

Amineanionogold(III) Complexes. II. Calculation of Equilibrium Constants from Multiwavelength Spectrophotometric Measurements. Application to the Exchange of Bromide for Chloride in *trans*-Diamminedichloridogold(III) in Acidic Aqueous Solution

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Tetraamminegold(III) reacts with chloride in acidic solution to give a diamminedichloridogold(III) species which was isolated as a chloride salt. The diamminegold(III) species is tentatively assigned the *trans* configuration and the fast exchange of the two chloride ligands with bromide ligands has been investigated spectrophotometrically in 1.0 M perchlorate solution. At 25 °C the stepwise equilibrium constants are: $K_1=122\pm 2$ and $K_2=29.9\pm 0.5$ with $\Delta H_1^\circ=-12.1\pm 1.2$ and $\Delta H_2^\circ=-13.5\pm 0.7$ kJ mol⁻¹, respectively. General equations for processing multiwavelength spectrophotometric data to give stability constants and spectra for polynuclear and mixed ligand complexes are presented in an appendix.

Substitution of the first two ammonia ligands in the tetraamminegold(III) ion by bromide or chloride are rather fast processes which give diamminedihalogenido species with much more robust ammonia ligands.^{1,2} This suggests that the charge of the complex and/or the nature of the non-reacting ligands is important for the rate of such gold(III) substitution reactions and provides a strong incentive for measuring thermodynamic parameters which might provide a better background for a correlation between structure, stability and reactivity. The robustness of the

diamminegold(III)-moiety ensures that the equilibrium constants for the halide exchange reactions at and around room temperature can be determined by standard spectrophotometric methods.

This simple system is well suited for a demonstration of the computational technique used to evaluate equilibrium constants and spectra from multiwavelength spectrophotometric data. The method has been used previously on other mononuclear systems³ but is equally applicable to systems involving polynuclear and mixed ligand complexes, for which generalized expressions are given in the Appendix.

EXPERIMENTAL

Materials. Potassium tetrachloridoaurate(III) from H. Drijfhout and Zoon's, Amsterdam, was used as the starting material for the preparation of the gold compounds. Other chemicals were of analytical grade. Hydrobromic acid was distilled before dilution. Stock solutions of hydrobromic acid, hydrochloric acid, and perchloric acid were analyzed using standard methods.

Spectrophotometric measurements were performed on a Zeiss DMR 21 spectrophotometer with thermostatted cell holder and cell compartment.

Analysis. Analyses for C, N, H and Au (the latter gravimetric) were made by the Microanalytical Laboratory of the H.C. Ørsted Institute. Gold was also determined spectrophotometrically as described previously.¹

Preparations. $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3^5$ and $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Br}_2]\text{Br}^1$ were both prepared and purified as previously described.

$\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}\cdot\frac{1}{3}\text{H}_2\text{O}$ *trans*-Diamminedichloridogold(III) chloride was synthesized by reacting 4.0 g, 8.9 mmol, of $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ in 40 ml of 4 M HCl at 45 °C for 20 min. The resulting yellow solution was filtered and mixed with 40 ml of saturated LiCl(aq) at room temperature. After cooling in ice the precipitate was filtered off, washed with 3 ml of ice-cold absolute ethanol and with ether. Yield 2.5 g. This crude product was dissolved in 10 ml of 0.01 M HClO₄ and reprecipitated by the slow addition of 5 ml of saturated LiCl(aq). After three such reprecipitations and drying in air at room temperature, the product appeared as a primrose-yellow microcrystalline powder. Yield 1.3 g of $[\text{Au}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}\cdot\frac{1}{3}\text{H}_2\text{O}$, corresponding to 43 %. Analysis Au, N, H, Cl. The absorption spectrum in the UV region in 0.10 M HCl+0.90 M HClO₄ showed no further changes after the second reprecipitation: $\lambda_{\text{max}}=277$ nm, $\epsilon_{\text{max}}=1180$

$\text{M}^{-1}\text{cm}^{-1}$, cf. Fig. 1. In 1.0 M HCl the absorption characteristics are 277 nm, $1300 \text{ M}^{-1} \text{ cm}^{-1}$. Drying the compound at 105 °C gave a loss in weight of less than 0.2 %.

The diamminedichloridogold(III) ion exists as two geometrical isomers. Arguments for assigning the *trans*-configuration to the present complex are presented in the Results section.

Equilibrium measurements. Stock solutions of $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+$ were freshly prepared by dissolution of weighed amounts of $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}\cdot\frac{1}{3}\text{H}_2\text{O}$ in 1.80 M HClO₄. By appropriate dilution with hydrobromic, hydrochloric, and perchloric acid, solutions with 0.100 M H(Br,Cl)+0.900 M HClO₄, $0.50 \leq [\text{Br}^-] \leq 0.100$ M, were prepared and equilibrated at 0.9, 15.1, 25.0 and 30.2 °C, respectively. Absorption spectra were recorded between 260 and 360 nm, and data for 18 solutions at the selected wavelengths: 270, 277, 291, 304, 310, 328, 340 and 350 nm and at the four different temperatures were used to evaluate the data in Table 1.

CALCULATIONS

The calculations to give spectra and stability constants for the diamminebromidochlorido- and

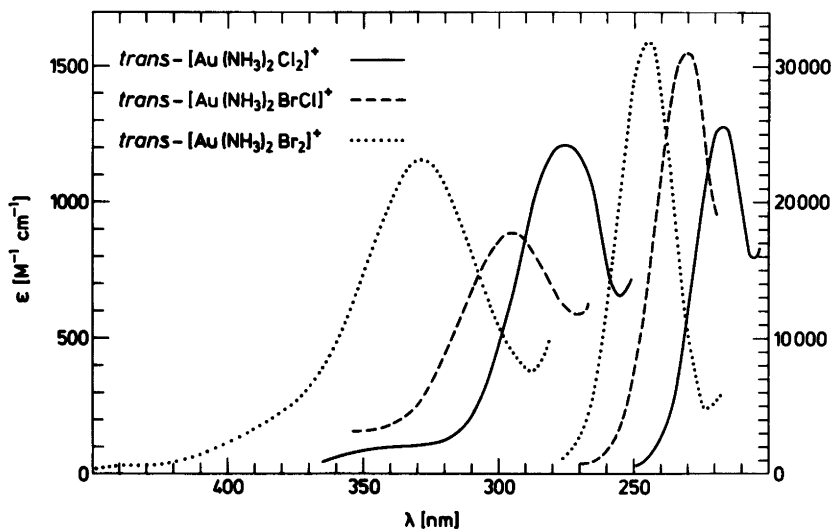


Fig. 1. Absorption spectra of $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+$, $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+$ and $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+$ in 0.10 M H(Cl,Br)+0.90 M HClO₄ (aqueous solution) at 25 °C. The spectra of the dichlorido and dibromido complexes were recorded after dissolution of $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}\cdot\frac{1}{3}\text{H}_2\text{O}$ in 0.10 M HCl+0.90 M HClO₄ and $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Br}_2]\text{Br}$ in 0.020 M HBr+0.98 M HClO₄, respectively. The spectrum of $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+$ was calculated from the recorded spectrum of a solution prepared to contain the maximum concentration of this species, using the $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+$ and the $\text{trans}-[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+$ spectra, and the stability constants of Table 1.

Table 1. Thermodynamic parameters for the stepwise exchange of chloride with bromide in $trans\text{-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+$ in aqueous 0.10 M H(Br, Cl)+0.90 M HClO_4 solution.

Equilibrium	$K(25^\circ\text{C})$	ΔH° ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS° ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
$trans\text{-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+ + \text{Br}^- \rightleftharpoons trans\text{-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Cl}^-$	122 ± 2	-12.1 ± 1.2	-1 ± 4
$trans\text{-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Br}^- \rightleftharpoons trans\text{-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+ + \text{Cl}^-$	29.9 ± 0.5	-13.5 ± 0.6	-17 ± 2

dibromidogold(III) species are readily performed by nonlinear regression analysis by the generalised method described in the Appendix. The method was programmed in the Algol 6 dialect for the RC4000 computer of the H.C. Ørsted Institute.

With the 3 initial species, $\mu=3$:

1: Cl^- , 2: Br^- and 3: $[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+$ and the 2 new species, $\nu=2$:

4: $[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+$ and 5: $[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+$, the stoichiometric relations are given by the C matrix as:

$$C \equiv \begin{Bmatrix} 1 & 0 & 0 & -1 & -2 \\ 0 & 1 & 0 & 1 & 2 \\ 0 & 0 & 1 & 1 & 1 \end{Bmatrix}$$

In the nomenclature of the Appendix this matrix defines the stability constants as:

$$[\text{MBrCl}^+] = \beta_4 [\text{Cl}^-]^{-1} [\text{Br}^-]^1 [\text{MCl}_2^+]^1$$

and

$$[\text{MBr}_2^+] = \beta_5 [\text{Cl}^-]^{-2} [\text{Br}^-]^2 [\text{MCl}_2^+]^1$$

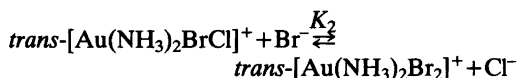
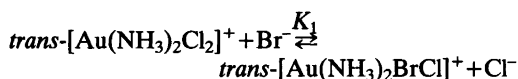
with $M \equiv \text{Au}(\text{NH}_3)_2$. These constants are of course easily transformed into the consecutive constants, K_1 and K_2 , by $K_1 = \beta_4$ and $K_2 = \beta_5/\beta_4$.

RESULTS AND DISCUSSION

Anation of $[\text{Au}(\text{NH}_3)_4]^{3+}$ by chloride in acidic aqueous solution where deprotonation and hydrolysis are suppressed⁵ takes place in two kinetically separated steps, thereby allowing the isolation and purification of an intermediate product as a chloride salt. This product was identified as $[\text{Au}(\text{NH}_3)_2\text{Cl}_2]\text{Cl} \cdot \frac{1}{3}\text{H}_2\text{O}$ from its elementary analysis. The UV-absorption spectrum of this salt dissolved in 0.020 M HBr+0.98 M HClO_4 had $\lambda_{\text{max}}=328.5$ nm and $\epsilon_{\text{max}}=1155$

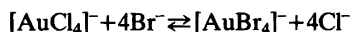
$\text{M}^{-1}\text{cm}^{-1}$, identical to that of $trans\text{-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]\text{Br}^*$ dissolved in the same medium¹ and this is taken as an indication of the same configuration for the dichlorido complex.

Further anation has half-lives larger than 12 h for the ammonia/bromide ligand substitution under the experimental conditions for the present equilibrium measurements, and is therefore insignificant for freshly prepared solutions. The stepwise equilibrium constants for



are presented in Fig. 2 and the calculated absorption spectra of the mixed bromido-chlorido and the dibromido complexes are given in Fig. 1.

The equilibrium constant for:



has the value $\beta_4=10^{7.50}$ in aqueous solution^{6,7} at 25 °C and is relatively insensitive to ionic strength changes.⁸ This value is comparable to the present finding of β_2 , for the equilibrium between $trans\text{-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+$ and $trans\text{-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+$, as $(\beta_4)^{1/4}=75$ and $\sqrt{\beta_2}=60$. The difference between the stability of bromido and chlorido complexes of Au(III) is higher than for other square planar d⁸ systems such as Pt(II) with $(\beta_4)^{1/4}=33^9$ and

* The assignment of a *trans* configuration to the dibromido complex is based upon kinetic arguments assuming the kinetic *trans* effect of coordinated bromide to be greater than that of coordinated ammonia. This *trans* effect order is well documented for a number of transition metal ions, including square planar platinum(II), and would have to be the opposite for gold(III) if a *cis* configuration should be accounted for.

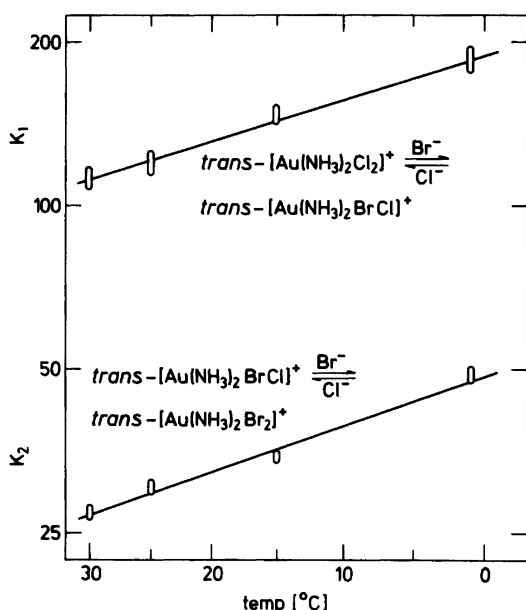
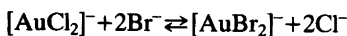


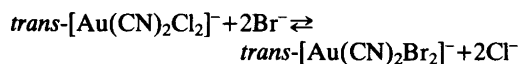
Fig. 2. Temperature dependence of K_1 and K_2 in the $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+ + \text{Br}^-$ system in 0.10 M $\text{H}(\text{Cl}, \text{Br}) + 0.90$ M HClO_4 . Experimental data are given with a range corresponding to \pm the estimated uncertainties and the solid curves computed from $\ln K = (-\Delta H^\circ/T + \Delta S^\circ)/R$ are the basis for the parameters, ΔH° and ΔS° .

$\text{Pd}(\text{II})$ with $(\beta_4)^{1/4} = 7^{10}$ and also higher than for $\text{Au}(\text{I})$ for which the equilibrium:

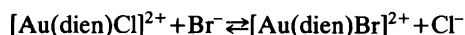


has $\sqrt{\beta_2} = 44$.^{6,7} These confirmations of $\text{Au}(\text{III})$ as an extremely soft acceptor^{8,11} also show that the introduction of two ammonia ligands *trans* to

each other in the coordination sphere has little if any modulating effect on the acceptor properties of $\text{Au}(\text{III})$. In contrast to this, two cyanide ligands strongly increase the softness of $\text{Au}(\text{III})$, as judged from the value of $\sqrt{\beta_2} \approx 750$ for the equilibrium:¹²



and introduction of an amine ligand *trans* to the halides works in the opposite direction, as indicated by the value $K \approx 15^{14}$ estimated for:



(dien = 1,4,7-triazaheptane).

The stepwise equilibrium constants for the exchange of bromide for chloride in $[\text{AuCl}_4]^-$, known from kinetic measurements,⁴ are compared in Table 2 with the present findings for the *trans*-diamminegold(III)-moiety. There is no significant difference between the statistically corrected¹³ constants and the affinity for exchange of a chloride with a bromide ligand at these $\text{Au}(\text{III})$ centres is thus independent of whether the *cis*-ligand is ammonia, chloride or bromide, or whether the *trans*-ligand is chloride or bromide. The observed high kinetic *cis*-effect^{1,2} of ammonia relative to the two halides therefore has no thermodynamic counterpart.

The ΔH° and ΔS° values of Table 1 also confirm that the difference between the K_1 and K_2 values is statistically determined, since the ΔH° values are identical within the estimated errors and the difference between the reaction entropies $\Delta S_1^\circ - \Delta S_2^\circ \approx 16 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ has the

Table 2. Comparison of some equilibrium constants for the exchange of chloride with bromide in gold(III) complexes in aqueous 1.0 M perchlorate solution at 25 °C.

Equilibrium	K	K_{corr}	Ref.
$\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+ + \text{Br}^- \rightleftharpoons \text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Cl}^-$	122 ± 2	61 ± 1	This work
$\text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Br}^- \rightleftharpoons \text{trans-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+ + \text{Cl}^-$	29.9 ± 0.5	59.8 ± 1.0	This work
$[\text{AuCl}_4]^- + \text{Br}^- \rightleftharpoons [\text{AuBrCl}_3]^- + \text{Cl}^-$	243 ± 40	61 ± 10	4
$[\text{AuBrCl}_3]^- + \text{Br}^- \rightleftharpoons \text{trans-}[\text{AuBr}_2\text{Cl}_2]^- + \text{Cl}^-$	34 ± 7	68 ± 14	4
$[\text{AuBrCl}_3]^- + \text{Br}^- \rightleftharpoons \text{cis-}[\text{AuBr}_2\text{Cl}_2]^- + \text{Cl}^-$	64 ± 13	64 ± 13	4
$\text{trans-}[\text{AuBr}_2\text{Cl}_2]^- + \text{Br}^- \rightleftharpoons [\text{AuBr}_3\text{Cl}]^- + \text{Cl}^-$	153 ± 15	77 ± 8	4
$\text{cis-}[\text{AuBr}_2\text{Cl}_2]^- + \text{Br}^- \rightleftharpoons [\text{AuBr}_3\text{Cl}]^- + \text{Cl}^-$	73 ± 15	73 ± 15	4
$[\text{AuBr}_3\text{Cl}]^- + \text{Br}^- \rightleftharpoons [\text{AuBr}_4]^- + \text{Cl}^-$	17 ± 5	68 ± 20	4

value expected from statistical arguments: $R \ln 4 = 12 \text{ J mol}^{-1} \text{ K}^{-1}$. Solvation of chloride is stronger than that of bromide as indicated by the difference between the entropies of these ions dissolved in water $S_{\text{Cl}^-}^\circ - S_{\text{Br}^-}^\circ = -26.1 \text{ J mol}^{-1} \text{ K}^{-1}$.¹⁵ For both reactions this difference in the solvational entropies gives a negative contribution to the overall reaction entropy and indicates that the difference between the solvation of the reactants and the products is the same for the two reactions or, in other words, the change in solvation of the complex is the same whether the first or the second chloride is exchanged with bromide.

APPENDIX

Determination of stability constants from spectrophotometric data. The determination of stability constants is most effectively accomplished by using nonlinear regression analysis. This involves the assumption of an initial set of parameter values followed by an iterative refinement of these values. Assuming the validity of the Lambert-Beer law, the problem is linear in the molar absorption coefficients and, therefore, initial values for only the stability constants are required in order to start the computations.

Stoichiometric relations of the form:

$$\tau_i = \sum_{j=1}^{\mu+\nu} \gamma_{ij} \sigma_j \quad i=1,2,\dots,\mu \quad (1)$$

for μ different species with total concentrations, τ_i , which interact to form ν new species, may be combined with the relevant mass action equations:

$$\sigma_i = \beta_i \prod_{j=1}^{\mu} \pi_j^{\gamma_{ij}} \quad i=1,2,\dots,\mu+\nu$$

with:

$$\beta_i \equiv 1 \quad \sigma_i \equiv \pi_i \quad i=1,2,\dots,\mu$$

to give μ nonlinear equations, in π_i , for the calculation of the free concentrations, σ_i , of all $\mu+\nu$ species.

Eqn. (1) may in matrix notation collectively be written:

$$\mathbf{t} = \mathbf{C}\mathbf{s} \quad (1a)$$

$$\mathbf{t} \equiv \{\tau_i\}, \mathbf{C} \equiv \{\gamma_{ij}\}, \mathbf{s} \equiv \{\sigma_j\} \quad \begin{cases} i=1,2,\dots,\mu \\ j=1,2,\dots,\mu+\nu \end{cases}$$

and Newton's method for the iterative solution to:

$$\mathbf{p} \equiv \{\pi_i\} \quad i=1,2,\dots,\mu$$

may be expressed as:

$$\mathbf{p}_{i+1} = \mathbf{p}_i + \left[\mathbf{C} \frac{\partial \mathbf{s}}{\partial \mathbf{p}} \right]^{-1} [\mathbf{t} - \mathbf{C}\mathbf{s}] \quad (2)$$

with

$$\frac{\partial \sigma_i}{\partial \pi_j} = \frac{\gamma_{ji} \sigma_i}{\pi_j}$$

The starting approximation $\mathbf{p}_0 = \mathbf{t}$ is usually sufficient to assure convergence by eqn. (2), particularly when only moderately stable species are formed.

For ξ different solutions measured at η different wavelengths the experimental set of data at unit pathlength, α_i^j , may be expressed, using the Lambert-Beer law, as:

$$\alpha_i^j = \sum_{k=1}^{\mu+\nu} \varepsilon_k^i \sigma_k^j \quad \begin{cases} i=1,2,\dots,\eta \\ j=1,2,\dots,\xi \end{cases} \quad (3)$$

where the superscripts are used to denote different solutions. Derivatives of the general form $\partial \alpha / \partial \varepsilon$ and $\partial \alpha / \partial \beta$ are necessary for the regression analysis. Numerical differentiation for the evaluation of these quantities can be used, but when many parameters are present such methods tend to be somewhat uneconomical in computer time and are unnecessary for problems of the present type since analytical expressions for the differential quotients are easily derived. The first type is calculated directly from eqn. (3), and is:

$$\frac{\partial \alpha_i^j}{\partial \varepsilon_k^l} = \delta_{ik} \sigma_l^j \quad \delta_{ik} = \begin{cases} 0 & i \neq k \\ 1 & i = k \end{cases} \quad (4)$$

To derive a formula for the remaining derivatives eqn. (3) may be written symbolically as:

$$\mathbf{a} = \mathbf{a}(\mathbf{s}(\mathbf{b}, \mathbf{p}(\mathbf{b})))$$

with

$$\mathbf{a} \equiv \{\alpha_i^j\} \quad \mathbf{b} \equiv \{\beta_i\} \quad \mathbf{p} \equiv \{\pi_i^j\} \quad \text{and} \quad \mathbf{s} \equiv \{\sigma_i^j\}$$

which upon differentiation yields:

$$\frac{\partial \mathbf{a}}{\partial \mathbf{b}} = \frac{\partial \mathbf{a}}{\partial \mathbf{s}} \left[\frac{\partial \mathbf{s}}{\partial \mathbf{b}} + \frac{\partial \mathbf{s}}{\partial \mathbf{p}} \frac{\partial \mathbf{p}}{\partial \mathbf{b}} \right]$$

Single elements in the matrices of this equation are given by:

$$\frac{\partial \alpha_k^i}{\partial \sigma_k^j} = \delta_{ij} \varepsilon_{ik}$$

$$\frac{\partial \sigma_k^j}{\partial \beta_i} = \delta_{ki} \frac{\sigma_k^j}{\beta_i}$$

and by the solution of the set of simultaneous linear equations derived by differentiation of eqn. (1a):

$$\frac{\partial \mathbf{p}}{\partial \mathbf{b}} = \left[\mathbf{C} \frac{\partial \mathbf{s}}{\partial \mathbf{p}} \right]^{-1} \mathbf{C} \frac{\partial \mathbf{s}}{\partial \mathbf{b}}$$

Application of the methods just outlined gives equations involving $\nu + \eta(\mu + \nu)$ parameters, which for even very simple systems may easily be so large a number that it will present difficulties when used without some modifications on a smaller computer:

If the parameter vector is defined as:

$$\mathbf{q} \equiv \begin{cases} \beta_i \\ \varepsilon_k^j \end{cases} \quad \begin{cases} i = \mu + 1, \mu + 2, \dots, \mu + \nu \\ j = 1, 2, \dots, \xi \\ k = 1, 2, \dots, \mu + \nu \end{cases}$$

then the normal equations for the parameter value corrections, $\Delta \mathbf{q}$, can be expressed as:

$$\left[\left(\frac{\partial \mathbf{a}}{\partial \mathbf{q}} \right)^T \left(\mathbf{V}(\mathbf{a}) \right)^{-1} \left(\frac{\partial \mathbf{a}}{\partial \mathbf{q}} \right) \right] \Delta \mathbf{q} = - \left(\frac{\partial \mathbf{a}}{\partial \mathbf{q}} \right)^T \left(\mathbf{V}(\mathbf{a}) \right)^{-1} \left(\mathbf{a}_{\text{obs}} - \mathbf{a}_{\text{calc}} \right)$$

or formally

$$\mathbf{B} \Delta \mathbf{q} = \mathbf{c}$$

where $\mathbf{V}(\mathbf{a})$ is the usually diagonal matrix of variances upon the experimental data. This equation has a coefficient matrix, \mathbf{B} , with the lower right part in block diagonal form, *i.e.*:

$$\begin{bmatrix} \mathbf{B}_{00} & \mathbf{B}_{01} & \mathbf{B}_{02} \cdots & \mathbf{B}_{0\eta} \\ \mathbf{B}_{01}^T & \mathbf{B}_{11} & \mathbf{O} & \cdots \mathbf{O} \\ \mathbf{B}_{02}^T & \mathbf{O} & \mathbf{B}_{22} \cdots & \mathbf{O} \\ \vdots & \vdots & \vdots & \vdots \\ \mathbf{B}_{0\eta}^T & \mathbf{O} & \mathbf{O} & \cdots \mathbf{B}_{\eta\eta} \end{bmatrix} \begin{bmatrix} \Delta \mathbf{q}_0 \\ \Delta \mathbf{q}_1 \\ \Delta \mathbf{q}_2 \\ \vdots \\ \Delta \mathbf{q}_\eta \end{bmatrix} = \begin{bmatrix} \mathbf{c}_0 \\ \mathbf{c}_1 \\ \mathbf{c}_2 \\ \vdots \\ \mathbf{c}_\eta \end{bmatrix} \quad (5)$$

This special form allows a considerable reduction in the need for both computer time and storage, since it is readily verified that eqn. (5) is equivalent to

$$\left[\mathbf{B}_{00} - \sum_{i=1}^{\eta} \mathbf{B}_{0i} \mathbf{B}_{ii}^{-1} \mathbf{B}_{0i}^T \right] \Delta \mathbf{q}_0 = \mathbf{c}_0 - \sum_{i=1}^{\eta} \mathbf{B}_{0i} \mathbf{B}_{ii}^{-1} \mathbf{c}_i \quad (6)$$

The spectrophotometric problem is linear in all the ε_k^i parameters. For a given set of stability constants these parameters may therefore be found directly by linear regression analysis from:

$$\mathbf{B}_{ii} \mathbf{e}^i = \mathbf{c}_i \equiv - \left(\frac{\partial \mathbf{a}}{\partial \mathbf{e}^i} \right)^T \left(\mathbf{V}(\mathbf{a}) \right)^{-1} \mathbf{a}_{\text{obs}} \quad (7)$$

with

$$\{ \varepsilon_k^i \} \equiv \mathbf{e}^i$$

and the matrix of partial derivatives given by eqn. (4).

Each iteration involving eqn. (5) is therefore most conveniently carried out by first finding suitable sets of ε_k^i parameters from eqn. (7), and then with these parameters adjusting the assumed initial values for the β_i parameters by eqn. (6) in which now

$$\mathbf{B}_{ii}^{-1} \mathbf{c}_i = 0 \quad i = 1, 2, \dots, \eta$$

which reduces the right-hand side to \mathbf{c}_0 . This calculation, of course, also gives implicit adjustments to the ε_k^i parameters. It therefore usually converges faster and gives more realistic error estimates than some alternative approaches in use which ignore off diagonal blocks in eqn. (5) and therefore only give conditional and sometimes unrealistically small variances upon the stability constants and spectral parameters.

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