was maintained to the freezing points of the solutions (about −60°) with the peak widths of I consistently smaller than those of II. As the temperature of III was progressively lowered from room temperature, the signal first broadened and then emerged at about −40° as two doublets characteristic of F_5PNCCH_3 and the hexafluorophosphate ion.

After 0.05 ml of 10% aqueous acetonitrile was added to I, the spectrum of the solution at room temperature consisted of a doublet (half-height width about 340 cps), very much broadened with respect to the doublet obtained from the anhydrous sample.

$F_5AsNCCH_3$.—The $F_5AsNCCH_3$ complex was prepared by warming mixtures of AsF_5 and conductivity grade acetonitrile from −196° to room temperature. Spectra were obtained from saturated acetonitrile solutions (yellow coloration) of the sublimed complex and consisted solely of a doublet and quintuplet of relative intensities 4.0 and 0.98, respectively. The relative sensitivities of the HR-60 and A-56 nmr instruments are such that the quintuplet was clearly visible only in spectra obtained with the HR instrument.

The spectrum of a hydrolyzed $F_5AsNCCH_3$ solution generated by addition of 0.25 ml of 30% aqueous acetonitrile to 1.27 mmoles of $F_5AsNCCH_3$ in 0.4 ml of acetonitrile had the quartet typical of the AsF_6^- ion[8] with peak positions at 2270, 3155, 4115, and 5020 cps to high field of the internal reference. The spectrum of a solution of similar solvent composition, containing 1.30 mmoles of potassium hexafluoroarsenate in 0.6 ml of solvent, exhibited peaks at 2257, 3170, 4117, and 5025 cps. The spectrum of a hydrolyzed $F_5AsNCCH_3$ solution generated by addition of an acetonitrile solution of $F_5AsNCCH_3$ (1.9 mmoles) to 0.4 ml of 25% sodium hydroxide in water also contained peaks characteristic of the hexafluoroarsenate ion.

$F_5SbNCCH_3$.—Acetonitrile, 0.4 ml, conductivity grade, was distilled into an nmr tube containing approximately 0.6 g (3 mmoles) of antimony pentafluoride. The mixture was warmed slowly to room temperature. The spectrum of the saturated solution, obtained with the HR-60 instrument, contained two broad singlets of relative intensities 4.0 and 1.14 appearing at +108 and +139 ppm from the internal standard.

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Thermodynamics of Metal Cyanide Coordination. VI. Copper(I)- and Silver(I)-Cyanide Systems[1a]

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Log K, $\Delta H°$, and $\Delta S°$ values reported for the consecutive interaction of CN^- with $Cu(CN)_2^-$ to form $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ are: $\log K = 5.30, 1.5$; $\Delta H° = -11.1, -11.2$ kcal/mole; and $\Delta S° = -13.4, -31$ cal/deg mole, respectively. Values of $\Delta H°$ and $\Delta S°$ for the formation of $Ag(CN)_3^{2-}$ from $Ag(CN)_2^-$ and CN^- are determined to be −0.6 kcal/mole and +5 cal/deg mole, respectively. Also, $\Delta H°$ and $\Delta S°$ values reported for the reaction $M^+ + 2CN^- = M(CN)_2^-$ (M = Cu, Ag) are: $\Delta H° = -29.1$ and -32.1 kcal/mole and $\Delta S° = +12$ and -16 cal/deg mole, respectively. The data are compared with those previously reported for the Zn^{2+}–CN^- system.

Introduction

Previous papers in this series have reported thermodynamic values for the interaction of CN^- with Ni^{2+} [2] and Zn^{2+}.[3] Two significant observations made in these studies concerning consecutive species intermediate between M^{2+} and $M(CN)_4^{2-}$ (M = Ni, Zn) were (1) that such species did not exist in detectable concentrations in the Ni^{2+}–CN^- system and (2) that, except for $ZnCN^+$, they were present in the Zn^{2+}–CN^- system. The $\Delta S°$ values for the formation of the $M(CN)_4^{2-}$ species from M^{2+} and CN^- were found to be nearly identical and very small for the two systems. Thus $\Delta G°$ (log K) is proportional to $\Delta H°$ in both systems but is much smaller (−26.77 *vs.* −41.1 kcal/mole) in the case of the Zn^{2+}–CN^- system.

Cuprous ion is isoelectronic with Zn^{2+} making a thermodynamic study of the Cu^+–CN^- system of interest in order to be able to compare the results with those of the corresponding Zn^{2+}–CN^- system. In addition, a knowledge of the thermodynamic quantities provides the necessary information to learn the relative importance of $\Delta H°$ and $\Delta S°$ in determining the stabilities of the species involved. Inclusion of Ag^+ in the study should contribute information on the effect of changing from the first to second transition series in d^{10} ions where ligand field effects are absent.

The species formed when CN^- interacts with Cu^+ have been identified by Cooper and Plane[4] and Penneman and Jones[5] to be $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$. Earlier spectral studies of the Cu^+–CN^- system have been summarized by Cooper and Plane.[4] Evidence based on infrared studies for corresponding complexes in the Ag^+–CN^- system has been reported by Jones and Penneman.[6] Equilibrium constant data valid at 25° and ionic strength $\mu = 0$ have been reported and previous work has been summarized for the

[1] (a) Supported by U. S. Atomic Energy Commission Contract AT (04-3)-299. Presented at the 20th Annual Northwest Regional American Chemical Society Meeting, Corvallis, Ore., June 14 and 15, 1965. (b) To whom inquiries should be directed. (c) Supported by a Public Health Service predoctoral fellowship (No. GM 20,545) from the Division of Research Grants, Public Health Service.

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formation of $M(CN)_2^-$ from M^+ ($M = Cu$,[7] Ag[8]) and CN^-. Corresponding calorimetric data have been reported[9] only in the case of Ag^+.

Available equilibrium constant data[6,8,10] indicate that formation of $Ag(CN)_3^{2-}$ and $Ag(CN)_4^{3-}$ from $Ag(CN)_2^-$ and CN^- occurs appreciably only in the presence of a large excess of CN^-. In contrast, the formation constants for the corresponding $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ species are relatively large,[5,11-13] log K_3 and log K_4 being of the order of 5 and 2, respectively. No calorimetric data have been reported for these reactions in the case of either Cu or Ag.

In this paper are reported log K_n, $\Delta H_n°$, and $\Delta S_n°$ values valid at 25° and $\mu = 0$ for the formation of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ from $Cu(CN)_2^-$ and CN^- together with $\Delta H°$ and $\Delta S°$ values for the formation of $M(CN)_2^-$ from M^+ ($M = Cu, Ag$) and CN^- and for the formation of $Ag(CN)_3^{2-}$ from $Ag(CN)_2^-$ and CN^-.

Experimental Section

Materials.—Reagent grade $CuCl_2 \cdot H_2O$ (Baker & Adamson), Na_2SO_3 (Baker & Adamson), KCN (Mallinckrodt), methanol (Baker & Adamson), CuCN (Fisher Certified), $HClO_4$ (Baker & Adamson), $AgNO_3$ (Baker & Adamson), and NaCN (Baker & Adamson) were used in the study. The salt $K_3Cu(CN)_4$ was prepared by dissolving CuCN powder in a 3.1:1 excess of KCN, filtering through a sintered-glass crucible, and precipitating the solid $K_3Cu(CN)_4$ from the filtrate using methanol. After separation from the filtrate, the salt was dried at 60° for 24 hr in a vacuum oven. Analysis for copper showed the salt to be 98.8% $K_3Cu(CN)_4$ while analysis for CN^- using Ag^+ showed an excess of KCN equal to 1% of the salt by weight which accounted quantitatively for the low copper analysis.

Cuprous chloride was prepared as described previously,[14] and analysis for Cu(I) showed it to be 99.8% CuCl.

Determination and Calculation of K_3 and K_4 for Cu^+–CN^- Systems.—A fresh solution of $K_3Cu(CN)_4$ was prepared daily by dissolving the salt in water. Aliquot portions of the solution were titrated with 0.2093 *F* $HClO_4$ and the pH was measured at appropriate intervals using a Beckman Model 1019 Research pH meter. The total copper concentration in the $K_3Cu(CN)_4$ solutions varied from 1.7×10^{-3} to 1.1×10^{-2} *F* with corresponding μ variations from 5.3×10^{-3} to 4.3×10^{-2}.

The ion product of water,[15] $K_w = 1.008 \times 10^{-14}$, the dissociation constant of HCN,[16] $K_d = 6.15 \times 10^{-10}$, and the measured pH values were corrected by means of the Debye–Hückel expression

$$\log \gamma_i = \frac{-Az_i^2\mu^{1/2}}{1 + B\mathring{a}\mu^{1/2}} \qquad (1)$$

to the corresponding quantities at the experimental μ values used at each point taken in the calculations. Values of $\mathring{a}$ from 3 to 10 A were substituted into eq 1. An $\mathring{a}$ value of 4 A was used since it gave thermodynamic constants which varied least with μ. A detailed discussion of the procedure[3] used in these determinations as well as recent refinements[17] have been published. The calculations were aided by an IBM 7040 computer.

Enthalpy Determinations and Calculations.—The calorimeter and auxiliary equipment have been described.[18] Because cuprous ion disproportionates in aqueous solution, it was not possible to determine the heat of formation of any of the copper(I) cyanide complexes by direct calorimetric procedures involving Cu^+ and CN^-. For this reason, the enthalpy values for the formation of the various cyano complexes of copper(I) were determined using an indirect method involving the known[19] enthalpy of formation of CuCl(s) from Cu^+ and Cl^-. A measured amount of CuCl(s) was dissolved in a known excess of sodium cyanide solution which was of such a concentration that only $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ were formed according to

$$n\text{CuCl(s)} + m\text{CN}^- = q\text{Cu(CN)}_3^{2-} + (n - q)\text{Cu(CN)}_4^{3-} + (m + q - 4n)\text{CN}^- + n\text{Cl}^- \qquad (2)$$

The total heat effect, Q_T (corrected for heats of dilution), when CuCl(s) is dissolved in excess CN^-, is given by

$$-\Delta H_{\text{CuCl(s)}}n_{\text{CuCl(s)}} + \Delta H_{0-3}q_{\text{Cu(CN)}_3^{2-}} + (\Delta H_{0-3} + \Delta H_{3-4})(n - q)_{\text{Cu(CN)}_4^{3-}} = Q_T \qquad (3)$$

where *n* and *q* are the number of moles of CuCl and $Cu(CN)_3^{2-}$, respectively, as defined in eq 2, and $\Delta H_{\text{CuCl(s)}}$, ΔH_{0-3}, and ΔH_{3-4} are the enthalpy change values for the formation of CuCl(s) from Cu^+(aq) and Cl^-(aq), $Cu(CN)_3^{2-}$ from Cu^+ and CN^-, and $Cu(CN)_4^{3-}$ from $Cu(CN)_3^{2-}$ and CN^-, respectively.

Equation 3 is simplified to eq 4 using the value[19] −4.58 kcal/mole for $\Delta H_{\text{CuCl(s)}}$ and the relationship $n_{\text{CuCl(s)}} = q_{\text{Cu(CN)}_3^{2-}} + (n\text{-}q)_{\text{Cu(CN)}_4^{3-}}$.

$$4.58n_{\text{CuCl(s)}} + \Delta H_{0-3}n_{\text{CuCl(s)}} + \Delta H_{3-4}(n - q)_{\text{Cu(CN)}_4^{3-}} = Q_T \qquad (4)$$

Values for $n_{\text{CuCl(s)}}$ and Q_T are obtained experimentally and $(n - q)_{\text{Cu(CN)}_4^{3-}}$ is calculated using the appropriate equilibrium constant determined in this study. Simultaneous solution of equations of type (4) using data from two separate determinations gives values for ΔH_{0-3} and ΔH_{3-4}. The two different equilibrium mixtures containing $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ have different μ values; therefore, the ΔH_{0-3} and ΔH_{3-4} values obtained from this treatment are not valid at either μ value. However, the resulting error should be small since previous studies[2,3] involving similar systems show the change in ΔH in this μ region (0.02–0.05) to be slight (±0.1 kcal/mole). The values of ΔH_{0-3} and ΔH_{3-4} obtained by the above method were corrected from $\mu = 0.03$ to $\mu = 0$ by applying a correction of −0.20 kcal/mole which was estimated from the results of similar systems.[2,3]

Values for ΔH_{2-3} for the formation of $M(CN)_3^{2-}$ ($M = Cu, Ag$) from $M(CN)_2^-$ and CN^- were also determined calorimetrically by mixing solutions of the $M(CN)_2^-$ complexes with known amounts of cyanide solutions.

The enthalpy change for the formation of $Cu(CN)_2^-$ from Cu^+ and CN^-, $\Delta H°_{0-2}$, can be calculated by appropriate combination of $\Delta H°_{0-3}$ and $\Delta H°_{2-3}$ as shown in eq 5–7.

$$\text{Cu}^+ + 3\text{CN}^- = \text{Cu(CN)}_3^{2-} \qquad \Delta H°_{0-3} \qquad (5)$$

$$\text{Cu(CN)}_3^{2-} = \text{Cu(CN)}_2^- + \text{CN}^- \qquad -\Delta H°_{2-3} \qquad (6)$$

$$\text{Cu}^+ + 2\text{CN}^- = \text{Cu(CN)}_2^- \qquad \Delta H°_{0-2} \qquad (7)$$

The enthalpy change for the formation of $Ag(CN)_2^-$ from Ag^+ and CN^- was determined by mixing NaCN and $AgNO_3$ solutions in a molar ratio of 2:1. The reaction was carried out as a func-

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tion of μ, and $\Delta H°$ values were obtained by extrapolation of a plot of ΔH *vs.* $\mu^{1/2}$ to $\mu = 0$.

Results

The calorimetric data used to calculate ΔH_{0-3} and ΔH_{3-4} are given in Table I.

Table I

Q_T Values for Calculation of ΔH_{0-3} and ΔH_{3-4}[a]

Run no.	Q_T, cal	n_{CuCl}, mmole	$n_{Cu(CN)_4^{3-}}$, mmole
1	−16.240	0.3650	0.2755
2	−13.217	0.2959	0.2247
3	−13.103	0.3197	0.1416
4	−10.390	0.2320	0.1800
5	−8.294	0.2006	0.09491

[a] CuCl(s) was dissolved in 199.9 ml of 0.02000 *F* NaCN (runs 3 and 5) or 199.9 ml of 0.05000 *F* NaCN (runs 1, 2, and 4), and Q_T was measured calorimetrically;[18] temperature, 25°.

A value for ΔH_{2-3} was obtained by mixing solutions of NaCN (9.992 ml, 0.05124 *F*) and $Cu(CN)_2^-$ (199.9 ml, 0.002561 *F*) in stoichiometric ratios to form $Cu(CN)_3^{2-}$. Since the equilibrium constant for this reaction is a little larger than 10^5 (Table IV), it can be considered to be quantitative and no correction for incomplete reaction is necessary.

The three determinations of ΔH_{2-3} for the Cu(I)–CN^- system gave Q values of −5.829, −5.829, and −5.794 cal. Correction of these Q values using −0.12 cal for the heat of dilution of the NaCN[20] gives ΔH_{2-3} values of −11.15, −11.15, and −11.08 kcal/mole, respectively. Because of the low μ value (0.00732) at which the determinations were made, their average was taken to be $\Delta H°_{2-3}$.

A ΔH value for the formation of $Ag(CN)_3^{2-}$ from $Ag(CN)_2^-$ and CN^- was estimated from two calorimetric measurements in which $Ag(CN)_2^-$ (199.9 ml, 0.01069 *F*) was mixed with a known, large excess of NaCN (9.99 ml, 0.500 *F*) to give −1.007 and −1.029 cal, respectively. The heat of dilution of NaCN under the conditions of the $Ag(CN)_2^-$–CN^- study was determined[20] to be zero. Using these Q and heat of dilution values and the concentration of $Ag(CN)_3^{2-}$ (0.00893 *M*) calculated using the equilibrium constants of Azzam and Shimi,[8] values of −0.565 and −0.575 kcal/mole, respectively, are calculated for ΔH_{2-3} for the Ag^+–CN^- system.

In Table II are given the calorimetric data for the reaction of CN^- with Ag^+ to produce $Ag(CN)_2^-$.

In Table III are given sample pH titration data, $\bar{n}$ and −log [CN^-] used in the calculation of log K_{2-3} and log K_{3-4} values for the Cu^+–CN^- system.

A summary of the thermodynamic quantities for the Cu^+– and Ag^+–CN^- systems together with previous results is given in Table IV.

Table II

Calorimetric Data for the Formation of $Ag(CN)_2^-$ from Ag^+ and CN^- at 25°[a,b]

$10^3\mu$	Q, cal[c]	ΔH, kcal/mole
10.4	−34.02, −34.06, −34.01	−33.42 ± 0.06
5.19	−16.92, −17.07, −16.99	−33.2 ± 0.3
2.53	−8.50, −8.54, −8.50	−33.0 ± 0.2

[a] Uncertainty of the average ΔH value calculated from the three duplicate determinations at each μ value is indicated as twice the standard deviation. [b] The volumes and concentrations, respectively, of $AgNO_3$ and NaCN solutions used in making Q determinations at each μ value are: μ = 0.01040, 199.9 ml, 5.065 × 10^{-3} *F*, 9.992 ml, 0.2076 *F*; μ = 0.00519, 199.9 ml, 2.532 × 10^{-3} *F*, 9.992 ml, 0.1038 *F*; μ = 0.00253, 199.9 ml, 1.265 × 10^{-3} *F*, 9.992 ml, 0.05065 *F*. [c] Q correction (cal) and millimoles of product for each μ value are: μ = 0.01040, −0.18, 1.013; μ = 0.00519, −0.17, 0.5063; μ = 0.00253, −0.14, 0.2530. The Q correction term in each case must be subtracted from Q to give Q_T.

Table III

Typical pH Titration Data for the Formation of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ from $Cu(CN)_2^-$ and CN^-

Ml. Titrant 0.2093 *F* HClO$_4$	pH	$\bar{n}$	−log [CN^-]
	Run 1^a		
1.568	9.140	1.128	2.481
1.698	9.072	1.126	2.516
1.818	9.008	1.125	2.552
1.950	8.941	1.120	2.589
2.117	8.852	1.114	2.644
2.258	8.781	1.105	2.688
2.377	8.707	1.103	2.741
2.500	8.627	1.101	2.800
2.629	8.538	1.096	2.869
4.733	6.064	0.679	5.106
4.810	6.014	0.657	5.150
4.850	5.988	0.645	5.172
4.932	5.938	0.621	5.216
5.020	5.888	0.596	5.258
	Run 2^a		
1.178	9.349	1.138	2.394
1.369	9.252	1.126	2.428
1.549	9.159	1.122	2.470
1.739	9.066	1.113	2.515
1.928	8.968	1.110	2.570
4.573	6.176	0.727	5.009
4.831	6.017	0.653	5.145
4.962	5.938	0.615	5.214
	Run 3^b		
0.132	9.954	1.080	2.839
0.304	9.727	1.051	2.867
0.443	9.566	1.039	2.902
0.632	9.368	1.033	2.967
0.765	9.238	1.030	3.021
0.902	9.106	1.027	3.086
1.623	8.037	1.005	3.909
2.360	6.640	0.629	5.148
2.683	6.273	0.437	5.460
2.963	5.884	0.270	5.808
	Run 4^b		
1.322	8.657	1.011	3.376
1.611	8.082	1.005	3.867
2.173	6.889	0.739	4.933
2.372	6.632	0.622	5.153
2.651	6.304	0.456	5.434
2.954	5.910	0.275	5.783

[a] Initial volume, 100.9 ml; initial $[Cu]_T$, 0.007158 *F*; initial $[CN]_T$, 0.02902 *F*. [b] Initial volume, 201.7 ml; initial $[Cu]_T$, 0.001731 *F*; initial $[CN]_T$, 0.007019 *F*.

Discussion

Equilibrium constant values[5, 11–13] reported previously for the formation of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ from $Cu(CN)_2^-$ and CN^- were, with the few exceptions noted below, determined under significantly different conditions of μ and/or temperature from those used in this study; therefore, no comparison with results of previous studies is attempted. Of the two

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TABLE IV

SUMMARY OF THERMODYNAMIC QUANTITIES FOR THE Cu^+– AND Ag^+–CN^- SYSTEMS[a]

Reaction	Log *K*	$\Delta G°$, kcal/mole	$\Delta H°$, kcal/mole	$\Delta S°$, cal/deg mole
$Cu^+ + 2CN^- = Cu(CN)_2^-$	$(23.94)^b$	−32.7	-29.1 ± 0.2	$+12. \pm 0.5$
$Cu(CN)_2^- + CN^- = Cu(CN)_3^{2-}$	5.30 ± 0.01 $(5.34)^c$ $(4.10)^d$	-7.23 ± 0.02	-11.1 ± 0.08	-13.4 ± 0.2
$Cu(CN)_3^{2-} + CN^- = Cu(CN)_4^{3-}$	1.5 ± 0.2 $(1.74)^c$	-2.0 ± 0.2	-11.2 ± 0.1	-31 ± 2
$Ag^+ + 2CN^- = Ag(CN)_2^-$	$(20.44)^e$	−27.89	-32.9 ± 0.1 $(-33.0)^f$	-16 ± 1
$Ag(CN)_2^- + CN^- = Ag(CN)_3^{2-}$	$(1.55)^e$	−2.11	-0.6 ± 0.2	$+5 \pm 2$

[a] Uncertainties of the values obtained in this study are expressed as twice the standard deviation. [b] Reference 7; value corrected using 9.21[16] as the dissociation constant of HCN. [c] Reference 11; $\mu = 0.01$. [d] Reference 13; $\mu = 0.001$. [e] Reference 8. [f] Reference 9.

previous studies reported for 25° and low μ values, the present results are seen to agree well with one[11] but to differ markedly from those of the second.[13]

The $\Delta H°$ values reported by Randall and Halford[9] for the heat of formation of $Ag(CN)_2^-$ from Ag^+ and CN^- are seen in Table IV to be in good agreement with those determined in this laboratory.

The smaller $-\Delta H°_{0-2}$ value for the formation of $Cu(CN)_2^-$ from Cu^+ and CN^- compared to the $\Delta H°_{0-2}$ value for the formation of $Ag(CN)_2^-$ from Ag^+ and CN^- is not predicted from electrostatic considerations. However, it is consistent with the known larger hydration energy of Cu^+. Values of $\Delta H°$ for the reaction $M^+(g) + 2CN^-(aq) = M(CN)_2^-(aq)$ (−277.5 and −252.8 kcal/mole for M = Cu and Ag, respectively) calculated using available data[19] for the hydration energies show the expected trend from electrostatic considerations alone. This comparison, however, assumes the relative hydration energies of $Cu(CN)_2^-$ and $Ag(CN)_2^-$ to be equal.

A possible explanation for the much larger $-\Delta H°_{2-3}$ value in the case of Cu compared to that in the case of Ag is the probable existence of multiple bonding in the $Cu(CN)_3^{2-}$ complex. Cooper and Plane[4] report D_{3h} (trigonal-planar) symmetry and high Raman intensities for the $Cu(CN)_3^{2-}$ complex in solution. These facts indicate that multiple bonding in $Cu(CN)_3^{2-}$ is quite probable, and this would be expected to cause ΔH to be more negative than it otherwise would be. Chantry and Plane[21] report no similar effects to be present in the Raman spectra for the aqueous $Ag(CN)_3^{2-}$ complex. Infrared spectra intensity measurements reported by Jones[5,22] also support the probability of π bonding in $Cu(CN)_3^{2-}$, but not in $Ag(CN)_3^{2-}$.

The large, nearly equal $-\Delta H°$ values for the stepwise formation of the $M(CN)_4^{3-}$ and $M(CN)_3^{2-}$ complexes from $M(CN)_2^-$ and CN^- are not peculiar to the Cu^+–CN^- system. A previous study of the Zn^{2+}–CN^- system[3] showed the $\Delta H°_{2-3}$ and $\Delta H°_{3-4}$ values (−8.4 and −8.6 kcal/mole, respectively) for the formation of $Zn(CN)_3^-$ and $Zn(CN)_4^{2-}$ to be large and nearly equal.

The $\Delta H°_{2-3}$ and $\Delta H°_{3-4}$ values determined in this study for the Cu^+–CN^- system are much more negative than the corresponding quantities for the Zn^{2-}–CN^- system. This difference is possibly the result of solvation effects caused by the larger negative charges of the $Cu(CN)_4^{3-}$ and $Cu(CN)_3^{2-}$ anions compared to the corresponding $Zn(CN)_4^{2-}$ and $Zn(CN)_3^-$ species. The much larger $\Delta S°_{2-3}$ and $\Delta S°_{3-4}$ values for the Cu(I)–CN^- system compared to the Zn(II)–CN^- system ($\Delta S°_{2-3}$ and $\Delta S°_{3-4}$ values[3] for the Zn(II)–CN^- system are −5.4 and −12 cal/deg mole, respectively) are consistent with the expected larger solvation effects in the Cu(I)–CN^- system. The larger $-\Delta H°$ values in the copper(I)–cyanide system could also be indicative of increased π bonding in the copper–cyanide compared to the zinc–cyanide complexes.

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