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Computer Evaluation of Equilibrium Constants from Spectrophotometric Data[1]

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A computer method of evaluating equilibrium constants from spectrophotometric data has been developed for the following type of chemical system

$$MX_m + nY \overset{\dagger\beta_n}{\rightleftharpoons} MY_nX_{m-n} + nX$$

The basis of the technique is a novel and simple method of graphing the error surface in the region of minimum error. Extinction coefficients for all species are also evaluated. Uncertainties in log $\dagger\beta_n$ are estimated by comparison of values obtained in separate experiments. Very precise spectrophotometric data (±0.001 absorbance unit) for the $PdBr_nCl_{4-n}^{2-}$ tetrahedral complexes were obtained for a wide range of lithium:bromide:chloride concentration ratios (ionic strength kept constant at 4.5 *M*, $[HClO_4] = 0.5$ *M*, and $[LiClO_4] = 2.0$ *M*). The calculated values of log $\dagger\beta_n$, log $\dagger\beta_1 = 1.40 \pm 0.025$, log $\dagger\beta_2 = 2.46 \pm 0.044$, log $\dagger\beta_3 = 3.18 \pm 0.07$, and log $\dagger\beta_4 = 3.45 \pm 0.10$ are in reasonable agreement with graphically analyzed data of previous workers.

Introduction

Methods of computer evaluation of equilibrium constants from spectrophotometric data have been reviewed by Rossotti, *et al.*[2] A few recent efforts are not cited.[3-5] Sillén and coworkers (see ref 2) are by far the most comprehensive in treating what might be termed "topological anomalies" of the error surface. The error surface is a multidimensional surface representing a plot of the sum of the squares of the deviations (or a plot of the standard deviation) as a function of all the problem variables. The combination of variables that produces the lowest point on the surface is generally accepted as the solution to the problem. There are, however, two types of topological anomalies which make it difficult to find that minimum. First is the possibility that the surface may exhibit several "pits" which might be mistaken for the minimum. Second and more serious is that the region of the true minimum may be very flat or skewed,[6] a consequence of high correlation among certain parameters.[7] The mathematics developed by Sillén to handle these problems is unfortunately cumbersome.

The analysis of two problems of interest to us, the equilibria of $PdBr_nCl_{4-n}^{2-}$ in aqueous and acetonitrile media, presented two examples of an extremely skewed minimum. (The acetonitrile data will be published in a subsequent paper.) In order to evaluate the equilibrium constants we developed what we believe is a relatively simple and quite general approach to problems of this type. The computer program, a modification of that described by Lieto and Liu,[5] is combined with a highly simplified alternative to Sillén's twist matrix method[6] which allows us to graph the pertinent regions of the error surface. Error estimates on the values of the equilibrium constants are obtained by analysis of repeat experiments or equivalently by analysis of nonoverlapping subsets of data. The approach accomplishes several desirable objectives.

(1) The probability of being "trapped" in a false minimum is reduced since the searches for the minimum are started from widely divergent points on the error surface.

(2) The minimum is found in a reasonable amount of computation time. By "reasonable" we mean that for 732 data points, 36 unknown extinction coefficients, and 4 unknown equilibrium constants, the minimum was found in less than 20 min of computation time with a Control Data Corp. 6600 computer. Computation time will increase with an increase in the number of data points and unknowns.

(3) Error estimates are obtained, albeit empirically. Sillén[6] has pointed out that, at least to his knowledge, for a nonlinear system there is "no generally recognized [mathematical] definition of $\sigma(\dagger\beta_n)$."

Our computer method is tested by application to highly precise spectrophotometric data (±0.001 absorbance unit) obtained for the aqueous $PdBr_nCl_{4-n}^{2-}$ system. The results of computer analysis are compared to the results of a graphical analysis of the same system presented in the earlier study.[8]

Calculations

Basic Equations.—The spectrophotometric behavior of the equilibria of the type

$$MX_m + nY \overset{\dagger\beta_n}{\rightleftharpoons} MY_nX_{m-n} + nX \qquad (1)$$

is described by the equation

$$A_{j,k} = \frac{C_M \sum_{n=0}^{m} \dagger\beta_n \epsilon_{j,n} R_k^{\,n}}{\sum_{n=0}^{m} \dagger\beta_n R_k^{\,n}} \qquad (2)$$

where

$$\dagger\beta_n = \frac{[MY_nX_{m-n}][X]^n}{[MX_m][Y]^n} \qquad (3)$$

$$R_k = [Y]/[X] \qquad (4)$$

and

$$\dagger\beta_0 = 1 \qquad (5)$$

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] F. J. C. Rossotti, H. S. Rossotti, and R. J. Whewell, *J. Inorg. Nucl. Chem.*, **33**, 2051 (1971), and references therein.

[3] C. Ropars and R. Viovy, *Bull. Soc. Chim. Fr.*, 3637, 3639 (1966).

[4] J. J. Kankare, *Anal. Chem.*, **42**, 1322 (1970).

[5] L. R. Lieto and C. H. Liu, Report ORNL-TM-2714, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1969; Dissertation, Arizona State University, 1969.

[6] L. G. Sillén, *Acta Chem. Scand.*, **18**, 1085 (1964).

[7] P. J. Lingane and Z Z. Hugus, Jr., *Inorg. Chem.*, **9**, 757 (1970).

[8] S. C. Srivastava and L. Newman, *ibid.*, **5**, 1506 (1966).

(Definitions of symbols are given in the Appendix.) There are $j_{\max}(m + 1) + m$ unknowns: an extinction coefficient for each species at each wavelength and an equilibrium constant for each reaction. For a given system a large number of experimental absorptions $A'_{j,k}$ measured at $j_{\max}$ different wavelengths and $k_{\max}$ different values of R_k should, in principle, allow one to evaluate the unknown parameters if

$$j_{\max}k_{\max} \geq j_{\max}(m + 1) + m \tag{6}$$

Generally the left-hand side of eq 6 is much greater than the right-hand side and eq 2 is overdetermined.

Least Squares.—Several workers have discussed the mathematics of problems of this type and the associated computer technique. The approach we use is similar to that described by Lieto and Liu.[5] The sum of the square of the deviations

$$S = \sum_{j}^{j_{\max}} \sum_{k}^{k_{\max}} \left[A'_{j,k} - \frac{C_{\mathrm{M}} \sum_{n=0}^{m} \dagger\beta_n \epsilon_{j,n} R_k^{\,n}}{\sum_{n=0}^{m} \dagger\beta_n R_k^{\,n}} \right]^2 \tag{7}$$

is the criterion of closeness of fit: the smaller S, the better the fit. If the values of $\dagger\beta_n$ are fixed (these can be guessed values) and the value of S minimized, then at a given jth wavelength, j

$$\frac{\partial S}{\partial \epsilon_{j,i}} = 0 = -2 \sum_{k=1}^{k_{\max}} \left[A'_{j,k} - \frac{C_{\mathrm{M}} \sum_{n=0}^{m} \dagger\beta_n \epsilon_{j,n} R_k^{\,n}}{\sum_{n=0}^{m} \dagger\beta_n R_k^{\,n}} \right] \frac{C_{\mathrm{M}} \dagger\beta_i R_k^{\,i}}{\sum_{n=0}^{m} \dagger\beta_n R_k^{\,n}} \tag{8}$$

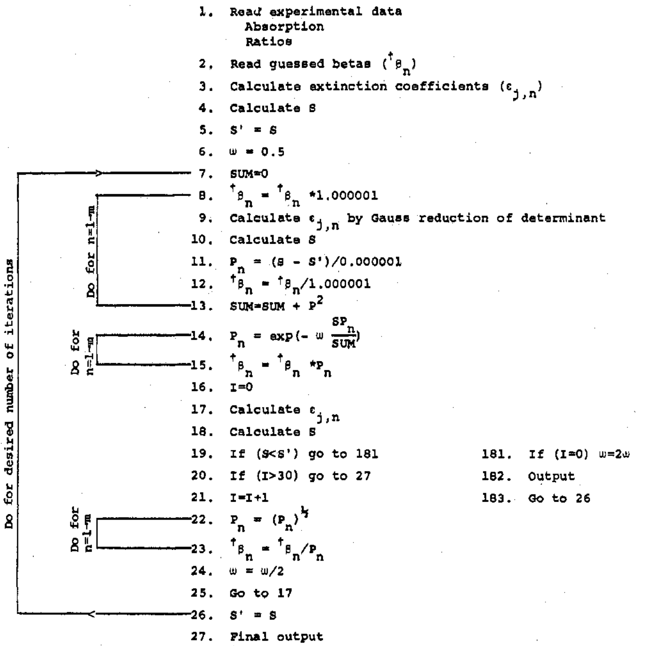
The resulting $m + 1$ linear equations allow evaluation of the $m + 1$ extinction coefficients at each wavelength. This is done by Gauss reduction[9] of the $(m + 1)^2$ determinant. In many cases some values of $\epsilon_{j,k}$ are known. Usually these are the values associated with the parent complexes ($n = 0$ and/or $n = m$) and the problem reduces to $m - 1$ equations and an $(m - 1)^2$ determinant. Still remaining is the problem of optimizing the values of $\dagger\beta_n$, remembering that adjusting these values in order to reduce S will modify eq 7 and necessitate recalculation of the extinction coefficients. The values of $\dagger\beta_n$ are adjusted according to the method of steepest descents[10] in which ln $\dagger\beta_n$ is changed in proportion to the magnitude of the partial derivative $\partial S/\partial \ln \dagger\beta_n$. The derivative for each $\dagger\beta_n$ is calculated by adding a very small change $(10^{-6} \cdot \dagger\beta_n)$, then recalculating $\epsilon_{j,n}$ and S, and noting the change, ΔS. Then

$$P_n = \frac{\partial S}{\partial \ln \dagger\beta_n} = 10^6 \Delta S \tag{9}$$

All values of $\dagger\beta_n$ are simultaneously readjusted according to

$$\dagger\beta_n' = \dagger\beta_n \exp\left[-\omega S P_n \Big/ \sum_{n=1}^{m} P_n^{\,2} \right] \tag{10}$$

followed by recalculation of $\epsilon_{j,n}$ and S. The constant ω is continually readjusted (generally becoming smaller) so that it will be as large as possible and still allow the value of S to decrease. In subsequent iterations the preceding sequence is repeated, beginning with the calculation P_n. The flow chart for the computer logic sequence is shown in Figure 1.



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1.  Read experimental data
      Absorption
      Ratios
2.  Read guessed betas (†βn)
3.  Calculate extinction coefficients (εj,n)
4.  Calculate S
5.  S' = S
6.  ω = 0.5
7.  SUM=0
8.  †βn = †βn *1.000001
9.  Calculate εj,n by Gauss reduction of determinant
10. Calculate S
11. Pn = (S - S')/0.000001
12. †βn = †βn/1.000001
13. SUM=SUM + P²
14. Pn = exp(- ω SPn/SUM)
15. †βn = †βn *Pn
16. I=0
17. Calculate εj,n
18. Calculate S
19. If (S<S') go to 181                181.  If (I=0) ω=2ω
20. If (I>30) go to 27                 182.  Output
21. I=I+1                              183.  Go to 26
22. Pn = (Pn)½
23. †βn = †βn/Pn
24. ω = ω/2
25. Go to 17
26. S' = S
27. Final output
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Figure 1.—Computer logic sequence.

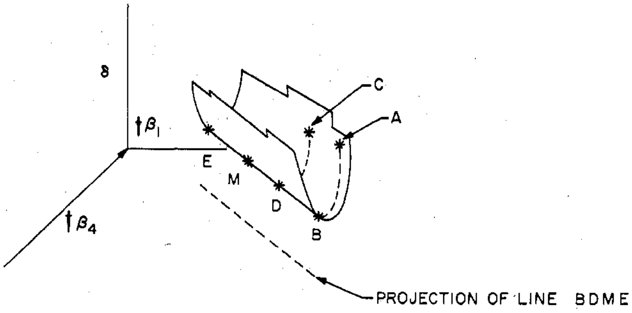

Figure 2.—An analogous two-dimensional error surface.

Finding the Bottom of a Skewed Pit.—The multidimensional surface described by S may be considered as an m-dimensional surface since for a given set of experimental data points, $A'_{j,k}$, explicit values of S and $\epsilon_{j,n}$ are obtained for any given set of $\dagger\beta_n$. The optimum values of $\dagger\beta_n$ are those associated with the lowest point on that surface (the minimum value of S). Initially guessed values of $\dagger\beta_n$ will locate a point on this surface that in all probability will be far from the minimum. The method of steepest descents will approach this minimum at a rate analogous to the rate of flow of water seeking its lowest level on the same surface. Sillén has pointed out that the region of the minimum (a pit) is often highly skewed.[6] Our studies indicate that this is certainly true for the $\mathrm{PdBr}_n\mathrm{Cl}_{4-n}{}^{2-}$ system in aqueous and acetonitrile media. In fact, the pit is almost trough shaped as indicated in Figure 2, drawn for an analogous two-dimensional surface. From a starting point on the surface (*e.g.*, point A, Figure 2) representing an initially guessed set of $\dagger\beta_n$ the iterative calculation quickly (less than 50 iterations)

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[9] V. L. Zaguskin in "Handbook of Numerical Methods for the Solution of Algebraic and Transcendental Equations," Pergamon Press, London, 1961, p 164.

[10] See ref 9, p 175.

descends the steep side of the trough to point B and then moves much more slowly toward the minimum M. In a sense one can conceive of two time constants for the process: a rapid convergence from almost any point on the surface to a point on the line BDME, occurring in less than 50 iterations, and slow convergence along the line BDME. Once the coordinates of this line are established, Sillén would invoke a "twist matrix" method in order to vary the values of $\dagger\beta_n$ in the most efficient way.

We have found a simple and efficient alternative to the complicated twist matrix method. As indicated in the projection of line BDME on the $\dagger\beta_4$, $\dagger\beta_1$ plane describes a straight line. Thus, one can write

$$\dagger\beta_1 = a_1\dagger\beta_4 + b_1 \tag{11}$$

For two systems that we have thoroughly investigated (the $PdBr_nCl_{4-n}{}^{2-}$ systems in water and in acetonitrile) we have found the following generalization of eq 11 to be an excellent approximation (in the vicinity of the minimum)[11]

$$\dagger\beta_n = a_n\dagger\beta_m + b_n \tag{12}$$

where $a_4 = 1$, $b_4 = 0$, $a_0 = 0$, and $b_0 = 1$, and for $n =$ 1–3 a_n and b_n are established experimentally. Equation 12 reduces the search for the minimum to a problem in one variable, $\dagger\beta_m$, and a plot of S (or σ) as a function of log $\dagger\beta_m$ quickly indicates the position of the minimum. The procedure may be briefly outlined. (1) Guess values of $\dagger\beta_n$ (*e.g.*, $\dagger\beta_1 = \dagger\beta_2 = \ldots = \dagger\beta_m =$ 1 or 10 or 100 or 0.1 or 0.01). (2) Calculate S, σ, and $\dagger\beta_n$ obtained after 50 iterations. It is important to point out here that some of these calculations will yield negative values for the extinction coefficients. In most cases the values become positive with subsequent iterations. In no case should they be artificially forced to zero. (3) Select those sets of refined $\dagger\beta_n$ which give the lowest S (or σ) and calculate a_n and b_n for any pair of sets or determine by plotting $\dagger\beta_n$ *vs.* $\dagger\beta_m$. Recalculate for any other pair and compare. (4) Use eq 12 to guess values of $\dagger\beta_n$ in the vicinity of the minimum and refine for 20 interactions. (5) Plot S (or σ) *vs.* log $\dagger\beta_m$ and estimate its value at the minimum. (6) Calculate $\dagger\beta_n$ from eq 12 for the optimum $\dagger\beta_m$ and refine for 20 iterations.

It is possible, of course, that some experimental systems will exhibit less skewed pits. This should manifest itself by producing more consistent sets of $\dagger\beta_n$ in spite of the very different initial guesses in step 1 above.

Estimating the Error in $\dagger\beta_n$ and $\dagger K_n$.—A simple method of estimating uncertainties in $\dagger\beta_n$ is by repetition of the experiment and recalculation of the unknowns. The variation in the value of a given unknown from one experiment to the next will indicate the uncertainty. We assume that computational errors caused by computer round-off, for example, are negligible—at least in the CDC 6600 whose single precision computation comprises 15 significant figures.

In the experiment which we discuss in this paper there are enough data to be divided into several nonoverlapping subsets. If there are $g_{\max}$ subsets of data, one can easily estimate the minimum in the σ *vs.* log $\dagger\beta_m$ plot for each subset. Then

$$\sigma_{\log\dagger\beta_{m,g}} = \left[\frac{\sum_{g=1}^{g_{\max}} (\overline{\log \dagger\beta_m} - \log \dagger\beta_{m,g})^2}{g_{\max} - 1}\right]^{1/2} \tag{13}$$

where

$$\overline{\log \dagger\beta_m} = \frac{1}{q_{\max}} \sum_{g=1}^{g_{\max}} \log \dagger\beta_{m,g} \tag{14}$$

We can equate

$$\sigma_{\log\dagger\beta_{m,g}} = \sigma_i/\sqrt{N/g_{\max}} \tag{15}$$

where $\sigma_i/\sqrt{N}$ is the standard deviation of log β_m based on all N data points, while $\sigma_{\log\dagger\beta_{m,g}}$ is the standard deviation for the mean of a given subset g. Thus

$$\sigma_i/\sqrt{N} = \sigma_{\log\dagger\beta_{m,g}}/\sqrt{g_{\max}} \tag{16}$$

An expression for the uncertainties in the other $\dagger\beta_n$ ($n \neq m$) may be derived from eq 12

$$\mathrm{d}\dagger\beta_n = a_n\, \mathrm{d}\dagger\beta_m \tag{17}$$

$$\dagger\beta_n\, \mathrm{d} \ln \dagger\beta_n = a_n\dagger\beta_m\, \mathrm{d} \ln \dagger\beta_m \tag{18}$$

and

$$\frac{\mathrm{d} \ln \dagger\beta_n}{\mathrm{d} \ln \dagger\beta_m} = \frac{\mathrm{d} \log \dagger\beta_n}{\mathrm{d} \log \dagger\beta_m} = \frac{a_n\dagger\beta_m}{\dagger\beta_n} \tag{19}$$

Thus

$$\frac{\sigma_{\log\dagger\beta_n}}{\sqrt{g_{\max}}} = \frac{\sigma_{\log\dagger\beta_m}}{\sqrt{g_{\max}}}\frac{a_n\dagger\beta_m}{\dagger\beta_n} \tag{20}$$

The expression for the error in $\dagger K_n$ may be analogously derived as

$$\dagger K_n = \dagger\beta_n/\dagger\beta_{n-1} \tag{21}$$

Thus from eq 12

$$\dagger K_n = \frac{a_n\dagger\beta_m + b_n}{a_{n-1}\dagger\beta_m + b_{n-1}} \tag{22}$$

and

$$\mathrm{d}\dagger K_n = \frac{a_n\, \mathrm{d}\dagger\beta_m}{a_{n-1}\dagger\beta_m + b_{n-1}} - \frac{(a_n\dagger\beta_m + b_n)a_{n-1}\, \mathrm{d}\dagger\beta_m}{(a_{n-1}\dagger\beta_m + b_{n-1})^2} \tag{23}$$

Thus

$$\mathrm{d} \ln \dagger K_n = \frac{\dagger\beta_m}{\dagger K_n}\mathrm{d} \ln \dagger\beta_m\left(\frac{a_n}{\dagger\beta_{n-1}} - \frac{\dagger K_n a_{n-1}}{\dagger\beta_{n-1}}\right) \tag{24}$$

and

$$\frac{\mathrm{d} \log \dagger K_n}{\mathrm{d} \log \dagger\beta_m} = \dagger\beta_m\left(\frac{a_n}{\dagger\beta_n} - \frac{a_{n-1}}{\dagger\beta_{n-1}}\right) \tag{25}$$

Then

$$\frac{\sigma_{\log\dagger K_n}}{\sqrt{g_{\max}}} = \frac{\sigma_{\log\dagger\beta_m}}{\sqrt{g_{\max}}}\dagger\beta_m\left(\frac{a_n}{\dagger\beta_n} - \frac{a_{n-1}}{\beta_{n-1}}\right) = \frac{\sigma_{\log\dagger\beta_n} - \sigma_{\log\dagger\beta_{n-1}}}{\sqrt{g_{\max}}} \tag{26}$$

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[11] Recalculation of the data of G. Wada and W. L. Reynolds, *Inorg. Chem.*, **5**, 1354 (1966), supports the validity of this approximation. The numbers obtained for $\dagger\beta_1$ and $\dagger\beta_2$ are in excellent agreement with the values recalculated by Lingane and Hugus.[7] Our program required some modifications in order to account for changes in ligand concentration due to complexation.

TABLE I

INITIAL GUESSES (IGV) AND RAPID CONVERGENCE VALUES (RCV) OF β'S

	IGV	RCV	IGV	RCV	IGV	RCV	IGV	RCV	IGV	RCV^a
$\dagger\beta_1$	10^5	2.808×10^3	10^4	261.1	10^3	29.83	10^2	19.41	10	14.95
$\dagger\beta_2$	10^5	5.552×10^4	10^4	4963	10^3	377.1	10^2	166.3	10	122.7
$\dagger\beta_3$	10^6	4.630×10^5	10^4	4.056×10^4	10^3	2255.5	10^2	490.7	10	277.4
$\dagger\beta_4$	10^5	1.248×10^6	10^4	$1,078 \times 10^5$	10^3	4813.9	10^2	139.8	10	153.25
σ	0.1176	0.0027630	0.116	0.0026157	0.105	0.0023365	0.0701	0.0025136	0.04428	0.0042209
Iterations		45		44		39		42		50
Real time, sec		151		147		133		142		167

^{a} At least one value of $\epsilon_{j,n}$ is negative.

Experimental Section. Obtaining Spectrophotometric Data for the Aqueous $PdBr_nCl_{4-n}^{2-}$ System

Previously published works[8,12-14] have established that palladium forms a series of mixed-halide complexes. It is tetracoordinate with a tetrahedral structure and thus exhibits no cis–trans isomerism. It was thought that the published chloride–bromide data were of insufficient accuracy to test our calculational approach. Consequently, the objective of this experiment was to obtain as precise spectrophotometric data as possible.

Reagents and Stock Solutions.—A 0.150 *M* solution of palladium(II) dichloride in 1.00 *M* HCl was prepared by weight from the anhydrous salt (Engelhard Industries). Suitable dilutions were made in preparing the experimental stock solutions. Baker Analyzed reagent grade perchloric acid (5.08 *M*) was standardized by titrating with 1.00 *M* sodium hydroxide. A 9.66 *M* solution of lithium bromide (Matheson Coleman and Bell) and a 8.70 *M* solution of lithium chloride (Baker and Adamson) were standardized with 0.1008 *M* silver nitrate titrant and dichlorofluorescein indicator. A 4.0 *M* solution of lithium perchlorate was prepared by weight from the anhydrous salt (G. Frederick Smith). Anhydrous salts were dried in a vacuum oven and stored in a vacuum desiccator prior to weighing. Doubly distilled water from a Barnstead still was used throughout.

Four experimental stock solutions were prepared: solution 1 comprised 1.5×10^{-4} *M* Pd^{2+}, 0.5 *M* $HClO_4$, 2.0 *M* $LiClO_4$, and 2.00 *M* LiCl; solution 2 was the same as solution 1 but contained 2.00 *M* LiBr instead of LiCl plus 1.3×10^{-3} *M* Cl^- (from the palladium stock solution); solutions 3 and 4 were the same as solutions 1 and 3, respectively, but contained no palladium.

Methods and Apparatus.—Experiments were carried out by titrating 50 ml of solution 1 with solution 2 (or 25 ml of solution 2 with solution 1) thus obtaining bromide:chloride ratios ranging from 6.7×10^3 down to zero. The ratio did not reach infinity because solution 2 contains 1.3×10^{-3} *M* chloride ion. A 1.00-cm silica adsorption cell fused to a 200-ml reservoir served as the titration vessel. Optical density measurements were made with a Cary 16 spectrophotometer (Cary Instruments). Readings for each of 63 different bromide:chloride ratios were taken at 12 different wavelengths from 375 to 265 nm at 10-nm increments. All readings were *vs.* air and the instrument was zeroed (air *vs.* air) prior to each reading. A constant temperature of 25.0 ± 0.05° was maintained in both the cell holder and the compartment. Ten minutes was the minimum time required for temperature equilibration of the absorption cell in the compartment.

Titrations were carried out with a syringe microburet (Micrometric Instruments, Model SB2). Solutions were mixed by shaking. The absorbance of a blank solution having a given bromide:chloride ratio, *R*, was determined indirectly. The absorbances of solutions 3 and 4 were measured at each of the 12 wavelengths. Several readings were taken at each wavelength and averaged. The absorbance at a given wavelength of a blank having a given *R* is

$$A_R = \left(\frac{R}{1+R}\right)A_3 + \left(\frac{1}{1+R}\right)A_4 \qquad (27)$$

where A_3 and A_4 are the absorbances of solutions 3 and 4 at that wavelength. In a brief experiment we measured the absorbances of several mixtures of solutions 3 and 4 and verified this relationship.

All absorbance measurements of Pd-containing solutions were corrected by subtracting the appropriately calculated blank.

Computer Analysis of the Data

Preliminary Data Reduction.—For the $PdBr_nCl_{4-n}^{2-}$ system there are five unknown extinction coefficients at each wavelength. When the bromide:chloride ratio is zero, only the $PdCl_4^{2-}$ species is present in solution and its extinction coefficients at all wavelengths are directly determined. Similarly, when the ratio is very large (6.7×10^3) $PdBr_4^{2-}$ is virtually the sole species present and its extinction coefficients are determined. Therefore, in eq 7 terms $\epsilon_{j,0}$ and $\epsilon_{j,m}$ become known constants thus reducing the determinant to 3 × 3.

Calculation of $\dagger\beta_n$ Starting from Divergent Initial Guesses.—Initial guesses of $\dagger\beta_n$ ($\dagger\beta_1 = \dagger\beta_2 = \dagger\beta_3 = \dagger\beta_4$) ranged from 10 to 10^5. For each set of initial guesses (IGV), the computer program calculated a set $\dagger\beta_n$ that we refer to as the rapid convergence values (RCV). Results are shown in Table I. Parameters a_n and b_n were evaluated from runs 2–4 (Table I). These values are compiled in Table II. A plot of σ *vs.* log $\dagger\beta_4$ is shown in Figure 3. This plot serves only to demonstrate the insensitivity of the standard deviation to a large variation in the RCV values of $\dagger\beta_n$. The value of $\dagger\beta_4$ varies over four orders of magnitude. The variations $\dagger\beta_3$, $\dagger\beta_2$, and $\dagger\beta_1$ are, of course, smaller as indicated by eq 12 and the values of a_n and b_n in Table II. More important is the expanded plot which indicates that the optimum combination of values of $\dagger\beta_n$ obtains when $\dagger\beta_4 = 10^{3.45} = 2.82 \times 10^3$. Using this value and the values of $\dagger\beta_1$, $\dagger\beta_2$, and $\dagger\beta_3$ calculated from eq 12 as a highly refined initial guess, a final set of $\dagger\beta_n$ was calculated

TABLE II

EVALUATION OF PARAMETER a_n AND b_n

n	a_n	b_n	n	a_n	b_n
0	0.0	1.0	3	0.378	436.0
1	0.00223	19.1	4	1.0	0.0
2	0.0451	160.0			

$$\dagger\beta_1 = 2.54 \times 10 = \frac{[PdBrCl_3^{2-}][Cl^-]}{[PdCl_4^{2-}][Br^-]}$$

$$\dagger\beta_2 = 2.87 \times 10^2 = \frac{[PdBr_2Cl_2^{2-}][Cl^-]^2}{[PdCl_4^{2-}][Br^-]^2}$$

$$\dagger\beta_3 = 1.51 \times 10^3 = \frac{[PdBr_3Cl^{2-}][Cl^-]^3}{[PdCl_4^{2-}][Br^-]^3}$$

$$\dagger\beta_4 = 2.81 \times 10^3 = \frac{[PdBr_4^{2-}][Cl^-]^4}{[PdCl_4^{2-}][Br^-]^4}$$

Estimation of the Standard Deviation in the Values of Log $\dagger\beta_n$.—Repetition of the entire experiment was deemed impractical. However, since there were 732 data points (in addition to those points used to establish

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[12] S. C. Srivastava and L. Newman, *Inorg. Chem.*, **6**, 762 (1967).

[13] S. C. Srivastava and L. Newman, *ibid.*, **11**, 2855 (1972).

[14] L. Newman and S. C. Srivastava, *Proc. Symp. Coord. Chem., 3rd, 1970*, **1**, 171 (1970).

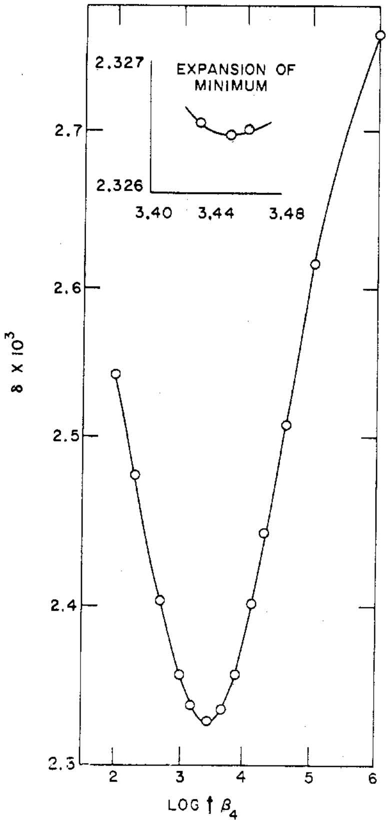

Figure 3.—Variation of standard deviation with $\dagger\beta_4$.

the extinction coefficients of the parent complexes), we decided to analyze subsets of the data. The subsets comprised experimental absorptions and corresponding ratios (bromide:chloride). If R_k represents the kth ratio, the data (all of it) for each wavelength are arranged so that $R_{k+1} > R_k$. Then, the data points in each of the $g_{\max}$ subsets will be R_k and $A_{j,k}$ values corresponding to the following values of k

subset 1: $k = 1, 1 + g_{\max}, 1 + 2g_{\max}, 1 + 3g_{\max}, 1 + 4g_{\max}, \ldots$

subset 2: $k = 2, 2 + g_{\max}, 2 + 2g_{\max}, 2 + 3g_{\max}, 2 + 4g_{\max}, \ldots$

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subset $g_{\max}$: $k = g_{\max}, 2g_{\max}, 3g_{\max}, 4g_{\max}, \ldots$

The evaluation of the set of $\dagger\beta_n$ for each subgroup is carried out in the same manner as described for a single group. Since the parameters for eq 1 (Table II) will be approximately the same for the subgroups as for the whole, reasonable refined initial guesses can be made. As before (Figure 3) σ was plotted *vs.* log $\dagger\beta_4$. The minimum was estimated with a parabolic fit. Results are given in Table III for several different values of $g_{\max}$. When $g_{\max} = 1$, of course, all the data are treated as a single group. As a regular procedure, using $g_{\max} = 4$ (in addition to $g_{\max} = 1$) would appear to be adequate.

TABLE III

OPTIMUM LOG $\dagger\beta_4$ FOR DIFFERENT SUBSETS

$g_{\max}$	No. of data points	Log $\dagger\beta_4$	(Log $\dagger\beta_4)_{\text{av}} \pm \sigma_{\log\dagger\beta_4}/\sqrt{g_{\max}}$[a]
1	732	3.45	
2	372	3.55	3.45 ± 0.10
	360	3.35	
3	252	3.25	3.45 ± 0.11
	240	3.61	
	240	3.50	
4	192	3.33	3.44 ± 0.10
	180	3.38	
	180	3.73	
	180	3.33	

[a] See eq 13–16.

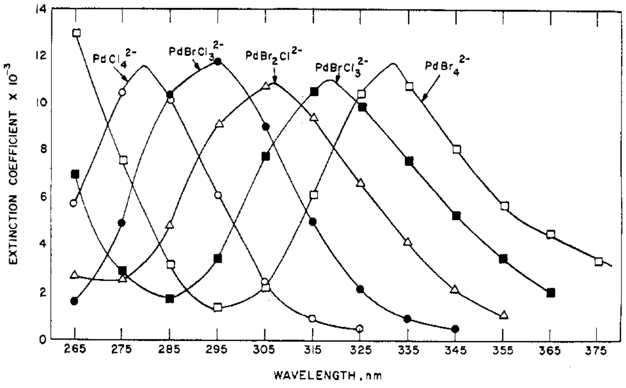

Figure 4.—Resolved spectra.

The uncertainties for $\dagger\beta_1$, $\dagger\beta_2$, and $\dagger\beta_3$ were estimated using eq 20 and the final results are given in Table IV.

TABLE IV

OPTIMUM VALUES OF $\dagger\beta_n$ AND THE ESTIMATED UNCERTAINTIES

n	Log $\dagger\beta_n \pm \sigma_i/\sqrt{N}$[a]	n	Log $\dagger\beta_n \pm \sigma_i/\sqrt{N}$[a]
1	1.40 ± 0.025	3	3.18 ± 0.07
2	2.46 ± 0.044	4	3.45 ± 0.10

[a] See eq 13–16 and 20.

Discussion

The results from this investigation are compared to those from the previous work[8] by looking at the stepwise equilibrium constants as given in Table V. The agreement is not quite as good as would be expected from the uncertainties given in either of the two works. The lower precision of the data of the previous work implies that their error estimates may be a bit optimistic. Thus, considering the shallowness of the minimum of the multidimensional error surface, it is unlikely that the graphical curve-fitting technique utilized in ref 8 could have found the real minimum.

TABLE V

COMPARISON OF THE STEPWISE CONSTANTS

Equilibrium	Log $\dagger K_n$: This work[a]	Log $\dagger K_n$: Ref 8
$PdCl_4^{2-} + Br^- = PdBrCl_3^{2-} + Cl^-$	1.40 ± 0.025	1.55
$PdBrCl_3^{2-} + Br^- = PdBr_2Cl_2^{2-} + Cl^-$	1.06 ± 0.02	1.09
$PdBr_2Cl_2^{2-} + Br^- = PdBr_3Cl^{2-} + Cl^-$	0.72 ± 0.026	0.95
$PdBr_3Cl^{2-} + Br^- = PdBr_4^{2-} + Cl^-$	0.27 ± 0.03	0.55

[a] See eq 26.

The resolved spectra for the mixed-ligand complexes are quite symmetrically distributed between the parent species (Figure 4). Indeed, even the extinction coefficients at the maxima are within 10% of those of the parents. These results agree quite well with those observed in the previous publication.

The theoretical statistical interrelationship of the equilibrium constants has been calculated for a tetrahedral system.[14,15] Comparison of these values with the appropriately normalized experimental constants (calculated from optimum values of $\dagger\beta_n$) is shown in Table VI. The results from this work yield almost purely statistical values[14,15] for the normalized equilibrium constants. In fact, we are tempted to believe that the system is perfectly statistical in its distribution and that the very slight differences are due to our experimental error. The previous data[8] are also reasonably close to a statistical distribution. The relative distribution of the various species as a function of the ligand ratio calculated for the optimum $\dagger\beta_n$ values (Table IV) is shown in Figure 5. The similarity of this figure to the statistical distribution given in ref 14 further reflects the nearly perfect statistical behavior of the system.

TABLE VI

COMPARISON OF THEORETICAL STATISTICAL CONSTANTS WITH NORMALIZED EXPERIMENTAL EQUILIBRIUM CONSTANTS

Reaction	Log (theoret)	Log (normalized exptl)[a] This work	Log (normalized exptl)[a] Ref 8
$^3/_4PdCl_4^{2-} + {}^1/_4PdBr_4^{2-} = PdBrCl_3^{2-}$	0.60	0.54	0.52
$^1/_2PdCl_4^{2-} + {}^1/_2PdBr_4^{2-} = PdBr_2Cl_2^{2-}$	0.78	0.74	0.57
$^1/_4PdCl_4^{2-} + {}^3/_4PdBr_4^{2-} = PdBr_3Cl^{2-}$	0.60	0.59	0.49

[a] Log (normalized experimental equilibrium constant) = log $\dagger\beta_n - (n/4) \log \dagger\beta_4$, where n (= 1–3) is the number of bromides in the product.

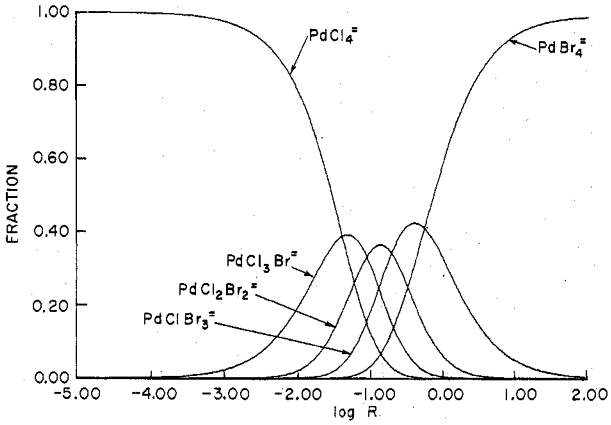

Figure 5.—Relative distribution as a function of ligand ratio.

The computer analysis presented here and the previous graphical analysis produce values of $\dagger K_n$ that are within reasonable agreement (Table V). Although graphical techniques can give reasonable values, a computer-fitting technique combined with error surface mapping is necessary in order to obtain the best set of values. We look forward to further applications of this computer approach by other workers as well as ourselves. Only then can it be determined if the method is generally applicable.

The observed nature of the error surface leads us to the obvious conclusion that it is desirable to obtain the most precise spectrophotometric data possible over a wide range of wavelengths and ligand concentration ratios. We still have found no way directly to correlate the precision of the data and the precision of the ultimately determined values of $\dagger\beta_n$. It has become clear to us, however, that this relationship depends very much upon the unique shape of the error surface existing for each problem. We have found, for example, that our analysis of the spectrophotometric data of Klotz, Feldberg, and Newman[16] (obtained with a Cary 14 for the $PdBr_nCl_{4-n}^{2-}$ system in acetonitrile) yielded nearly the same precision in the values of $\dagger\beta_n$ as we obtained in this paper with data that are an order of magnitude more precise. We attribute this difference to a more well-defined minimum as defined by a plot of σ *vs.* log β_4 (see Figure 3, this paper).

The data which are the basis of this work are available on request.

Acknowledgment.—We wish to thank Dr. Manny Hillman for many enlightening discussions on the topic of least-squares techniques.

Appendix

Definition of Symbols

m	Number of ligands coordinated by central atom
n	Species index ($n = 0\text{–}m$)
$\dagger\beta_n$	Overall equilibrium constant for reaction 1
$\dagger K_n$	Stepwise equilibrium constant ($\dagger K_n = \dagger\beta_n/\dagger\beta_{n-1})_{n=1,2,\ldots,m}$
C_M	Total concentration of central metal atom
j_{max}	Number of different wavelengths used in given experiment
j	Wavelength index ($j = 1\text{–}j_{max}$)
R_k	Ratio [Y]/[X]
k	Ratio index ($k = 1\text{–}k_{max}$)
k_{max}	Number of different ratios used in given experiment
$\epsilon_{j,n}$	Extinction coefficient of nth species at jth wavelength
$A_{j,k}$	Absorption at kth ratio and jth wavelength
S	Sum of square of deviation
σ	Standard deviation $\sigma = \sqrt{S/(j_{max}k_{max} - 1)}$
a_n b_n	Parametric constants (see eq 11)
$\sigma_{\log\dagger\beta_n}$	Uncertainties in log $\dagger\beta_n$
g_{max}	Number of subsets of data
N	Total number of data points

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(15) Y. Marcus and I. Eliezer, *Coord. Chem. Rev.*, **4**, 273 (1969).

(16) P. Klotz, S. Feldberg, and L. Newman, *Inorg. Chem.*, **12**, 164 (1973).