

ported<sup>27</sup> on the basis of n.m.r. investigations. Finally, Wojcicki and Farona<sup>28</sup> have just reported the isolation of the linkage isomers  $[\text{Mn}(\text{CO})_5\text{SCN}]$  and  $[\text{Mn}(\text{CO})_5\text{NCS}]$ .

(27) O. W. Howarth, R. E. Richards, and L. M. Venanzi, in press.

(28) A. Wojcicki and M. F. Farona, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964; Proceedings of the Eighth International Conference on Coordination Chemistry, Springer-Verlag, Vienna and New York, 1964, pp. 262-264.

**Acknowledgments.**—This research was supported by the U. S. Atomic Energy Commission, COO-1087-80. We also wish to thank Professors R. G. Pearson and D. F. Shriver for stimulating and helpful discussions. Special expressions of gratitude are due the latter, for advice and assistance with some of the spectral measurements, and Dr. A. J. Poë, who supervised a year of this research.

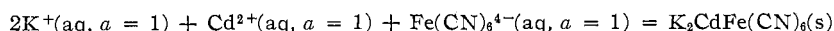
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## Free Energies of Some Heavy-Metal Ferrocyanides<sup>1</sup>

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The free energies of formation (kcal.) of the following ferrocyanides from their ions at 25° have been determined by e.m.f. measurement using cells without liquid junctions:  $\text{Pb}_2\text{Fe}(\text{CN})_6$ , -24.58;  $\text{Ag}_4\text{Fe}(\text{CN})_6$ , -60.11;  $\text{Cd}_2\text{Fe}(\text{CN})_6$ , -23.70;  $\text{K}_2\text{CdFe}(\text{CN})_6$ , -23.32;  $\text{Zn}_2\text{Fe}(\text{CN})_6$ , -21.40;  $\text{KZn}_{1.5}\text{Fe}(\text{CN})_6$ , -28.77;  $\text{K}_2\text{Cu}_2\text{Fe}(\text{CN})_6$ , -36.36; *i.e.*, the reported free energy change refers, *e.g.*, to the reaction



X-Ray diffraction data, taken from powder patterns run on analyzed samples, for several metal ferrocyanide salts are also reported.

There are few thermodynamic data on heavy-metal ferrocyanides,<sup>2-4</sup> perhaps because experimental thermodynamicists do not like to work with solids that tend to be colloidal.<sup>5</sup> We report here a method for preparing them in high purity and noncolloidal form, and the free energies of a number of them at 25° from e.m.f. measurements.

### Experimental

**Reagents.**—Solutions were made from reagent grade chemicals and nitrogen-saturated water. Lead, cadmium, and zinc amalgams were made from reagent grade metals and triple-distilled mercury, and just before use were washed with 6 *M*  $\text{HNO}_3$  and distilled water. Potassium amalgam was made by electrolysis of 2 *M* KOH with a platinum anode and mercury cathode, dried on the vacuum line, and transferred under dry nitrogen. Tetraethylammonium ferrocyanide solution was prepared by neutralizing tetraethylammonium hydroxide with freshly prepared (*vide infra*) ferrocyanic acid solution. Reagent grade  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  was recrystallized from nitrogen-saturated distilled water below 60° and stored in a darkened desiccator over saturated aqueous  $\text{NaBr} \cdot 2\text{H}_2\text{O}$ .

**Synthesis of Ferrocyanides.**—The following procedure served for preparing  $\text{Cu}_2\text{Fe}(\text{CN})_6$ ,  $\text{Zn}_2\text{Fe}(\text{CN})_6$ , and  $\text{Cd}_2\text{Fe}(\text{CN})_6$ : A column of cation-exchange resin, Dowex AG-50W-X8, was prepared in the hydrogen ion form. A 0.5 *M* solution of  $\text{K}_4\text{Fe}(\text{CN})_6$  was poured onto the column and the effluent  $\text{H}_4\text{Fe}(\text{CN})_6$  run directly into a stirred twofold excess of 0.8 *M* cupric, zinc, or cadmium acetate solution. After stirring for 1 hr. at room tempera-

ture the precipitate was washed by repeated decantation (about 15 washings) until the wash water gave no test for metal ion.

We prefer the ion-exchange method for making ferrocyanic acid to the ether adduct method described by Weiser and coworkers,<sup>5</sup> since solid ferrocyanic acid is rather susceptible to decomposition on storage. The acetate salt is used in this synthesis so that its buffer action can prevent the buildup of hydrogen ion, which if present makes the precipitate more colloidal and at high concentration can even incorporate in the crystal.

Samples of  $\text{Pb}_2\text{Fe}(\text{CN})_6$  and  $\text{Ag}_4\text{Fe}(\text{CN})_6$  were prepared by simply mixing solutions of the corresponding soluble salts, since they do not precipitate as colloids or incorporate alkali in the crystals.<sup>6-8</sup>

Cuprous ferrocyanides were prepared by making cupric sulfate solution ammoniacal, reducing it with hydroxylamine sulfate, then adding potassium ferrocyanide. We did not make use of the solid resulting when cuprous was in excess, which was pale green (possibly  $[\text{Cu}(\text{NH}_3)_2]_4\text{Fe}(\text{CN})_6$ ) but turned white on treatment with dilute sulfuric acid, had a  $\text{Cu}:\text{Fe}(\text{CN})_6$  ratio of  $4.08 \pm 0.05$ , and was presumably  $\text{Cu}_4\text{Fe}(\text{CN})_6$ . The solid we used in our measurements was precipitated when  $\text{K}_4\text{Fe}(\text{CN})_6$  was in excess, was white, and analysis showed it to have a  $\text{Cu}:\text{Fe}(\text{CN})_6$  ratio of  $2.00 \pm 0.01$ , corresponding to  $\text{K}_2\text{Cu}_2\text{Fe}(\text{CN})_6$ .

A sample of  $\text{K}_2\text{CdFe}(\text{CN})_6$  was made by preparing dilute (0.01 *M*)  $\text{CdSO}_4$  solution, almost saturated with  $\text{KNO}_3$ , and adding to it an equal volume of almost saturated  $\text{K}_4\text{Fe}(\text{CN})_6$ . The same procedure was followed in an attempt to prepare the corresponding zinc salt, as reported by Rigamonti.<sup>9</sup> However, the product was always the sesquizinc ferrocyanide,  $\text{KZn}_{1.5}\text{Fe}(\text{CN})_6$ , the same product produced by mixing stoichiometric amounts of the zinc and ferrocyanide reagents, as indicated by analysis and X-ray pattern.

(1) This work constitutes part of the Ph.D. thesis of Peter A. Rock, University of California, Berkeley, 1964.

(2) E. V. Tananaev, M. A. Glushkova, and G. B. Seifer, *Zh. Neorgan. Khim.*, **1**, 66 (1956).

(3) J. N. Pearce and L. D. Ough, *J. Am. Chem. Soc.*, **60**, 80 (1938).

(4) M. W. Grieb and W. H. Cone, *J. Phys. Colloid Chem.*, **54**, 658 (1950).

(5) Cf. H. B. Weiser, W. O. Milligan, and J. B. Bates, *ibid.*, **42**, 945 (1938).

(6) H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 1543 (1933).

(7) W. Steyer, *Z. anal. Chem.*, **74**, 108 (1928); I. M. Kolthoff, *Rec. trav. chim.*, **41**, 425 (1922); ref. 3 and 6.

(8) Our results give no evidence for the solid  $\text{KAg}_3\text{Fe}(\text{CN})_6$  sometimes reported.

(9) R. Rigamonti, *Gazz. chim. ital.*, **68**, 803 (1938).

TABLE I

|  | d-VALUES IN Å. (WITH RELATIVE INTENSITIES) OF THE EIGHT STRONGEST LINES |            |            |            |            |           |           |           |
|--|---|------------|------------|------------|------------|-----------|-----------|-----------|
| Cu <sub>2</sub> Fe(CN) <sub>6</sub> ·9H <sub>2</sub> O<br>(brown)  | 5.00 (100)  | 3.52 (100) | 2.49 (75)  | 2.23 (50)  | 7.02 (20)  | 5.77 (10) | 5.59 (10) | 4.45 (10) |
| Cu <sup>I</sup> <sub>2</sub> Cu <sup>II</sup> Fe(CN) <sub>6</sub> ·xH <sub>2</sub> O<br>(purple)                             | 5.50 (100)  | 5.09 (100) | 3.54 (50)  | 2.09 (50)  | 4.75 (10)  | 4.29 (10) | 3.17 (10) | 2.49 (10) |
| K <sub>2</sub> Cu <sub>2</sub> Fe(CN) <sub>6</sub> ·xH <sub>2</sub> O<br>(white)   | 5.97 (100)  | 4.54 (100) | 3.75 (100) | 3.29 (100) | 2.82 (100) | 4.18 (50) | 3.14 (50) | 2.67 (50) |
| K <sub>2</sub> CdFe(CN) <sub>6</sub> ·xH <sub>2</sub> O<br>(pale yellow)   | 5.10 (100)  | 3.57 (100) | 2.53 (75)  | 2.02 (50)  | 1.60 (50)  | 2.25 (40) | 1.78 (20) | 5.28 (10) |
| [(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ] <sub>2</sub> Cd <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub><br>(white) | 4.29 (100)  | 7.4 (50)   | 6.5 (50)   | 5.18 (50)  | 3.08 (50)  | 2.50 (50) | 2.48 (50) | 4.77 (10) |
| Cd <sub>2</sub> Fe(CN) <sub>6</sub> ·7H <sub>2</sub> O<br>(white)  | 6.35 (100)  | 4.12 (100) | 5.56 (50)  | 5.39 (50)  | 5.13 (10)  | 3.17 (10) | 4.76 (5)  | 4.40 (5)  |
| Ag <sub>4</sub> Fe(CN) <sub>6</sub> ·H <sub>2</sub> O<br>(white)   | 3.01 (100)  | 3.70 (100) | 2.34 (50)  | 3.22 (30)  | 1.84 (10)  | 1.73 (10) | 1.58 (10) | 1.52 (10) |
| Pb <sub>2</sub> Fe(CN) <sub>6</sub> ·3H <sub>2</sub> O<br>(white)  | 3.71 (100)  | 3.63 (100) | 6.15 (60)  | 5.61 (50)  | 3.79 (50)  | 2.58 (50) | 2.16 (50) | 3.24 (20) |
| Zn <sub>2</sub> Fe(CN) <sub>6</sub> ·2H <sub>2</sub> O<br>(white)  | 4.32 (100)  | 3.80 (100) | 2.85 (75)  | 2.63 (75)  | 2.28 (75)  | 1.90 (60) | 2.19 (50) | 2.16 (50) |
| K <sub>2</sub> Zn <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> ·8H <sub>2</sub> O<br>(white)                             | 5.40 (100)  | 4.06 (100) | 4.50 (75)  | 3.62 (60)  | 3.10 (50)  | 2.70 (50) | 2.45 (50) | 2.19 (50) |

**X-Ray Characterization of Ferrocyanides.**—The *d*-values, in Angstroms, for the eight strongest lines of the powder patterns of the several ferrocyanides are collected in Table I. The data were taken by P. A. R., but we thank Professor D. H. Templeton for the use of his X-ray apparatus and Mrs. Helena Ruben for technical guidance.

**Analysis.**—Tetraethylammonium ferrocyanide was assayed by titration with ceric ammonium sulfate. Pb<sub>2</sub>Fe(CN)<sub>6</sub> was decomposed with 3 *M* H<sub>2</sub>SO<sub>4</sub>; the PbSO<sub>4</sub> was determined gravimetrically and the ferrocyanide with ceric. Cu<sub>2</sub>Fe(CN)<sub>6</sub> was decomposed with 2 *M* KOH; the Cu(OH)<sub>2</sub> was dissolved in acid and determined iodometrically and the ferrocyanide with ceric. K<sub>2</sub>Cu<sub>2</sub>Fe(CN)<sub>6</sub> was oxidized by a brief treatment with acidic peroxydisulfate to cupric ferrocyanide, which was dissolved in aqueous ammonia and determined spectrophotometrically. The cadmium ferrocyanides were decomposed with 2 *M* KOH; the cadmium was determined gravimetrically as the pyrophosphate and the ferrocyanide with ceric. The zinc ferrocyanides were dissolved in 12 *M* HCl, the ferrocyanide was decomposed to ferric ion by prolonged boiling with HNO<sub>3</sub>, the ferric ion was extracted by isopropyl ether from 7.75 *M* HCl,<sup>10</sup> and the zinc and iron were determined conventionally. We did not find a satisfactory procedure for decomposing silver ferrocyanide, and the analysis here reported was deduced from its C, H, and N analysis. There is always the danger, in e.m.f. work, that a trace of more soluble solid contaminating the principal solid is the one actually controlling the activity of ions in solution; consequently, it is prudent to measure each cell e.m.f. at several electrolyte concentrations, so as to check by means of Nernst's equation the cell reaction. We have done so for the silver, zinc, and cadmium salts here studied (see text).

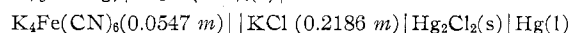
TABLE II

|                                     | Metal:ferro-<br>cyanide<br>ratio |  | Metal:ferro-<br>cyanide<br>ratio |
|-------------------------------------|----------------------------------|--|----------------------------------|
| Pb <sub>2</sub> Fe(CN) <sub>6</sub> | 2.00 ± 0.01                      | KZn <sub>1.5</sub> Fe(CN) <sub>6</sub>             | 1.50 ± 0.01                      |
| Cd <sub>2</sub> Fe(CN) <sub>6</sub> | 2.00 ± 0.03                      | K <sub>2</sub> CdFe(CN) <sub>6</sub>               | 0.98 ± 0.03                      |
| Cu <sub>2</sub> Fe(CN) <sub>6</sub> | 2.00 ± 0.01                      | K <sub>2</sub> Cu <sub>2</sub> Fe(CN) <sub>6</sub> | 2.00 ± 0.01                      |
| Zn <sub>2</sub> Fe(CN) <sub>6</sub> | 2.00 ± 0.01                      | Ag <sub>4</sub> Fe(CN) <sub>6</sub>                | 4.03 ± 0.02                      |

**Electrical Cell Measurements.**—Voltages were measured with a Leeds and Northrup Type K-3 potentiometer and a Leeds and Northrup No. 2430C galvanometer. The voltage standard was an Eppley Laboratory unsaturated Weston cell, with Bureau of Standards calibration. Electrode compartments were like that

described by Hills and Ives,<sup>11</sup> and the calomel cell was set up according to their prescription. The silver electrode was made by rapid electrolysis of AgNO<sub>3</sub> solution. The copper electrode was made by electrodepositing copper under the conditions used for its analytical determination. Air was excluded from all cells by a stream of nitrogen from a presaturator filled with cell electrolyte. Cells were kept in a water bath, at 25 ± 0.002°.

**Cells with Liquid Junction.**—In order to find out whether satisfactory measurements could be made with cells including liquid junctions of the type K<sub>4</sub>Fe(CN)<sub>6</sub> || KCl, the voltage of the cell Pb(5 wt. % in Hg) | Pb<sub>2</sub>Fe(CN)<sub>6</sub>(s) |



was measured first with a liquid-junction connector like that described by Gordon and co-workers<sup>12</sup> and then with an amalgam-junction connector like that of Harned,<sup>13</sup> using 0.01% potassium amalgam. Note that the two electrolytes had the same equivalent concentration, as required for the later application of the Lewis-Sargent equation. The e.m.f. of the cell with liquid junction was 0.6539 ± 0.0002 v., and that of the same cell without liquid junction was 0.6380 ± 0.0002 v., *i.e.*, the liquid-junction correction amounted to 15.9 mv. The Lewis-Sargent equation for a liquid junction of this type

$$E(\text{liquid junction}) = \frac{RT}{nF} \ln \frac{\Delta_2}{\Delta_1}$$

predicts a liquid-junction correction amounting to<sup>14</sup> (0.05916/4) log (126/107) = 1.1 mv. It appears that the uncritical use of the Lewis-Sargent equation could lead to substantial errors. The reason for its failure here is surely that the extrathermodynamic assumptions necessary to obtain it are very badly satisfied by pairs of salts so dissimilar as K<sub>4</sub>Fe(CN)<sub>6</sub> and KCl. However that may be, we are led to distrust the interpretation of thermodynamic measurements involving cells with liquid junctions. In the studies reported here, we have gone over entirely to cells without liquid junction.

**Cells without Liquid Junction.**—In our first measurements with a flowing amalgam junction, we followed Harned's<sup>12</sup> design. However, if the cell requires several days to become steady, his design uses up an extravagant amount of amalgam. The connector pictured in Fig. 1 avoids this difficulty and in our hands gave extremely steady and reproducible results.

(11) G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 311 (1951).

(12) W. J. Hornibrook, G. J. Janz, and A. R. Gordon, *J. Am. Chem. Soc.*, **64**, 513 (1942).

(13) H. S. Harned, *ibid.*, **51**, 417 (1929).

(14) Equivalent conductivity data from "International Critical Tables," Vol. VI, p. 234, 253.

(10) R. W. Dodson, G. J. Forney, and E. H. Swift, *J. Am. Chem. Soc.*, **58**, 2573 (1936).

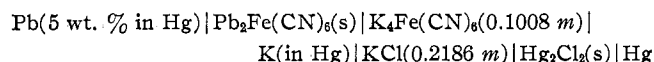
Cells of the type



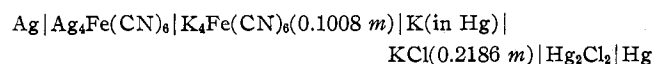
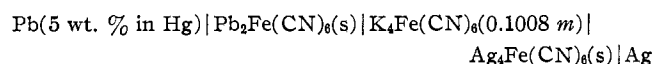
inherently involve a negligible liquid junction. They were set up using in each electrode compartment the cell electrolyte with a slurry of the corresponding sparingly soluble solid, with a connecting tube filled with the cell electrolyte and loosely plugged with cotton at each end. These cells quickly became steady and remained so for days.

## Results

**Lead Ferrocyanide.**—The potential of the Pb–Pb<sub>2</sub>–Fe(CN)<sub>6</sub> electrode was determined in two ways: by direct measurement with the cell



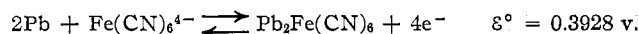
and by combination of the measurements with the two cells



The e.m.f. of the lead ferrocyanide *vs.* calomel cell was  $0.6490 \pm 0.0001$  v. (lead negative), that of the lead ferrocyanide *vs.* silver ferrocyanide cell was  $0.5348 \pm 0.0002$  v., and that of the silver ferrocyanide *vs.* calomel cell was  $0.1142 \pm 0.0003$  v., so that the two determinations agree within our experimental uncertainty of a few tenths of a millivolt.

A two-phase amalgam was used as the lead electrode<sup>15</sup> because it gives a constant metal activity over its range of existence and therefore does not have to be analyzed precisely. This lead ferrocyanide electrode is simple to prepare, comes to equilibrium rapidly, and is very stable, so it is a satisfactory reference electrode for e.m.f. studies with ferrocyanides.

Making use of the auxiliary data that the e.m.f. of the Pb(5 wt. % in Hg)|satd. PbCl<sub>2</sub>|Pb cell is<sup>15</sup> 0.0058 v., that the mean activity coefficient<sup>16</sup> of 0.1008 *m* K<sub>4</sub>Fe(CN)<sub>6</sub> is 0.1384 and that of 0.2186 *m* KCl is 0.712, and that the standard oxidation potential of the calomel half-cell is<sup>10</sup> –0.2680 v., we compute the standard oxidation potential of the half-cell.



**Silver Ferrocyanide.**—The cells used for determining the potential of the Ag–Ag<sub>4</sub>Fe(CN)<sub>6</sub> electrode were referred to in the preceding section. The e.m.f. of the lead ferrocyanide *vs.* silver ferrocyanide cell was the same, within less than 1 mv., for 0.05, 0.1, and 0.25 *m* K<sub>4</sub>Fe(CN)<sub>6</sub>, as it ought to be if the solid silver ferrocyanide controlling the activity of Ag<sup>+</sup> is in fact Ag<sub>4</sub>Fe(CN)<sub>6</sub> and not one incorporating potassium ion. Silver ferrocyanide is somewhat photosensitive, and if the cell was not protected from direct light the solid became grayish or blue while the cell voltage became erratic. The measurements reported here were made

(15) W. R. Carmody, *J. Am. Chem. Soc.*, **51**, 2905 (1929).

(16) Interpolated from tabulations in R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, New York, N. Y., 1955.

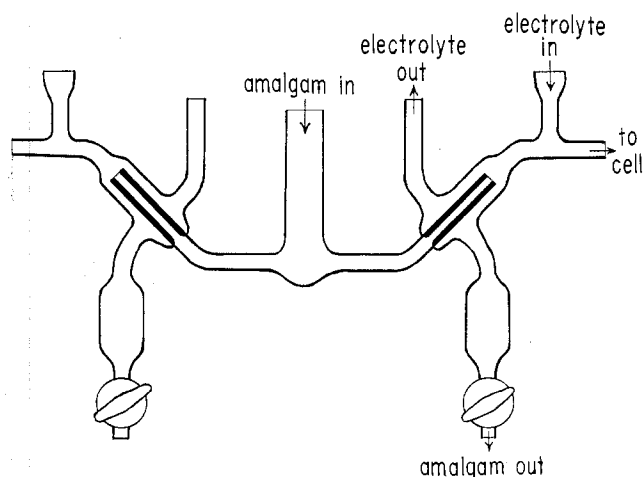
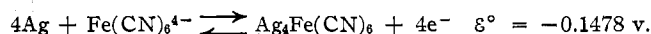


Fig. 1.—Flowing amalgam junction.

in subdued light and the solid was white at the end of the measurement.

From the observed e.m.f. of the lead ferrocyanide *vs.* silver ferrocyanide cell,  $0.5348 \pm 0.0002$  v. (lead negative), and the standard oxidation potential here reported for the lead ferrocyanide half-cell, we compute for the silver ferrocyanide half-cell



**Mercury Ferrocyanides.**—Mercurous ferrocyanide is precipitated as a bright yellow solid, but within less than 1 hr. it decomposes to mercuric ferrocyanide and metallic mercury, so it is not suitable for e.m.f. study. Mercuric ferrocyanide is readily precipitated as a deep yellow solid, but, upon washing for several days to free it of adsorbed ions, invariably decomposes to give Prussian blue. Emschwiler<sup>17</sup> has already noticed that mercuric ion catalyzes the decomposition of ferrocyanide to Prussian blue, and since we have seen the same decomposition with Ag<sub>4</sub>Fe(CN)<sub>6</sub> and Cd<sub>2</sub>Fe(CN)<sub>6</sub> allowed to stand a number of days, we conjecture that the reaction is common to all metallic ions themselves forming comparatively stable cyanides or cyanide complexes. The limited stability of mercuric ferrocyanide discouraged us from cell measurements with it.

**Cadmium Ferrocyanides.**—The potential of the Cd–Cd<sub>2</sub>Fe(CN)<sub>6</sub> electrode was determined with the cell Cd(11 wt. % in Hg)|Cd<sub>2</sub>Fe(CN)<sub>6</sub>(s)|[(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>4</sub>Fe(CN)<sub>6</sub>(aq)|Pb<sub>2</sub>Fe(CN)<sub>6</sub>(s)|Pb(5 wt. % in Hg)

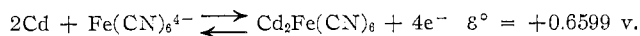
The cadmium amalgam was two-phase.<sup>18</sup> Tetraethylammonium ferrocyanide was used as the cell electrolyte, with the idea that the large (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup> ion would not incorporate in the Cd<sub>2</sub>Fe(CN)<sub>6</sub> lattice; this idea proved successful, since we obtained the same cell e.m.f.,  $0.2224 \pm 0.0002$  v. (cadmium negative), with 0.0056, 0.0280, 0.0601, and 0.1258 *M* tetraethylammonium ferrocyanide solutions. The e.m.f. became steady within 1 or 2 hr. It must be recorded,

(17) G. Emschwiler, *Compt. rend.*, **242**, 1610 (1956).

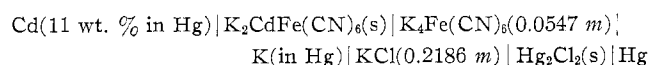
(18) H. S. Harned and M. E. Fitzgerald, *J. Am. Chem. Soc.*, **58**, 2624 (1936).

however, that if e.m.f. measurement was continued for a longer time, it rather suddenly began to drift upward, the onset of the drift occurring in from one to several days; and, concomitantly, the solid phase changed, giving a different X-ray pattern and an analysis corresponding to bis(tetraethylammonium) cadmium ferrocyanide.

From the observed e.m.f., the standard oxidation potential here reported for the lead ferrocyanide half-cell, and the known<sup>17</sup> e.m.f. of the Cd *vs.* Cd(11 wt. % in Hg) cell, 0.0505 v., we compute for the dicadmium ferrocyanide half-cell

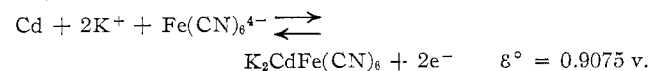


The potential of the Cd-K<sub>2</sub>CdFe(CN)<sub>6</sub> electrode was determined with the cell

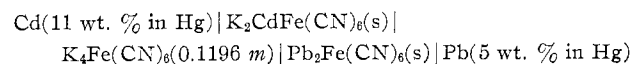


The observed e.m.f., steady for several days, was 0.9836 ± 0.0003 v. (cadmium negative).

The mean activity coefficient of 0.0547 *m* K<sub>4</sub>Fe(CN)<sub>6</sub> cannot be extrapolated accurately enough from the tables of Robinson and Stokes,<sup>15</sup> so we measured it by setting up the cell Pb(amalgam) *vs.* calomel, as in the first paragraph of this section, but with 0.0547 *m* K<sub>4</sub>Fe(CN)<sub>6</sub>. From the observed e.m.f., 0.6380 ± 0.0001 v., we compute the mean activity coefficient to be 0.181, in adequate agreement with the value estimated from a log-log plot of Robinson and Stokes' data, namely 0.189. From the observed e.m.f. and our value of the activity coefficient, we compute for the dipotassium cadmium ferrocyanide half-cell

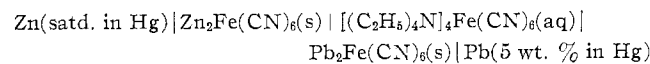


As a check that the solid cadmium ferrocyanide controlling the activity of Cd<sup>2+</sup> was in fact K<sub>2</sub>CdFe(CN)<sub>6</sub>, we measured the e.m.f. of a cell with a different concentration of electrolyte, namely



From its observed e.m.f., 0.369 ± 0.001 v. (cadmium negative), we compute the standard oxidation potential of the dipotassium cadmium ferrocyanide half-cell within 1 mv. of the value previously obtained.

**Zinc Ferrocyanides.**—The potential of the Zn-Zn<sub>2</sub>Fe(CN)<sub>6</sub> electrode was determined with the cell

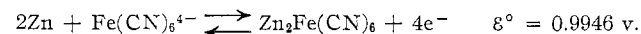


After 1–2 days to become steady, this cell gave an e.m.f. of 0.6076 ± 0.0003 v. (zinc negative), the same e.m.f. being obtained with 0.0280 and 0.0601 *M* tetraethylammonium ferrocyanide.

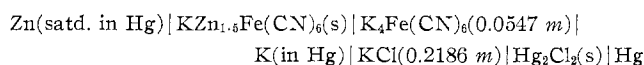
From this observed e.m.f., our standard oxidation potential of the lead ferrocyanide half-cell, and Clayton and Vosburgh's<sup>19</sup> observation that the e.m.f. is zero

(19) W. J. Clayton and W. C. Vosburgh, *J. Am. Chem. Soc.*, **68**, 2093 (1936).

between metallic zinc and saturated zinc amalgam, we compute for the zinc ferrocyanide half-cell

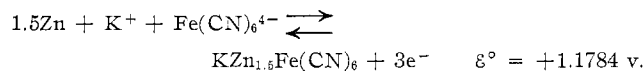


The potential of the Zn-KZn<sub>1.5</sub>Fe(CN)<sub>6</sub> electrode was determined with the cell

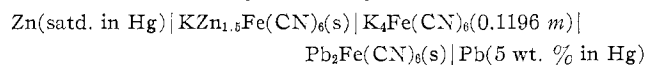


which reached a steady e.m.f. in 1–2 days. The e.m.f. was 1.3907 ± 0.0020 v. (zinc negative), using several different preparations of solid sesquizinc ferrocyanide.

From this observed e.m.f. and the value already used for the mean activity coefficient of the potassium ferrocyanide electrolyte, we compute for the potassium sesquizinc ferrocyanide half-cell



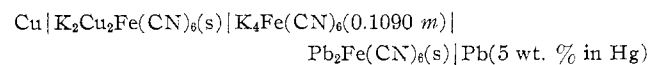
As a check that the solid zinc ferrocyanide controlling the activity of Zn<sup>2+</sup> was in fact KZn<sub>1.5</sub>Fe(CN)<sub>6</sub>, we measured the e.m.f. of a cell with a different concentration of electrolyte, namely



From its observed e.m.f., 0.7595 ± 0.0005 v. (zinc negative), we compute the standard oxidation potential of the potassium sesquizinc half-cell within 1 mv. of the value previously obtained.

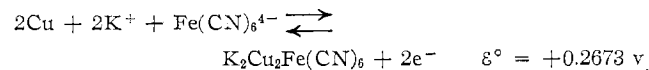
**Copper Ferrocyanides.**—Pure Cu<sub>2</sub>Fe(CN)<sub>6</sub> was prepared without difficulty by the recipe we have given, but a cell set up with it in contact with metallic copper drifted at the rate of some 20 mv./hr., for hours on end, and a look at the cell compartment showed that a purple solid was being formed. This same solid was formed upon merely mixing Cu<sub>2</sub>Fe(CN)<sub>6</sub> with powdered copper in the presence of ferrocyanide solution, and analysis showed it to be Cu<sub>3</sub>Fe(CN)<sub>6</sub>. It is, presumably, dicuprous cupriferoferrocyanide, *i.e.*, the analog of K<sub>2</sub>CuFe(CN)<sub>6</sub> with cuprous ions replacing alkali ions in the interstitial positions. Its formation precluded our making further e.m.f. studies with Cu<sub>2</sub>Fe(CN)<sub>6</sub>.

A sample of K<sub>2</sub>Cu<sub>2</sub>Fe(CN)<sub>6</sub> was prepared as described in the Experimental section, and its electrode potential was determined with the cell



Although this cuprous ferrocyanide is sensitive to oxidation by air, being converted thereby to the purple Cu<sub>3</sub>Fe(CN)<sub>6</sub>, it remained white in the cell for many days if air was excluded, the e.m.f. gradually becoming steady and remaining so for several days at 0.2200 ± 0.0002 v. (lead negative).

From this observed e.m.f. and the standard oxidation potential for lead ferrocyanide and mean activity coefficient previously used, we compute for the dipotassium dicuprous ferrocyanide half-cell



So far as we are aware, the salts  $\text{Cu}_3\text{Fe}(\text{CN})_6$  (purple),  $\text{Cu}_4\text{Fe}(\text{CN})_6$  (white, not red-brown), and  $\text{K}_2\text{Cu}_2\text{Fe}(\text{CN})_6$  (white) have not previously been reported.

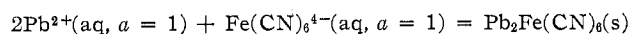
### Discussion

Adopting Latimer's<sup>20</sup> values for the free energies of ions, we calculate from our results the corresponding solubility products and free energies of formation from the ions and from the elements collected in Table III.

TABLE III  
DERIVED THERMODYNAMIC PROPERTIES

| Solid <sup>a</sup>                            | $K_{sp}$ (25°)        | $\Delta F^\circ$<br>(resp.<br>ions),<br>kcal. | $\Delta F^\circ$<br>(resp.<br>elements),<br>kcal. |
|---|-----------------------|---|---|
| $\text{Pb}_2\text{Fe}(\text{CN})_6$           | $9.6 \times 10^{-19}$ | -24.58  | 134.2   |
| $\text{Ag}_4\text{Fe}(\text{CN})_6$           | $8.6 \times 10^{-46}$ | -60.11  | 184.0   |
| $\text{Cd}_2\text{Fe}(\text{CN})_6$           | $4.2 \times 10^{-18}$ | -23.70  | 109.5   |
| $\text{K}_2\text{CdFe}(\text{CN})_6$          | $8.1 \times 10^{-18}$ | -23.32  | -6.4  |
| $\text{Zn}_2\text{Fe}(\text{CN})_6$           | $2.1 \times 10^{-16}$ | -21.40  | 78.6  |
| $\text{KZn}_{1.5}\text{Fe}(\text{CN})_6$      | $8.2 \times 10^{-22}$ | -28.77  | 21.4  |
| $\text{K}_2\text{Cu}_2\text{Fe}(\text{CN})_6$ | $2.2 \times 10^{-27}$ | -36.36  | 23.1  |

<sup>a</sup> Our analytical C, H, and N data indicate that the lead salt is a trihydrate, the silver salt a monohydrate, the cadmium salt a heptahydrate, the zinc salt a dihydrate, the sesquizinc salt a tetrahydrate. These free energy data do not include the contribution from water of crystallization, since at the cell electrolyte concentrations used the correction is in all cases within the experimental error.  $\Delta F^\circ$  (resp. ions) refers, *e.g.*, to the process



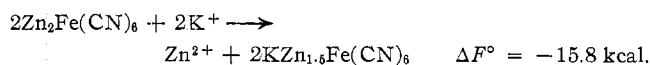
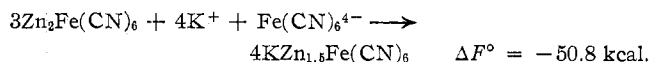
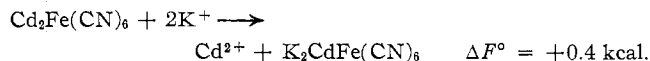
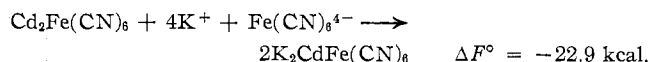
Tananaev's<sup>2</sup> value for the free energy of  $\text{Pb}_2\text{Fe}(\text{CN})_6$ , upon which his values for the other ferrocyanides rest, is -19.7 kcal. with respect to the ions. We are unable to explain the considerable discrepancy between his results and ours, although it seems to us that his technique, depending on the relative amounts of  $\text{PbSO}_4$  and  $\text{Pb}_2\text{Fe}(\text{CN})_6$  precipitated from a solution containing  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_4\text{Fe}(\text{CN})_6$ , might suffer from slowness to reach equilibrium and from analytical errors arising from adsorption. Tananaev's values for  $\text{Cd}_2\text{Fe}(\text{CN})_6$ , -22.5 kcal., and  $\text{Zn}_2\text{Fe}(\text{CN})_6$ , -21.0 kcal., are in rather good agreement with ours, but the agreement is probably fortuitous, both because his are based upon his value for lead ferrocyanide and because his assumption that  $\text{Li}^+$  does not incorporate in heavy-metal ferrocyanides is invalid.<sup>21</sup> Pearce and Ough's<sup>3</sup> measurement on  $\text{Ag}_4\text{Fe}(\text{CN})_6$  leads to a free energy of -55.8 kcal. with respect to the ions. Their result differs from ours by rather more than we can ascribe to their erroneous liquid-junction correction, and since they did not comment on the need to work in subdued light with silver ferrocyanide electrodes

(20) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952.

(21) R. Rigamonti, *Gazz. chim. ital.*, **67**, 148 (1937); S. Saito, *Bull. Inst. Phys.-Chem. Res. (Tokyo)*, **11**, 593 (1932).

we rather suspect that their cells may have been affected by sunlight. Grieb and Cone's<sup>4</sup> value for  $\text{KZn}_{1.5}\text{Fe}(\text{CN})_6$  leads to a free energy for that solid of -44 kcal. with respect to the ions, but their cell involves such large and uncertain liquid-junction and activity coefficient corrections, to say nothing of uncertainty as to what the solid phase is, that we cannot assign it much weight.

When we started this investigation, we fully expected to find solid solutions of the type  $\text{K}_{2x}\text{Cd}_{2-x}\text{Fe}(\text{CN})_6$  and  $\text{K}_{2x}\text{Zn}_{2-x}\text{Fe}(\text{CN})_6$ , with  $0 < x < 1$ . However, the observation that the dicadmium and dizinc ferrocyanides are not isomorphous with the corresponding alkali-containing ferrocyanides (*cf.* Table I) immediately makes solid-solution formation implausible, and our analytical and e.m.f. results are entirely consistent with the existence of well-defined stoichiometric  $\text{K}_2\text{CdFe}(\text{CN})_6$  and  $\text{KZn}_{1.5}\text{Fe}(\text{CN})_6$ . From our thermodynamic data we can calculate the free energy changes for the transposition of the dicadmium into monocadmium and dizinc into sesquizinc ferrocyanides.



These calculations show that  $\text{K}_2\text{CdFe}(\text{CN})_6$  and  $\text{KZn}_{1.5}\text{Fe}(\text{CN})_6$  are the stable solid phases in the presence of excess potassium ferrocyanide solution. Moreover,  $\text{KZn}_{1.5}\text{Fe}(\text{CN})_6$  is the stable solid in the presence of even a small concentration of  $\text{K}^+$ , without excess soluble ferrocyanide. Cadmium ferrocyanide,  $\text{Cd}_2\text{Fe}(\text{CN})_6$ , on the other hand, will not suffer transposition to  $\text{K}_2\text{CdFe}(\text{CN})_6$  in the absence of soluble ferrocyanide until the ratio  $(\text{K}^+)^2/(\text{Cd}^{2+})$  reaches a value of approximately 2. We suggest that this transposition accounts for the observation by Britton and Dodd<sup>6</sup> that the electrometric titration of  $\text{Cd}^{2+}$  with  $\text{Fe}(\text{CN})_6^{4-}$  gave an "early" break not corresponding to any particular stoichiometry; such behavior would be observed if the solid formed in the earliest stages were  $\text{Cd}_2\text{Fe}(\text{CN})_6$ , but at an intermediate stage the  $(\text{K}^+)^2/(\text{Cd}^{2+})$  ratio became high enough so that the solid was transposed, at least partially in the time available, into  $\text{K}_2\text{CdFe}(\text{CN})_6$ .

**Acknowledgment.**—Peter A. Rock is pleased to acknowledge the tenure of a Woodrow Wilson Fellowship during 1961–1962 and of National Science Foundation Predoctoral Fellowships during 1962–1963 and 1963–1964.