atoms may be, there appears to be an appreciable decrease in going from the aquo cation to the anion. This may result from an increase in the utilization of s character in the tin–oxygen bonds as these become more covalent in going from the aquo cation to the anion.

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Thermodynamics of Metal Cyanide Coordination. III. $\Delta G°$, $\Delta H°$, and $\Delta S°$ Values for Ferrocyanide and Ferricyanide Ion Formation in Aqueous Solution at 25°[1a]

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Values for $\Delta H°$ of -85.77 and -70.14 kcal./mole have been determined calorimetrically for the formation of ferrocyanide and ferricyanide ions, respectively, from their constituent ions in aqueous solution at 25°. Combination of these $\Delta H°$ values with literature $\Delta S°$ values gave $\Delta G°$ values of -48.23 and -59.50 kcal./mole for the formation of ferrocyanide and ferricyanide ions, respectively. Corresponding log β_6 values (valid at zero ionic strength) are 35.4 and 43.6.

Introduction

This paper is part of a study to determine the thermodynamic quantities, $\Delta G°$, $\Delta H°$, and $\Delta S°$, for the interaction of cyanide ion with selected metal ions.[2] As recently pointed out by Griffith,[3] reliable formation constants for cyanide complexes are virtually unknown. Equilibrium constants are difficult to measure by the usual procedures for the formation of many of these complexes because of their extremely stable nature, their slow kinetics, and the evolution of gaseous HCN in their acidic solutions.

Ferrocyanide and ferricyanide ions are typical of complexes whose formation constants are not amenable to direct measurement. Formation constant and $\Delta G°$ values for such complexes can be obtained from $\Delta H°$ and $\Delta S°$ data, however, provided these latter data can be experimentally determined. This approach has been used by Stephenson and Morrow,[4] who estimated log β_6 values of 24 and 31 for the formation of ferrocyanide and ferricyanide ions, respectively, from their respective constituent ions in aqueous solution. However, these values appear to be unusually low when compared with the formation constant of $Ni(CN)_4^{2-}$ (log $\beta_4 = 30.1$) determined recently in this laboratory.[5] Stephenson and Morrow[4] state that their β_6 values are uncertain due to the approximate $\Delta S°$ and $\Delta H°$ values used in their calculations. Since no accurate calorimetric $\Delta H°$ value for the formation of the ferricyanide ion was available to these workers, their estimated β_6 value for the formation of this species is particularly uncertain. Recently reported standard entropy values[6] ($S°_{H^+} = 0$) for the ferrocyanide and ferricyanide ions make possible better estimations of the $\Delta S°$ values for the formation of these complexes in aqueous solution by combination of these standard entropy values with available entropy values for Fe^{2+},[7] Fe^{3+},[8] and CN^-.[8]

Müller[9] measured the heat of formation of ferrocyanide ion by the reaction of CN^- with Fe^{2+}. Guzzetta and Hadley[10] report ΔH values for ferrocyanide and ferricyanide ion formation from the interaction of Fe^{2+} and solid ferric alum, respectively, with 1 F CN^- solutions. The ΔH values reported by Müller[9] and Guzzetta and Hadley[10] are not thermodynamically useful because of the high ionic strengths, μ, of the solutions used by these investigators. Also, in the latter study[10] no mention is made of corrections for the dilution of the cyanide ion solution by the metal ion solutions, the heat of dissolution of the ferric alum, and heat effects due to H_2O and HCN formation. Such corrections could be considerable, and the reported values are, therefore, uncertain.

In the present study, $\Delta H°$ values are reported for the formation of ferrocyanide and ferricyanide ions from their respective constituent ions in aqueous solution at 25°. These $\Delta H°$ values are combined with $\Delta S°$ values calculated from literature data[6–8] to give corresponding formation constant values.

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[2] The standard state for the solute species in this study is a hypothetical 1 M solution. The superscript degree sign when used with the thermodynamic quantities refers to the standard changes in these quantities with respect to this standard state.

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Experimental

Materials.—All solutions were prepared and standardized by conventional procedures. Because of their susceptibility to air oxidation ferrous sulfate and potassium ferrocyanide solutions (both prepared from reagent grade Baker and Adamson chemicals) were prepared and stored in a nitrogen atmosphere. The ferrous solutions were found to be free of ferric ion. The effects of hydrolytic decomposition of the cyanide ion were minimized by using cyanide solutions freshly prepared from reagent grade potassium cyanide (Baker and Adamson) or sodium cyanide (Baker and Adamson).

Enthalpy Determinations.—The calorimeter and auxiliary equipment have been described.[11] The heat of formation of $Fe(CN)_6^{4-}(aq)$ from aqueous ferrous and cyanide ions was determined in the following manner. The concentrations of the ferrous sulfate (*ca.* 1×10^{-3} *F*) and potassium cyanide solutions were adjusted so that 10 ml. of the cyanide solution would react completely and rapidly with 200 ml. of the ferrous solution. Reaction of CN^- with Fe^{2+} was observed to be essentially instantaneous when the molar CN^- to Fe^{2+} ratio was greater than about 50:1. In solutions of lower CN^- to Fe^{2+} ratios the reaction was not consistently instantaneous. The cyanide ion solutions were sealed in thin-walled glass capsules which were then attached to a glass manifold rod within the calorimeter. Before the 200 ml. of ferrous solution was added, the calorimeter was purged with nitrogen gas for several minutes. The calorimeter and contents were then placed in position and the solution was brought to the desired temperature by an internal heater. The initial temperature prior to the reaction between cyanide and ferrous ions was chosen in each case to be 25.000 ± 0.005°. After thermal equilibrium had been established the capsule was broken by turning it into the sharpened blades of the stirring rod. The reaction between the ferrous and cyanide ions was rapid, resulting in a clear, colorless solution. The contents of the calorimeter were cooled immediately at 25.00° or lower by removing the calorimeter from the water bath. The calorimeter was then returned to the water bath and brought to thermal equilibrium at 25.00°. Heat capacity determinations were immediately made on the contents in a manner which duplicated as nearly as possible the just completed reaction between ferrous and cyanide ions. Since the acid concentration of the ferrous ion solution was approximately 10^{-3} *M*, it was necessary to correct the measured heat of reaction, Q_{total}, for the interaction of excess CN^- with this acid. This was done by running blanks which contained the same concentrations of acid and excess cyanide ion as were present in the determinations described above, but no ferrous ion.

The heat of formation of the ferricyanide ion could not be determined by direct reaction of the constituent ions as was done in the case of the ferrocyanide ion. A large amount of HCN was immediately evolved when capsules containing cyanide ion were broken into ferric ion solutions due to the low pH necessary to minimize hydrolysis of the Fe^{3+}. Also, the basic cyanide ion solution caused immediate precipitation of ferric hydroxide which took several days to redissolve making the reaction unsuitable for our calorimetric equipment. An indirect method was devised to measure the heat of formation of the ferricyanide ion which avoided the difficulties mentioned. This method is illustrated by the following equations.

$$Fe^{2+}(aq) + 6CN^-(aq) = Fe(CN)_6^{4-}(aq) \qquad \Delta H_1^\circ \quad (1)$$

$$Fe(CN)_6^{4-}(aq) + {}^1/_5MnO_4^-(aq) + {}^8/_5H^+(aq) = Fe(CN)_6^{3-}(aq) + {}^1/_5Mn^{2+}(aq) + {}^4/_5H_2O(aq) \qquad \Delta H_2^\circ \quad (2)$$

$$Fe^{3+}(aq) + {}^1/_5Mn^{2+}(aq) + {}^4/_5H_2O = Fe^{2+}(aq) + {}^1/_5MnO_4^-(aq) + {}^8/_5H^+(aq) \qquad \Delta H_3^\circ \quad (3)$$

$$Fe^{3+}(aq) + 6CN^-(aq) = Fe(CN)_6^{3-}(aq) \qquad \Delta H_4^\circ \quad (4)$$

$$\Delta H_4^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ$$

TABLE I

CALORIMETRIC DATA FOR REACTIONS 1, 2, AND 3 AT 25°

Uncertainties of the ΔH values at each μ are indicated as the standard deviation

Reaction	μ	Q_{total}, cal.[a]	ΔH, kcal./mole
1	0.072	−18.563	−85.6*1*
		−18.596	−85.7*7*
		−18.603	−85.8*0*
		−18.586	−85.7*2*
			−85.73 ± 0.08
	0.051	−7.418	−85.9*1*
		−7.391	−85.6*4*
		−7.424	−85.9*7*
		−7.408	−85.8*1*
			−85.83 ± 0.12
	0.036	−9.435	−85.7*8*
		−9.428	−85.7*1*
		−9.440	−85.8*3*
		−9.427	−85.7*0*
			−85.76 ± 0.06
2	0.030	−7.288	−14.4*5*
		−7.290	−14.4*5*
		−7.315	−14.5*0*
		−7.302	−14.4*8*
			−14.47 ± 0.02
	0.0215	−7.215	−14.3*4*
		−7.203	−14.3*2*
		−7.203	−14.3*2*
		−7.194	−14.3*0*
			−14.32 ± 0.02
3	0.090	−15.345	−30.6*0*
		−15.327	−30.5*6*
		−15.353	−30.6*2*
		−15.342	−30.5*9*
			−30.59 ± 0.02
	0.045	−7.594	−30.2*9*
		−7.592	−30.2*8*
		−7.612	−30.3*6*
		−7.612	−30.3*6*
			−30.32 ± 0.04

[a] $Q_{\text{correction}}$ (cal.), and mmoles of product, respectively, for each reaction at each μ value are (1) μ = 0.072, −1.442, 0.2000; μ = 0.051, 1.173, 0.1000; μ = 0.036, −0.857, 0.1000; (2) μ = 0.030, 0.064, 0.5000; μ = 0.0215, −0.045, 0.500; and (3) μ = 0.090, 0.045, 0.5000; μ = 0.045, −0.022, 0.2500. The $Q_{\text{correction}}$ term in each case is subtracted from Q_{total}.

Reactions 1 and 2 were carried out as written. A value of ΔH_3° was obtained from the measured heat of reaction between potassium permanganate and ferrous sulfate solutions, (3). Appropriate combination of the heats of reaction for (1), (2), and (3) gives the heat of reaction of CN^- with Fe^{3+}, (4).

Results

In Table I are given the calorimetric data for the reactions indicated in (1), (2), and (3). The corrections (see footnote *a*, Table I) given for reaction 1 are those due to the interaction of CN^- with H^+ as indicated in the Experimental section and to the dilution of the CN^- solution, while those for reactions 2 and 3 are the sums of the $KMnO_4$[12] and $HClO_4$[13] dilution corrections.

All reactions were carried out at the μ values indicated in Table I, and the resulting data were corrected to μ = 0 either by extrapolation of a plot of ΔH *vs.* μ to μ = 0

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

[12] This correction as determined by us was of the order 0.005 cal.

[13] C. E. Vanderzee and J. A. Swanson, *J. Phys. Chem.*, **67**, 285 (1963).

TABLE II

THERMODYNAMIC QUANTITIES VALID AT 25° AND $\mu = 0$ FOR THE FORMATION IN AQUEOUS SOLUTION OF FERROCYANIDE AND FERRICYANIDE IONS FROM THEIR RESPECTIVE CONSTITUENT IONS (PREVIOUS WORK IS GIVEN IN PARENTHESES)

Reaction	$\Delta H°$, kcal./mole	$\Delta S°$, cal./deg.-mole	$\Delta G°$, kcal./mole	log β_6
$Fe^{3+} + 6CN^- = Fe(CN)_6{}^{3-}$	−70.14	−35.7	−59.50	43.6
	(−70.96)[a]			(31)[c]
				(42)[d]
$Fe^{2+} + 6CN^- = Fe(CN)_6{}^{4-}$	−85.77	−125.9	−48.23	35.4
	(−76.93)[a]			(24)[c]
	(−68.90)[b]			(35)[d]

[a] Reference 10, no data corrections made, μ *ca.* 1 *M*. [b] Reference 9, no data corrections made, μ unknown. [c] Reference 4, estimated value. [d] Reference 8, estimated value.

(reaction 1) or by using appropriate heat of dilution data for ferrous,[14] ferric,[15] ferrocyanide,[16] and ferricyanide[16] ions (reactions 2 and 3). Resulting $\Delta H_1°$, $\Delta H_2°$, $\Delta H_3°$, and $\Delta H_4°$ values with their estimated uncertainties for the reactions given by eq. 1, 2, 3, and 4 are -85.77 ± 0.08, -14.09 ± 0.01, -29.72 ± 0.03, and -70.14 ± 0.10 kcal./mole, respectively. These uncertainties do not include those due to uncertainties in the heats of dilution data used in the correction since these latter uncertainties were not given.[15,16] Errors due to this source are probably small because of the small correction (approximately 1%) involved.

In Table II are summarized the thermodynamic data determined in the present study together with results of previous wokers. Values for $\Delta S°$ are calculated from literature data.[6-8] The $\Delta G°$ and β_6 values in Table II were calculated by combination of the $\Delta S°$ values with the corresponding $\Delta H°$ values determined in the present study.

Discussion

The $\Delta H°$ values reported in Table II for ferricyanide ion formation are in fair agreement with those of previous workers; however, since no previous data were obtained in the μ region used in the present study, more detailed comparisons are not given.

The formation constants reported in Table II for these systems are the first to be based entirely on reliable calorimetric $\Delta H°$ data. These formation constants are in excellent agreement with those calculated by Latimer,[8] but are larger than those calculated by Stephenson and Morrow[4] by a factor of approximately 10^{11}. The agreement with Latimer[8] is fortuitous since the value calculated by him is based on incorrect $\Delta H°$ and $\Delta S°$ data.

A check on the $\Delta H°$ value for reaction 3 is provided by combining the data of Hugus and Latimer[17] and Magnusson and Huizenga,[18] who report values of 196.71 and −9.7 kcal./mole, respectively, for the reduction by $H_2(g)$ of MnO_4^- and Fe^{3+}, respectively. Appropriate combination of these values gives a $\Delta H°$ value for reaction 3 of −29.64 kcal./mole, in excellent agreement with that reported here, −29.72 kcal./mole.

The $\Delta G°$ data in Table II show the ferricyanide ion to be less dissociated than the ferrocyanide ion. This is in agreement with cell potential data for oxidation of ferrocyanide ion to ferricyanide ion.[8]

Appropriate combination of the data in Table II give $\Delta G°$, $\Delta H°$, and $\Delta S°$ values of −11.27 kcal./mole, 15.63 kcal./mole, and 90.2 cal./mole deg., respectively, for the reaction $Fe^{3+} + Fe(CN)_6{}^{4-} = Fe^{2+} + Fe(CN)_6{}^{3-}$. It is apparent from these data that formation of the products is favored by the large $\Delta S°$ value, but not by the $\Delta H°$ value. The large $\Delta S°$ value reflects the relative ion charges of the reactants and products since there is no change in the number of particles during the reaction.

The relative magnitudes of the $\Delta H°$ values in Table II are at first sight unexpected. One would expect from electrostatic considerations alone that the $\Delta H°$ value for ferricyanide ion formation would be much larger than the corresponding $\Delta H°$ value for ferrocyanide ion formation. However, the following effects combine to decrease the $\Delta H°$ value of ferricyanide relative to that of ferrocyanide ion formation: (a) the larger hydration energy of Fe^{3+} compared to Fe^{2+}, (b) the larger ligand field stabilization of the d^6 (ferrocyanide) relative to the d^5 (ferricyanide) states of iron, and (c) the destabilization of iron(III) relative to iron(II) in the reaction of the high-spin aqueous ions with CN^- to form the low-spin cyanide complexes. As recently pointed out,[19] (c) is a result of the special stability of the half-filled 3d energy level of iron(III).

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