For the case considered, $\alpha_1 = \alpha_2 = 109°$, $B = A = (16/9)\ \mu^2$, and the average of the square of the dipole moment is

$$\overline{\mu^2} = \frac{\int_0^\pi \mu^2(\theta) \exp[-V(\theta)/RT]\mathrm{d}\theta}{\int_0^\pi \exp[-V(\theta)/RT]\mathrm{d}\theta} \qquad (9)$$

Substitute into (7)

$$\overline{\mu^2} = A + Bf$$

$$f = \frac{\int_0^\pi \cos\theta \exp[-V(\theta)/RT]\mathrm{d}\theta}{\int_0^\pi \exp[-V(\theta)/RT]\mathrm{d}\theta} \qquad (10)$$

Evaluation of (8) and substitution into (10) gave $B = A = 0.44$, $f = 0.69$. With $a = (V_0/2RT)$ and $T = 293°$K.

$$0.69 = \frac{e^{-a/2}\int_0^{\pi/2} \exp[(a/2)\cos 2\theta] \cos\theta\, \mathrm{d}\theta + \int_{\pi/2}^{\pi} \exp[a \cos 2(\theta - \pi)] \cos\theta\, \mathrm{d}\theta}{e^{-a/2}\int_0^{\pi/2} \exp[(a/2)\cos 2\theta]\mathrm{d}\theta + \int_{\pi/2}^{\pi} \exp[a \cos 2(\theta - \pi)]\mathrm{d}\theta} \qquad (11)$$

The integrals in (11) were evaluated graphically, giving $a = 2.56$, $V_0 = 3$ kcal., the depth of the s-*trans* barrier; *i.e.*, the magnitude of V for $\theta = \pi/2$. The s-*cis* barrier was assumed to be $V_0/2$ or 1.5 kcal.; *i.e.*, the magnitude of V for $\theta = \pi$. The value of V_0 thus obtained is less than that for butadiene,[28] which was 5 kcal., although it is expected to be larger due to the enhanced interaction between halogen atoms as contrasted to the hydrogen atoms.

The ratio of the number of molecules in the *trans* configuration to those in the *cis* configuration is given by $N_{trans}/N_{cis} = \exp(-a) = 12.9$, while the ratio of the number of molecules N_t/N_c, with θ in the interval $0 \leqslant \theta \leqslant \pi/2$, to those with θ in the interval $\pi/2 \leqslant \theta \leqslant \pi$ is given by

$$N_t/N_c = \frac{\int_0^{\pi/2} \exp[a \cos 2(\theta - \pi)]\mathrm{d}\theta}{e^{-a/2}\int_{\pi/2}^{\pi} \exp[(a/2) \cos 2\theta]\ \mathrm{d}\theta} = 7.8 \qquad (12)$$

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[CONTRIBUTION FROM COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Thermodynamics of Aqueous Ferricyanide, Ferrocyanide and Cobalticyanide Ions

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We have measured heats of solution of $K_3Fe(CN)_6$(c) and $K_3Co(CN)_6$(c) and the solubility of $K_3Co(CN)_6$(c) in water at 25°. The resulting data have been used in calculating that the standard partial molal entropies of $Fe(CN)_6^{-3}$ (aq) and $Co(CN)_6^{-3}$ (aq) are 63.4 and 55.7 cal./deg. mole, respectively. The heat of oxidation of $Fe(CN)_6^{-4}$(aq) by Br_2(liq) was measured and used with the above entropy of $Fe(CN)_6^{-3}$(aq) to obtain 17 cal./deg. mole for the standard partial molal entropy of $Fe(CN)_6^{-4}$(aq). The uncertainty in the entropy of $Fe(CN)_6^{-4}$(aq) is large, mainly because of the uncertainty of the oxidation potential used in the calculation. Heats of solution of $K_4Fe(CN)_6$(c) and $K_4Fe(CN)_6 \cdot 3H_2O$ (c) also were measured. The as yet undetermined Third Law entropies of $K_4Fe(CN)_6$(c) and $K_4Fe(CN)_6 \cdot 3H_2O$(c) can be combined with data now available to give a reliable thermodynamic value for the standard oxidation potential of the ferrocyanide–ferricyanide couple.

Stephenson and Morrow[2] have investigated the heat capacities of $K_3Fe(CN)_6$(c) and $K_3Co(CN)_6$ (c) from 15 to 300°K. and have calculated entropies at 298.16°K. They used the standard entropy of $K_3Fe(CN)_6$(c) with thermodynamic data from the literature in calculating the standard partial molal entropy of $Fe(CN)_6^{-3}$(aq) and other derived thermodynamic quantities. They also pointed out the approximate nature of these derived quantities and suggested that careful determination of some heats of solution would be desirable.[3]

Heats of solution of $K_3Fe(CN)_6$(c), $K_4Fe(CN)_6$ (c), $K_4Fe(CN)_6 \cdot 3H_2O$(c) and $K_3Co(CN)_6$(c) and the heat of oxidation of $Fe(CN)_6^{-4}$(aq) to $Fe(CN)_6^{-3}$(aq) by Br_2(liq) were measured. The solubility of $K_3Co(CN)_6$(c) in water at 25° was also determined.

Experimental

The solution calorimeter used in this investigation has been described previously.[4,5] All of our heat determinations were at 25.0 ± 0.3° with 950 ml. of water or solution in the calorimeter.

Commercial C.P. $K_3Fe(CN)_6$(c) was purified according to the method of Stephenson and Morrow.[2] Baker "Purified" $K_4Fe(CN)_6 \cdot 3H_2O$(c) was recrystallized three times from distilled water. Aqueous solutions of $K_4Fe(CN)_6$ were never heated above 60°. Anhydrous $K_4Fe(CN)_6$(c) was obtained by drying the recrystallized trihydrate at 110° or by prolonged drying over P_2O_5 in a vacuum desiccator. No significant differences in analysis or heats of solution of $K_4Fe(CN)_6$(c) samples prepared in these two ways were noted.

Two samples of $K_4Fe(CN)_6 \cdot 3H_2O$(c) for heat of solution measurements were prepared. One sample was prepared by storing damp, recrystallized $K_4Fe(CN)_6 \cdot 3H_2O$(c) in a black-

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(1) Alfred P. Sloan Research Fellow.

(2) C. C. Stephenson and J. C. Morrow, THIS JOURNAL, **78**, 275 (1956).

(3) We are grateful to Professor Morrow for calling this suggestion to our attention.

(4) R. L. Graham and L. G. Hepler, THIS JOURNAL, **78**, 4846 (1956).

(5) C. N. Muldrow and L. G. Hepler, *ibid.*, **79**, 4045 (1957).

painted desiccator with a saturated solution of NaBr (solid phase $NaBr\cdot 2H_2O$) for one to six months.[6] Another sample was prepared by storing damp, recrystallized $K_4Fe(CN)_6\cdot 3H_2O$(c) in a similar desiccator with a solution that was saturated with respect to NaCl and sucrose.[6] Heats of solution of these two samples were the same and loss of weight on heating agreed with that calculated from the formula weights.

Reagent grade bromine was used without further purification. Because of the volatility of liquid bromine and the reactivity of bromine vapor our usual calorimetric sample bulbs were unsatisfactory for these heat of oxidation experiments. Special bulbs having a capillary side-arm sticking out from the bulb stem were blown from 8 mm. Pyrex tubing. The stem was sealed off just above the capillary side-arm and then a short piece of 8 mm. Pyrex tube was sealed to the remaining stem to facilitate fastening the bulb to the bottom of the stirrer. These bulbs were loaded with bromine through the capillary and then, while the bromine was cooled by imbedding the bulb in a small pile of crushed Dry Ice, the capillary side-arm was sealed off.

Three different samples of $K_3Co(CN)_6$(c) were prepared by a procedure nearly the same as those already described by Benedetti-Pichler[7] and Bigelow.[8] Each of these batches was purified by recrystallization (three times) from distilled water and then dried in a vacuum desiccator over P_2O_5.

The density of saturated solutions of $K_3Co(CN)_6$ in water at 25.0 ± 0.1° was determined by taking 10-ml. aliquots from the saturated solutions with a calibrated pipet and weighing the aliquots in stoppered weighing bottles. All weights were corrected to vacuum. The density of the saturated solutions was calculated to be 1.1805 ± 0.0012 g./ml. The solubility of $K_3Co(CN)_6$(c) in water at 25° was determined by evaporating aliquots from the density determinations to dryness and then weighing the residue. The concentration of $K_3Co(CN)_6$(aq) in saturated solution was 1.303 ± 0.010 molal at 25°. The experimental procedure was checked by adding water to a known weight of $K_3Co(CN)_6$(c), evaporating the water by heating and then weighing.

Results

Heats of solution of $K_3Fe(CN)_6$(c) in water are given in Table I. Each measured heat of solution was combined with a heat of dilution of $K_3Fe(CN)_6$(aq)[9] to obtain standard heats of solution of $K_3Fe(CN)_6$(c) that are also given in Table I.

Table I

Heats of Solution of $K_3Fe(CN)_6$(c)

Moles $K_3Fe(CN)_6 \times 10^3$/950 ml. soln.	ΔH (kcal./mole)	ΔH^0 (kcal./mole)
0.9682	13.13	12.95
2.324	13.32	13.05
2.975	13.23	12.95
3.194	13.36	13.07
4.288	13.32	13.00
4.720	13.35	13.02
5.910	13.38	13.03
6.505	13.41	13.05
14.102	13.39	12.97
14.570	13.40	12.98

Av. ΔH^0 = 13.01 } kcal./mole
Av. dev. = 0.04 }

The average standard heat of solution is ΔH^0 = 13.01 ± 0.04 kcal./mole where ±0.04 indicates the average deviation from the average. It may be seen from the consistency of the ΔH^0 values in Table I that crude heats of dilution of $K_3Fe(CN)_6$(aq) calculated from differences in heats of solution of $K_3Fe(CN)_6$(c) agree with the accurate results of Lange and Miederer.[9]

Heats of solution of $K_4Fe(CN)_6$(c) and $K_4Fe(CN)_6\cdot 3H_2O$(c) are given in Tables II and III, respectively. They were combined with heats of dilution of $K_4Fe(CN)_6$(aq)[9] to obtain the standard heats of solution given in Tables II and III. Averages are ΔH^0 = 9.61 ± 0.06 kcal./mole $K_4Fe(CN)_6$(c) and ΔH^0 = 13.15 ± 0.03 kcal./mole $K_4Fe(CN)_6\cdot 3H_2O$(c).

Table II

Heats of Solution of $K_4Fe(CN)_6$(c)

Moles $K_4Fe(CN)_6 \times 10^3$/950 ml. soln.	ΔH (kcal./mole)	ΔH^0 (kcal./mole
2.173	10.31	9.67
3.182	10.25	9.56
4.290	10.35	9.62
5.574	10.41	9.66
5.075	10.41	9.65
6.835	10.32	9.53
7.095	10.37	9.57
9.288	10.57	9.73
10.034	10.41	9.56
12.766	10.42	9.54

Av. ΔH^0 = 9.61 } kcal./mole
Av. dev. = 0.06 }

Table III

Heats of Solution of $K_4Fe(CN)_6\cdot 3H_2O$(c)

Moles $K_4Fe(CN)_6 \times 10^3$/950 ml. soln.	ΔH (kcal./mole)	ΔH^0 (kcal./mole)
5.281	13.95	13.18
8.165	13.99	13.17
12.027	13.99	13.12
13.353	14.06	13.16
26.910	14.06	13.10

Av. ΔH^0 = 13.15 } kcal./mole
Av. dev. = 0.03 }

Heats of solution of $K_3Co(CN)_6$(c) in water are given in Table IV. To calculate standard heats we assumed that heats of dilution of $K_3Co(CN)_6$(aq) and $K_3Fe(CN)_6$(aq) are the same in dilute solutions. The average ΔH^0 for solution of $K_3Co(CN)_6$(c) is 12.27 ± 0.02 kcal./mole. The consistency of the ΔH^0 values in Table IV supports our assumption that heats of dilution of $K_3Co(CN)_6$(aq) and $K_3Fe(CN)_6$(aq) are the same in dilute solutions.

Table IV

Heats of Solution of $K_3Co(CN)_6$(c)

Moles $K_3Co(CN)_6 \times 10^3$/950 ml. soln.	ΔH (kcal./mole)	ΔH^0 (kcal./mole)
4.2250	13.00	12.27
5.6767	13.04	12.29
6.8951	13.08	12.28
6.9043	13.06	12.26
12.711	13.10	12.24

Av. ΔH^0 = 12.27 } kcal./mole
Av. dev. = 0.02 }

Heats of oxidation of $Fe(CN)_6^{-4}$(aq) to $Fe(CN)_6^{-3}$(aq) by Br_2(liq) are given in Table V in terms of the reaction

$$Br_2(liq) + 2Fe(CN)_6^{-4}(aq) = 2Br^-(aq) + 2Fe(CN)_6^{-3}(aq)$$

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[6] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952.

[7] A. A. Benedetti-Pichler, *Z. anal. Chem.*, **70**, 258 (1927).

[8] J. H. Bigelow, *Inorg. Syntheses*, **II**, 225 (1946).

[9] E. Lange and W. Miederer, *Z. Elektrochem.*, **60**, 34 (1956).

TABLE V

HEATS OF OXIDATION OF $Fe(CN)_6^{-4}$(AQ) BY Br_2(LIQ)

Moles Br_2 (liq)/ 950 ml. soln.	Moles $Fe(CN)_6^{-4}$/ 950 ml. soln.	ΔH (kcal./mole Br_2)
0.01221	0.0452	−4.0
.01501	.0452	−4.4
.01872	.0485	−4.4
.01954	.0900	−4.6

Because of the slowness of this reaction (15–40 minutes to calorimetric completion), these results are considerably more uncertain than our heats of solution. Uncertainties in the results of the individual calorimetric runs have been estimated from consideration of the drift uncertainties. Heats of dilution in solutions of mixed electrolytes are difficult to estimate, especially when some of the ionic species in the solution are highly charged as in the reaction under consideration. Considering heats of dilution of $K_3Fe(CN)_6$(aq), $K_4Fe(CN)_6$(aq) and KBr(aq), it is probable that in dilute solution the standard heat of reaction is slightly more endothermic than the measured heats. We have therefore taken ΔH^0 of oxidation of $Fe(CN)_6^{-4}$ (aq) by Br_2(liq) to be −4.2 ± 0.8 kcal./mole of Br_2(liq) with ±0.8 the estimated maximum total uncertainty.

Derived Thermodynamic Quantities

The simplest and most straight-forward calculation we can make with our results and data from the literature is the calculation of the standard partial molal entropy of $Fe(CN)_6^{-3}$(aq). The standard free energy of solution of $K_3Fe(CN)_6$(c) is

$$\Delta F^0 = -RT \ln (3m)^3 m\, \gamma^4 = 2.12 \text{ kcal./mole}$$

with m the molal solubility of $K_3Fe(CN)_6$(c) at 298.16°K. and γ the mean (molal) activity coefficient in the saturated solution.[10,11] This free energy of solution combined with ΔH^0 of solution gives 36.52 cal./deg. mole for ΔS^0. From ΔS^0 of solution, the standard partial molal entropy of K^+(aq)[12] and the standard entropy of $K_3Fe(CN)_6$(c)[2] we obtain 63.4 cal./deg. mole for the standard partial molal entropy of $Fe(CN)_6^{-3}$(aq). Our estimate of the *total* uncertainty for the entropy of $Fe(CN)_6^{-3}$(aq) is about 1 cal./deg. mole.

The standard partial molal entropy of $Co(CN)_6^{-3}$(aq) calculated in similar fashion is 55.7 cal./deg. mole. For this calculation we have used our solubility and ΔH^0 of solution of $K_3Co(CN)_6$(c) with Stephenson and Morrow's[2] entropy of $K_3Co(CN)_6$(c) and the mean molal activity coefficient for $K_3Co(CN)_6$(aq) in saturated solution.[13] The uncertainty in this entropy is about the same as the uncertainty in the entropy of $Fe(CN)_6^{-3}$(aq).

The heat of reaction of Br_2(liq) with $Fe(CN)_6^{-4}$(aq), together with the heat of formation of Br^-(aq), the standard oxidation potential for the ferrocyanide–ferricyanide couple,[14] the entropy of $Fe(CN)_6^{-3}$(aq) and the entropy of H_2(g) yields 17 cal./deg. mole for the standard partial molal entropy of $Fe(CN)_6^{-4}$(aq). The uncertainty in our heat of reaction leads to an uncertainty of about 2 cal./deg. mole in the entropy of $Fe(CN)_6^{-4}$(aq). A still more important possible source of error is the oxidation potential used. Several other values for this potential have been reported (see Reynolds[15] for other references). The results of several workers are consistent with the idea of extensive association of cations (usually K^+) with anions in these solutions and that this association is more important for $Fe(CN)_6^{-4}$(aq) than for $Fe(CN)_6^{-3}$(aq). This is as expected from electrostatics.

The calculated standard partial molal entropy for $Fe(CN)_6^{-4}$(aq) may be in error by 5–15 cal./deg. mole. More precise values for the difference in heats of formation of $Fe(CN)_6^{-4}$(aq) and $Fe(CN)_6^{-3}$(aq) and the standard oxidation potential of the ferrocyanide–ferricyanide couple are needed. Reinvestigation of the ferrocyanide–ferricyanide standard oxidation potential at 25° is desirable but not sufficient. The temperature dependence of the potential must also be known before more extensive thermodynamic calculations and comparisons can be made.

Another approach to this problem is through measurement of the heat capacities of $K_4Fe(CN)_6$(c) and $K_4Fe(CN)_6 \cdot 3H_2O$(c) and direct calculation of the entropies at 298°K. These Third Law entropies then can be combined with heats and free energies of solution to obtain a reliable value for the standard partial molal entropy of $Fe(CN)_6^{-4}$(aq). The calorimetric heat of oxidation of $Fe(CN)_6^{-4}$(aq) to $Fe(CN)_6^{-3}$(aq) and the known standard partial molal entropy of $Fe(CN)_6^{-3}$(aq) can be combined with the entropy of $Fe(CN)_6^{-4}$(aq) to give a reliable thermodynamic value for the standard oxidation potential of the ferrocyanide–ferricyanide couple. Comparison of this calculated E^0 with the results of e.m.f. experiments [also comparison of dE^0/dT with a calorimetric ΔH^0 of oxidation of $Fe(CN)_6^{-4}$(aq)] should shed some light on the thermodynamic behavior of solutions of highly charged ions as well as provide useful information about ferrocyanide and ferricyanide ions.

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