

"dip" refer to 1,10-phenanthroline and α, α' -dipyridyl, respectively. The rate constant for (7) is approximately $4(\text{mole/l.})^{-1} \text{ sec.}^{-1}$ and those for (8), (9) and (10) are greater than $10^5(\text{mole/l.})^{-1} \text{ sec.}^{-1}$ at 25° . If it is assumed that electron tunnelling occurs when the reactants approach to such a distance that the first coordination shells are in contact and that reorientation of the first coordination shells is unnecessary, then equations 11 and 12 relating the free energy of activation, ΔF^* , and the over-all standard free energy change, ΔF^0 , of the reaction may be employed.

$$\Delta F^* = \frac{z_1^* z_2^* e^2}{RD_s} + m^2 (\Delta z)^2 e^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) \quad (11)$$

$$- (2m + 1)(\Delta z)^2 e^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) =$$

$$\Delta F^0 + T\Delta S_0 + (z_1 z_2 - z_1^* z_2^*) e^2 \quad (12)$$

where z_1^* and z_2 are the charges on the reactant ions before electron tunnelling, z_1 and z_2 are the charges on the reactant ions after tunnelling, Δz

is equal to $|z_1^* - z_1|$, e is the electronic charge, r_1 and r_2 are the radii of reactant ions 1 and 2, respectively, and each is equal to one-half the diameter of the indicated metal ion plus first coordination shell, R is equal to the sum ($r_1 + r_2$), D_{op} is the optical dielectric constant, D_s is the low-frequency, small-field-strength dielectric constant of the solvent, $T\Delta S_e$ is the free energy change resulting from a change in the number of unpaired electrons and m is a constant determined by (12). The value of r_1 , the radius of $\text{Fe}^{+2}_{(\text{aq})}$, is the same for all reactions listed and is approximately 3.44 \AA . The value of r_2 is approximately 3.44 for (7), 4.4 for (3), 7.08 for (8), 5.92 for (9) and 4.05 \AA for (10). The value of $T\Delta S_e$ is zero for all five reactions.

If the relative rates of these reactions are compared, the theory predicts that the rate constants of (8), (9) and (10) will be greater than that of (7) by at least a factor of 10^4 – 10^5 and this is observed. Also the theory predicts that the rate constant of (7) will be at least 10^2 times greater than that of (3) as observed. However, the values of the calculated rate constants are a factor of 10^6 too large for (7) and a factor of at least 10^7 too large for (3). Application of Marcus' theory for reorientation of inner shell ligands^{10a} may remove this discrepancy; these calculations have not been made yet for this series of reactions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

Reactions of Amminepentacyanoferrates(II) and (III) with Azide and Thiocyanate

BY BRUNO JASELSKIS

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Aqueous solution of amminepentacyanoferrate(III) in the presence of azide or thiocyanate develops an intense purple or blue color, respectively. The colored complexes are shown to be azidopentacyanoferrate(III) or pentacyanothiocyanatoferrate(III). Tetrabutylammonium salts of these complexes have been crystallized and analyzed. The log ratio method for the exchange reactions of ammonia in aqueous solutions of amminepentacyanoferrate(III) with azide or thiocyanate gives a combining ratio of 1:1. In addition, apparent equilibrium constants for various exchange reactions have been calculated, with an over-all reproducibility of approximately $\pm 5\%$. The calculated equilibrium constants for the exchange reactions of azidopentacyanoferrate(III) with ammonia (K_1), pyridine (K_2), hydroxyl (K_3) are $K_1 = 3.9$, $K_2 = 3.25$, $K_3 = 200$ and the calculated equilibrium constants for pentacyanothiocyanatoferrate(III) with ammonia (K_1), pyridine (K_2) and hydroxyl (K_3) are $K_1 = 29.7$, $K_2 = 24.4$ and $K_3 = 1500$.

Aquo- and amminepentacyanoferrates(II) yield color tests with azide, thiocyanate and a number of organic functional groups, like aromatic amines, aromatic aldehydes, thioaldehydes, hydrazides. These reactions have been recommended by Feigl¹ as suitable spot tests for identification purposes. The reactions of amminepentacyanoferrate(II) with aromatic amines have been described by Herington.²⁻⁴ However, most of these reactions are not understood. In fact, the

purple color for the reaction of azide with amminepentacyanoferrate(II) in presence of an oxidizing agent has been attributed by Baudisch⁵ to the aquopentacyanoferrate(III). In a recent publication Jaselskis and Edwards⁶ suggest that this color definitely is caused by a distinct azide complex; also they observe that thiocyanate reacts in a manner similar to azide. Thus, it seems of interest to investigate not only the reactions of azide and thiocyanate with amminepentacyanoferrate(II) but also with amminepentacyanoferrate(III). Both of these complexes have

(1) F. Feigl, "Spot Tests in Organic Analyses," Elsevier Publishing Co., 1956.

(2) E. F. G. Herington, *J. Chem. Soc. (London)*, 2747 (1956).

(3) E. F. G. Herington, *ibid.*, 4683 (1958).

(4) E. F. G. Herington, *ibid.*, 4771 (1958).

(5) O. Baudisch, *Science*, **108**, 443 (1948).

(6) B. Jaselskis and J. C. Edwards, *Anal. Chem.*, **32**, 381 (1960).

intense color and are quite stable. This paper describes studies on combining ratios, apparent equilibrium constants and the preparation of these colored complexes as crystalline tetrabutylammonium salts.

Experimental

Materials.—Sodium salts of amminepentacyanoferrates (II) and (III) were prepared by the procedure described in Brauer's "Handbuch der Präparativen Anorganischen Chemie"⁷ from reagent grade sodium nitroprusside. These compounds were recrystallized from ice cold water-ethanol mixtures.

Tetrabutylammonium pentacyanathiocyanatoferrate(III) was prepared by the addition of pentacyanathiocyanatoferric and thiocyanic acid mixtures to tetrabutylammonium hydroxide. A mixture of these acids was prepared by passing sodium amminepentacyanoferrate(III) and sodium thiocyanate (in a molar ratio 1:2) through a cation exchange resin, Amberlite IR 120, in a hydrogen cycle. The eluent was added directly to the tetrabutylammonium hydroxide and the neutralization was stopped at pH 7.0. However, when the order of neutralization was reversed, a blue insoluble precipitate resulted at pH 2-3. Water was removed under vacuum at room temperature and the resulting precipitate was dissolved in a minimum amount of absolute alcohol; anhydrous ethyl ether was added until the precipitate appeared. The precipitate was dissolved on cooling in Dry Ice-acetone bath and then the solution was gradually warmed to room temperature. On standing, orange-red, needle like crystals of tetrabutylammonium pentacyanathiocyanatoferrate(III) were formed. The best results were obtained if the concentration of salt were low and alcohol to ether ratio were approximately 1:9. If the concentrations of the salt and ether were too high an oily residue resulted. The crystalline salt was readily recrystallized by the above procedure from an alcohol-ether mixture.

Tetrabutylammonium hydroxide was prepared either by passing a solution of tetrabutylammonium halide through an anion exchange resin, Amberlite IRA 400, in hydroxyl cycle or by the reaction with silver hydroxide.

Tetrabutylammonium azidopentacyanoferrate(III) was prepared by the neutralization of azidopentacyanoferric and hydrazoic acids with tetrabutylammonium hydroxide. The mixture of hydrazoic and pentacyanoferric acids was prepared by passing sodium salts of these acids through a cation exchange column as described above. The resulting eluent was neutralized to approximately pH 6.0. The excess of hydrazoic acid was evaporated under vacuum for about 10 minutes. Then the solution was neutralized to pH 7.0 and water was removed under vacuum. On crystallization from an ether-ethanol mixture, red needle-like crystals of tetrabutylammonium azidopentacyanoferrate(III) were obtained.

On the basis of analyses empirical formulas for the above compounds were assigned for tetrabutylammonium azidopentacyanoferrate(III), $(\text{Bu}_4\text{N})_3\text{Fe}(\text{III})(\text{CN})_5\text{N}_3$, and for tetrabutylammonium pentacyanathiocyanatoferrate(III), $(\text{Bu}_4\text{N})_3\text{Fe}(\text{III})(\text{CN})_5\text{SCN}$. The results are summarized in Table I.

TABLE I
SUMMARY OF ANALYSES

Compound		Analyzed for. %				
		C	H	N	Fe	S
$(\text{Bu}_4\text{N})_3\text{Fe}(\text{III})(\text{CN})_5\text{N}_3$	Found	66.90	11.12	16.21	5.90	..
	Calcd.	66.78	11.36	16.12	5.85	..
$(\text{Bu}_4\text{N})_3\text{Fe}(\text{III})(\text{CN})_5\text{SCN}$	Found	66.57	10.82	12.85	5.68	3.33
	Calcd.	66.73	11.19	12.97	5.75	3.30

Sodium azide produced by Eastman Kodak Co. was recrystallized from a water-ethanol mixture. A 2M standard solution was prepared by weight, and the resulting con-

centration of azide was determined titrimetrically. Another 2M standard solution of thiocyanate was prepared by weighing our reagent grade sodium thiocyanate, manufactured by J. T. Baker Co. The thiocyanate concentration was checked by argentometric titration. Ammonium hydroxide-ammonium perchlorate buffer was prepared from the reagent grade chemicals by neutralization of perchloric acid with ammonium hydroxide. Total ammonium concentration in an aliquot was determined by the Kjeldahl method. The ammonia concentration in a buffer solution was calculated using pH and ionization constant data.

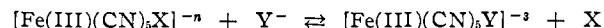
Standard pyridine-pyridinium perchlorate was prepared by weighing out reagent grade pyridine and adjusting the pH to 7.5-8.0 with perchloric acid.

A standard solution of approximately $2.0 \times 10^{-3} M$ amminepentacyanoferrate(III) was prepared by weight. The solution was kept in the dark and only freshly prepared solutions were used. Aliquots were taken for iron and ammonia analyses. In ordinary runs it was not necessary to know exact concentration.

The ionic strength of the solutions was adjusted using 2.0M neutralized sodium perchlorate.

Apparatus.—The absorption spectra were recorded with a Cary automatic recording spectrophotometer, Model XI, and individual absorbance measurements were made with a Beckman Model DU spectrophotometer using 1.0 cm. cells. The cell compartment was thermostated at 25°. The pH of the solutions was measured using a Beckman Model G pH meter at 25°.

Procedure. Reactions of Amminepentacyanoferrate(III) with Azide and Thiocyanate.—A number of reactions based on the equation



(where Y⁻ is thiocyanate or azide and X is ammonia, pyridine or hydroxyl) were carried out. Two ml. of a freshly prepared $2.0 \times 10^{-3} M$ amminepentacyanoferrate(III) solution was added to 25 ml. volumetric flasks. Then varying amounts of either sodium thiocyanate or azide were added from a 25 ml. buret (volumes ranging from 10.0 to 2.5 ml.). The resulting concentration of azide or thiocyanate in these runs varied from 0.8 to 0.1 M. The ionic strength of the solution was adjusted by the addition of 2 M neutral sodium perchlorate. Finally, after 1 hr. a known amount of the desired ion used in the exchange reaction was added from a buret. The exchange reactions were carried out with ammonia, pyridine and hydroxyl, which were obtained from the standard solutions. The contents were diluted to a volume and the flasks were placed in a 25° thermostated bath and kept in the dark. Absorbances of thiocyanate and azide complexes were measured after 4 hr. at 590 and 560 mμ. The optimum time was determined by observing absorbance and time under various conditions.

In another set of experiments the concentration of amminepentacyanoferrate(III) and thiocyanate were kept constant: only the concentration of ammonia or pyridine was varied. In particular, this method was necessary with the thiocyanate complex in the ammonia exchange reaction because the competitive hydroxyl reaction could not be neglected. The concentration of ammonia was varied from 0.02 to 0.1 M.

The pH for these solutions was determined following the absorbance measurements. Molar absorptivities of the pentacyanathiocyanatoferrate(III) and azidopentacyanoferrate(III) were determined at pH 7.0 by extrapolating absorbance to a constant value with increasing thiocyanate or azide concentrations.

Reaction of Amminepentacyanoferrate(II) with Azide and Thiocyanate.—Aminepentacyanoferrate(II) in the absence of oxygen and oxidizing agents such as hydrogen peroxide or ferricyanide failed to develop a color. The number of equivalents necessary to oxidize amminepentacyanoferrate(II) solutions containing azide or thiocyanate were determined by a photometric titration using a standard ferricyanide solution. In the beginning of the titration color developed rapidly. However, after the midpoint it was necessary to wait for about 1 hr. between each reading. A similar titration was repeated using a standard solution of hydrogen peroxide. In both cases only one equivalent was used to oxidize amminepentacyanoferrate(II) to amminepentacyanoferrate(III).

(7) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke, Stuttgart, 1954, pp. 1129, 1364.

TABLE II

RATIO METHOD FOR THE REACTIONS OF PENTACYANOTHIOCYANATO- AND AZIDOPENTACYANOFERRATES(III) WITH HYDROXYL, PYRIDINE AND AMMONIA

reagent (Y)	Nature and concn. of displacing ion (X)	Absorbance at 590 m μ	Absorbance at 560 m μ	Absorbance difference (A ₅₉₀ - A ₅₆₀)	Ratio $\frac{A}{A_{590} - A_{560}}$	
[SCN ⁻] ^a	0.80 [OH ⁻] ^b	2.82 × 10 ⁻⁴	0.217	...	0.115	1.886
[SCN ⁻] ^a	.56 [OH ⁻] ^b	2.82 × 10 ⁻⁴	.190142	1.338
[SCN ⁻] ^a	.40 [OH ⁻] ^b	2.82 × 10 ⁻⁴	.157175	0.897
[SCN ⁻] ^a	.20 [OH ⁻] ^b	2.82 × 10 ⁻⁴	.105227	.462
[SCN ⁻] ^a	.80 [NH ₃] ^c	0.047	.119213	.559
[SCN ⁻] ^a	.56 [NH ₃] ^c	.047	.098234	.418
[SCN ⁻] ^a	.40 [NH ₃] ^c	.047	.074258	.287
[SCN ⁻] ^a	.20 [NH ₃] ^c	.047	.043289	.149
[SCN ⁻] ^a	.80 [Py] ^d	.080	.097235	.413
[SCN ⁻] ^a	.60 [Py] ^d	.080	.079253	.312
[SCN ⁻] ^a	.40 [Py] ^d	.080	.057275	.207
[SCN ⁻] ^a	1.0332	0.284
[SCN ⁻] ^f	1.0 [NH ₃] ^e	.074	.127288	.441
	1.0 [NH ₃] ^e	.062	.143272	.523
	1.0 [NH ₃] ^e	.049	.160255	.627
[N ₃ ⁻] ^g	0.80 [NH ₃] ^e	.10	...	0.213	.104	2.048
[N ₃ ⁻] ^g	.60 [NH ₃] ^e	.10195	.122	1.598
[N ₃ ⁻] ^g	.40 [NH ₃] ^e	.10165	.152	1.085
[N ₃ ⁻] ^g	.20 [NH ₃] ^e	.10112	.205	0.546
[N ₃ ⁻] ^g	.80 [OH ⁻] ^b	4.17 × 10 ⁻³156	.161	.969
	.60 [OH ⁻] ^b	4.17 × 10 ⁻³128	.189	.677
[N ₃ ⁻] ^g	.40 [OH ⁻] ^b	4.17 × 10 ⁻³107	.210	.509
	.20 [OH ⁻] ^b	4.17 × 10 ⁻³087	.230	.378
[N ₃ ⁻] ^g	.80 [Py] ^d	0.16138	.179	.770
	.60	.16110	.207	.531
	.40	.16092	.235	.391
[N ₃ ⁻] ^g	1.00	...	0.281	.317
[SCN ⁻] ^h			.275	.235
[N ₃ ⁻] ^g	.60246	.257
[SCN ⁻] ^h	.20					

^a The concentration of pentacyanoferrate(III) in all the "a" runs is 1.68×10^{-4} and the ionic strength is 0.95. ^b The hydroxyl ion concentration is measured by pH meter. ^c The ammonia concentration is calculated using the pH, ionization constant ($K^b = 1.80 \times 10^{-5}$) and total concentration of ammonia. ^d The pyridine concentration is calculated using the pH, ionization constant and total concentration of pyridine. ^e The concentration of pentacyanoferrate(III) in all the "e" runs is 1.38×10^{-4} M and the ionic strength is 0.95. ^f The concentration of pentacyanoferrate(III) and thiocyanate are constant.

TABLE III

SUMMARY OF RESULTS ON COMBINING RATIOS AND APPARENT FORMATION CONSTANTS

Reaction	Slope (combining ratio)	Apparent equilibrium constant
Fe(III)(CN) ₅ SCN ⁻³ + OH ⁻ ⇌ Fe(III)(CN) ₅ OH ⁻³ + SCN ⁻	1.04 ± 0.03	1500 ± 150
Fe(III)(CN) ₅ SCN ⁻³ + NH ₃ ⇌ Fe(III)(CN) ₅ NH ₃ ⁻² + SCN ⁻	1.02 ± .03	29.7 ± 1.5
Fe(III)(CN) ₅ SCN ⁻³ + py ⇌ Fe(III)(CN) ₅ py ⁻² + SCN ⁻	1.04 ± .03	24.4 ± 1.2
Fe(III)(CN) ₅ SCN ⁻³ + N ₃ ⁻ ⇌ Fe(III)(CN) ₅ N ₃ ⁻³ + SCN ⁻	7.65 ^a ± 0.38
Fe(III)(CN) ₅ N ₃ ⁻³ + OH ⁻ ⇌ Fe(III)(CN) ₅ OH ⁻² + N ₃ ⁻	1.06 ± .03	200 ± 20
Fe(III)(CN) ₅ N ₃ ⁻³ + NH ₃ ⇌ Fe(III)(CN) ₅ NH ₃ ⁻² + N ₃ ⁻	1.02 ± .03	3.90 ± 0.20
Fe(III)(CN) ₅ N ₃ ⁻³ + py ⇌ Fe(III)(CN) ₅ py ⁻² + N ₃ ⁻	1.04 ± .03	3.25 ± 0.16

^a The apparent formation constant is calculated using molar absorptivities for azide and thiocyanate mixture.

Results and Discussion

Spectra of the pentacyanothiocyanatoferrate(III) and azidopentacyanoferrate(III) show strong absorption bands at 590 and 560 m μ , which have approximate molar absorptivities of 2680 and 3700, respectively. The absorption bands are relatively broad as shown in Fig. 1. It is of interest to note

that the spectrum of aquopentacyanoferrate(III) resembles that of azidopentacyanoferrate(III). The latter complex has been thought to be the aquopentacyanoferrate(III). Ammine-, hydroxo- and pyridinepentacyanoferrates(III) do not absorb at 560 and 590 m μ . However, they exhibit a strong absorption at approximately 400 m μ in

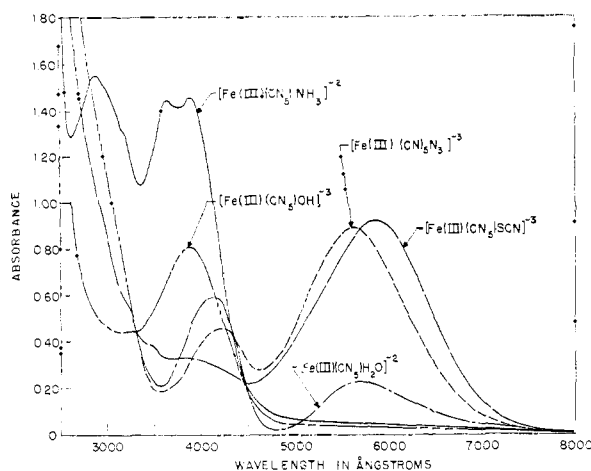


Fig. 1.—Spectra of aquo-, ammine-, azido-, hydroxo- and thiocyanate-pentacyanoferrates (III).

ultraviolet. The spectrum of amminepentacyanoferrate(III) has been described by Shiura and Masuda.⁸

Combining Ratio and Apparent Stability Constants of Amminepentacyanoferrate(III) with Azide or Thiocyanate, Log Ratio Method.—The log ratio method has been applied successfully for the identification of complexes and calculation of the apparent stability constants by numerous workers.^{9,10} In particular, this method is useful (i) when the stability constants are low, (ii) when relatively high concentrations of reagents are necessary, and (iii) when the purity of the reagents is not well established.

The reaction of amminepentacyanoferrate(II) with an oxidizing agent in slightly acid solution yields a purple color attributable to aquopentacyanoferrate(III). A similar color is obtained by the reaction of amminepentacyanoferrate(II) with azide in the presence of an oxidizing agent or by the reaction of amminepentacyanoferrate(III) with azide alone. Baudisch⁵ attributes the latter color to the aquopentacyanoferrate(III). Although the color produced by the reaction of amminepentacyanoferrate(III) with azide is similar to the aquopentacyanoferrate(III), the molar absorptivities and spectra are different. In addition, the reaction of amminepentacyanoferrate(III) with thiocyanate yields a distinctly different color. Both of these observations suggest formation of thiocyanato or azido complexes with pentacyanoferrate(III). The preparation of crystalline tetra-butylammonium salts of azidopentacyanoferrate(III) and pentacyanothiocyanatoferrate(III), without a doubt, confirms the presence of these complexes in a solid form. However, in solution this may be a different case. The combining ratio and apparent equilibrium constants for these reactions are obtained by the log ratio method.

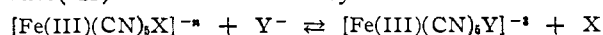
The equilibrium constants for the reaction of

(8) I. K. Shiura and I. Masuda, *J. Chem. Soc., Japan*, **76**, 1211 (1954).

(9) Harvey Diehl and R. R. Sealock, *Record Chem. Progress (Kresge-Hooker Sci. Libr.)*, **13**, 10 (1952).

(10) W. D. Kingery and D. N. Hume, *THIS JOURNAL*, **71**, 2393 (1949).

ammine-, pyridine- and hydroxopentacyanoferrate(III) with azide or thiocyanate



can be expressed as

$$K = \frac{[\text{Fe(III)(CN)}_5\text{Y}^{-3}][\text{X}]}{[\text{Fe(III)(CN)}_5\text{X}^{-n}][\text{Y}^-]}$$

A linear equation is obtained by rearranging the latter equation and taking logarithms

$$\log K/[X] + \log [Y^-] = \log \frac{[\text{Fe(III)(CN)}_5\text{Y}^{-3}]}{[\text{Fe(III)(CN)}_5\text{X}^{-n}]}$$

A plot of the logarithm ratio vs. $\log [Y^-]$ is a straight line with a slope equal to the number of Y^- used in this displacement reaction; and an intercept at the concentration $1.0 M \text{Y}^-$ is $K/[X]$ (or $K/[X][\text{CN}^-]$ if more than one mole of Y^- is used per mole of amminepentacyanoferrate(III)). Absorbancies of pentacyanoferrates-

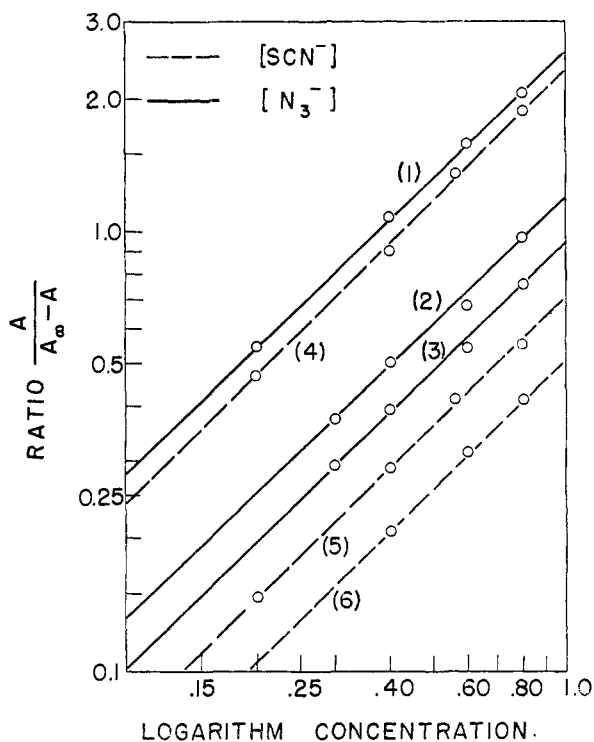


Fig. 2.—Logarithm ratio plot vs. concentration of azide or thiocyanate.

(III) in the presence of azide or thiocyanate at 560 and 590 $m\mu$, respectively, are proportional to the colored complexes, $[\text{Fe(III)(CN)}_5\text{Y}^{-3}]$, formed. Since the absorbance of reactants at the above wavelengths is negligible, the concentration of unreacted pentacyanoferrate(III) species is directly proportional to the difference of absorbancies $[A_\infty - A]$. The A_∞ is the extrapolated value of absorbance for azide or thiocyanate complexes in the absence of a displacing ion (X), and A is the measured absorbance in the presence of the displacing ion $[\text{X}]$. The log ratio simply becomes $\log A/(A_\infty - A)$. Typical results are summarized in Table II.

The slopes for the log ratio method can be best evaluated from the plot of $\log A/(A_\infty - A)$ vs. $\log [Y^-]$ as shown in Fig. 2. A summary of the results

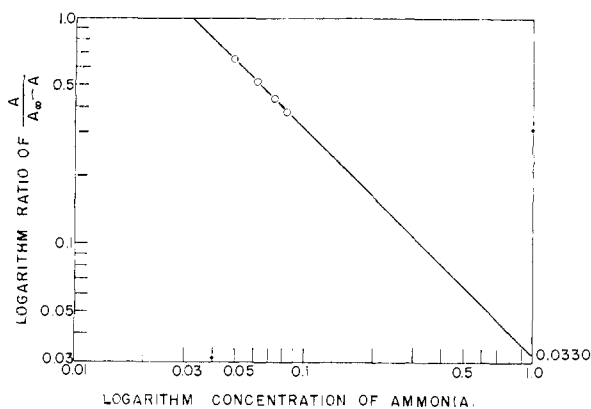


Fig. 3.—Logarithm ratio plot vs. concentration of ammonia.

on combining ratios and the apparent equilibrium constants are presented in Table III. These results clearly indicate that the combining ratio is 1:1. Similar results have been reported by Herington²⁻⁴ for the reactions of aromatic amines with amminepentacyanoferrate(II) in presence of an oxidizing agent.

The apparent equilibrium constants are calculated at a specified ionic strength using molarities rather than activities and using literature values for the ionization constants of ammonium hydroxide and pyridine.

Equilibrium constants for the exchange reaction of pentacyanathiocyanoferrate(III) with ammonia vary with pH . This is attributed to the reaction of hydroxyl with pentacyanathiocyanoferrate(III). The apparent equilibrium constant K for the ammonia exchange reaction can be obtained directly by plotting $\log(A/A_0 \approx -A)$ vs. \log ammonia at a constant thiocyanate concentration, as shown in Fig. 3. The extrapolated line to 1.0 M ammonia concentration yields the $K/(Y)$ value directly. In the exchange reaction of amminepentacyanoferrate(III) with azide in ammonia buffer solutions there is practically no effect up to pH 10.0. This is in agreement with the calculated results using K values for the hydroxyl exchange reaction.

In determining exchange reactions of hydroxypentacyanoferrate(III) with azide or thiocyanate in alkaline buffer solutions best results are obtained if pOH of the buffer corresponds approximately to the pK for the reaction.

The reproducibility of the apparent equilibrium constants is rather poor, because of the secondary reactions, relatively long time necessary to reach equilibrium and the order of addition of reagents. Some of these factors are shown in a plot of absorbance vs. time in Fig. 4. It is apparent that not only the order of addition of reagents is important but also that on standing the color decays at a rather slow rate.

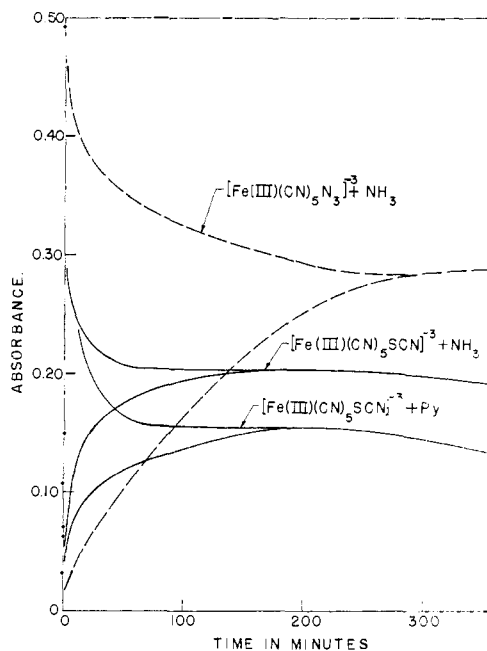


Fig. 4.—Absorbance dependence on time.

The presence of impurities such as ferro- or ferricyanides has a definite effect on the achievement of equilibrium and decay of the color. In addition, the presence of sunlight has a very marked effect on the color decay. Ferricyanide on hydrolysis yields pentacyanoferrate(III), which in turn produces colored complexes of thiocyanate or azide. Ferrocyanide on oxidation by air and hydrolysis again can produce colored complexes. In general, on prolonged standing (over two days) in alkaline solution a brown or white precipitate is formed, which resembles hydrous ferric hydroxide. In addition, some of the iron(III) is reduced to iron(II) by photocatalytic processes. Even though the individual equilibrium constants can be reproduced to within $\pm 2\%$, the over-all reproducibility is in the order of $\pm 5.0\%$ and for the hydroxy exchange is in the order of $\pm 10\%$.

The reaction of amminepentacyanoferrate(II) with azide or thiocyanate is essentially the same as for the ammine-pentacyanoferrate(III), except that one equivalent of an oxidizing agent such as oxygen, hydrogen peroxide or ferricyanide is necessary. The slope values and the equilibrium constants calculated are in good agreement with the amminepentacyanoferrate(III).

The formation of color by amminepentacyanoferrate(III) in spot tests for a number of organic reagents as described by Feigl¹ apparently resembles the ammonia exchange reaction with azide or thiocyanate. Eventually, it is hoped to develop new colorimetric methods for the analysis of organic functional groups.