AUG 8 1967

COO-299-2
CONF-661128--1

CESTI PRICES

(December 19, 1966)

HQ \$ 3.00, MN .65

Computer Evaluation of "Entropy" Titration

Data: Determination of β_i^0 , ΔH_i^0 and ΔS_i^0 Values for the Silver (I) Pyridine System^{la}

By: James J. Christensen^{lb}, Delbert Eatough^{lc}, Reed M. Izatt^{lb}, and Richard L. Snow

Departments of Chemical Engineering and Chemistry

Brigham Young University, Provo, Utah

1. (a) Supported by United States Atomic Energy Commission Contract AT(04-3)-299 and National Institutes of Health Grant RG 9430-06.
- (b) To whom inquiries should be directed.
- (c) National Defense Education Act Predoctoral Fellow 1964-67.

Abstract

$\log K_i$, ΔH_i^0 and ΔS_i^0 values have been determined for the stepwise formation of AgPy_2^+ (Py = pyridine) from Ag^+ and Py using a thermometric titration procedure. The results agree well with previously determined values and demonstrate that titration calorimetry can be used to determine $\log K$, ΔH^0 , and ΔS^0 values for metal-ligand systems. Four iterative methods of data analysis are compared and discussed.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Introduction

The shape of a thermometric titration curve is a function of the equilibrium constants and enthalpy changes for all the reactions involved in the titration. For example, in the simple reaction $A + B = AB$ where A is titrated with B, the resulting thermometric titration curve will be sufficiently non-linear if $\log K$ for the reaction is less than approximately 4 to allow calculation of $\log K$, ΔH and ΔS values for the reaction. This procedure, called the "entropy titration" method has been successfully applied to many acid-base systems involving single protonation reactions.²⁻⁴

-
- (2) J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, J. Phys. Chem., 70, 2003 (1966).
 - (3) R. M. Izatt, J. H. Rytting, L. D. Hansen, and J. J. Christensen, J. Am. Chem. Soc., 88, 2641 (1966).
 - (4) J. J. Christensen, D. P. Wrathall, R. M. Izatt, and D. O. Tolman, J. Phys. Chem. submitted for publication.
-

However, in general the equations involved in the calculations cannot be solved exactly for the desired thermodynamic values and an iterative process must be used to analyze the data. Although iterative calculation methods have been used in the past for the analysis of potentiometric and calorimetric data,^{5,6} an extensive study of the problems involved in such calculations as

-
- (5) L. G. Sillen, Acta. Chem. Scand., 16, 159 (1962)
 - (6) P. Paoletti, A. Vacca, and D. Arenare, J. Phys. Chem., 70, 193 (1966).
-

applied to entropy titration data has not been reported. This study was therefore undertaken (1) to compare several different iterative methods for the analysis of entropy titration data, and (2) to investigate the applicability

of the entropy titration procedure to a metal ion-ligand system involving simultaneous equilibria.

The Ag(I)-pyridine (Py) system was chosen for this study because (1) the equilibrium constants are expected to be independent of ionic strength, μ , (2) competing reactions are negligible, (3) the system is more complex than those previously studied by us in that simultaneous equilibria occur, providing a better test of the various methods of data analysis used, and (4) the system has been previously investigated and the results of this study could be compared with reliable thermodynamic values in the literature. Formation constants for the Ag^+ -Py system have been determined from potentiometric^{7,8} solubility⁹, and calorimetric^{6,10} data.

(7) W. C. Vosburgh, and S. A. Cogswell, J. Am. Chem. Soc., **65**, 2412 (1943).

(8) R. J. Bruehlman, and F. H. Verhoek, J. Am. Chem. Soc., **70** 1401 (1948).

(9) R. K. Murmann and F. Basolo, J. Am. Chem. Soc., **77**, 3484 (1955).

(10) F. Becker, J. Barthel, N. G. Schmahl and H. M. Luscov, Z. Physik. Chem., **37**, 52 (1963).

Corresponding ΔH° values have been determined calorimetrically.^{6,10}

Experimental

Materials - Reagent Grade AgNO_3 (Baker 'Analyzed') and NaNO_3 (Baker 'Analyzed') were dried at 100° for four hours and used as a primary standard in the preparation of their solutions. Reagent grade Py (Eastman 'white label') was purified by distillation under reduced pressure over lithium aluminum hydride and stored under a N_2 atmosphere.

Thermometric Titrations - The calorimetric equipment and operational procedure have been described^{11,12}. Titrations were made using both Py and

(11) J. J. Christensen and R. M. Izatt, J. Phys. Chem. **66**, 1030 (1962).

(12) J. J. Christensen, R. M. Izatt and L. D. Hansen, Rev. Sci., Instr., **36** 779 (1965).

AgNO₃ as titrant. The μ values of the runs were varied from 0.02 to 0.005. Heat of dilution data¹³ were determined as a function of μ

(13) D. Eatough, Ph. D. Dissertation, Brigham Young University, 1967.

for both the Py and AgNO₃ titrants by titration of each into H₂O and also into NaNO₃ solutions. The heat of dilution data were fitted by the method of least squares to a power series in $\sqrt{\mu}$, resulting in values of $(-300 + 45.5\sqrt{\mu})$ and $(507 - 482\sqrt{\mu} + 609\mu)$ cal/mole for the heats of dilution of 0.9886 F Py and 0.9858 F AgNO₃ solutions (to final μ values 0.0005 to 0.03), respectively.

Calculations - The thermodynamic values associated with the reaction of Ag⁺ and Py are defined by equations (1) and (2).

The heat, Q_c , liberated during the reaction of Ag⁺ with Py can be calculated from the following expression,

$$Q_c = ([\text{AgPy}^+] \Delta H_1^{\circ} + [\text{AgPy}_2^+] \Delta H_2^{\circ}) V_t \quad (3)$$

where V_t is the volume of solution in the calorimeter at time t_1 . Q_c can be expressed as a function of β_1 , β_2 , ΔH_1° , ΔH_2° , and [Py] by combining equation (3), $\text{Ag}^+_{\text{total}} = [\text{Ag}^+] + [\text{AgPy}^+] + [\text{AgPy}_2^+]$, and the expressions for β_1 (eq. (1)) and β_2 (eq. (2)) to give equation (4).

$$Q_c = [\text{Ag}^+_{\text{total}}] V_t ([\text{Py}] \Delta H_1^{\circ} + [\text{Py}]^2 \Delta H_2^{\circ}) / (1 + \beta_1 [\text{Py}] + \beta_2 [\text{Py}]^2)$$

The best values of β_1 , β_2 , ΔH_1° and ΔH_2° for a given thermometric titration curve can be obtained by comparing Q_c values calculated from equation (4) with the corresponding experimentally measured Q_e (experimentally measured heat corrected for H₂O formation, HPy⁺ formation, titrant dilution and calorimeter heat leaks) value. This comparison is carried out in the following manner. Values of β_1 and β_2 are assumed. These β_1 and β_2 values are used

to calculate [Py] as a function of titrant added to the calorimeter. A least squares analysis of equation (4) where Q_c is taken to be equal to Q_e is used to calculate the best values of ΔH_1^0 and ΔH_2^0 for the β_1 and β_2 values chosen. An indication of how well the β_1 and ΔH_1^0 values describe the thermometric titration curve is obtained by calculation of the error square sum, $U(\beta_1, \beta_2)$,

$$U(\beta_1, \beta_2) = \sum_{i=1}^N (Q_{e_i} - Q_{c_i})^2 \quad (5)$$

where the sum is over all data points. New values of β_1 and β_2 are chosen and the procedure is repeated. This iterative process is repeated with different values of β_1 and β_2 until the minimum error square sum is obtained. The problem of calculating the β_i and ΔH_i^0 values for the interaction of Ag^+ with Py then reduces to finding the minimum value of U , U_{min} . In the past, three different methods have been used to find U_{min} .

(1) Schematic map of $U(\beta_1, \beta_2)$. β_i values may be varied over a large domain and U_{min} found by trial and error. This method has been successfully used in the analysis of data for studies involving single equilibria.⁴ However, for systems involving more than one constant, the computer time required for complete data analysis may be extremely large.

(2) "Pit Mapping." A functional relationship may be assumed for $U(\beta_1, \beta_2)$ and U_{min} found by direct differentiation. The "pit mapping" method described by Sillen^{5,6} assumes U to be quadratic and therefore of the form

$$U = C_{00} + 2 \sum_{r=1}^n C_{0r} \Delta \beta_r + \sum_{r=1}^n \sum_{s=1}^n C_{rs} \Delta \beta_r \Delta \beta_s \quad (6)$$

where $\Delta \beta_i$ is the deviation of β_i from the initial approximation, β_i^0 , and the C_{ij} terms are the coefficients in the expression. For a system of n reactions, $1/2 (n+1) (n+2)$ sets of $\Delta \beta_i$ values are required to evaluate the parameters in equation (6). U_{min} can then be evaluated, yielding a new approximation for the β_i values. The cycle is repeated until the cal-

culations are self-consistent.

(3) Simultaneous solution of equations. Values for β_i and ΔH_1^0 can be calculated directly if four equations of the form of equation (4) are solved simultaneously for four t_i values. Corrections are made for activity coefficients and $[Py]$ until the results are self-consistent. It is then assumed that the average of the β_i values calculated from all possible combinations of data points corresponds to those giving U_{min} . There is no way in this method to check this assumption. Entropy titration data for proton dissociation from HSO_4^- and HPO_4^{2-} have been analyzed by this method.²

The major drawback with the iterative methods used in the past is that some assumptions must be made about the behavior of the function $U(\beta_1, \beta_2)$. A computer program which does not contain such assumptions has been developed by Davidon¹⁴. This program uses a numerical variable metric method of

(14) W. C. Davidon, "Variable Metric Method for Minimization" Argonne National Laboratory Report (ANL 5990 Rev. 2) (1966).

minimization (VMM) to find relative minima for any well behaved function, and can be directly adapted to the problem of least-squares fitting of experimental data. The program uses an iterative gradient method in which calculated values of $\partial U / \partial \beta_i$ and approximated values of $\partial^2 U / \partial \beta_i \partial \beta_j$ for various values of β_i are used to locate those values of β_i for which $\partial U / \partial \beta_i$ is zero and for which the Hessian matrix,

$$\left\| \frac{\partial^2 U}{\partial \beta_i \partial \beta_j} \right\|$$

is positive definite.

After a relative minimum has been located the values of β_i may be randomly varied and a new relative minimum located. Thus, it is possible to calculate a U_{min} value and to explore a given region around this value to determine if it is the only relative minimum in that region.

Each of the above mentioned methods of data analysis ((1), (2), (3), and the VMM method) are used in the calculation of β_i and ΔH_i^0 values from the thermometric titration data for the interaction of Ag^+ with Py. Due to the complexity of the functions involved it was found more convenient in the VMM method to approximate the derivatives by assuming

$$\frac{\partial U}{\partial \beta_i} = \frac{\Delta U}{\Delta \beta_i}$$

where $\Delta U = U_2 - U_1$ and $\Delta \beta_i = \beta_i - (1-k) \beta_i = k\beta_i$

Calculations indicated that for the functions involved in these studies, the $\partial U / \partial \beta_i$ values were essentially constant for $k \leq 10^{-2}$.

Corrections for pyridine hydrolysis were made using the pK value, 5.175⁹, and ΔH^0 value -4.90 kcal/mole.¹⁶ The ion product, 1.008×10^{-14} , K_w , and heat of ionization, -13.34 kcal/mole, of water were taken from Harned and Owen¹⁷ and Hale, *et. al.*,¹⁸ respectively. A Debye Hückel ex-

(16) Unpublished data this laboratory.

(17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Edition, Reinhold Pub. Corp., New York, 1958.

(18) J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, **67**, 2605 (1963).

pression of the form

$$\log \gamma = \frac{AZ^2\sqrt{\mu}}{1 + Ba^0\sqrt{\mu}}$$

where the various terms have their usual significance¹⁷, was used to convert the thermodynamic K_w value to a concentration quantity. The value $a^0 = 4\text{\AA}$ was used in the calculations. Calculations were aided by the use of an IBM 7040 Computer.

Results

The thermometric titration data are given in Table 1.

Table 1

Thermometric titration data for the interaction of Ag^+ with Py^{a} .

T^{b}	Run 1 -Qe	Run 2 -Qe	Run 3 -Qe	Run 4 -Qe	Run 5 -Qe	Run 6 -Qe	Run 7 -Qe	Run 8 -Qe	Run 9 -Qe	Run 10 -Qe
1	0.42	0.42	0.39	0.32	0.33	0.35	0.24	0.25	0.27	0.26
2	0.85	0.85	0.85	0.67	0.67	0.69	0.52	0.53	0.55	0.54
3	1.34	1.34	1.32	1.03	1.04	1.05	0.81	0.82	0.84	0.83
4	1.77	1.77	1.74	1.42	1.42	1.43	1.09	1.10	1.12	1.13
5	2.27	2.27	2.21	1.77	1.80	1.80	1.39	1.40	1.41	1.42
6	2.77	2.74	2.71	2.17	2.16	2.18	1.68	1.69	1.70	1.72
7	3.24	3.20	3.18	2.56	2.53	2.54	1.96	1.96	1.98	2.00
8	3.74	3.71	3.68	2.92	2.90	2.93	2.23	2.23	2.25	2.27
9	4.21	4.21	4.15	3.29	3.29	3.29	2.50	2.50	2.50	2.53
10	4.72	4.71	4.69	3.65	3.65	3.66	2.74	2.75	2.75	2.77
11	5.19	5.19	5.17	4.05	4.01	4.02	2.99	2.98	2.99	3.01
12	5.70	5.67	5.68	4.38	4.36	4.37	3.21	3.20	3.21	3.24
13	6.17	6.14	6.15	4.71	4.67	4.68	3.42	3.41	3.42	3.44
14	6.61	6.62	6.63	5.01	4.99	5.00	3.61	3.61	3.62	3.65
15	7.09	7.10	7.07	5.31	5.29	5.31	3.79	3.79	3.80	3.83
16	7.57	7.58	7.55	5.61	5.60	5.60	3.97	3.96	3.97	4.00
17	8.05	8.06	8.03	5.91	5.88	5.88	4.12	4.12	4.12	4.16
18	8.54	8.51	8.52	6.21	6.16	6.16	4.26	4.25	4.26	4.36
19	8.99	9.00	8.93	6.48	6.41	6.39	4.39	4.38	4.38	4.43
20	9.44	9.45	9.42	6.71	6.66	6.63	4.51	4.51	4.51	4.56
21	9.89	9.87	9.83	6.91	6.89	6.87	4.63	4.61	4.61	4.67
22	10.34	10.33	10.28	7.15	7.09	7.06	4.73	4.72	4.72	4.77
23	10.70	10.74	10.74	7.35	7.30	7.26	4.83	4.82	4.81	4.87
24	11.18	11.13	11.16	7.58	7.49	7.46	4.93	4.90	4.91	4.97
25	11.57	11.55	11.58	7.71	7.69	7.63				
26	11.88	11.91	11.89	7.88	7.84	7.79				
27	12.27	12.26	12.28	8.05	8.01	7.95				
28	12.63	12.65	12.62	8.21	8.16	8.09				
29	12.98	13.01	13.02	8.31	8.29	8.23				
30	13.37	13.37	13.37	8.44	8.42	8.35				
31	13.73	13.72	13.72	8.58	8.54	8.47				
32	14.09	14.05	14.08	8.68	8.66	8.58				
33	14.37	14.37	14.40	8.77	8.76	8.68				
34	14.70	14.66	14.69	8.87	8.85	8.78				
35	14.99	14.96	14.97	8.97	8.94	8.86				
36	15.28	15.28	15.30	9.07	9.10	8.95				
37	15.53	15.54	15.55	9.14	9.09	9.03				
38	15.79	15.80	15.86	9.20	9.15	9.09				
39	16.04	16.06	16.06	9.26	9.22	9.15				
40	16.26	16.28	16.27	9.33	9.29	9.21				
41	16.56	16.50	16.53	9.36	9.35	9.27				
42	16.79	16.73	16.74	9.42	9.41	9.32				
43	16.97	16.95	16.97	9.49	9.46	9.37				
44	17.15	17.14	17.15	9.56	9.51	9.42				
45	17.34	17.33	17.33	9.62	9.57	9.47				
46	17.53	17.52	17.52	9.65	9.61	9.52				
47	17.72	17.72	17.71	9.72	9.65	9.57				

Table I (con't)

	Run 11	Run 12	Run 13	Run 14	Run 15	Run 16	Run 17	Run 18
	-Qe	-Qe	-Qe	-Qe	-Qe	-Qe	-Qe	-Qe
1	0.48	0.40	0.41	0.39	0.42	0.36	1.80	1.27
2	0.98	1.00	0.97	0.93	0.99	0.89	3.26	2.85
3	1.54	1.58	1.49	1.48	1.52	1.42	4.88	4.40
4	2.14	2.17	2.02	2.06	2.03	1.95	6.41	5.83
5	2.73	2.77	2.60	2.64	2.60	2.50	8.06	7.20
6	3.35	3.40	3.21	3.24	3.18	3.07	9.55	8.48
7	3.96	4.05	3.80	3.83	3.77	3.66	11.12	9.66
8	4.62	4.70	4.42	4.45	4.33	4.22	12.60	10.73
9	5.24	5.33	5.05	5.13	4.88	4.80	13.97	11.67
10	5.58	5.95	5.68	5.66	5.41	5.34	15.30	12.46
11	6.45	6.55	6.31	6.30	5.92	5.88	16.58	13.23
12	7.06	7.11	6.93	6.91	6.45	6.41	17.78	13.83
13	7.66	7.71	7.56	7.52	6.98	6.92	18.82	14.32
14	8.25	8.32	8.14	8.12	7.46	7.43	19.85	14.79
15	8.82	8.90	8.71	8.68	7.95	7.89	20.74	15.22
16	9.38	9.48	9.26	9.26	8.40	8.36	21.50	15.57
17	9.94	10.04	9.81	9.80	8.84	8.81	22.21	15.86
18	10.48	10.61	10.34	10.35	9.26	9.24	22.86	16.12
19	10.98	11.12	10.89	10.87	9.69	9.66	23.42	16.36
20	11.49	11.66	11.44	11.45	10.10	10.04	23.89	16.58
21	12.05	12.17	11.98	11.89	10.38	10.40	24.32	16.76
22	12.53	12.63	12.47	12.36	10.77	10.74	24.69	16.95
23	12.99	13.09	12.93	12.79	11.09	11.07	25.03	17.09
24	13.42	13.53	13.32	13.25	11.44	11.41	25.34	17.21
25	13.82	13.95	13.72	13.71	11.70	11.66	25.61	17.33
26	14.21	14.37	14.10	14.14	11.95	11.91	25.85	17.45
27	14.62	14.76	14.48	14.54	12.17	12.16	26.05	17.57
28	14.98	15.13	14.83	14.87	12.38	12.37	26.24	17.69
29	15.22	15.47	15.20	15.18	12.59	12.58	26.42	17.81
30	15.59	15.79	15.51	15.47	12.76	12.78	26.56	17.93
31	15.90	16.09	15.82	15.75	12.95	12.96	26.70	18.03
32	16.23	16.37	16.06	16.01	13.12	13.14	26.83	18.07
33	16.52	16.63	16.30	16.27	13.26	13.37	26.95	18.19
34	16.77	16.88	16.56	16.52	13.41	13.44	27.04	18.26
35	17.06	17.15	16.80	16.79	13.53	13.59	27.14	18.31
36	17.19	17.36	17.00	17.01	13.65	13.69	27.23	18.35

a Qe (cal.) values corrected for the heat of dilution of the titrant and calorimeter heat leaks. $T = 25.0^{\circ}$. The I value refers to the column heading "Mmole of Titrant at Point I" in footnote b (i.e. for Run 4, Point 10, mmole of titrant = $0.1267 \times 10^{-3} - 0.000 = 1.267$)

b Run	Titrant	Calorimeter Solution	Mmole of Titrant at Point I	Ml. of Solution Initially in Cal.
1-3	0.9886 F Py	0.01996 F AgNO ₃	0.1267xI - 0.000	100.00
4-6	0.9886 F Py	0.01000 F AgNO ₃	0.1267xI - 0.000	100.00
7-10	0.9886 F Py	0.00599 F AgNO ₃	0.1267xI - 0.000	100.00
11	0.9886 F Py	0.01967 F AgNO ₃	0.1686xI - 0.053	99.95
12	0.9886 F Py	0.01967 F AgNO ₃	0.1686xI - 0.046	99.95
13	0.9886 F Py	0.01967 F AgNO ₃	0.1686xI - 0.054	99.95
14	0.9886 F Py	0.01967 F AgNO ₃	0.1686xI - 0.062	99.95
15	0.9886 F Py	0.01472 F AgNO ₃	0.1686xI - 0.026	99.95
16	0.9886 F Py	0.01472 F AgNO ₃	0.1686xI - 0.046	99.95
17	0.9858 F AgNO ₃	0.05922 F Py	0.1682xI - 0.033	99.95
18	0.9858 F AgNO ₃	0.03949 F Py	0.1682xI - 0.040	99.95

The thermodynamic $\log \beta_i$, ΔH_i^0 and ΔS_i^0 values determined in this study together with literature values for the interaction of Ag^+ with Py are summarized in Table II. The thermodynamic values reported in Table II are the average of those for 18 runs and the uncertainties are expressed as standard deviations between runs.

Table II

$\log \beta_i$, ΔH_i^0 and ΔS_i^0 ($i = 1, 2$) values valid at 25° for the interaction of Ag^+ with Py^a.

<u>$\log \beta$</u>	<u>ΔH^0 (kcal/mole)</u>	<u>ΔS^0 (cal/mole-deg)</u>
	$\text{Ag}^+ + \text{Py} = \text{AgPy}^+$	
2.04 ± 0.06^b	-4.6 ± 0.2	-6.2 ± 0.8
2.05 ± 0.05^c	-4.6 ± 0.2	-6.0 ± 0.9
2.05 ± 0.03^d	-4.5 ± 0.2	-5.8 ± 0.8
$(2.00)^e$	(-4.83)	(-7.0)
$(2.24)^f$	(-4.77)	(-5.2)
$(2.04)^g$		
$(2.00)^h$		
	$\text{Ag}^+ + 2\text{Py} = \text{AgPy}_2^+$	
4.09 ± 0.05^b	-11.25 ± 0.09	-19.0 ± 0.4
4.10 ± 0.07^c	-11.24 ± 0.12	-18.9 ± 0.4
4.11 ± 0.05^d	-11.21 ± 0.12	-18.8 ± 0.4
$(4.11)^e$	(-11.43)	(-19.2)
$(4.21)^f$	(-11.53)	(-19.0)
$(4.22)^g$		
$(4.11)^h$		

^aThe uncertainties are expressed as standard deviations. ^bThis study, $\mu=0$. determined by the entropy titration procedure using the VMM method with random steps to analyze the data. ^cThis study, $\mu=0$. Same as ^b except random steps were not taken. Initial values used were $\log \beta_1 = 2.05$ and $\log \beta_2 = 4.15$. ^dThis study, $\mu=0$. Determined by the entropy titration procedure using the "pit mapping" method to analyze the data. Initial values used were $\log \beta_1 = 2.05$ and $\log \beta_2 = 4.15$.

$\Delta_{\text{Ref. 6}}$, Determined by conventional calorimetry using the "pit mapping" method to analyze the data. Valid at $\mu = 0.5$. $\Delta_{\text{Ref. 10}}$, Determined by incremental calorimetry using an initial slope method to analyze the data. Valid at $\mu = 0.2$. $\Delta_{\text{Ref. 7}}$, Determined by potentiometry. Valid at $\mu = 0.6$. $\Delta_{\text{Ref. 9}}$, Determined by solubility measurements. Valid at $\mu = 0$.

DISCUSSION

The $\log \beta_i$ values determined in this study are generally in good agreement with those reported previously, indicating that the entropy titration method can be applied to the determination of the thermodynamic quantities for metal-ligand interaction involving simultaneous equilibria. The ΔH° values reported in Table II are slightly less negative than those reported previously. This difference could result from the large concentration of NO_3^- present in the earlier studies. The presence of NO_3^- would be expected to change the nature of the hydrated Ag^+ with a resulting difference in the ΔH° value.

The shape of a thermometric titration curve will often yield information concerning the nature of the reactions taking place. An example is seen in Fig. 1 where a thermometric titration curve and corresponding species distribution are given for the data in Run 4 of Table I. The S shape of the titration curve shows that AgPy_2^+ is formed in a step-wise manner when a solution containing Ag^+ is-titrated with Py. This S-shaped titration curve can only be explained if two species are formed in the calorimeter and the heat for the stepwise formation of AgPy_2^+ from AgPy^+ is more exothermic than the heat of formation of AgPy^+ from Ag^+ .

The standard deviation for ΔH_1° is large compared to that for ΔH_2° . This is not unexpected since $(\Delta H_2^\circ - \Delta H_1^\circ)$ is more negative than ΔH_1° and the $[\text{AgPy}^+]$ in the calorimeter is always small compared to $[\text{Ag}_{\text{total}}^+]$ making the contribution of AgPy^+ to the shape of the thermometric titration curve less than

the contribution of the AgPy_2^+ species.

The relative merits of the four methods of data analysis can be shown by comparison of the results obtained when each method is used to analyze the data in Run 4 of Table I.

(1) Schematic map of $U(\beta_1, \beta_2)$. The dependence of $U(\beta_1, \beta_2)$ on β_1 and β_2 was extensively studied by varying $\log \beta_1$ values from 1.90 to 2.25 and $\log \beta_2$ values from 3.95 to 4.30. These results are summarized in Fig. 2.

Two close lying minima were found for this run with $U_{\min}$, $\log \beta_1$ and $\log \beta_2$ values of 0.0136, 1.92, 4.06 and 0.0130, 1.99, 4.10, respectively. Since the second $U_{\min}$ value lies lower than the first, the β_i values corresponding to the minima are the "best" values.

(2) Pit Mapping." In several runs as many as four minima were found in the region close to $U_{\min}$. The existence of such pits complicates analysis by the pit mapping method. If the initial guess for the β_i values lies close to either point A or point C in Fig. 1, then the corresponding minimum is calculated. If the initial β_i values, however, lie close to point B then, since the pit mapping method locates extreme only, the value of U at the saddle point B is calculated for $U_{\min}$. The pit mapping method assumes U to be quadratic around the point $U_{\min}$, however, for initial guesses of β_i values which do not lie close to A, B or C, the shape of the pit is much more complicated. If initial β_i values were not close to one of the extreme (within 0.05 log unit), the calculations did not generally zero in on a $U_{\min}$ value.

(3) VMM Procedure. Using this procedure with random steps points A and C were both calculated as relative minima. Point B was not calculated since the Hessian matrix is not positive definite in this region. The VMM method of data analysis then has three main advantages over the "pit mapping" method described by Sillen. (a) Only relative minima are calculated as $U_{\min}$ values, saddle points are not calculated. (b) Extreme values other than the proper $U_{\min}$ value

may be located and eliminated. (c) For complex functions the region of convergence to a relative minima is much larger. The first two disadvantages of the "pit mapping" method can be partially eliminated by use of some type of random step program to assist in locating all minima and determining saddle point regions. The third disadvantage, however, is inherent in the assumptions used in the method and cannot be easily overcome. However, the "pit mapping" method has the advantage that it is easier to program and uses approximately 25% less computer time.

(4) Simultaneous solution of equations. All attempts to calculate $\log \beta_i$ and ΔH_1^0 values using this method were unsuccessful, presumably because of the importance of small errors in the solution of large numbers of independent equations.

The advantages and disadvantages of the four methods of data analysis are summarized in Table III.

Table III

Comparison of Methods of Data Analysis

<u>Method</u>	<u>Advantages</u>	<u>Disadvantages</u>
1. Schematic map of $U(\beta_1, \beta_2)$	The method is thorough and accurate	Computer time required is long. (approximately 1 hr./run).
2. "Pit Mapping"	Computer time is short. (approximately 1 min./run).	Locates saddle points as well as minima. Area of convergence is smaller than in the VMM method.
3. VMM	Only relative minima are located. Area of convergence is much larger than in the "pit mapping" method.	Requires approximately 25% more computer time than "pit mapping."
4. Simultaneous solution of equations	None	Apparently not applicable to systems involving more than one reaction.

Acknowledgements

The authors wish to express their appreciation to the Argonne National Laboratories, Argonne, Illinois for information on the variable metric minimization program,¹⁹ and to Mr. Glen Enke of the Brigham Young University Computer Research Center for a random number generating subroutine.

¹⁹Fortran IV copies of the basic metric minimization program are available through the Argonne National Laboratories, Argonne, Illinois. Two subroutines must be written to utilize this basic program, a FCN subroutine to calculate $U(\beta_1, \beta_2)$ and $\partial U / \partial \beta_i$ and a RANDM2 subroutine to control the random step routine. A Fortran II copy of the basic metric minimization program with accompanying RANDM2 subroutine is also available through Dr. Reed M. Izatt, Department of Chemistry, or Dr. James J. Christensen, Department of Chemical Engineering, Brigham Young University, Provo, Utah.

TITRATION of Ag^+ WITH PYRIDINE

Figure 1

Figure 2