Further evidence is furnished by the saturation study (Fig. 5) when $[Cu(en)_2]^{2+}$ and D-mannosan interact. Regardless of whether the mannosan was added to the $[Cu(en)_2]^{2+}$ or *vice versa*, the peak of the curve was located at a mole fraction 0.5. This indicates that the reaction takes place in a molecular ratio of 1:1, which is identical with the results of the spectrophotometric continuous variation studies with erythritol anhydride.[2] A saturation study could not be made with the $[Cu(en)_2]^{2+}$ ion because it is unstable in the presence of sodium hydroxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Heat Capacities of Potassium Ferricyanide and Potassium Cobalticyanide from 15 to 300°K. A Magnetic Transition in Potassium Ferricyanide

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The heat capacities of potassium ferricyanide and potassium cobalticyanide have been measured from 15 to 300°K. The standard entropies of the salts at 298.16°K. are 100.4 and 96.0 ± 0.2 cal. $deg.^{-1}$ $mole^{-1}$, respectively. The thermodynamic properties of ferricyanide and ferrocyanide ions have been calculated. A gradual transition, magnetic in nature, occurs at about 131°K. in the paramagnetic potassium ferricyanide. Ordering of the spin moments may not be complete at 15°K. in this salt.

The calorimetric determination of the entropy of paramagnetic substances by means of heat capacity measurements and by use of the third law of thermodynamics frequently requires measurements to temperatures below 15°K. A paramagnetic substance, which is in a disordered state, must become ordered at some low temperature, and if the substance is magnetically dilute, as in paramagnetic alums and hydrates, this ordering may occur at temperatures well below 15°K. In the relatively few cases where complete heat capacity measurements have been made at these low temperatures, the entropy change associated with the ordering process has agreed with that calculated from theory. The addition of the magnetic entropy contribution to the usual Debye extrapolation is justified in such cases. However, considerable discretion is required, because the anomalous heat capacities caused by a changing population of the electronic energy levels in the solid may extend to higher temperatures where a differentiation from the lattice heat capacities becomes difficult.

The magnetic properties of potassium ferricyanide, $K_3Fe(CN)_6$, which correspond to $S = {}^1/_2$, have been the subject of a number of experimental[2,3] and theoretical studies.[4] According to Howard, crystalline field theory gives three doubly degenerate energy levels of which only the lowest will be occupied at room temperature. Hence, the total magnetic entropy to be expected at low temperatures is not $R \ln 6$, as in a ferric alum, but $R \ln 2$. This magnetic entropy of $R \ln 2$ should be lost at temperatures below 15°K. The susceptibility measurements also indicate the potassium ferricyanide is disordered magnetically at 15°K., and there are no abnormal changes in the susceptibility at higher temperatures. Nevertheless, Dr. Richard Bersohn suggested to us that a transition might occur at higher temperatures due to interaction between ferricyanide ions in the crystal. We have measured the heat capacity of potassium ferricyanide from 15 to 300°K. for this reason, as well as to obtain the thermodynamic properties of the substance.

A gradual transition was found in potassium ferricyanide, with a maximum occurring in the heat capacity at about 131°K. In order to show that this transition is magnetic in nature, it was then necessary to measure the heat capacity of the diamagnetic potassium cobalticyanide, $K_3Co(CN)_6$, which is presumably isomorphous with the ferricyanide. The heat capacity of potassium cobalticyanide, which was measured from 15 to 300°K., is normal. The entropy change associated with the gradual transition in the ferricyanide, which is an important factor in the interpretation of the nature of such a transition, was estimated by using the normal heat capacities of the cobalticyanide as a guide. Unfortunately, a complete interpretation of these results is not yet possible.

Material.—Potassium ferricyanide for the calorimetric determination was commercial C.P. material (maximum impurities less than 0.02%) recrystallized three times from distilled water. This product was subjected to vacuum desiccation to remove most of the water. All measurements were made on a single loading of 160.8990 g. *in vacuo*, or 0.488689 mole. Correction has been made for the presence of 0.0109 weight per cent. water indicated by slight distortion of the heat capacity curve near the ice point. The molecular weight of potassium ferricyanide was taken as 329.246.

Potassium cobalticyanide (potassium hexacyanocobaltate-(III)) was prepared by the method of Benedetti-Pichler.[5] To an aqueous solution of cobaltous chloride potassium cyanide was added dropwise; the finely divided precipitate of cobaltous cyanide was filtered and washed once with cold water. The moist product was transferred to a solution of potassium cyanide sufficiently concentrated to dissolve the cobaltous cyanide completely. This solution was heated and held at the boiling point for 15 minutes, whereupon hydrogen was evolved, and the solution turned yellow. Pale yellow crystals of potassium cobalticyanide precipitated from the cold solution. The product was recrystallized from distilled water five times in order to remove all traces of potassium cyanide. Potassium cyanide undergoes a non-isothermal transition[6] near 168°K. with a total heat effect of 300 cal./mole; 0.05 weight per cent. potassium cyanide would be detected by distortion of the heat capacity curve

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[1] Allied Chemical and Dye Corporation Fellow, academic year 1948–1949.

[2] L. C. Jackson, *Proc. Roy. Soc.* (*London*), **A140**, 695 (1933).

[3] L. C. Jackson, *Proc. Phys. Soc.* (*London*), **50**, 707 (1938).

[4] J. Howard, *J. Chem. Phys.*, **3**, 813 (1935).

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

[6] C. Messner and W. Ziegler, THIS JOURNAL, **63**, 2703 (1941).

near 168°K. The absence of any distortion sets a maximum cyanide impurity at 0.05%, but the amount of potassium cyanide is believed to be less than 0.01% as the result of extensive recrystallization. Nickel impurities in the cobaltous chloride were removed quantitatively by the preparation procedure itself. After the final purification, the sample was analyzed polarographically[7] and found free from aquo-cyanide impurities. Vacuum desiccation was employed to remove water from the moist product. All measurements were made on a single loading of 129.8682 g. *in vacuo*, or 0.390774 mole. Correction has been made for the presence of 0.0447 weight per cent. water indicated by distortion of the heat capacity curve near the ice point. The molecular weight of potassium cobalticyanide was taken as 332.336.

Apparatus and Method.—The cryostat employed in this investigation has been described previously.[8] Temperatures and energy inputs were measured by means of a platinum-rhodium resistance thermometer with laboratory designation R222. The ice-point resistance of this thermometer, which had been calibrated with a helium gas thermometer, agreed with the original calibration. The calorie was taken as 4.1833 international joules. The absolute temperature of the ice point was taken as 273.16°K.

Heat Capacity Measurements.—Results of the heat capacity determinations are listed for potassium ferricyanide in Table I and for potassium colbalticyanide in Table II; graphical presentation is made in Fig. 1. For both salts, accuracy is believed to be within 0.2% above 30°K., 1.0% between 20 and 30°K., and 5.0% below 20°K. Series II and III for potassium ferricyanide consist of measurements with very short heating intervals for careful examination of the transition region. Points of all three series in this region are consistent with one another to 0.1%, a value well within limit of error. In all instances, the temperature increments were chosen small enough for the results to yield true differential heat capacities.

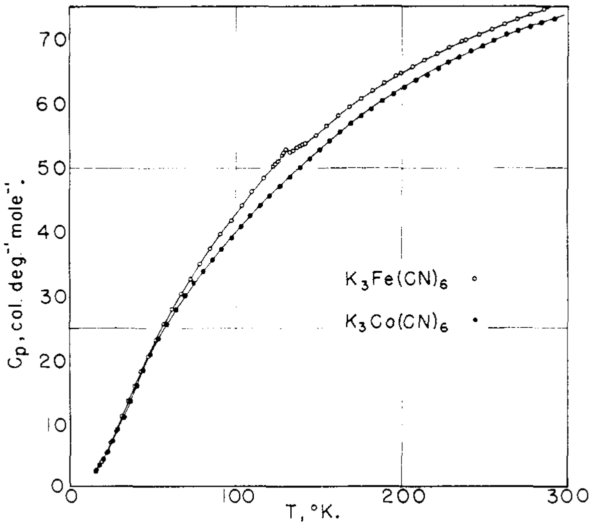

Fig. 1.—The heat capacity of $K_3Fe(CN)_6$ and of $K_3Co(CN)_6$.

Table I

The Heat Capacity of $K_3Fe(CN)_6$, Cal. Deg.$^{-1}$ Mole^{-1}

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		Series I			
16.20	2.71	84.70	37.48	189.59	63.11
19.35	4.03	90.92	39.73	196.74	64.18
22.02	5.41	97.13	41.93	199.16	64.61
24.77	6.95	103.39	44.08	206.41	65.70
28.01	8.90	109.75	46.20	213.76	66.70
31.70	11.20	116.23	48.37	221.24	67.62
35.57	13.57	122.66	50.42	228.55	68.64
39.51	15.95	129.11	52.32	235.96	69.49
43.48	18.27	135.61	52.99	238.82	69.77
47.55	20.64	141.92	53.79	246.51	70.60
52.05	23.11	148.28	55.15	254.05	71.35
56.93	25.59	154.67	56.58	261.77	72.28
61.84	27.94	161.90	58.07	269.59	73.02
66.96	30.30	168.51	59.42	277.55	73.88
72.47	32.70	175.47	60.66	285.94	74.61
78.46	35.01	182.50	61.86	294.73	75.36
		Series II			
123.24	50.57	129.88	52.86	136.30	53.22
125.49	51.04	132.04	52.46	138.39	53.40
127.71	52.12	134.18	52.65	140.47	53.57
		Series III			
128.41	52.33	129.98	52.81	131.55	52.51
129.20	52.45	130.77	52.93	132.33	52.40

Table II

The Heat Capacity of $K_3Co(CN)_6$, Cal. Deg.$^{-1}$ Mole^{-1}

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
15.51	2.34	85.86	35.63	188.47	60.32
17.92	3.37	91.55	37.42	195.14	61.47
20.25	4.37	97.38	39.23	201.94	62.51
22.87	5.60	103.12	40.96	208.86	63.62
25.77	7.24	108.89	42.60	215.62	64.44
28.92	9.13	114.71	44.22	222.23	65.46
32.44	11.26	120.53	45.77	228.18	66.28
36.35	13.58	126.39	47.27	234.97	67.23
40.43	15.98	132.27	48.69	241.94	68.10
44.53	18.43	138.41	50.12	248.77	68.89
48.92	20.83	144.57	51.50	255.77	69.76
53.54	23.33	150.52	52.90	262.92	70.72
58.21	25.71	156.55	54.26	263.14	70.76
63.87	27.91	162.94	55.62	270.13	71.35
69.37	30.12	169.40	56.86	277.41	71.88
74.84	32.08	175.68	58.16	284.84	72.60
80.31	33.86	181.93	59.20	292.13	73.17

Through the entire range of temperatures, the heat capacity of the diamagnetic salt increases smoothly without maxima, minima or discontinuities. In the neighborhood of 131°K., potassium ferricyanide exhibits in its heat capacity curve a definite maximum. At all temperatures in the range studied, the heat capacity of potassium ferricyanide lies higher than that of potassium cobalticyanide, although the two are very close below 40°K. This difference has a qualitative explanation in the fact that there is a corresponding difference in metal-to-cyanide bonding. The exceptional stability of the cobalticyanide complex as compared with the ferricyanide group is, at high temperatures, reflected in the heat capacities, to which so much is contributed by the M–CN vibrational frequency.

Entropy of the Transition.—The entropy of the gradual transition was estimated by drawing a hypothetical normal heat capacity curve for potassium ferricyanide. The slope of this curve was chosen to be that of the potassium cobalticyanide curve, with a slight shift of orientation. Ordinates were chosen so that the hypothetical curve was

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(7) D. W. Hume and I. M. Kolthoff, This Journal, **71**, 867 (1949).

(8) R. W. Blue and J. F. G. Hicks, *ibid.*, **59**, 1962 (1937).

identical with the experimental values except in the interval from 57 to 160°K. The entropy associated with the higher heat capacities in this range was found to be 0.9 ± 0.2 cal. deg.$^{-1}$ mole^{-1} by graphical integration. The estimate of the error in this quantity is somewhat arbitrary because the anomalous heat capacities extend over a range of about one hundred degrees.

This transition is considered to be magnetic in nature because of the absence of a corresponding transition in the diamagnetic potassium cobalticyanide. The failure of the energy level scheme of Howard is then attributed to interaction between ferricyanide ions. The total magnetic entropy to be expected for potassium ferricyanide at low temperatures is $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1}. At present, we can only suggest that the difference between $R \ln 2$ and the measured value of 0.9, about 0.5 cal. deg.$^{-1}$ mole^{-1}, will be lost at temperatures below 15°K. A completely satisfactory interpretation will no doubt require additional experimental evidence as well as revisions of theory.

The Entropies of $K_3Co(CN)_6$ and $K_3Fe(CN)_6$ at 298.16°K.—For the diamagnetic salt, potassium cobalticyanide, the third law of thermodynamics can be employed in a straightforward manner to give the entropy of the solid. Graphical integration of $\int C_p \, d \ln T$ between 15 and 298.16°K gives 95.19 cal. deg.$^{-1}$ mole^{-1} to which is added a Debye extrapolation with $4D(139)$ of 0.81 cal. deg.$^{-1}$ mole^{-1} for the interval from 0° to 15°K. The entropy of $K_3Co(CN)_6$ is then 96.0 ± 0.2 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.

The entropy increase between 15 and 298.16°K. for potassium ferricyanide is 99.58 cal. deg.$^{-1}$ mole^{-1} by graphical integration. To this a Debye extrapolation of 0.81 for the interval from 0 to 15°K. is added, giving 100.4 cal. deg.$^{-1}$ mole^{-1} at 298.16°K. Since the Debye extrapolation ignores any magnetic contribution, an additional term may be necessary. We have suggested that this amounts to 0.5 cal. deg.$^{-1}$ mole^{-1}; its maximum value could be 1.38 cal. deg.$^{-1}$ mole^{-1}.

Derived Thermodynamic Values.—The entropy of potassium ferricyanide may be combined with other thermodynamic data[9] to give the values listed in Table III, at 298°K. The value chosen for the entropy of potassium ferricyanide in these calculations ignores any magnetic contribution below 15°K.; any error thus introduced is trivial in comparison to the probable errors in the heats of formation and solution of the potassium ferro- and ferricyanides which may amount to several thousand calories. Standard free energies of solution were obtained from activity coefficients[10] and solubilities. The dissociation pressure[11] of $K_4Fe(CN)_6 \cdot 3H_2O$ was required for the difference in standard free energy between the anhydrous salt and the hydrate, and the potential[12] of the ferrocyanide–ferricyanide couple was used for the standard free energy difference between the ferrocyanide and ferricyanide ions.

TABLE III

	ΔH_f^0, cal. mole^{-1}	ΔF_f^0, cal. mole^{-1}	S^0, cal. deg.$^{-1}$ mole^{-1}
$K_3Fe(CN)_6$ (s)	− 41,400	− 12,400	100.4
$Fe(CN)_6^{---}$ (aq)	151,800	192,100	64
$Fe(CN)_6^{----}$ (aq)	126,700	183,900	22
$K_4Fe(CN)_6 \cdot 3H_2O$(s)		−262,300	
$K_4Fe(CN)_6$(s)	−125,100	− 90,900	98

The approximate nature of the calculated results in Table III is indicated by the fact that the entropy of $K_4Fe(CN)_6$ turns out to be less than that of $K_3Fe(CN)_6$, whereas it is probably several units higher. The errors in the entropies of the aqueous ions may be even greater; modern measurements of the heats of solution of these salts would be desirable to reduce these uncertainties. Nevertheless, the equilibrium constants calculated for the following equations are of the right order of magnitude

$$Fe(CN)_6^{---} = Fe^{+++} + 6CN^- \quad K = 10^{-31}$$
$$Fe(CN)_6^{----} = Fe^{++} + 6CN^- \quad K = 10^{-24}$$

Acknowledgments.—We are indebted to Dr. Richard Bersohn for discussions of the magnetic properties of potassium ferricyanide. This research was assisted by a contribution from the Linde Air Products Division of Union Carbide and Carbon Corporation.

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[9] National Bureau of Standard Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

[10] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

[11] H. Schottky, *Z. physik. Chem.*, **64**, 430 (1908).

[12] I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 945 (1935).