Activity Coefficients of $Na_4Fe(CN)_6$ in Water and in $Na_4Fe(CN)_6(aq)$ + NaCl(aq) Solutions at 25°C

Leonard F. Silvester and Peter A. Rock[1]
Department of Chemistry, University of California, Davis, Calif. 95616

The mean ionic activity coefficients of $Na_4Fe(CN)_6(aq)$ at 25°C over the concentration range 0–0.10*m* in water and in NaCl(aq) solutions at a constant total ionic strength of 1.0 are reported. The results are obtained from electrochemical measurements on cells without liquid junction by use of Na^+-specific glass electrodes. Harned's rule is obeyed for $Na_4Fe(CN)_6(aq)$ in the presence of NaCl(aq) at a total ionic strength of 1.0. The Harned rule coefficient differs in sign and magnitude from that calculated from the Brönsted-Guggenheim β-parameters for the NaCl(aq) and $Na_4Fe(CN)_6(aq)$.

There have been a considerable number of investigations in recent years on the thermodynamic behavior of strong electrolytes in multicomponent electrolyte solutions (*1, 2*). These investigations have been confined to mixtures involving 1-1, 2-1, and 1-2 electrolytes. On the other hand, numerous equilibrium studies (*11*) involving multivalent, transition-metal complex ions have been carried out in solutions of constant total ionic strength, in which the ionic strength is maintained by various 1-1 supporting electrolytes.

Thermodynamic data (e.g., ΔG_f° values) for a species obtained from such studies cannot be combined with other data for the same species based on a conventional choice of standard states (i.e., in the absence of the supporting electrolyte) without first adjusting all data to the same (preferably the conventional) standard state. To do this requires activity coefficient data on the salt involving the complex ion in the presence of the supporting electrolyte.

If it can be established that Harned's rule holds in such systems and, in addition, that the Harned-rule coefficient can be calculated reliably from the Brönsted-Guggenheim β parameters, obtained from data on the individual salts in solution, then the problem of converting from one type of standard state to the other would be considerably simplified. For this reason, we have undertaken an electrochemical study of salts involving multivalent, transition-metal complex ions in the presence of 1-1 electrolytes, and our results are reported for the activity coefficients of $Na_4Fe(CN)_6(aq)$ at 25°C in the presence of NaCl(aq) at a total ionic strength of 1.000. We also have determined $\gamma_\pm$ at 25°C for $Na_4Fe(CN)_6(aq)$ from $I = 0$ to $I = 1$.

The measurements have been carried out on cells without liquid junction of the type

$$\mathrm{Pb(Hg)}|\mathrm{Pb_2Fe(CN)_6 \cdot 3H_2O(s)}|\mathrm{Na_4Fe(CN)_6(aq,}m_2\mathrm{),\ NaCl(aq,}m_3\mathrm{)}|\mathrm{Na\text{-}glass} \quad (1)$$

(2-phase 5 wt % Pb)

$$\mathrm{Na\text{-}glass}|\mathrm{NaCl(aq,}m_1\mathrm{)}|\mathrm{Hg_2Cl_2(s)}|\mathrm{Hg(l)} \quad (2)$$

where Na-glass represents a sodium ion-specific glass electrode. The problem of liquid-junction potentials has been avoided by the use of the same glass electrode in both cells 1 and 2 (*3*). The algebraic sum of the measured emf values for cells 1 and 2 is equal to the emf of the hypothetical double cell (*4, 6, 9*)

$$\mathrm{Pb(Hg)}|\mathrm{Pb_2Fe(CN)_6 \cdot 3H_2O(s)}|\mathrm{Na_4Fe(CN)_6(}m_2\mathrm{),\ NaCl(}m_3\mathrm{)}|\mathrm{Na\text{-}glass}|\mathrm{NaCl(}m_1\mathrm{)}|\mathrm{Hg_2Cl_2(s)}|\mathrm{Hg(l)} \quad (3)$$

The emf of cell 3 is independent of the particular Na-glass electrode used (to within ±0.2 mV), and the net cell reaction for cell 3 has been used to obtain the activity coefficient data reported.

Experimental

Voltage measurements were made with a Keithley 630 potentiometric electrometer which was calibrated with an NBS-certified Leeds and Northrup K-3 potentiometer. The cells were thermostated at 25.00 ± 0.01°C in a grounded water bath. The cell construction was essentially the same as that used in earlier work (*4, 6, 10*). Oxygen was excluded from the cells by means of nitrogen, which was first passed through a glass frit, then through a presaturator, and then through the cell itself. The calomel electrodes were prepared according to the method of Hills and Ives (*3*). The $\mathrm{Pb(Hg)}|\mathrm{Pb_2Fe(CN)_6 \cdot 3H_2O(s)}|\mathrm{Fe(CN)_6^{4-}(aq)}$ electrode was prepared by methods already described (*10*). The sodium ion-specific glass electrodes used were obtained from Beckman #39278. These electrodes were fitted with a Teflon sleeve to facilitate placement in the cells. The distilled water used to prepare the cell solutions was deoxygenated with nitrogen. Solutions were prepared on a molality concentration basis; buoyancy corrections were applied to all weights.

The NaCl(s) used was Thorn Smith primary standard grade. The $Na_4Fe(CN)_6 \cdot 10H_2O(s)$ used was Baker reagent grade. The salt was recrystallized from deoxygenated water and stored over a saturated solution of $NaBr \cdot 2H_2O(s)$ in a desiccator. The waters of hydration of $Na_4Fe(CN)_6 \cdot 10H_2O$ were taken into account in the preparation of the $Na_4Fe(CN)_6(aq)$ solutions. Solutions were stored in the dark under nitrogen in brown nalgene bottles. Sodium ferrocyanide solutions were used in the cells within 12 hr of preparation, and new solutions were used for each experiment.

The voltage of the hypothetical double cell 3 was obtained as follows: Measurements were made of the voltages of cells 1 and 2 by use of the same sodium ion-specific glass electrode; readings were taken in pairs (1, 2, then 2, 1) and added to obtain two values of $\epsilon_1 + \epsilon_2$; the two values of $\epsilon_1 + \epsilon_2$ usually agreed to within ±0.3 mV. The cells usually required 3–6 hr to reach a stable (±0.2 mV) voltage, and the period of stability ranged from 6 to 48 hr. The values of $\epsilon_1 + \epsilon_2$ obtained were averaged over the stable period of the cell life. The average value of $\epsilon_1 + \epsilon_2$ for a given pair of cells was the same (within ±0.2 mV) for the two different sodium ion-specific glass electrodes used in the study. The calculations described in the results were carried out in double precision on a DEC PDP-8 computer.

Results

The results of our measurements are presented in Tables I and II. The net reaction of the double cell 3 was

---

[1] To whom correspondence should be addressed.

obtained as follows: For cell 1 we have [on choosing strong electrolyte standard states and assuming that the internal part of the ion-specific electrode involves a Ag$|$AgCl electrode in 0.1M NaCl(aq)]:

$$2\text{Pb(Hg)} + \text{Fe(CN)}_6{}^{4-}(\text{m}_2) + 3\text{H}_2\text{O(l)} \rightarrow \text{Pb}_2\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O(s)} + 4e^-$$

$$4\text{Na}^+(4\text{m}_2 + \text{m}_3) \rightarrow 4\text{Na}^+(\text{glass})$$

$$4\text{Na}^+(\text{glass}) \rightarrow 4\text{Na}^+(0.1M\ \text{NaCl})$$

$$4\text{AgCl(s)} + 4e^- \rightarrow 4\text{Ag(s)} + 4\text{Cl}^-(0.1M\ \text{NaCl})$$

whereas for cell 2 we have:

$$4\text{Cl}^-(0.1M\ \text{NaCl}) + 4\text{Ag(s)} \rightarrow 4\text{AgCl(s)} + 4e^-$$

$$4\text{Na}^+(0.1M\ \text{NaCl}) \rightarrow 4\text{Na}^+(\text{glass})$$

$$4\text{Na}^+(\text{glass}) \rightarrow 4\text{Na}^+(\text{m}_1)$$

$$2\text{Hg}_2\text{Cl}_2\text{(s)} + 4e^- \rightarrow 4\text{Hg(l)} + 4\text{Cl}^-(\text{m}_1)$$

The summation of all of these reactions yields the net cell reaction for cell 3:

$$2\text{Pb(Hg)} + 4\text{Na}^+(4\text{m}_2 + \text{m}_3) + \text{Fe(CN)}_6{}^{4-}(\text{m}_2) + 3\text{H}_2\text{O(l)} + 2\text{Hg}_2\text{Cl}_2\text{(s)} \rightarrow 4\text{Hg(l)} + 4\text{Na}^+(\text{m}_1) + 4\text{Cl}^-(\text{m}_1) + \text{Pb}_2\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O(s)} \qquad (4)$$

Application of the Nernst equation to the cell reaction yields ($\omega = RT/\mathfrak{F}$).

$$\epsilon = \epsilon^\circ - \frac{\omega}{4} \ln \left\{ \frac{a^4{}_{\text{Na}^+(\text{m}_1)} a^4{}_{\text{Cl}^-(\text{m}_1)}}{a^4{}_{\text{Na}^+(4\text{m}_2+4\text{m}_3)} a_{\text{Fe(CN)}_6{}^{4-}(\text{m}_2)} a^3{}_{\text{H}_2\text{O}}} \right\} \qquad (5)$$

where we have set the activities of mercury, mercurous chloride, lead ferrocyanide trihydrate, and lead in the amalgam equal to unity (the same 2-phase lead amalgam was used in all experiments). Substitution of the relationship $a_i = \text{m}_i\gamma_i$ for each ion in Equation 5, followed by conversion to mean ionic activity coefficients yields

$$\epsilon = \epsilon^\circ - \frac{\omega}{4} \ln \left\{ \frac{\gamma^8{}_{\pm(\text{NaCl})} \text{m}_1{}^8}{\gamma^5{}_{\pm[\text{Na}_4\text{Fe(CN)}_6]} (4\text{m}_2 + \text{m}_3)^4 \text{m}_2 a^3{}_{\text{H}_2\text{O}}} \right\} \qquad (6)$$

Equation 6 can be rewritten as

$$\epsilon + 2\,\omega \ln (\gamma_{\pm(\text{NaCl})}\text{m}_1) - \omega \ln (4\text{m}_2 + \text{m}_3) - \frac{\omega}{4} \ln \text{m}_2 - \frac{3\,\omega}{4} \ln a_{\text{H}_2\text{O}} = \epsilon^\circ + \frac{5\,\omega}{4} \ln \gamma_{\pm[\text{Na}_4\text{Fe(CN)}_6]} \qquad (7)$$

All of the quantities on the left-hand side of Equation 7 are known, except for the relatively small term $-(3\,\omega/4) \ln a_{\text{H}_2\text{O}}$ which can be estimated (see below). The value of ϵ° can be obtained from an extrapolation of our data on $\text{Na}_4\text{Fe(CN)}_6$(aq) solutions ($\text{m}_3 = 0$ in Equation 7) to zero ionic strength. The left-hand side of Equation 7 is the Hitchcock extrapolation function ϵ_H for cell 3

$$\epsilon_H = \epsilon^\circ + \frac{5\,\omega}{4} \ln \gamma_\pm \qquad (8)$$

Table I. Cell Data Used to Determine $\gamma_\pm$ for $\text{Na}_4\text{Fe(CN)}_6$(aq) at 25°C

(1) Pb(Hg)$|$$\text{Pb}_2\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}(s)|$$\text{Na}_4\text{Fe(CN)}_6$(aq,$\text{m}_2$)$|$Na-glass

(2) Na-glass$|$NaCl(aq,$\text{m}_1 = 1.000$)$|$$\text{Hg}_2\text{Cl}_2(s)|$Hg(l)

m_2	$\epsilon_1 + \epsilon_2$, mV[a]	$-\ln a_{\text{H}_2\text{O}}$[b]	ϵ_H, mV[c]	ϵ_G, mV[d]	$I^{1/2}/(1 + I^{1/2})$
0.1000	582.6 ± 0.3	0.00541	599.5	675.0	0.5000
0.05000	565.7 ± 0.2	0.00282	604.8	667.3	0.4142
0.01000	535.2 ± 0.2	0.00065	625.9	662.2	0.2403
0.005000	519.3 ± 0.2	0.00032	632.2	659.8	0.1827
0.003000	507.4 ± 0.2	0.00020	636.7	659.0	0.1476
0.001000	479.6 ± 0.2	0.00006	644.2	657.9	0.0909
0.000500	465.8 ± 0.7	0.00003	(652.7)[e]	(662.6)[e]	0.0660

[a] Cell voltage is taken to be positive when the left electrode in the cell diagram is negative. [b] Estimated by use of osmotic coefficient data for $\text{K}_4\text{Fe(CN)}_6$(aq) solutions from References *7* and *10*. [c] See Equation 8. [d] See Equation 11. [e] This point was not used in the least-squares analysis.

Table II. Activity Coefficients for $\text{Na}_4\text{Fe(CN)}_6$(aq) at 25°C in $\text{Na}_4\text{Fe(CN)}_6$(aq) + NaCl(aq) Solutions with $I_\text{tot} = 1.000$ Calculated from Data on Cells

(1) Pb(Hg)$|$$\text{Pb}_2\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}(s)|$$\text{Na}_4\text{Fe(CN)}_6$($\text{m}_2$),NaCl($\text{m}_3$),Na-glass

(2) Na-glass$|$NaCl($\text{m}_1 = 1.000$)$|$$\text{Hg}_2\text{Cl}_2(s)|$Hg(l)

m_2	m_3	$\epsilon_1 + \epsilon_2$, mV	$-\ln a_{\text{H}_2\text{O}}$[a]	$-\ln \gamma_\pm$	$\gamma_\pm$
0.1000	0	582.6 ± 0.3	0.00541	1.8477	0.158 ± 0.004
0.0900	0.1000	585.0 ± 0.1	0.00736	1.8636	0.155 ± 0.004
0.0800	0.2000	586.2 ± 0.2	0.00955	1.8998	0.150 ± 0.004
0.0700	0.3000	588.1 ± 0.2	0.01193	1.9017	0.149 ± 0.004
0.0600	0.4000	589.2 ± 0.2	0.01449	1.9148	0.147 ± 0.004
0.0400	0.6000	590.2 ± 1.0	0.02015	1.9351	0.144 ± 0.006
0.0300	0.7000	588.2 ± 0.5	0.02326	1.9987	0.136 ± 0.004
0.0200	0.8000	588.1 ± 0.3	0.02656	1.9753	0.139 ± 0.004
0.0100	0.9000	584.9 ± 0.4	0.03004	1.9870	0.137 ± 0.004

[a] Calculated from the expression $-\ln a_{\text{H}_2\text{O}} = (5\text{m}_2 + 2\text{m}_3)(5.95\text{m}_2 + 0.9355\text{m}_3)/(55.516)$.

As $I \rightarrow 0$, the Debye-Hückel theory requires that $\ln \gamma_\pm \rightarrow -4\,\alpha I^{1/2}/(1 + I^{1/2})$, where $\alpha = 1.1762$ (25°C). Therefore, a plot of ϵ_H vs. $I^{1/2}/(1 + I^{1/2})$ (where $I = 10\,\text{m}_2$) should have a theoretical limiting slope of $-(5\,\omega/4)(4\,\alpha) = -151.1$ mV. The water activity in $\text{Na}_4\text{Fe(CN)}_6$(aq,$\text{m}_2$) solutions is given by

$$\ln a_{\text{H}_2\text{O}} = -5\text{m}_2\phi/55.516 \qquad (9)$$

where ϕ is the osmotic coefficient. The osmotic coefficients of water in our $\text{Na}_4\text{Fe(CN)}_6$(aq,$\text{m}_2$) solution were estimated from the isopiestic data of Robinson and Stokes (*7, 8*) on $\text{K}_4\text{Fe(CN)}_6$(aq). For $\text{m}_2 < 0.01$, the $(3\,\omega/4) \ln a_{\text{H}_2\text{O}}$ term is insignificant (<0.02 mV).

A least-squares analysis of a plot of ϵ_H vs. $I^{1/2}/(1 + I^{1/2})$ for the cells (Table I) with $0.001 \leq \text{m}_2 \leq 0.05$ yields an intercept of $\epsilon^\circ = 654.8 \pm 0.4$ mV and a slope of -121.0 ± 1.6 mV (theoretical slope -151.1 mV). Inclusion of the $\text{m}_2 = 0.0005$ point improves the agreement with the theoretical slope but greatly increases the uncertainty in ϵ°. The ϵ° value computed by requiring the data to fit the theoretical slope is $\epsilon^\circ = 661.3 \pm 3.7$ mV. The magnitude of the deviation of our experimental limiting slope from the theoretical slope suggests that our data do not extend far enough into the Debye-Hückel region to obtain ϵ° to the desired accuracy and precision (i.e., better than ±0.5 mV) from a Hitchcock plot.

If we assume that the Brönsted-Guggenheim equation (5) is valid for $\text{Na}_4\text{Fe(CN)}_6$(aq) within the range of our data, then we can write (25°C)

$$\ln \gamma_\pm = -4\,\alpha I^{1/2}/(1 + I^{1/2}) + 8\,\beta\text{m}_2/5 \qquad (10)$$

where β is the Brönsted-Guggenheim parameter (natural logarithms, $\beta = 2.303$ B). Combination of Equation 10 with Equation 8 yields

$$\epsilon_G = \epsilon_H + 5\,\alpha\omega I^{1/2}/(1 + I^{1/2}) = \epsilon^\circ + 2\,\omega\beta m_2 \quad (11)$$

where ϵ_G is the Guggenheim extrapolation function. If Equation 10 holds for $\ln \gamma_\pm$, then a plot of ϵ_G vs. m_2 should be a straight line with intercept ϵ° and slope of $2\,\omega\beta$.

A least-squares analysis of a plot of ϵ_G vs. m_2 for the cells (Table I) with $0.001 \le m_2 \le 0.1$ yields an intercept of $\epsilon^\circ = 658.9 \pm 0.5$ mV and a slope of 163.3 ± 11.5 mV. The slope of the Guggenheim plot yields $\beta = 3.18 \pm 0.23$. Thus, the activity coefficients at 25°C of $Na_4Fe(CN)_6$(aq) over the molality range $0 \le m_2 \le 0.10$ are given by

$$\ln \gamma_\pm = -4.705(10\,m_2)^{1/2}/[1 + (10m_2)^{1/2}] + (5.08 \pm 0.37)m_2 \quad (12)$$

The results of our measurements on $Na_4Fe(CN)_6$(aq,m_2) + NaCl(aq,m_1) solutions at a total ionic strength of $1.000 = 10m_2 + m_3$ are given in Table II. The water activity in our mixed electrolyte solution is given by

$$\ln a_{H_2O} = -\left(\frac{5m_2 + 2m_3}{55.516}\right)\phi_{\text{mix}} \quad (13)$$

where ϕ_{mix} is the osmotic coefficient of water in the mixture. The value of ϕ_{mix} was estimated from the expression (2)

$$\phi_{\text{mix}} = \frac{I_2}{I_t}\phi_2 + \frac{I_3}{I_t}\phi_3 \quad (14)$$

where I_i/I_t is the ionic strength fraction of i in the mixture, and ϕ_i is the osmotic coefficient of water in a solution containing only electrolyte i at a concentration equivalent to the total ionic strength in the mixture. For our system $I_t = 1.000$, $I_2 = 10m_2$, $I_3 = m_3$, $\phi = 0.595$, and $\phi_3 = 0.9355$ (7). Thus,

$$\ln a_{H_2O} = -(5m_2 + 2m_3)(5.95m_2 + 0.9355m_3)/55.516 \quad (15)$$

The mean ionic activity coefficients given in Table II for $Na_4Fe(CN)_6$(aq) in the mixed electrolyte solutions were calculated from Equation 7 with $\epsilon^\circ = 658.9$ mV, and with $\ln a_{H_2O}$ calculated from Equation 15.

Discussion

If the Brönsted-Guggenheim equation (5) holds for the activity coefficients of $Na_4Fe(CN)_6$(aq) in the constant ionic strength $Na_4Fe(CN)_6$(aq,m_2) + NaCl(aq,m_3) solutions, then the activity coefficient of $Na_4Fe(CN)_6$ in the solution is given by

$$\ln \gamma_{\pm(\text{mix})} = \ln \gamma_\pm{}^\circ + \left(\frac{4}{5}\beta_{\text{NaCl}} + \frac{1}{25}\beta_{\text{Na}_4\text{Fe(CN)}_6}\right)m_3 \quad (16)$$

where $\gamma_\pm{}^\circ$ is the activity coefficient of $Na_4Fe(CN)_6$(aq) at the same total ionic strength as in the mixture. The β values are the Brönsted-Guggenheim parameters for pure NaCl(aq) and pure $Na_4Fe(CN)_6$(aq) at the total ionic strength of the mixture. Equation 16, with the coefficient of the m_3 term equal to a constant at fixed total ionic strength, is Harned's rule applied to our system. If Equation 16 holds, then it is clear that the activity coefficients of $Na_4Fe(CN)_6$ in the mixture can be calculated from data on the pure salt solutions.

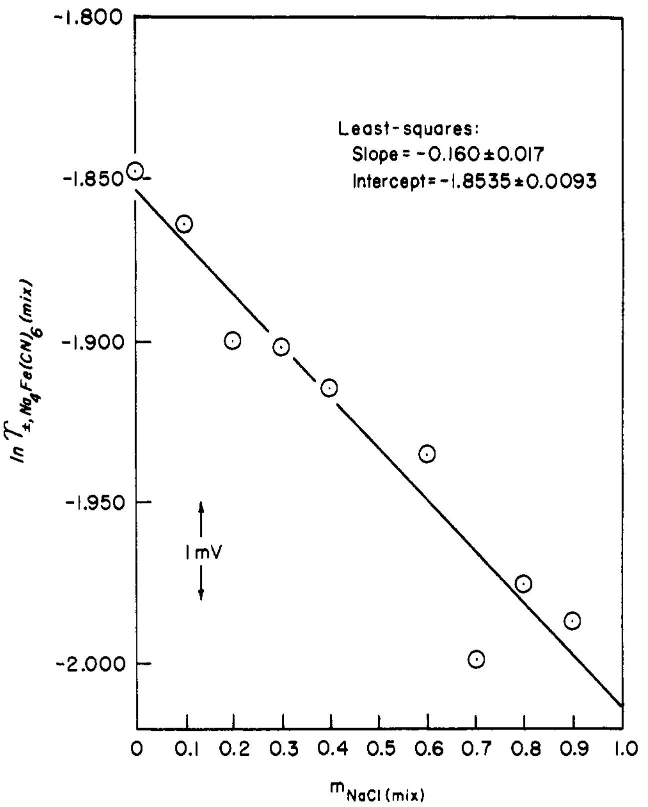

Figure 1. Test of Harned's rule for $\ln \gamma_\pm$ of $Na_4Fe(CN)_6$ in $Na_4Fe(CN)_6$(aq) + NaCl(aq) mixtures ($I_{\text{tot}} = 1.00$, $t = 25°C$)

We have tested Equation 16 by use of the data in Table II. A least-squares analysis of our data yields a slope of -0.160 ± 0.017 and an intercept of -1.8535 ± 0.0093 (Figure 1). The theoretical intercept is $\ln \gamma_\pm{}^\circ$ (at $I = 1$) $= -1.8477$. The theoretical slope is $\{(4/5)(0.167) + (1/25)(3.18)\} = +0.261 \pm 0.010$. Figure 1 shows that Harned's rule holds surprisingly well for these mixed electrolyte solutions, but the experimental Harned's rule coefficient is different in sign and magnitude from that predicted by the Brönsted-Guggenheim equation. It is encouraging that Harned's rule holds for a high-charge electrolyte in the presence of a 1-1 electrolyte. However, the failure of the Brönsted-Guggenheim equation to predict even the correct sign of the Harned rule coefficient for $Na_4Fe(CN)_6$ in the mixed electrolyte solution suggests that the Brönsted-Guggenheim equation should be used with caution in such systems.

Literature Cited

(1) Butler, J. N., "Activity Coefficient Measurements Using Dilute Metal Amalgam Electrodes," Office of Saline Water Research and Development Report No. 388, U.S. Government Printing Office, Washington, D.C., 1968.
(2) Harned, H. S., Robinson, R. A., Multicomponent Electrolyte Solutions, Topic 15, Vol 2, "International Encyclopedia of Physical Chemistry and Chemical Physics," Pergamon Press, Oxford, England, 1968.
(3) Hills, G. J., Ives, D. J. G., *J. Chem. Soc.*, **1951**, p 311.
(4) Kim, J. J., Rock, P. A., *Inorg. Chem.*, **8**, 563 (1969).
(5) Lewis, G. N., Randall, M., "Thermodynamics," rev. by K. S. Pitzer and L. Brewer, p 346, McGraw-Hill, New York, N.Y., 1961.
(6) Murray, Jr., R. C., Rock, P. A., *Electrochim. Acta*, **13**, 969 (1968).
(7) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions," 2nd rev. ed., Butterworths, London, England, 1959.
(8) Robinson, R. A., Stokes, R. H., *Trans. Faraday Soc.*, **45**, 612 (1949).
(9) Rock, P. A., *J. Chem. Educ.*, **47**, 683 (1970).
(10) Rock, P. A., Powell, R. E., *Inorg. Chem.*, **3**, 1593 (1964).
(11) Sillén, L. G., Martell, A. E., "Stability Constants of Metal Ion Complexes," Publication No. 17, London: The Chemical Society, Burlington House, W.1, England, 1964.

Received for review February 1, 1973. Accepted April 23, 1973. This work was supported in part by funds from the Committee on Research, UCD.