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Thermodynamics of Metal Cyanide Coördination. II. ΔG^0, ΔH^0, and ΔS^0 Values for Tetracyanoniccolate(II) Ion Formation in Aqueous Solution at 25°[1a]

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The thermodynamic formation constant of $Ni(CN)_4^{-2}$ in aqueous solution has been determined potentiometrically at 25°. The resulting log K value is 30.1 ± 0.2 ($\Delta G^0 = -41.1 \pm 0.3$ kcal./mole). A ΔH^0 value of -43.2 ± 0.2 kcal./mole for the formation of $Ni(CN)_4^{-2}$ in aqueous solution has been determined calorimetrically at 25° using a simple calorimeter and a thermometric titration procedure at high and low ionic strengths, respectively. Combination of the ΔG^0 and ΔH^0 values gives a value of -7 e.u. for ΔS^0.

Introduction

The development of the ligand field theory has resulted in an increased interest in the thermodynamic properties of coördination compounds of transition metals. Few thermodynamic studies have been made using ligands of high ligand field strength, *i.e.*, CN^-, although such studies would be of theoretical interest in that they would provide data involving spin-paired complexes. Therefore, a study has been initiated in this Laboratory to determine the thermodynamics of formation of transition metal cyanides in aqueous solution. The initial step in this study involved the necessary determination of the thermodynamic properties of HCN in aqueous solution.[2] Nickel(II) was selected for the present study since tetracoördinated complexes of nickel have long occupied a prominent position in the development of the theory of inorganic complex ions.

As recently pointed out by Griffith,[3] very few facts are available concerning the stabilities of cyanide complexes. Hume and Kolthoff,[4] who reviewed the earlier determinations of the formation constant of $Ni(CN)_4^{-2}$ in aqueous solution, present convincing evidence of the unreliability of the data. These authors give a maximum value of 10^{-24} for the dissociation constant based on their polarographic study. Latimer's[5] calculated value for the dissociation constant, 10^{-22}, is based on a very approximate, estimated value for the entropy of $Ni(CN)_4^{-2}$. Freund and Schneider[6] used ultraviolet absorption as a means of quantitatively determining $Ni(CN)_4^{-2}$. Their value for the dissociation constant of $Ni(CN)_4^{-2}$ at 25° and infinite dilution is $1.0 \pm 0.2 \times 10^{-31}$.

A ΔH value for the formation of $Ni(CN)_4^{-2}$ was determined calorimetrically at 14° and high ionic strength, μ, by Varet[7] in 1896. This author reported several values for the heat of formation of $Ni(CN)_2(s)$ in various salt solutions. He also reported the heat of solution of $Ni(CN)_2(s)$ in various metal cyanide solutions with the resultant formation of $Ni(CN)_4^{-2}$. Assuming that the heat of hydration of the solid nickel cyanide is negligible, values ranging from 42 to 44 kcal./mole for the heat of formation of $Ni(CN)_4^{-2}$ can be calculated from Varet's data. $Ni(CN)_2$, as has been pointed out by Hume and Kolthoff[4] and demonstrated by Long,[8] is actually $Ni[Ni(CN)_4]$; however, this fact does not affect the heat of formation value.

This study was undertaken to obtain log K and ΔH values for $Ni(CN)_4^{-2}$ formation from Ni^{++} and CN^- in aqueous solution at 25° and at infinite dilution. Log K values were determined potentiometrically and compared with the recently determined spectrophotometric value.[6] ΔH values were determined by direct calorimetry.

Experimental

Materials.—Reagent grade NaCN (Baker analyzed), $HClO_4$ (Baker and Adamson), NaOH (Baker and Adamson), and nickel shot (Baker analyzed) were used in the preparation of solutions for the equilibrium constant and heat determinations. Standard nickel solutions were prepared by refluxing nickel shot in 5 *F* $HClO_4$. Nickel solutions made in this manner gave negative tests for Cl^-. The concentration of excess $HClO_4$ in the Ni^{++} solutions was determined by titration with standard carbonate-free NaOH solution. All water used in the preparation of solutions was recently boiled distilled water of pH approximately 6.5. NaCN solutions were standardized frequently by both Liebig and acidimetric titration in order to take into account the rapid CN^- decomposition.[2] A stable, standard $Na_2Ni(CN)_4$ solution was prepared for the equilibrium constant determinations by mixing known quantities of $Ni(ClO_4)_2$, NaCN, and NaOH and diluting the resulting solution with water. The resulting solution was slightly basic as determined by an acidimetric titration.

Equilibrium Constant Determination.—The first attempts to determine the formation constant of $Ni(CN)_4^{-2}$ were made by mixing HCN and $Ni(ClO_4)_2$ solutions and titrating with NaOH solution. However, considerable HCN volatilization occurred

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from the acidic solution while waiting for equilibrium to be attained; therefore, consistent pH data were not obtained. The best estimate of the log K value based on these widely divergent results was 29 ± 1. In order to minimize HCN volatilization, subsequent determinations were made in the following manner. Four separate $Ni(CN)_4^{-2}$ solutions having μ values ranging from 1.9×10^{-4} to 3.9×10^{-3} were prepared from the stock $Na_2Ni(CN)_4$ solution (low μ values were necessary to avoid $Ni[Ni(CN)_4]$ precipitation). Each of these solutions was divided into three equal portions, and to each portion was added standard $HClO_4$ in such quantity as to result in each portion having a different $\bar{n}$ value ($\bar{n}$ being the average number of CN^- ions bound per Ni^{++}). Immediately after preparation each of the twelve resulting solutions was divided into two or three portions which were contained in small polyethylene bottles. The bottles were almost completely filled, leaving little or no air space, and were sealed with paraffin to prevent subsequent HCN volatilization. The small bottles were attached to a rotating drum and allowed to equilibrate in a water bath maintained at 25.0 ± 0.1°. After 2 days, bottles representing each of the twelve solutions were opened while remaining partially submerged in the water bath, the pH was measured, and the contents were discarded. This process was repeated after several days, the final bottles being analyzed after 7 days. pH measurements were taken with a Leeds and Northrup pH indicator (No. 7401) equipped with Beckman glass E-2 and saturated calomel electrodes. A heliopot and microdial were used with the pH indicator, giving a tenfold sensitivity increase and a Leeds and Northrup recorder (pH ND 46-96(100) Model S) was employed to eliminate possible errors due to drifting. The pH meter was standardized before and after each reading with a pH 4.007 buffer (NBS Standard Sample No. 185c).

Enthalpy Determinations.—The heat of formation of $Ni(CN)_4^{-2}$ at 25° in aqueous solution was determined by direct calorimetry. Measurements were made at very low μ values using a thermometric titration procedure. In this procedure, solutions containing varying concentrations of $Ni(ClO_4)_2$, $HClO_4$, and NaCN were titrated with NaOH solution. The equipment and procedure used in these determinations have been described[9] as well as more recent refinements.[2]

Measurements at higher μ values (0.04 to 0.26) were carried out in a simple bench top calorimeter. Ampoules containing NaCN solutions were imploded into $Ni(ClO_4)_2$ solutions after sufficient time was allowed for temperature equilibrium to be attained. Care was taken to ensure that no large excess of CN^- was present over that necessary to stoichiometrically form $Ni(CN)_4^{-2}$. Temperature changes were measured using a Beckmann thermometer with an accuracy of 0.001°. The temperature of the calorimeter was maintained near 25° by submerging it in a controlled temperature water bath. The effective heat capacity of the calorimeter was determined by successive HCl–NaOH reactions. The heats of formation of water at the different ionic strengths used in our calculations are those given by Laidler.[10]

Calculations.—μ is defined in the usual manner. A Debye–Hückel equation of the form $-\log \gamma_{\pm} = A\sqrt{\mu}/(1 + B\sqrt{\mu})$ was used to convert pH to $[H^+]$. The formation constant of $Ni(CN)_4^{-2}$ was calculated by the $\bar{n}$ method.[11] $\bar{n}$ was calculated from electroneutrality and mass balance expressions using the pH readings in $\bar{n}$ regions ranging from 1.1 to 3.2 at each of the four μ values (see section on Equilibrium Constant Determination). It was assumed in the mass balance equation that the total Ni^{++} was present either as free Ni^{++} or $Ni(CN)_4^{-2}$. All calculations, including a recycling process between μ and γ until the approximation attained the desired self-consistence, were done on an IBM 650 electronic computer.

The method used to calculate heats of formation from the thermometric titration data at low μ values has been described.[9,12] Heats of formation at high μ values were calculated directly from the immediate temperature change and the determined heat capacity of the bench-top calorimeter. Heats of dilution and stirrer rates were taken into account.

Results

Log K values corrected to $\mu = 0$ for the formation of $Ni(CN)_4^{-2}$ in aqueous solution calculated from data at various μ values are given in Table I together with the pH reading for each sample taken. The subscripts on the pH values refer to the solution portions which were analyzed at time intervals as described in the Experimental section. pH values of at least two samples of each solution were read at each μ value, and an average log K value was calculated from these data. pH values are not given in the cases of those samples which were read before equilibrium had been obtained (2 samples), those whose pH value differed from the others by more than four times the standard deviation (2 samples), and those in which only two portions of the solution were equilibrated (5 samples). The average log K value with its standard deviation which was calculated before "rounding off" the data in Table I is 30.1 ± 0.2 ($\Delta G^0 = -41.1 \pm 0.3$ kcal./mole).

Table I

Log K Values for the Formation of $Ni(CN)_4^{-2}$ in Aqueous Solution at 25° and Corresponding μ, pH, and $\bar{n}$ Data

$\mu \times 10^3$	pH_1	pH_2	pH_3	$\bar{n}$	Av. log K
3.9	4.39	4.32	...	1.2	30.4
4.4	4.41	4.68	...	2.0	30.4
5.1	5.06	5.10	...	3.2	29.8
1.3	4.87	4.86	...	1.1	30.2
1.3	5.06	5.08	5.07	1.9	30.2
1.3	...	5.68	5.67	3.2	30.0
0.54	5.30	...	5.29	1.1	30.0
.52	5.48	...	5.51	1.85	30.1
.49	6.09	5.97	5.96	3.0	30.0
.22	5.72	5.72	...	1.1	29.9
.21	5.85	5.89	5.88	1.85	30.2
.19	...	6.26	6.22	3.0	30.5

In Table II are given the heats for $Ni(CN)_4^{-2}$ formation at 25° in aqueous solution at low μ values calculated from thermometric titration data. The ΔH data in Table II do not vary significantly with μ; therefore a ΔH^0 value of -43.2 ± 0.5 kcal./mole was calculated using all of the data.

In Table III are given the heats of formation of $Ni(CN)_4^{-2}$ at high μ values as determined in the bench-top calorimeter. Several runs were carried out at each μ value, and an average ΔH value is given for each μ value together with its standard deviation. Extrapolation of a plot of the ΔH data in Table III *vs.* μ to $\mu = 0$ gives a ΔH^0 value of -43.2 kcal./mole with an estimated uncertainty of ±0.2 kcal./mole, in good

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

[10] K. J. Laidler, *Can. J. Chem.*, **34**, 1677 (1956).

[11] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961.

[12] J. J. Christensen, R. M. Izatt, and L. Hansen, "Proceedings of the Seventh International Conference on Coördination Chemistry," Stockholm, 1962, Paper 7F1, p. 354.

TABLE II

ΔH VALUES (KCAL./MOLE) DETERMINED AT LOW μ VALUES FOR $Ni(CN)_4^{-2}$ FORMATION IN AQUEOUS SOLUTION AT 25°

$\mu \times 10^3$	$-\Delta H$	$\mu \times 10^3$	$-\Delta H$
1.17	43.85	4.67	43.61
1.17	42.57	4.67	43.73
1.17	43.45	4.67	43.63
2.30	42.56	6.98	43.33
2.30	43.18	6.98	43.88
2.30	42.90	6.98	42.99
3.56	42.96	6.98	43.44
3.56	42.85		
3.56	43.40		
3.56	42.96		

TABLE III

ΔH VALUES (KCAL./MOLE) DETERMINED AT HIGH μ VALUES FOR $Ni(CN)_4^{-2}$ FORMATION IN AQUEOUS SOLUTION AT 25°

μ	$-\Delta H$
0.040	43.35 ± 0.12
.082	43.50 ± 0.07
.134	43.73 ± 0.05
.255	44.30 ± 0.03

agreement with the ΔH^0 value obtained by thermometric titration.

Discussion

The equilibrium constant and enthalpy data in the present study are adequately explained by assuming the nickel to be present only as Ni^{++} and $Ni(CN)_4^{-2}$. It is possible that species intermediate between Ni^{++} and $Ni(CN)_4^{-2}$ exist in small concentration at any $\bar{n}$ value, although as indicated by Freund and Schneider[6] no such species have been reported. The constancy of log K with changing $\bar{n}$ values in Table I indicates that $Ni(CN)_4^{-2}$ is the predominant cyanide-containing species over the $\bar{n}$ range studied. This result also is confirmed by the thermometric titration data in which a plot of temperature rise *vs.* ml. of NaOH titrant added from $\bar{n} = 0$ to $n = 4$ gives a straight line, indicating that the same reaction is occuring throughout the titration. Complexes in which the concentrations of the intermediate species are small relative to that of a higher species are unusual in aqueous solution chemistry, but have been discussed recently by Sillén[13] and Rossotti.[14]

In Table IV is found a comparison taken from the literature and the present study of the potentiometrically and spectrophotometrically determined formation constants of HCN and $Ni(CN)_4^{-2}$. The formation constant of HCN is included in the comparison because the formation constant of $Ni(CN)_4^{-2}$ is dependent on it to the fourth power. It is interesting that these independent methods give results which agree within the experimental limits of error.

TABLE IV

COMPARISON OF FORMATION CONSTANT VALUES FOR HCN AND $Ni(CN)_4^{-2}$ DETERMINED POTENTIOMETRICALLY AND SPECTROPHOTOMETRICALLY

Species	log K (potentiometric)	log K (spectrophotometric)
HCN	9.21 ± 0.01[a]	9.216[c]
$Ni(CN)_4^{-2}$	30.1 ± 0.2[b]	30.3 ± 0.1[d]

[a] See ref. 2. [b] Present work. [c] K. P. Ang, *J. Chem. Soc.*, 3822 (1959). [d] This value is calculated from data given by Freund and Schneider[3] using the recently determined pK of HCN reported by Ang.[c] Freund and Schneider reported a log K value of 31.0 ± 0.1 using a value of 4×10^{-10} for HCN dissociation.

Values reported by Varet[7] for the heat of formation of $Ni(CN)_4^{-2}$ in aqueous solution were determined under significantly different conditions from those in this study, therefore no further comparison can be made between the data obtained in the two studies.

Combination of the calorimetric ΔH^0 value for $Ni(CN)_4^{-2}$ formation in aqueous solution at 25° with the corresponding ΔG^0 value results in a ΔS^0 value of -7 e.u. Using thermochemical data obtained in this study and literature data,[5] a standard heat of formation of 85.9 kcal./mole is calculated for the formation of aqueous $Ni(CN)_4^{-2}$ from the elements in their respective standard states. The corresponding free energy change is 105.8 kcal./mole, while the calculated standard entropy change is -66.6 e.u. A value of $+69$ e.u. is calculated for the ionic entropy of $Ni(CN)_4^{-2}$ in aqueous solution. This value is much larger than the value of $+33$ e.u. estimated by Latimer[5] ($\bar{S}_{H^+}{}^0 = 0$). The value calculated for the ionic entropy of aqueous Ni^{++}, -37 e.u., agrees well with the value, -38.1 e.u., given by the National Bureau of Standards.[15]

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