A Procedure for the Calculation of Enthalpy Changes from Continuous-titration Calorimetric Experiments

By **Alberto Vacca**, **Antonio Sabatini**,* and **Lucia Bologni**, Istituto di Chimica Generale ed Inorganica della Università, Laboratorio C.N.R., Via J. Nardi 39, 50132 Florence, Italy

An isoperibolic titration calorimeter has been modified to perform continuous-titration measurements. In order to take into account the unavoidable time-lag in the response of the sensor element to temperature changes, the process of heat transfer inside the calorimeter has been schematized. A calculation procedure, based on this model, allows the interpretation of the experimental data and the determination of enthalpies of reaction. The method has been tested by measurement of the heat of ionization of water and the heat of protonation of aminotris(hydroxymethyl)methane at 298 K. The results are in good agreement with previously reported data. The stepwise enthalpies of protonation of the phosphate ion in 0.15 mol dm^{-3} NaCl at 298 K have also been determined.

CALORIMETRIC titration has been widely used and several monographs have been published on this method.[1] It can be applied both for analytical purposes and for determinations of enthalpies of reaction, and in appropriate circumstances may be used for the simultaneous determination of equilibrium constants and enthalpy changes (entropy titration).[2]

Continuous-titration calorimetry is performed by adding the titrant at a rigorously constant rate to the solution contained in the calorimetric vessel. The continuous record of the temperature change during the addition of titrant makes it possible (*i*) to follow the progress of the reaction, (*ii*) to detect eventual end-points, and (*iii*) to obtain, from a single experiment, the equivalent of a large number of determinations performed by the incremental technique. However, for kinetically hindered reactions, the continuous method gives erroneous results and the incremental method must be used. Another stringent requirement is that the equipment based on the continuous addition must have a quick response to temperature changes. The response time of commercially available titration calorimeters is usually of the order of a few seconds. This is mainly due to the interval needed for thermal equilibration of the sensor element and the solution contained in the calorimetric vessel, and is a function of the temperature difference between the sensor and solution.

In order to take account of this effect, the process of heat transfer between the various regions inside an isoperibolic calorimeter has been schematized, and a mathematical model for the analysis of the calorimetric data has been developed.[3] The present paper deals with the detailed description of the whole calculation procedure, which has already been applied in recent publications.[3,4] The results of the chemical calibration, carried out for evaluation of the performance of the whole procedure, are also reported. As part of a more general investigation on solution equilibria involving biologically important ligands, this method has been used for the determination of the enthalpies of protonation of the phosphate ion at 298 K in 0.15 mol dm^{-3} NaCl.

EXPERIMENTAL

Materials.—Analytical grade sodium chloride (Merck), disodium hydrogenphosphate dihydrate (Merck), and aminotris(hydroxymethyl)methane (NBS, solution calorimetry standard) were used without further purification.

An aqueous solution of hydrochloric acid was prepared by dilution of the constant-boiling solution and standardized against $NH_2C(CH_2OH)_3$ by pH-metric titrations. Aqueous solutions of sodium hydroxide were prepared and stored as previously described.[5] These solutions were standardized by means of pH-metric titration against potassium hydrogenphthalate (Erba, primary standard) and periodically re-checked with the standard solution of hydrochloric acid.

The end-points of all titrations were calculated according to the Gran method.[6]

Potentiometric Measurements.—The apparatus and the experimental procedure have been described previously.[5] As supporting electrolyte, 0.15 mol dm^{-3} NaCl was used. For the determination of the basicity constants of the phosphate ion, solutions containing $Na[H_2PO_4]$ and HCl (total volume *ca.* 110 cm^3) were titrated with the Na[OH] solution (*ca.* 0.15 mol dm^{-3}). The experimental details of the potentiometric measurements are shown in Table 1.

TABLE 1

Experimental details of the e.m.f. measurements

Initial concentration/(mol m^{-3})			
$Na_2[HPO_4]$	HCl	pH range	Number of data points
2.182	9.205	2.2—11.4	59
2.545	9.186	2.2—11.8	89
3.351	4.553	6.0—11.9	40
4.230	13.96	2.1—7.6	41
7.046	17.10	2.1—7.8	31
8.323	22.20	2.0—8.1	40

The hydrogen-ion concentration was calculated from the experimental e.m.f. values E (expressed in mV) using equation (1). Each measurement was preceded by a

$$[H^+] = \exp[(E - E^{\ominus} + E_{ja} - E_{jb})/25.693] \quad (1)$$

HCl–Na[OH] titration in the same ionic medium and covering the same e.m.f. range. This allowed the calculation of the standard potential, $E^{\ominus}$, and the correction terms due to the liquid junction, E_{ja} and E_{jb}, for strongly acidic and strongly basic regions, respectively.[7]

Calorimetric Measurements.—The calorimetry system used in the continuous-titration experiments has been described previously.[3] A device was constructed so as to make the experiments fully automatic. It performs the following functions: (*i*) analogue-to-digital conversion of the output voltage of the unbalanced Wheatstone bridge; (*ii*) data acquisition at constant and predetermined time intervals; and (*iii*) generation, at preselected times, of electrical pulses, which simulate all manual interventions of the operator and remotely control the beginning and the length of each step of the measurement. The experimental details of the calorimetric measurements on the protonation of phosphate are shown in Table 2.

The heat of ionization of water was determined by adding the Na[OH] solution to a HCl solution contained in the calorimetric vessel. The enthalpy of protonation of $NH_2C(CH_2OH)_3$ was measured by adding either the Na[OH] solution or the HCl solution to buffered solutions of the amine having a total concentration of *ca.* 40 mol m^{-3}.

TABLE 2

Experimental details of the calorimetric titrations

Initial quantity/mmol		Volume of initial solution/cm^3	Amount of Na[OH] added mmol	Rate of addition/ µmol s^{-1}	Number of data points
$Na_2[HPO_4]$	HCl				
0.1938	1.0080	80.4	0.9923	1.3084	62
0.1966	0.4011	80.9	0.9919	1.3084	64
0.2516	1.0110	83.9	1.0152	1.3087	65
0.5299	0.4819	79.8	1.5333	2.5701	30

CALCULATIONS

Potentiometric Data.—The computer program MINIQUAD [8] was used to calculate the basicity constants of the phosphate ion. The stepwise equilibrium constants and the corresponding standard deviations were obtained by the procedure already reported.[5]

Calorimetric Data.—The output voltages of the unbalanced Wheatstone bridge were converted into the corresponding values of thermistor resistance using the known values of bridge resistances, e.m.f. and internal resistance of the d.c. power supply, voltmeter input resistance, and filter time constant. Using the thermistor resistance–temperature relation (2), the value of θ_t can be obtained

$$R = A \exp(B/\theta_t) \qquad (2)$$

(for symbols not defined in the text, see the Appendix). The values of A and B for each thermistor employed were determined by suitable calibration experiments. The program TRANS written in FORTRAN was used to transform the voltage values directly into thermistor temperatures for both the calorimetric vessel and thermostat bath.

As previously described,[3] it can be assumed that heat flows inside the calorimeter between four different regions at different temperatures (Figure). According to this scheme the differential equations (3)—(5) can be obtained,[3] and formulated in matrix notation as in equation (6).

$$\theta_t' = [W_t + K_{ts}(\theta_s - \theta_t)]/C_t \qquad (3)$$

$$\theta_h' = [W_h + K_{hs}(\theta_s - \theta_h)]/C_h \qquad (4)$$

$$\theta_s' = [W_s + K_{ts}(\theta_t - \theta_s) + K_{hs}(\theta_h - \theta_s) + K_s(\theta_b - \theta_s)]/C_s \qquad (5)$$

$$\boldsymbol{\theta}' = \boldsymbol{A\theta} + \boldsymbol{b} \qquad (6)$$

The system of differential equations can be solved if the terms in matrix $\boldsymbol{A}$ and vector $\boldsymbol{b}$ are constant. However, in titration experiments, some of these terms, in particular the heat capacity of the solution and the thermal power generated in the solution, change when the titrant is added. Thus, a method of numerical integration must be used.

The vector $\boldsymbol{\delta}$ of the temperature changes in a finite time interval h is given by the Taylor series (7). The non-constant terms in $\boldsymbol{A}$ and $\boldsymbol{b}$ can be approximated by their

$$\boldsymbol{\delta} = \boldsymbol{\theta}'h + (\boldsymbol{\theta}''h/2) + (\boldsymbol{\theta}'''h/6) + (\boldsymbol{\theta}''''h/24) + \cdots \qquad (7)$$

mean values in the interval h, if it is sufficiently short. Using this approximation, a matrix $\boldsymbol{A}$ and a vector $\boldsymbol{b}$, which are constant within each interval, are obtained. Accordingly equation (6) becomes (8). By differentiating equation (8)

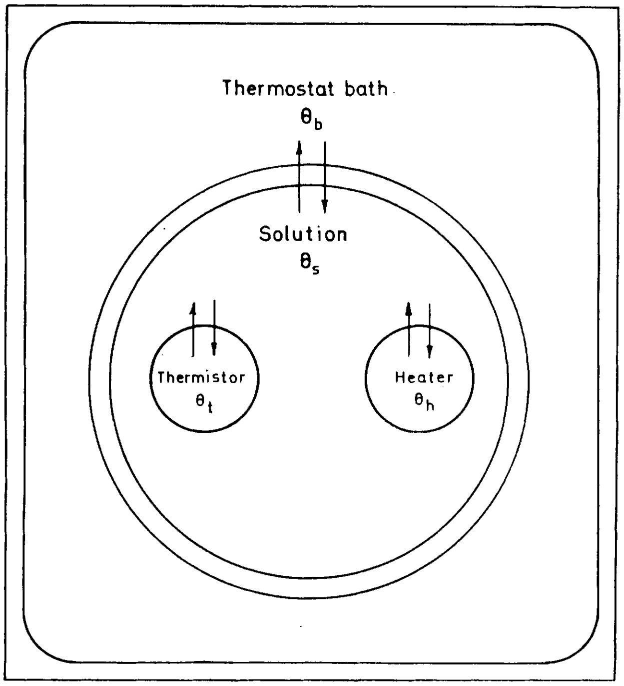
$$\boldsymbol{\theta}' = \boldsymbol{A\theta} + \boldsymbol{b} \qquad (8)$$

and remembering that $\boldsymbol{A}$ and $\boldsymbol{b}$ are constant, the higher derivatives of $\boldsymbol{\theta}$ are obtained according to equations (9).

$$\boldsymbol{\theta}'' = \boldsymbol{A\theta}'; \ \boldsymbol{\theta}''' = \boldsymbol{A}^2\boldsymbol{\theta}'; \ \boldsymbol{\theta}'''' = \boldsymbol{A}^3\boldsymbol{\theta}', \ etc. \qquad (9)$$

Substitution of equations (9) into (7) results in (10).

$$\boldsymbol{\delta} = \sum_{i=1}^{\infty} (\boldsymbol{A}^{i-1}\boldsymbol{\theta}')(h/i!) \qquad (10)$$



Schematic representation of the heat flow between different regions inside the calorimeter

Assuming that all the terms in $\boldsymbol{A}$ and $\boldsymbol{b}$ and the values of the temperatures $\boldsymbol{\theta}$ at the beginning of the measurement are known, $\boldsymbol{\theta}'$ can be obtained by solving equation (8). The vector $\boldsymbol{\delta}$ is calculated by using equation (10), where the Taylor expansion is conveniently truncated (see below). This allows the calculation of the temperatures $\boldsymbol{\theta}$ after the first interval h. By applying the same procedure to the following time intervals, the temperatures $\boldsymbol{\theta}$ are obtained as a function of time over the whole measurement.

As pointed out above, three pieces of information are needed regarding the initial conditions of the measurement (*i.e.* the three temperatures θ_t, θ_h, and θ_s). In this calculation procedure the problem of chosing the boundary conditions is solved as follows: a guessed value, θ_0, is assigned to the initial temperature of the solution and, assuming that $\theta_t' = \theta_h' = \theta_s'$, the values of the other two initial temperatures, θ_t and θ_h, are obtained. The values of some quantities in $\boldsymbol{A}$ and $\boldsymbol{b}$, such as W_t, W_h, and θ_b, are known; C_t, C_h, K_{ts}, and K_{hs} were obtained from separate calibration experiments. Guessed values are attributed to the remaining quantities, which are refined in the calculation procedure.

The quantities C_s, K_s, and W_{tit} change during the addition of titrant according to equations (11)—(13). As

$$C_s = C_0 + \alpha_c v_{tit} \tag{11}$$

$$K_s = K_0 + \alpha_k v_{tit} \tag{12}$$

$$W_{tit} = c_{tit} R(\theta_b - \theta_s) \tag{13}$$

described above, their mean values in the interval h are used. Also W_r, the thermal power contribution due to the reaction, is a non-constant term, whose mean value in the step h is given by equation (14), where Δn_j is the amount of

$$W_r = -\Sigma(\Delta n_j/h)\Delta H_j^{\ominus} \tag{14}$$

the j-th species formed in the interval h and $\Delta H_j^{\ominus}$ is the corresponding heat of formation.

Tentative calculations have shown that the right compromise between speed and precision of calculation is achieved when h is *ca.* 5 s. The infinite Taylor expansion is truncated at the term giving a contribution less than 10^{-6} K.

The analysis of the data obtained from continuous-titration experiments was performed in two steps. First, measurements were examined one at a time, using the FORTRAN program TITCA. This calculates the thermistor temperature as a function of time using the method of numerical integration described above. The data points referring to the titration period are not taken into account. Gauss–Newton least-squares refinement of the parameters, such as W_{st}, α_c, C_0, K_s, and θ_0, which are peculiar to each measurement, is performed. This allows us to obtain the best agreement between observed and calculated values of the thermistor temperature for all measurement steps except that of titrant addition. When convergence is attained, a data file is constructed which contains the following: all the data points of the titration period; the values of all quantities needed for the solution of equation (8); the temperatures calculated at the beginning of this period; the amounts of reactant used; the initial volume in the vessel; the concentration of the titrant solution; the standard deviations of the parameters refined by TITCA and their correlation coefficients.

The resulting data, pertaining to one or more measurements on the same chemical system, were then treated by the FORTRAN program CALTC. Further input data are the formation constants of the species involved in the reaction and guessed values of the corresponding enthalpies of formation, $\Delta H_j^{\ominus}$. The amounts of the different species present at equilibrium in the reaction period are calculated. The mean value of the thermal power generated by the reaction in the time interval h is given by equation (14).

By the method of numerical integration outlined above one obtains the values of the thermistor temperatures for the period of titrant addition. The best $\Delta H^{\ominus}$ values are obtained by Gauss–Newton least-squares refinement, together with the standard deviations of the parameters and their correlation coefficients. The calculation of the standard deviations of $\Delta H^{\ominus}$ takes into account the estimated errors and correlation terms of parameters refined by the program TITCA and of formation constants given, using the rules of error propagation.

All calculations were performed using a SEL 32/77 computer (524 kbytes of core memory). Details of the programs TRANS, TITCA, and CALTC and input instructions are available from the authors.

RESULTS AND DISCUSSION

The heat of neutralization of hydrochloric acid and sodium hydroxide has been determined using 60 data points from two experiments of continuous titration. The value obtained, $\Delta H^{\ominus} = -55.85 \pm 0.08$ kJ mol^{-1}, is in excellent agreement with previous calorimetric determinations.[9]

The enthalpy of protonation of $NH_2C(CH_2OH)_3(aq)$ (80 data points, four measurements) is found to be $\Delta H^{\ominus} = -47.39 \pm 0.06$ kJ mol^{-1}. This reaction has been investigated by several workers [10] and the calorimetric $\Delta H^{\ominus}$ values determined at 298 K range from -47.5 to -45.7 kJ mol^{-1}. Our value is in close agreement with most literature values (*e.g.* -47.49,[11] -47.45,[9] -47.43,[12] and -47.36 kJ mol^{-1} [13]).

The results obtained are considered to be very satisfactory. They show clearly that, using this procedure, calorimetric equipment with reasonably quick responses can be used to perform accurate experiments of continuous-titration calorimetry. However, the two chemical calibrations carried out to test the accuracy and the precision of both apparatus and method are based upon single-step complete reactions, which generate constant thermal power.

In order to evaluate the performance of the whole method for multi-step reactions, the protonation of phosphate in 0.15 mol dm^{-3} NaCl at 298 K has been studied. The basicity constants of phosphate and the ionic product of water and its heat of ionization under these conditions have been determined. Table 3 shows the thermodynamic functions obtained. The standard deviations reported have been calculated by the procedure described previously.[5]

In processing the potentiometric data with the program MINIQUAD, the dimeric hydrogen-bonded species $H_5(PO_4)_2^-$, $H_4(PO_4)_2^{2-}$, and $H_3(PO_4)_2^{3-}$ considered by Childs [14] have also been taken into account. The introduction of such species did not produce a significant improvement of the fit. Since the concentrations of these species would be negligible under the experimental conditions used in this work they have been ignored.

The enthalpy of ionization of water in 0.15 mol dm^{-3} NaCl is higher than the value obtained without the supporting electrolyte. The effect of the ionic strength on the enthalpy of ionization of water in NaCl solutions has been investigated previously by e.m.f. measurements.[15] By applying correction terms for the present ionic strength, a value of $\Delta H^\ominus = -56.24$ kJ mol^{-1} is obtained, in good agreement with our value.

TABLE 3

Thermodynamic functions for the protonation of phosphate ion and for the ionization of water at 298 K in 0.15 mol dm^{-3} NaCl *

Reaction	log K	$\Delta H^\ominus$/ kJ mol^{-1}	$\Delta S^\ominus$/J K^{-1} mol^{-1}
$PO_4^{3-} + H^+ \longrightarrow HPO_4^{2-}$	11.545(5)	−18.6(2)	158.7(6)
$HPO_4^{2-} + H^+ \longrightarrow H_2PO_4^-$	6.638(3)	−4.70(5)	111.3(2)
$H_2PO_4^- + H^+ \longrightarrow H_3PO_4$	1.843(3)	8.6(7)	64(2)
$H_2O \longrightarrow H^+ + OH^-$	−13.748(1)	56.49(5)	73.69(2)

* Values in parentheses are standard deviations in the last significant figure.

A large number of values for the basicity constants and for the heats of protonation of phosphate have been reported in the literature under different conditions of temperature and ionic medium.[16] Unfortunately, no previous study has been carried out in 0.15 mol dm^{-3} NaCl at 298 K, and thus comparison with the data reported here is difficult. The values reported in the literature lie within the following ranges: log K_1 11.1—12.37, log K_{12} 6.1—7.22, log K_{13} 1.68—2.36; $-\Delta H_1^\ominus$ 10.8—21.8, $-\Delta H_{12}^\ominus$ 2.5—5.0, $\Delta H_{13}^\ominus$ 7.7—8.7 kJ mol^{-1}. As can be seen from Table 3, the values obtained in this work are also within these ranges.

Conclusions.—The results of this work show that the schematic description of the heat flow inside the calorimeter is a good approximation of the real behaviour. Furthermore, the mathematical treatment developed correctly reproduces the postulated model.

For the application of this method commercially available titration calorimeters can be used, only small instrumental changes being required. However, the calorimetric data must be of high accuracy. The use of a digital controlling device, allowing full automation of the measurements, makes the continuous-titration experiments simple and rapid.

APPENDIX

θ_s, θ_t, θ_h, and θ_b are the temperatures (in K) of the solutions in the vessel, thermistor, heater, and thermostat bath, respectively, as shown in the Figure. Other symbols are defined as follows:

θ_t' = derivative (in K s^{-1}) of thermistor temperature with respect to time
θ_h' = derivative (in K s^{-1}) of heater temperature with respect to time
θ_s' = derivative (in K s^{-1}) of solution temperature with respect to time
K_{ts} = thermal leakage constant (in J K^{-1} s^{-1}) between the thermistor and solution
K_{hs} = thermal leakage constant (in J K^{-1} s^{-1}) between the heat and solution
K_s = thermal leakage constant (in J K^{-1} s^{-1}) between the solution and thermostat bath
C_t = heat capacity (in J K^{-1}) of the thermistor
C_h = heat capacity (in J K^{-1}) of the heater
C_s = heat capacity (in J K^{-1}) of the solution
W_t = power (in J s^{-1}) generated in the thermistor by the Joule effect
W_h = power (in J s^{-1}) generated in the heater by the Joule effect
W_s = power (in J s^{-1}) generated in the solution as the resultant of several terms ($W_s = W_{st} + W_r + W_{dil} + W_{tit}$)
W_{st} = power contribution (in J s^{-1}) due to stirring
W_r = power contribution (in J s^{-1}) due to chemical reaction
W_{dil} = power contribution (in J s^{-1}) due to dilution of titrant
W_{tit} = power contribution (in J s^{-1}) due to the temperature difference between the titrant and solution
C_0 = heat capacity (in J K^{-1}) of the solution before addition of titrant
K_0 = thermal leakage constant (in J K^{-1} s^{-1}) between the solution and thermostat bath before addition of titrant
α_c = change of heat capacity (in J K^{-1} cm^{-3}) of the solution per unit volume of titrant added
α_k = change of thermal leakage constant (in J K^{-1} s^{-1} cm^{-3}) between the solution and thermostat bath per unit volume of titrant added
v_{tit} = volume (in cm^3) of titrant added
θ_0 = initial value (in K) of the temperature of the solution
R = titrant delivery rate (in cm^3 s^{-1})
c_{tit} = heat capacity (in J K^{-1} cm^{-3}) of titrant per unit volume
$\boldsymbol{\theta}$ = column vector $[\theta_t, \theta_h, \theta_s]$

$$\boldsymbol{A} = \text{square matrix} \begin{vmatrix} -K_{ts}/C_t & 0 & K_{ts}/C_t \\ 0 & -K_{ts}/C_h & K_{hs}/C_h \\ K_{ts}/C_s & K_{hs}/C_h & -(K_{ts} + K_{hs} + K_s)/C_s \end{vmatrix}$$

$\boldsymbol{b}$ = column vector $[W_t/C_t, W_h/C_h, (W_s + K_s\theta_b)/C_s]$

We thank Mr. S. Vasacci for his assistance in assembling the electronic device used to control the calorimetric experiments.

[0/1514 *Received, 3rd October,* 1980]

REFERENCES

[1] H. J. V. Tyrrel and A. E. Beezer, 'Thermometric Titrimetry,' Chapman and Hall, London, 1968; L. S. Bark and S. M. Bark, 'Thermometric Titrimetry,' Pergamon, Oxford, 1969; D. J. Eatough, J. J. Christensen, and R. M. Izatt, 'Experiments in Thermometric Titrimetry and Titration Calorimetry,' Brigham Young University Press, Provo, 1974; G. A. Vaughan, 'Thermometric and Enthalpimetric Titrimetry,' Van Nostrand Reinhold, New York, 1973; J. Barthel, 'Thermometric Titrations,' Wiley–Interscience, New York, 1975 and refs. therein.

[2] J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, *J. Phys. Chem.*, 1966, **70**, 2003.

[3] A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1980, 519.

[4] M. Micheloni, P. Paoletti, and A. Vacca, *J. Chem. Soc., Perkin Trans. 2*, 1978, 945; R. Barbucci, V. Barone, M. Micheloni, and L. Rusconi, *J. Phys. Chem.*, in the press.

[5] M. Micheloni, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1977, **25**, 41.

[6] G. Gran, *Analyst* (*London*), 1952, **77**, 661; F. J. C. Rossotti and H. Rossotti, *J. Chem. Educ.*, 1965, **42**, 365.

[7] R. G. Bates, 'Determination of pH. Theory and Practice,' Wiley, New York, 1973, pp. 263—268.

[8] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

[9] I. Grenthe, H. Ots, and O. Ginstrup, *Acta Chem. Scand.*, 1970, **24**, 1067 and refs. therein.

[10] J. J. Christensen, L. D. Hansen, and R. M. Izatt, 'Handbook of Proton Ionization Heats and Related Thermodynamic Quantities,' Wiley, New York, 1976, p. 159.

[11] G. Öjelund and I. Wadsö, *Acta Chem. Scand.*, 1968, **22**, 2961.

[12] H. Ots, *Acta Chem. Scand.*, 1972, **26**, 3810.

[13] L. D. Hansen and E. A. Lewis, *J. Chem. Thermodyn.*, 1971, **3**, 35.

[14] C. W. Childs, *J. Phys. Chem.*, 1969, **73**, 2956.

[15] H. S. Harned and G. E. Mannweiler, *J. Am. Chem. Soc.*, 1935, **57**, 1873.

[16] L. G. Sillén and A. E. Martell, 'Stability Constants of Metal–Ion Complexes,' *Special Publ.*, The Chemical Society, London, 1971, no. 25; J. J. Christensen and R. M. Izatt, 'Handbook of Metal-Ligand Heats and Related Thermodynamic Quantities,' Marcel Dekker, New York, 1970.