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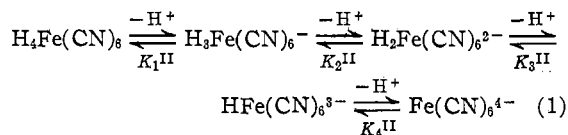
The Protonation of Hexacyanoferrates^{1,2}

By JOSEPH JORDAN AND GORDON J. EWING

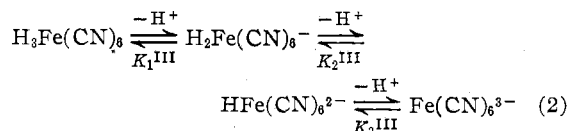
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The protonation of ferrocyanide and ferricyanide ions has been investigated by potentiometric pH titration in aqueous solutions. The precision and accuracy of the actual pH measurements was such that the limits of confidence were comparable to those inherent in the reference scales defined by the National Bureau of Standards. The successive ionization constants of (a) ferricyanic acid, $\text{H}_3\text{Fe}^{\text{III}}(\text{CN})_6$, and (b) ferrocyanic acid, $\text{H}_4\text{Fe}^{\text{II}}(\text{CN})_6$, were evaluated at 25° yielding: (a) $K_1^{\text{III}} > K_2^{\text{III}} > K_3^{\text{III}} > 0.1$; (b) $K_1^{\text{II}} > K_2^{\text{II}} > 0.1$; $K_3^{\text{II}} = (6 \pm 2) \times 10^{-3}$; $K_4^{\text{II}} = (6.7 \pm 0.3) \times 10^{-5}$. This corresponds to virtually complete dissociation of ferricyanic acid whenever $\text{pH} > 1$, whereas ferrocyanide is extensively protonated: At $\text{pH} \approx 1$ the concentration of $\text{Fe}(\text{CN})_6^{4-}$ is negligible and $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ is the predominating species. Formal potentials, E_0' , of the ferrocyanide-ferricyanide couple in acidic media were computed utilizing protonation data from this study in conjunction with the standard potentials assigned in Latimer to the unprotonated oxidation-reduction couple. The calculated values of E_0' in 0.1 and 0.5 *M* sulfuric acid were identical with corresponding experimental data. This agreement offers definitive verification of the standard potential as well as the protonation thermodynamics reported herein. The entropies of protonation of the ions $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ and $\text{HFe}^{\text{II}}(\text{CN})_6^{3-}$ differed by 6 cal./mole-deg., which approximates the entropy of fusion of water. A reasonable interpretation is postulated accordingly, suggesting a corresponding difference in the amount of hydration-water "immobilized" around each ion.

One hundred and forty years ago Berzelius isolated, from an acidified aqueous potassium ferrocyanide solution,³ a solid which analyzed as $\text{H}_4\text{Fe}(\text{CN})_6$. A century later Kolthoff⁴ published evidence that the ferrocyanide ion may be protonated in aqueous solution. These findings suggest that the ferrocyanide ion may exhibit, in principle, the behavior of a quadrivalent Brønsted base. The corresponding base strengths can be expressed conveniently in terms of the successive ionization constants of the respective conjugate acids, *viz.*



A priori, a similar sequence of proton transfer equilibria is conceivable for ferricyanide, as explicated in eq. 2.



It has been reported⁵ that $\text{H}_3\text{Fe}(\text{CN})_6$ has in-

deed been prepared. The *K*'s in eq. 1 and 2 denote equilibrium constants of the type

$$K_3^{\text{II}} = \frac{a_{\text{H}^+} a_{\text{HFe}(\text{CN})_6^{3-}}}{a_{\text{H}_2\text{Fe}(\text{CN})_6^{2-}}} = a_{\text{H}^+} \frac{[\text{HFe}(\text{CN})_6^{3-}] f_3^{\text{II}}}{[\text{H}_2\text{Fe}(\text{CN})_6^{2-}] f_2^{\text{II}}} \quad (3)$$

$$K_4^{\text{II}} = \frac{a_{\text{H}^+} a_{\text{Fe}(\text{CN})_6^{4-}}}{a_{\text{HFe}(\text{CN})_6^{3-}}} = a_{\text{H}^+} \frac{[\text{Fe}(\text{CN})_6^{4-}] f_4^{\text{II}}}{[\text{HFe}(\text{CN})_6^{3-}] f_3^{\text{II}}} \quad (4)$$

$$K_3^{\text{III}} = \frac{a_{\text{H}^+} a_{\text{Fe}(\text{CN})_6^{3-}}}{a_{\text{HFe}(\text{CN})_6^{2-}}} = a_{\text{H}^+} \frac{[\text{Fe}(\text{CN})_6^{3-}] f_3^{\text{III}}}{[\text{HFe}(\text{CN})_6^{2-}] f_2^{\text{III}}} \quad (5)$$

etc., where the superscripts refer to the oxidation state of iron. The subscripts of the activity coefficients (*f*) specify the charge of the ionic species to which they refer, while the subscripts of the equilibrium constants (*K*) identify the ionization step involved. Values of K_4^{II} at 25° have been reported previously,⁶⁻⁸ ranging from 5×10^{-5} to 6.8×10^{-5} . Nekrasov and Zotov⁸ have estimated $K_3^{\text{II}} \approx 10^{-3}$ and indicated that the trinegative ferricyanide ion was a weak Brønsted base. Definitive and complete knowledge of the protonation thermodynamics of the hexacyanoferrates is crucial in the quantitative treatment and evaluation of important reversible electrode potentials. In view of this situation, an extensive investigation has been carried out in order to re-assess quantitatively the importance of the various proton-transfer

(1) Based on a doctoral thesis by the junior author.
(2) Work supported by the U. S. Atomic Energy Commission under Contract AT(30-1)2133 with the Pennsylvania State University.
(3) J. J. Berzelius, *Schw. J.*, **30**, 44 (1820).
(4) I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **110**, 143 (1920).
(5) See, e.g., W. M. Cumming and D. G. Brown, *J. Soc. Chem. Ind., Japan*, **44**, 110T (1925).

(6) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 955 (1935).

(7) O. E. Lanford and S. J. Kiehl, *ibid.*, **45**, 300 (1941).

(8) B. Nekrasov and G. Zotov, *J. Appl. Chem. USSR*, **14**, 264 (1941).

equilibria governing the behavior of the hexacyanoferrates. Ionization constants at various ionic strengths have been evaluated to the limits of accuracy accessible by current experimental methods. The results reported in this study indicate that in 0.5 *M* aqueous sulfuric acid (which is a favorite medium for carrying out many analytically important oxidation-reduction titrations), as much as 98% of the total ferrocyanide may exist as the diprotonated species. The thermochemistry of the protonation of the hexacyanoferrates also has been studied, with the corresponding heats of dissociation being determined by an accurate "thermometric titration" procedure. Entropies have been calculated and interpreted in terms of reasonable solvation assumptions.

Methodology

Determination of Ionization Constants.—The equilibrium constants in eq. 1 and 2 were estimated or determined from accurate acidimetric titration curves. Dilute aqueous solutions ($\approx 10^{-3} F$) of known concentration of potassium ferricyanide and of potassium ferrocyanide were titrated with standard 0.1 *F* aqueous hydrochloric acid and the concomitant change in the pH was monitored with a precision and accuracy of ± 0.003 pH unit. Rigorous treatment (*vide infra*) of the data permitted the determination (within the specified limits of precision) of all *K* values smaller than 10^{-1} .

One-hundred-ml. samples of hexacyanoferrate solution were titrated. Whenever desired, the ionic strength was maintained at constant levels by adding appropriate concentrations of potassium chloride. The titrant, 3 to 4 ml. total, was delivered with the aid of a microburet which was precise and accurate to 0.005 ml. Volume changes occurring during the titrations and variations in ionic strength (when applicable, see Fig. 2, curve IV) were taken into account in calculating the ionization constants. The pH varied in a range between 2.5 and 6 and was determined with a Beckman Model GS pH meter. A Beckman No. 39270 fiber type saturated calomel half-cell and a Beckman No. 39290 glass electrode served as reference and indicator electrodes, respectively. The pH meter was calibrated with reference to a 0.050 *M* potassium hydrogen phthalate solution (a recommended NBS pH scale standard⁹) which has been assigned a pH of 4.008 ± 0.003 at 25°.

Determination of Heats of Protonation.—The heats of protonation of the hexacyanoferrates were determined by means of thermometric "enthalpy" titrations. Dilute (10^{-3} to $10^{-2} F$) hexacyanoferrate solutions were titrated with a strong acid under adiabatic conditions. The titrant was dispensed from a constant-speed motor-driven, syringe buret. Any temperature change occurring during a titration resulted in a potential unbalance across a thermistor bridge which was monitored automatically

with the aid of a recording d.c. millivoltmeter. The method, which has been described previously,^{10,11} yielded plots of temperature change *vs.* volume of titrant. The temperature sensing system had a sensitivity threshold of 0.0001°, corresponding to a detection limit of 0.01 kcal./mole in terms of heat of reaction.

Materials.—Reagent grade chemicals were used throughout. Potassium ferrocyanide and potassium ferricyanide were recrystallized twice from aqueous solution, yielding material of primary standard purity. Triply distilled, degassed water served as the solvent. To obviate air oxidation, experiments were carried out in an argon atmosphere.

Reference States and Temperatures.—In all potentiometric titrations, temperatures were maintained at $25.00 \pm 0.02^\circ$. In the enthalpy titrations the initial temperatures also were adjusted to $25.00 \pm 0.02^\circ$. The actual temperature at the beginning of each specific thermometric titration was constant within $\pm 0.0001^\circ$. Thus the thermodynamic parameters reported in this paper correspond to virtually isothermal conditions at 25.0°, since their variability is negligible within $\pm 0.1^\circ$. Potentials have been referred to the normal hydrogen electrode, which, of course, has no effect on the values reported for changes in thermodynamic quantities (*e.g.*, ΔH , ΔF , and ΔS).

Results

Potentiometric titrations of 0.01 *F* potassium ferricyanide with hydrochloric acid showed no evidence of protonation. Individual points on the titration curve of ferricyanide coincided with an analogous blank titration of pure water to within 0.05 pH unit. Pertinent calculations indicated that all three ionization constants of $H_3Fe(CN)_6$ must necessarily be larger than 0.1 in order to account for the results obtained. Consequently, it is possible to specify the order of magnitude of the ionization constants of $H_3Fe(CN)_6$ as

$$K_1^{III} > K_2^{III} > K_3^{III} > 0.1 \quad (6)$$

In contradistinction to the behavior of ferricyanide, titrations of 0.001 *F* potassium ferrocyanide exhibited significant differences from "the dilution curve" of hydrochloric acid. Figure 1 is a representative "ferrocyanide protonation titration." The titration curves obtained were inflectionless and concave upward throughout. This gives some indication of the relative values of the constants, since in order to obtain discrete inflections all dissociation constants must be less than 10^{-4} and each pair of successive constants must differ by 10^4 or more.¹² Speakman¹³ has described a

(10) J. Jordan and T. G. Alleman, *Anal. Chem.*, **29**, 9 (1957).

(11) J. Jordan, J. Meier, E. J. Billingham, Jr., and J. Pendergrast, *ibid.*, **32**, 651 (1960).

(12) I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1931, pp. 36-37.

(13) J. C. Speakman, *J. Chem. Soc.*, 855 (1940).

(9) D. I. Hitchcock, Natl. Bur. Std. (U.S.), Circ. 524, 1953, p. 205.

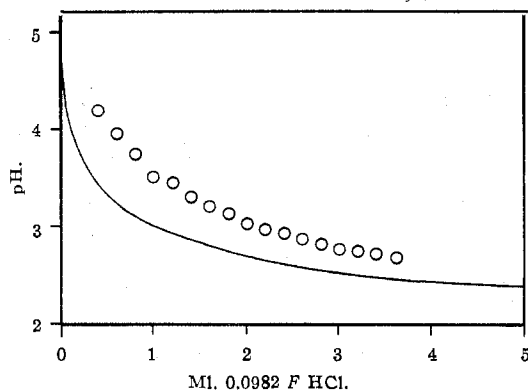


Fig. 1.—Protonation titration of 100 ml. of 0.001 *F* potassium ferrocyanide; circles—experimental points obtained with ferrocyanide; continuous line—calculated curve for pure water.

method whereby the ionization constants of weak dibasic acids can be determined from inflectionless titration curves of the type obtained in this study. Speakman's mathematical treatment (*vide infra*) fitted satisfactorily our ferrocyanide data, indicating that the ionization constants K_3^{II} and K_4^{II} were necessary and sufficient to account for the observed protonation behavior of the ion $\text{Fe}(\text{CN})_6^{4-}$. In other words, the following approximation was warranted under experimental conditions prevailing in this study

$$b \equiv [\text{Fe}(\text{CN})_6^{4-}] + [\text{HFe}(\text{CN})_6^{3-}] + [\text{H}_2\text{Fe}(\text{CN})_6^{2-}] + [\text{H}_3\text{Fe}(\text{CN})_6^-] + [\text{H}_4\text{Fe}(\text{CN})_6] \approx [\text{Fe}(\text{CN})_6^{4-}] + [\text{HFe}(\text{CN})_6^{3-}] + [\text{H}_2\text{Fe}(\text{CN})_6^{2-}] \quad (7)$$

the contribution of $\text{H}_3\text{Fe}(\text{CN})_6^-$ and $\text{H}_4\text{Fe}(\text{CN})_6$ being negligible. Using approximation 7, Speakman's treatment was applied as follows to the specific case of the titration of potassium ferrocyanide with hydrochloric acid. Considering the applicable mass balance and electroneutrality relationships 8 and 9,

$$[\text{H}_2\text{Fe}(\text{CN})_6^{2-}] = \frac{1}{2}[\text{Cl}^-] + [\text{OH}^-] - [\text{H}^+] - [\text{HFe}(\text{CN})_6^{3-}] \quad (8)$$

$$[\text{H}^+] + [\text{K}^+] = [\text{Cl}^-] + [\text{OH}^-] + 4[\text{Fe}(\text{CN})_6^{4-}] + 3[\text{HFe}(\text{CN})_6^{3-}] + 2[\text{H}_2\text{Fe}(\text{CN})_6^{2-}] \quad (9)$$

and solving (3), (4), (8), and (9) as a simultaneous system of equations, expression 10 was obtained.

$$\left(\frac{2b}{L} - 1\right) (a_{\text{H}^+})^2 \frac{f_4^{\text{II}}}{f_2^{\text{II}}} = K_3^{\text{II}} \left(1 - \frac{b}{L}\right) (a_{\text{H}^+}) \frac{f_4^{\text{II}}}{f_3^{\text{II}}} + K_3^{\text{II}} K_4^{\text{II}} \quad (10)$$

where

$$L \equiv [\text{Cl}^-] + [\text{OH}^-] - [\text{H}^+] \quad (11)$$

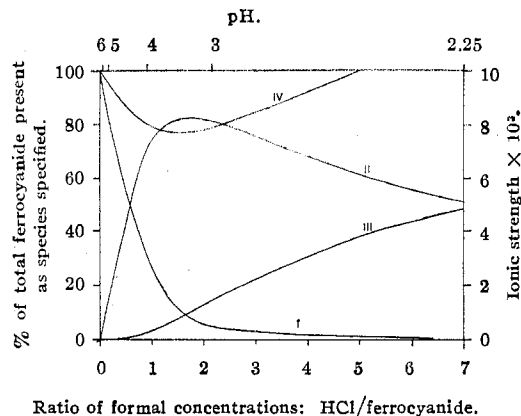


Fig. 2.—Relative abundance of hexacyanoferrate(II) species in 0.001 *F* aqueous $\text{K}_4\text{Fe}(\text{CN})_6$ in the presence of varying amounts of hydrochloric acid: I, $\text{Fe}(\text{CN})_6^{4-}$; II, $\text{HFe}(\text{CN})_6^{3-}$; III, $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$; IV, ionic strength.

Equation 10 is of the form

$$Y = K_3^{\text{II}} X + K_3^{\text{II}} K_4^{\text{II}} \quad (12)$$

permitting the graphical determination of K_3^{II} and K_4^{II} from the slope and intercept of a plot of

$$X \equiv (1 - b/L)(a_{\text{H}^+})(f_4^{\text{II}}/f_3^{\text{II}}) \quad (13)$$

vs.

$$Y \equiv (2b/L - 1)(a_{\text{H}^+})^2 (f_4^{\text{II}}/f_2^{\text{II}}) \quad (14)$$

X and Y are experimentally accessible for each point of a titration curve (*e.g.*, Fig. 2), except for the activity coefficient ratios. However, eq. 10 permits the *direct* determination from actual experimental data of the "apparent constants"

$$k_3^{\text{II}} \equiv k_3^{\text{II}} \frac{f_2^{\text{II}}}{f_3^{\text{II}}}; \quad k_4^{\text{II}} \equiv K_4^{\text{II}} \frac{f_8^{\text{II}}}{f_4^{\text{II}}} \quad (15)$$

at a given ionic strength. In applying eq. 12, the uncertainty in the value obtained for K_3^{II} necessarily affects the reliability of the value assigned to K_4^{II} . Actually K_4^{II} , being smaller than K_3^{II} , should be measurable with a better precision and accuracy than the latter. Rearrangement of eq. 13 to

$$X/Y = -K_4^{\text{II}}/Y + 1/K_3^{\text{II}} \quad (16)$$

yielded an expression which was amenable to a graphic evaluation of K_4^{II} that did not depend on a previously assigned value of K_3^{II} . However, eq. 16 did not lend itself to the precise determination of K_3^{II} because of uncertainties involved in reading the intercept. Consequently, K_3^{II} was determined from the slope of the line corresponding to eq. 12 and K_4^{II} was determined from a plot of eq. 16.

The values of the ionization constants that were

TABLE I
FERROCYANIC ACID DISSOCIATION CONSTANTS AT 25°

Ionic strength ^a	k_3^{II}	k_4^{II}
0.01 ^b	$(7 \pm 2) \times 10^{-3}$	$(1.4 \pm 0.2) \times 10^{-4}$
.02 ^b	$(3 \pm 1) \times 10^{-2}$	$(1.8 \pm 0.1) \times 10^{-4}$
.1 ^b	$(6 \pm 2) \times 10^{-2}$	$(6.8 \pm 0.3) \times 10^{-4}$
.5 ^b	$(1.2 \pm 0.5) \times 10^{-2}$	$(1.9 \pm 0.1) \times 10^{-3}$
Zero ^c	$K_3^{\text{II}} = (6 \pm 2) \times 10^{-3}$	$K_4^{\text{II}} = (6.7 \pm 0.3) \times 10^{-3}$

^a Controlled by the presence of appropriate concentrations of potassium chloride. ^b Determined experimentally. ^c Extrapolated to infinite dilution.

determined are listed in Table I as a function of ionic strength.

The thermodynamic constants K_3^{II} and K_4^{II} were calculated by utilizing an applicable Debye-Hückel expression¹⁴ to evaluate the relevant activity coefficient ratios for the data obtained at ionic strengths of 0.01 and 0.02.

Thermometric titrations of potassium ferrocyanide with hydrochloric acid in pure water yielded isothermal lines, indicating that the heat of protonation was negligible, *i.e.*

$$\Delta H_4^{\text{II}} = \Delta H_3^{\text{II}} = 0.0 \text{ kcal./mole} \quad (17)$$

Discussion

Prevalence of Protonated Ferrocyanide Species.—The significance of the constants listed in Table I becomes evident upon consideration of the relative abundance of the various hexacyanoferrate(II) species in aqueous solution when hydrochloric acid is added to $K_4\text{Fe}(\text{CN})_6$. Representative data are presented in Fig. 2. As can be seen from the curves, the concentration of unprotonated ferrocyanide is negligible below pH 3, while $\text{HFe}(\text{CN})_6^-$ reaches its maximum concentration between pH 3 and 4. It also is evident that $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ is the predominating species at pH 2. The quadrivalent ferrocyanide base, $\text{Fe}(\text{CN})_6^{4-}$, the prevalence of which is implied in normal usage, is conspicuous by its virtual absence in acid solution where the ferrocyanide-ferricyanide oxidation-reduction couple serves as an important electron donor-acceptor system.

Ferrocyanide-Ferricyanide Oxidation-Reduction Potential.—When the solvent is carefully specified, a Nernst type expression (eq. 18) describes adequately the reversible potential of the ferrocyanide-ferricyanide couple

(14) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Academic Press, Inc., New York, N. Y., 1959, p. 231, eq. 9.12.

$$E = E_0' - 0.0591 \log \frac{F_{\text{Fe}(\text{CN})_6^{3-}}}{F_{\text{Fe}(\text{CN})_6^{4-}}} \quad (18)$$

E denotes the actual potential prevailing in a specified medium when the total concentration summed over all forms of each oxidation state (the formality) is $F_{\text{Fe}(\text{CN})_6^{3-}}$ and $F_{\text{Fe}(\text{CN})_6^{4-}}$. E_0' is Swift's¹⁵ "formal potential" which is correlated with the standard potential, E_0 , of the couple by eq. 19.

$$E_0' = E_0 - 0.0591 \log \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]} \times \frac{f_3^{\text{III}}}{f_4^{\text{II}}} \quad (19)$$

when

$$F_{(\text{FeCN})_6^{3-}} = F_{(\text{FeCN})_6^{4-}}$$

Kolthoff and Tomsicek¹⁶ reported $E_0 = -0.356$ v. and $f_3^{\text{III}}/f_4^{\text{II}} = 12$ and 39 for ionic strengths of 0.1 and 0.5, respectively. By combining these values with the pertinent concentration ratios $[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$ calculated with the aid of Table I, the data listed in Table II were obtained.

TABLE II
COMPARISON OF CALCULATED AND EXPERIMENTALLY REPORTED VALUES OF FERROCYANIDE-FERRICYANIDE POTENTIALS AT 25°

[H ⁺]	Formal potential	
	Calcd. ^a	Exptl. values ¹⁷⁻²⁰
0.1	-0.57 ± 0.01	$-0.567, -0.57$ $-0.56, -0.564$
0.5	-0.69 ± 0.01	-0.689

^a Assuming, for $\text{H}_3\text{Fe}(\text{CN})_6$: $K_1^{\text{III}}, K_2^{\text{III}}, K_3^{\text{III}} > 0.1$; for $\text{H}_4\text{Fe}(\text{CN})_6$: $K_1^{\text{II}}, K_2^{\text{II}} > 0.1, K_3^{\text{II}} = 6 \times 10^{-3}, K_4^{\text{II}} = 6.7 \times 10^{-3}$.

The excellent agreement between the calculated and experimental formal oxidation potentials is a conclusive verification, not only of the protonation constants determined in this study, but also of the value of E_0 reported by Kolthoff and Tomsicek¹⁶ and accepted in Latimer.²¹ This agreement is particularly significant when it is considered that the formal potentials in Table II are twice as large as the standard potential of the

(15) E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1939, p. 50.

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

(17) E. Müller, *Z. Phys. Chem.*, **88**, 46 (1914).

(18) H. H. Willard and G. D. Manalo, *Ind. Eng. Chem., Anal. Ed.*, **19**, 462 (1947).

(19) E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1939, pp. 540-543.

(20) I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **110**, 143 (1920).

(21) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 225.

ferrocyanide-ferricyanide half-cell. In the light of these findings, the recent suggestion by Hepler, *et al.*,²² that the Kolthoff and Tomsicek assignment may have been in error must be restricted to a possible uncertainty of ± 0.01 v.

Protonation Thermodynamics of the Hexacyanoferrates.—Since the heats of dissociation of the acids $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ and $\text{HFe}(\text{CN})_6^{3-}$ were found to be zero, the following interesting situation prevails

$$-RT \ln K_4^{\text{II}} = (\Delta F^0)_4^{\text{II}} = -T(\Delta S^0)_4^{\text{II}} \quad (20)$$

$$-RT \ln K_3^{\text{II}} = (\Delta F^0)_3^{\text{II}} = -T(\Delta S^0)_3^{\text{II}} \quad (21)$$

With the aid of the dissociation constants listed in Table I, the thermodynamic parameters for the equilibria described by eq. 22, 23, and 24 have been calculated and are listed in Table III.

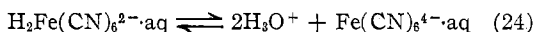
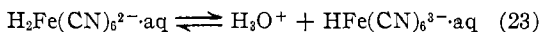
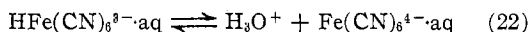


TABLE III

Thermodynamic Parameters for the Ionization of Protonated Ferrocyanide Species at 25.0°

Reaction no.	ΔF^0 , kcal./mole	ΔS^0 , cal./mole-deg.	ΔH^0 , kcal./mole
22	$+5.70 \pm 0.02$	-19.1 ± 0.1	0.0
23	$+3.1 \pm 0.2$	-10.3 ± 0.7	0.0
24	$+8.8 \pm 0.2$	-29.4 ± 0.7	0.0

The entropy changes involved can be interpreted satisfactorily in terms of hydration phenomena. It is noted that the entropies reported in Table III are all approximate multiples of 5 to 6 e.u., which is equal to the molar entropy of fusion of water. Accordingly, we suggest that

(22) L. G. Hepler, G. R. Sweet, and R. A. Jessor, *J. Am. Chem. Soc.*, **82**, 304 (1960).

the entropies in Tables III and IV can be accounted for by postulating that they reflect appropriate differences in the hydration of the hexacyanoferrate species involved. We assign an entropy change of -6 e.u. per mole of water involved in the hydration process, the water being considered immobilized ("frozen") in the vicinity of the solvated species. If the entropy changes listed in Table III are entirely attributed to hydration differences, eq. 22, 23, and 24 can be reformulated as

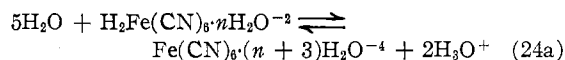
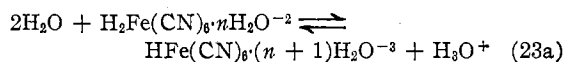
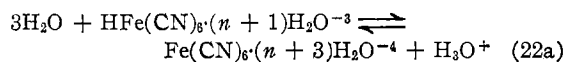


TABLE IV

Comparison of "Theoretical" and Actual Entropies

Reaction no.	Moles of water "frozen" in transformation	ΔS (e.u.)	
		Calcd. ^a	Found
22a	3	-18	-19
23a	2	-12	-10
24a	5	-30	-29

^a By assigning an entropy change of -6 cal./mole-deg. of water "frozen."

The entropy changes listed in column 2 of Table IV were calculated by assigning an entropy change of -6 cal./mole-deg. to the water "frozen" in the course of the processes 22a, 23a, and 24a. The agreement between experimental and calculated entropy changes is considered satisfactory, indicating that the entropies of protonation of ferrocyanide are indeed quasi-quantized in multiples of 6 cal./mole-deg.