3+}$ and $FeCl^{2+}$ at 400 nm, 840 *vs.* 1040, so that even a rather considerable shift in the position of the equilibrium has but a small effect on the measured absorbance.

(18) K. Magnell, private communication.

Table II

Partial Correlation Coefficients for the Parameters of the Iron(III)–Chloride System in DMSO

| | $k_1$ | $k_2$ | $\epsilon_{FeCl^{2+}}$ | $\epsilon_{FeCl_2^+}$ |
|---|---|---|---|---|
| $k_1$ | ... | −0.39 | −0.89 | −0.29 |
| $k_2$ | | ... | −0.73 | −0.96 |
| $\epsilon_{FeCl^{2+}}$ | | | ... | −0.59 |
| $\epsilon_{FeCl_2^+}$ | | | | ... |
| | $\beta_1$ | $\beta_2$ | $\epsilon_{FeCl^{2+}}$ | $\epsilon_{FeCl_2^+}$ |
| $\beta_1$ | ... | 0.998 | 0.68 | 0.97 |
| $\beta_2$ | | ... | −0.72 | −0.96 |
| $\epsilon_{FeCl^{2+}}$ | | | ... | −0.59 |
| $\epsilon_{FeCl_2^+}$ | | | | ... |

Partial correlation coefficients, defined as $-c_{ij}/(c_{ii}c_{jj})^{1/2}$, where the $c_{ij}$ are the elements in the normal equation coefficient matrix,[17] are given in Table II. These values are insensitive to the weighting scheme. Since a partial correlation coefficient greater than 0.5 is significant at the 99% confidence level for 25 degrees of freedom,[17] it is clear that there is strong pairwise correlation between errors in the estimates of the equilibrium constants and errors in the estimates of the molar absorptivities.

Table III

Residuals of the Spectrophotometric Measurements for the Iron(III)–Chloride System in DMSO (Absorbance Units × $10^4$)

| | Residual = exptl − adjusted | | |
|---|---|---|---|
| Exptl absorbance | Wada and Reynolds[9] | Present work | $FeCl_2^+$ absent |
| 2160 | 25 | −6 | −15 |
| 2220 | 26 | −2 | −2 |
| 2265 | 18 | −5 | 5 |
| 2310 | 15 | −2 | 19 |
| 2340 | 0 | −9 | 22 |
| 2385 | 4 | 2 | 45 |
| 2415 | −4 | 3 | 55 |
| 2445 | −9 | 6 | 68 |
| 2472 | 27 | −5 | 118 |
| 2679 | 1 | 7 | 38 |
| 2820 | 3 | 2 | 66 |
| 2880 | 0 | −7 | 73 |
| 2970 | 18 | 4 | 99 |
| 3030 | 12 | −5 | 98 |
| 3150 | 18 | 7 | 104 |
| 3240 | 12 | 14 | 89 |
| 3300 | −9 | 2 | 53 |
| 3360 | −20 | −4 | 25 |
| 3420 | −23 | −5 | 3 |
| 3480 | −20 | −3 | −13 |
| 3510 | −42 | −29 | −53 |
| 3600 | −1 | 9 | −28 |
| 3630 | −16 | 11 | −59 |
| 3690 | 1 | 0 | −55 |
| 3750 | 20 | 14 | −48 |
| 3780 | 11 | 0 | −67 |
| 3840 | 33 | 18 | −54 |
| 3870 | 27 | 7 | −67 |
| 3900 | 22 | −2 | −78 |

The values of $H_0$ calculated from eq 9 using parameters reported by Wada and Reynolds[9] and using values reported here appear in Table III. Although the values of $H_0$ for the Wada and Reynolds parameters are distinctly larger and the distribution of posi-

TABLE IV

EFFECT OF CORRELATION OF EXPERIMENTAL ERRORS ON THE PARAMETERS OF THE MERCURY(II)–IODIDE SYSTEM IN DMSO[a]

| | $s^2(A) > \alpha^2 s^2(C_{Hg})$ | | $s^2(A) < \alpha^2 s^2(C_{Hg})$ | |
|---|---|---|---|---|
| | Included | Ignored | Included | Ignored |
| $10^{-5}K_3$ | 5.46 ± 0.76 | 5.41 ± 0.70 | 6.77 ± 1.9 | 4.90 ± 0.94 |
| $K_4$ | 75.7 ± 2.4 | 75.8 ± 2.5 | 74.8 ± 2.7 | 76.1 ± 3.8 |
| $\epsilon_{HgI_2}$, 286 nm | 7140 ± 41 | 7135 ± 41 | 7147 ± 57 | 7142 ± 57 |
| 304 nm | 6679 ± 49 | 6671 ± 49 | 6720 ± 120 | 6744 ± 120 |
| 334 nm | 2630 ± 33 | 2621 ± 33 | 2659 ± 88 | 2668 ± 88 |
| $\epsilon_{HgI_3}$, 286 nm | 9683 ± 42 | 9683 ± 42 | 9669 ± 62 | 9704 ± 65 |
| 304 nm | 13,748 ± 65 | 13,752 ± 63 | 13,670 ± 110 | 13,770 ± 100 |
| 334 nm | 7523 ± 46 | 7532 ± 46 | 7461 ± 72 | 7540 ± 73 |
| $\epsilon_{HgI_4}$, 286 nm | 23,400 ± 220 | 23,390 ± 220 | 23,410 ± 300 | 23,320 ± 310 |
| 304 nm | 7170 ± 69 | 7170 ± 71 | 7190 ± 92 | 7175 ± 110 |
| 334 nm | 21,720 ± 210 | 21,720 ± 210 | 21,790 ± 290 | 21,730 ± 300 |
| $\chi^2/115$ | 2.72 | 3.01 | 1.32 | 1.19 |

[a] Data are from ref 12 and weighted assuming a spectrophotometric error of 0.005 transmittance unit and concentration errors of 0.5 or 2.0%.

tive and negative values is less even, the data are reasonably well fit by either set of parameters. This indicates that the least-squares minimum is very shallow and this in turn is a consequence of the correlations between parameters. The high correlation seen here appears to be a frequent phenomenon[3,11,19–21] and one which greatly restricts the utility of the spectrophotometric method for the determination of equilibrium constants.

The fit by either set of parameters is almost too good in comparison to reasonable estimates of the experimental errors involved. Since a too good fit might arise because we are assuming more species than actually exist thereby introducing more adjustable parameters than are required, the spectrophotometric data were analyzed assuming only $Fe(DMSO)_6^{3+}$ and $Fe(DMSO)_5Cl^{2+}$ to be present. The residuals calculated under this assumption (Table III) exhibit a definite nonrandomness in that the negative values are grouped together at the higher absorbance values. For this reason, we are inclined to accept the presence of significant amounts of $FeCl_2^+$.

A principal prediction of the larger values of $k_1$ and $k_2$ reported here is that a larger fraction of the iron will exist as $FeCl_2^+$. However, this is not in disagreement with the isosbestic point at 280 nm observed[9] at low Cl:Fe ratios $\{[Fe(III)] \approx 1.5 \times 10^{-4}\ M$, $[NaCl] \approx (1.5–3.0) \times 10^{-4}\ M\}$ since $FeCl_2^+$ amounts to only 2.3% of the total iron for $[Fe(III)] = 1.5 \times 10^{-4}\ M$ and $[NaCl] = 2.3 \times 10^{-4}\ M$, with $k_1 = 5.5 \times 10^4$ and $k_2 = 280$.

## Discussion

If the ligand is transparent, the measured absorbance of a series of mononuclear complexes is proportional to $C_M$. Consequently, $\alpha(\lambda,J)$, the factor by which concentration errors are propagated into nonzero values of $H_0$, may be approximated as the average molar absorptivity $A/C_M$. Hence $\alpha^2 s^2(C_M) \approx (A \times$ relative error in $C_M)^2$. Since concentration errors can be easily reduced to 0.1% by taking aliquots of a stock solution or by preparing solutions by weight, for example, $10^{-6}A^2$ is a reasonable estimate for $\alpha^2 s^2(C_M)$.

Errors in the ligand concentration will generally be of less importance because small errors in $C_L$ will seldom cause more than a slight shift in the position of equilibrium. If there are several absorbing species, the effect on the spectrophotometric measurements is further attenuated. Consequently, $\beta^2 s^2(C_L) \ll \alpha^2 s^2 \cdot (C_M)$.

We can estimate the lower limit on the reproducibility of the spectrophotometric measurements from manufacturers' specifications. For the Cary Model 14, "photometric reproducibility" is 0.002 absorbance unit[22] so that $s^2(A) \approx 4 \times 10^{-6}$. For the Beckman Model DU-2, "reproducibility" is better than 0.001 transmittance unit[23] so that $s^2(A) \approx 2 \times 10^{-6}$ for absorbance measurements near 0.5. While some spectrophotometers are more precise than these, $(2–4) \times 10^{-6}$ is probably a realistic estimate of $s^2(A)$.[24]

These arguments suggest that the experimental conditions can be controlled so that $s^2(A)$ is the dominant term in eq 18. This conclusion is important because it suggests that it is valid to neglect the correlation among the data due to concentration errors and to use the normal equations appropriate to the one-wavelength case for the multiwavelength case as well.

It appears[11,12,21] that spectrophotometric error is indeed the dominant term in eq 18 for concentration errors on the order of a few tenths of 1% and spectrophotometric errors on the order of a few thousandths of a unit. Moreover, it appears that even when this is not the case, the correlation among data for the same solution but at different wavelengths can often be neglected. This is illustrated by the data in Table IV. Note that there is no significant change in the parameters or in their standard errors when the correlation among the data is ignored even when concentration errors are dominant ($s^2(A) < \alpha^2 s^2(C_{Hg})$). Furthermore, the value of $\chi^2$, which is calculated from eq 22 in the multiwavelength case,[16] does not change

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appreciably when the correlation among the data is ignored.

$$\chi^2 = \mathbf{H}'\mathbf{M}^{-1}\mathbf{H} = \Sigma h'_i m_i^{-1} h_i \qquad (i = 1, J) \quad (22)$$

In fact, it appears that the only error that is made upon ignoring the correlation among experimental errors is that one would always conclude, upon examining the matrix of partial correlation coefficients, that the molar absorptivities of the same species at different wavelengths are linearily uncorrelated whereas in reality this is only true if $s^2(A) > \alpha^2 s^2(C_M)$. One obtains accurate values for the linear correlation among the other parameters whether or not one considers the correlation among the errors in the data.

It is fortunate that significant correlation of the equilibrium constants with each other and with the molar absorptivities does not adversely affect the iteration to the minimum because the degree of correlation between parameters cannot be altered dramatically by simple changes in the experimental procedure. For example, a uniform change in the precision of the data does not change the correlation between parameters since a partial correlation coefficient is the *ratio* of elements in the $\mathbf{A}'\mathbf{M}^{-1}\mathbf{A}$ matrix. An increase in the number of wavelengths at which measurements are made is also ineffective for reducing the correlation between parameters although this does decrease the estimated error in the formation constants by increasing the number of degrees of freedom in the system. The only effective way to reduce the correlation between parameters appears to be to include in the calculation data for solutions of known composition.

From a purely practical point of view, it should be noted that it is considerably simpler to write computer programs based on the matrix formulation than on the normal equations implicit in eq 15–18. If the matrix formulation is used, it is a trivial matter to include the correlation of experimental errors, and therefore we recommend that this be done even though ignoring this correlation will probably not change the results significantly.

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# The Crystal Structure of Di-$\mu$-hydrido-diphenylsiliconbis(tetracarbonylrhenium), $(C_6H_5)_2SiH_2Re_2(CO)_8$

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The crystal structure of di-$\mu$-hydrido-diphenylsiliconbis(tetracarbonylrhenium), $(C_6H_5)_2SiH_2Re_2(CO)_8$, has been determined from three-dimensional X-ray data collected by counter methods. Refinement by least-squares techniques gave a final $R$ factor of 5.6% for 1297 independent above-background reflections. The space group is orthorhombic, $D_{2h}^{14}$-Pbcn, with cell parameters $a$ = 17.657 (7) Å, $b$ = 17.294 (7) Å, and $c$ = 15.426 (5) Å. The calculated density of 2.20 (1) g cm$^{-3}$ (26°) for eight molecules per unit cell agrees with the value of 2.23 (2) g cm$^{-3}$ measured by flotation. The molecule exhibits an Re–Re bond of 3.121 (2) Å which is bridged symmetrically by the silicon atom with Re–Si distances of 2.544 (9) Å. The carbonyl groups occupy octahedral positions about the rhenium atoms while the two ligand hydrogen atoms are assumed to occupy the vacant octahedral coordination site of each rhenium atom, bridging the Re–Si bonds and lying in the ReReSi plane. The molecular symmetry approximates closely to $C_{2v}$.

## Introduction

The ultraviolet irradiation of a solution of $Re_2(CO)_{10}$ and $(C_6H_5)_2SiH_2$ in benzene yields the compound $(C_6H_5)_2SiH_2Re_2(CO)_8$.[2] The mass spectrum indicates that there are 12 hydrogen atoms in the molecule and the proton nmr and the infrared spectra are consistent with the presence of two hydrogen atoms, bridging the Re–Si bonds. Hydrogen bridges are known in rhenium and manganese carbonyls such as $HRe_2Mn(CO)_{14}$[3a] and $H_2Re_3(CO)_{12}^-$,[3b] and there are a number of compounds with hydrogen bridges involving boron and a transition metal, such as $HMn_3(CO)_{10}(BH_3)_2$,[4] $[(C_6H_5)_3P]_2CuBH_4$,[5] and $[(CH_3)_4N][Cr(CO)_4B_3H_8]$,[6] but this is the first such mixed bridge where a nontransition element other than boron is involved. With the availability of good crystals the crystal structure analysis was undertaken in order to provide stereochemical evidence as to the structure of this new compound.

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