356. *Ferric Thiocyanate. Part II.* The Distribution of Ferric Thiocyanate between Ether and Water.*

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The distribution of ferric thiocyanate between ether and water has been used to investigate the equilibrium between the various complexes. All complexes from $FeCNS^{2+}$ to $Fe(CNS)_6{}^{3-}$ have been shown to occur, and the mass-action constants of all except the neutral molecule been determined. The factor limiting accuracy seems to be the change of activity coefficient with composition, which occurs at high concentration even at constant ionic strength. Bjerrum's relationship, K_2/K_1, etc. = const., holds to a first approximation.

The object of this work is to determine the nature of the complexes responsible for the colour in solutions of ferric thiocyanate. Migration experiments (*e.g.*, Schlesinger, *J. Amer. Chem. Soc.*, 1941, **63**, 1765; Bent and French, *ibid.*, p. 568) show that under suitable conditions either positively or negatively charged complexes may exist; and the fact that ether, amyl alcohol, and other solvents can extract the red colour from such solutions indicates the presence of a neutral complex which molecular-weight experiments (Part I *) show to have a formula $Fe(CNS)_3$ (for simplicity, the co-ordinated water molecules will be omitted in this discussion). A number of workers (references given in Part I) have proved the existence of the complex $FeCNS^{2+}$ in dilute solution, and have found some evidence of higher complexes in more concentrated solutions. The possibility of a complex $Fe(CNS)_6{}^{3-}$ is indicated both by analogy with the ferricyanides and by the existence of crystalline compounds of the type $M_3Fe(CNS)_6$ (Rosenheim and Cohn, *Z. anorg. Chem.*, 1901, **27**, 280).

In this work the possibility will be assumed that there exists a series of complexes of general formula $Fe(CNS)_x^{(3-x)+}$, where x is an integer from 1 to 6, and an attempt will be made to determine the stability constant of each. The stability constant is the reciprocal of the ionisation constant, *i.e.*,

$$K_x = [Fe(CNS)_x^{(3-x)+}]/[Fe(CNS)_{x-1}^{(4-x)+}][CNS^-] \quad . \quad . \quad . \quad . \quad (1)$$

and will be zero if the complex has no real existence.

The relationships expressed in equation (1) can be combined and rearranged so that the neutral complex appears in the denominator of each equation, thus,

$$[Fe(CNS)_x^{(3-x)+}][CNS^-]^{3-x}/[Fe(CNS)_3] = k_x \quad . \quad . \quad . \quad . \quad (2)$$

The simple ferric ion ($x = 0$) may conveniently be included in this series.

It is important to observe from this equation that the relative proportions of the different complexes, though dependent on the thiocyanate concentration, are quite independent of the iron concentration so long as this is not sufficiently great as to reduce appreciably the thiocyanate concentration by complex formation. Hence the importance in the colorimetric determination of ferric iron by thiocyanate of keeping the thiocyanate concentration constant.

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* Part I, *J.*, 1951, 1310.

The effect is well seen in Figs. 1 and 2, which show families of curves, (1) at constant ferric concentration and (2) at constant thiocyanate concentration. In Fig. 1 the variation of the wave-length of maximum absorption indicates a change in the proportions of the various complexes.

If an aqueous solution is extracted with ether, then by the partition law,

$$[\mathrm{Fe(CNS)_3}]_{\mathrm{Water}} = n[\mathrm{Fe(CNS)_3}]_{\mathrm{Ether}} = n(\mathrm{Fe})_{\mathrm{E}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

whence, from (2),

$$[\mathrm{Fe(CNS)}_x^{(3-x)+}][\mathrm{CNS}^-]^{3-x}/(\mathrm{Fe})_{\mathrm{E}} = nk_x \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If, under given conditions, nearly all the iron in the water were in the form of a single complex,

$$(\mathrm{Fe})_{\mathrm{W}} = [\mathrm{Fe(CNS)}_x^{(3-x)+}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

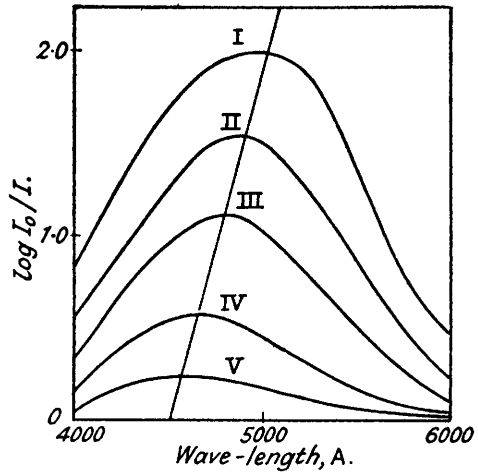
then, from (4)

$$[\mathrm{CNS}^-]^{3-x} = nk_x(\mathrm{Fe})_{\mathrm{E}}/(\mathrm{Fe})_{\mathrm{W}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The value of x can now be determined by plotting log $[\mathrm{CNS}^-]$ against log $(\mathrm{Fe})_{\mathrm{E}}/(\mathrm{Fe})_{\mathrm{W}}$; $[\mathrm{CNS}^-]$ is equal to the total thiocyanate concentration when this is in large excess. In other cases, a correction for the thiocyanate combined in the complex must be made, after an approximate value for x has been found. The method becomes impracticable when the iron is in excess, and also when several complexes are simultaneously present in significant proportions.

FIG. 1.

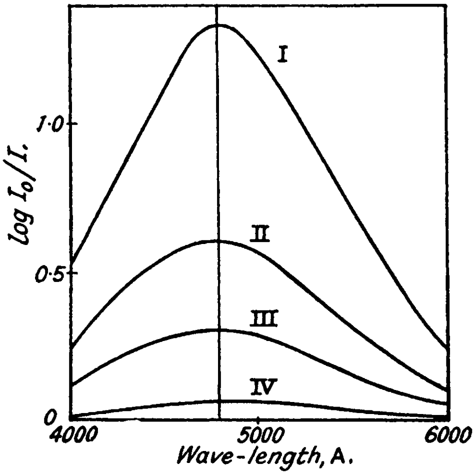
Absorption curves at varying thiocyanate concentration : $\lambda_{\mathrm{max.}}$ varies.



$[\mathrm{Fe}^{+++}] = 0{\cdot}000303$M.; $[\mathrm{CNS}^-] =$ (I) 0·91M.; (II) 0·28M.; (III) 0·091M.; (IV) 0·028M.; (V) 0·009M.

FIG. 2.

Absorption curves at constant thiocyanate concentration : $\lambda_{\mathrm{max.}}$ is constant, and Beer's law is obeyed.



$[\mathrm{CNS}^-] = 0{\cdot}37$M.; $\mathrm{Fe}[^{+++}] =$ (I) 0·00024M.; (II) 0·00012M.; (III) 0·00006M.; (IV) 0·000012M.

Fig. 3 shows plots of log $[\mathrm{CNS}^-]$ against log $(\mathrm{Fe})_{\mathrm{E}}/(\mathrm{Fe})_{\mathrm{W}}$ for two experiments, and it will be seen that the slope in fact varies, over the range covered, from about $+2$ ($= \mathrm{FeCNS}^{2+}$) to -1 ($= \mathrm{Fe(CNS)_4}^-$), the curve passing through a maximum where the mean charge on the complex is zero. As it is evident that several complexes are present together, a more general solution of equation (4) must be found.

Since the total iron in the aqueous layer is the sum of the iron in the different complexes present, we may write, using equation (2),

$$(\mathrm{Fe})_{\mathrm{W}} = \sum_{x=6}^{x=0} [\mathrm{Fe(CNS)}_x^{(3-x)+}] = [\mathrm{Fe(CNS)_3}] \sum_{x=6}^{x=0} k_x[\mathrm{CNS}^-]^{(x-3)} \quad . \quad . \quad . \quad (7)$$

and hence, from (3),

$$(\mathrm{Fe})_{\mathrm{W}}/(\mathrm{Fe})_{\mathrm{E}} = nk_0[\mathrm{CNS}^-]^{-3} + nk_1[\mathrm{CNS}^-]^{-2} + \ldots\ldots + nk_6[\mathrm{CNS}^-]^3 \quad . \quad . \quad (8)$$

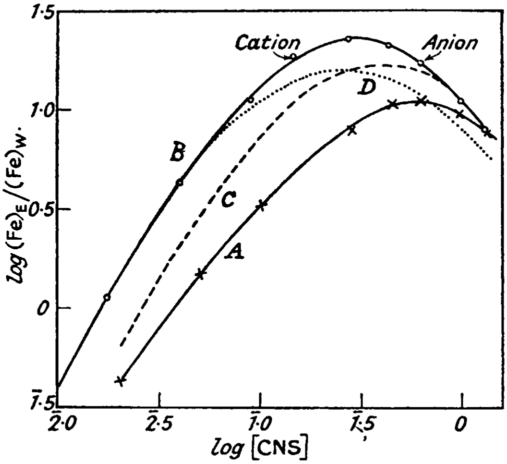
By making a sufficient number of accurate measurements of the partition ratio $(Fe)_W/(Fe)_E$ at different thiocyanate concentrations it is possible, in theory, to determine all the values of nk_x, and hence of the stability constants K_x, which are connected with them by the relationship $K_x = k_x/k_{x-1}$.

The number of parameters in equation (8) is too large for practical purposes, but may be reduced as follows. First, it will be seen from equation (2) that $k_3 = 1$. Secondly, Frank and Ostwalt (*J. Amer. Chem. Soc.*, 1947, **69**, 1321) have shown that the value of K_1 $(= k_1/k_0)$ can be found from measurements of the optical density of solutions of low thiocyanate concentration. Thirdly, an empirical relationship has been found (see p. 1578) relating k_0 to k_6, k_1 to k_5, and k_2 to k_4. Thus the total number of unknowns to be found from the experiment may be reduced to the manageable number of three.

Equation (8) has been derived above without any reference to activity coefficients. A rigorous treatment, however, shows that the activity-coefficient factors all cancel out, and that precisely the same equation results, provided that these activity coefficients remain constant at constant ionic strength.

FIG. 3.

Logarithmic plot of extraction ratio against thiocyanate concentration.



Experimental points : × = *Series A,* ⊙ = *Series B.*

A, B, curves calculated from constants in Table III, cols. 2 *and* 3; *D, calculated from constants in Table III, col.* 4; *C, curve A, partly corrected for variation in activity coefficients.*

EXPERIMENTAL.

Partition experiments were carried out at 18·0° ± 0·1° at a constant acidity of 0·18N. and an ionic strength of 1·8. The choice of acid and salt used in making up the solutions was limited, as many anions form complexes with ferric iron. It is generally believed that neither nitrate nor perchlorate forms such complexes in dilute solution, and Rabinowitch and Stockmayer (*J. Amer. Chem. Soc.*, 1942, **64**, 335) found no evidence of complex formation up to concentrations of 3M. Two series of solutions were therefore made : series A with ferric nitrate, potassium thiocyanate, potassium nitrate, and nitric acid; series B with ferric perchlorate, ammonium thiocyanate, sodium perchlorate, and perchloric acid. According to Bray and Hershey's data (*ibid.*, 1934, **56**, 1889), an acidity of 0·18N. should reduce hydrolysis to about 1% of the simple ferric ion present, at the ionic strengths used in these experiments.

The solutions, especially those containing nitric acid, were rather unstable and the experiments were carried out as quickly as possible and to a strict timetable. Equilibrium is rapidly established, and the solutions were always shaken for 15 minutes, allowed to settle for 15 minutes, separated, and analysed at once. Basically, 200 ml. of 2M-thiocyanate were mixed with 50 ml. of 0·03M-ferric salt which had been made 0·9N. with respect to acid, and the whole extracted with 150 ml. of ether. In other runs of the series, varying amounts of the thiocyanate were replaced by equal amounts of 2M-salt. (In series B, the fall in ionic strength caused by the extraction of ferric thiocyanate and thiocyanic acid by the ether was calculated from preliminary experiments, and extra salt was added to maintain it at the value 1·8. This correction was not made in series A, where μ may have fallen to 1·65 in some cases.) The ether (AnalaR quality) was shaken with ferrous sulphate, washed, stored over copper wire to remove peroxides which interfere the determination of ferric iron, and distilled. The iron was determined by titanous sulphate, and the thiocyanate by silver nitrate. The total iron and total thiocyanate in the two layers were always checked against the amount originally taken, allowance being made for the change of volume of the ether and water layers caused by their mutual solubility. Agreement to within about 2% was obtained. The results are summarised in Fig. 3.

Optical density measurements were made in order to determine the value of K_1, at an ionic strength of 1·8 in the presence of several different salts, and also at ionic strengths of 1 and 0·2. The solutions used here consisted of 20 ml. of the base salt (sodium perchlorate, potassium nitrate, or lithium nitrate) to which were added 1 ml. of 0·005M-ammonium thiocyanate and 1—4 ml. of 0·05M-ferric salt, both acidified to 0·9N. with the appropriate acid, and the whole was made up to 25 ml. with 0·9N-acid. Small volumes were measured with a micrometer syringe. The resulting solutions were stable for several hours and were measured at room temperature in a Unicam spectrophotometer, concordant values of K_1 being obtained over the visible range from 3900 to 5500 A. The equation given by Frank and Ostwalt (*loc. cit.*) is : $ab/D = (a + b)/\varepsilon + 1/\varepsilon K_1$ where a = total ferric iron, b = total thiocyanate, D = optical density, and ε = molecular extinction coefficient. In a few cases, runs were made at several values of a, and both ε and K_1 were obtained graphically over the range of wave-lengths; but for the most part, pairs of runs were made with $a = 0{\cdot}002$ and 0·008, and the resulting simultaneous equations were solved. ε, depending as it does on the difference of two values of ab/D, is rather sensitive to experimental error, but as it is independent of the ionic strength or the nature of the base salt used, it was possible to take mean values from all the 26 experiments made at each wave-length, and these mean values, which are given in Table I, were used to determine K_1 in each separate run. The values of K_1 for all wave-lengths and every run of a particular salt solution were then collected and averaged, the results being given in Table II.

TABLE I.

Molecular extinction coefficients of $FeCNS^{2+}$, ($\log I_0/I)/lc$; *standard error* ±40.

λ	3800	3900	4000	4100	4200	4300	4400	4500	4600	4700	4800	4900	5000	5500	6000
ε	1617	1954	2646	3189	3793	4321	4693	4983	4946	4781	4474	4065	3578	1367	437·1

TABLE II.

Value of K_1 *in different salt solutions and ionic strengths.*

			Activity coefficients.			
Salt.	μ.	K_1.	Pure salt.*[1]	AgOAc.[2]	$CH_2Cl{\cdot}CO_2Ag$.[2]	$CaSO_4$.[3]
$NaClO_4$	1·8	122·5 ± 1·0	(0·54)	—	—	0·6
KNO_3	1·8	91·0 ± 0·9	0·34	0·60	0·48	0·3
$LiNO_3$	1·8	114·4 ± 5	(0·85)	0·47	0·49	0·4
$NaClO_4$	1·0	127·9 ± 6	0·576	—	—	—
KNO_3	1·0	98·8 ± 4	0·439	0·75	0·53	—
$LiNO_3$	1·0	109·5 ± 5	0·54	0·55	—	—
$HClO_4$	0·2	178·2 ± 7	—	—	—	—
HNO_3	0·2	196·4 ± 8	—	—	—	—

* Values in parentheses were obtained by extrapolation.

[1] Landolt–Börnstein " Tabellen." [2] MacDougall and Rehner, *J. Amer. Chem. Soc.*, 1934, **56**, 368.

[3] This work (approximate value only).

A few migration experiments were performed to confirm the conclusions reached as to the mean charge on the complexes at different thiocyanate concentrations. To be of value, conditions must be arranged so that the thiocyanate concentration on each side of the moving boundary is nearly the same, so that the equilibrium between the different complexes is not disturbed as the boundary is crossed. The apparatus used was a U-tube with a wide-bore stop-cock in each limb. The portion between the stop-cocks was filled with acidified thiocyanate, coloured by the addition of a trace of ferric iron. The remaining portions were filled with the same acidified solution of thiocyanate but without the iron. After the whole had been brought to uniform temperature in a thermostat, the boundaries were formed by opening the stop-cocks. These boundaries were apt to become unstable, but by use of a low potential gradient definite results were obtained. Only small movements were obtained, however, as on prolonged running secondary effects intervened, such as the migration of hydroxyl ions from the cathode, with consequent hydrolysis and bleaching of the boundary.

DISCUSSION.

It will be seen from Fig. 3 that the slope of the graph of $\log (Fe)_E/(Fe)_W$ against $\log [CNS^-]$ changes direction, showing that positive complexes predominate at low thiocyanate concentrations and negative complexes at high concentrations (equation 6). This was confirmed by migration experiments. With a concentration of thiocyanate of 0·09287N., the boundary moved towards the cathode : at 0·6339N., it moved to the anode (both solutions being made up to $\mu = 1{\cdot}8$ with sodium perchlorate). The two points are marked " cation " and " anion " in Fig. 3.

Fig. 3 indicates that the series in potassium nitrate (A) and that in sodium perchlorate (B) are generally similar though they do not follow exactly the same course, and that curve B, at least, shows a remarkable symmetry. This symmetry, which is assumed to apply also to curve A, means that if the equation is transformed to bring the origin to the point of maximum extraction, positive and negative logarithmic terms become interchangeable, and therefore that in equation (8), the coefficients of like powers (but opposite signs) of $[CNS^-]$ become equal. The origin is shifted by multiplying $[\mathrm{CNS}^-]$ by a factor P (the maximum in Fig. 3 lies at $-\log P$), and equation (8) can then be written as

$$
\begin{aligned}
(\mathrm{Fe})_\mathrm{W}/(\mathrm{Fe})_\mathrm{E} &= \frac{nk_0}{P^{-3}}P^{-3}[\mathrm{CNS}^-]^{-3} + \frac{nk_1}{P^{-2}}P^{-2}[\mathrm{CNS}^-]^{-2} + \ldots + \frac{nk_6}{P^3}P^3[\mathrm{CNS}^-]^3 \\
&= k_0'P^{-3}[\mathrm{CNS}^-]^{-3} + k_1'P^{-2}[\mathrm{CNS}^-]^{-2} + \ldots. + k_6'P^3[\mathrm{CNS}^-]^3 \qquad (9)
\end{aligned}
$$

in which $k_0' = k_6'$, $k_1' = k_5'$, and $k_2' = k_4'$. Remembering that $k_1/k_0 = K_1$, we may write

$$(\mathrm{Fe})_\mathrm{W}/(\mathrm{Fe})_\mathrm{E} = uk_0' + vk_2' + k_3' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $u = (P^3[\mathrm{CNS}^-]^3 + P^{-3}[\mathrm{CNS}^-]^{-3} + K_1P^{-3}[\mathrm{CNS}^-]^{-2} + K_1P[\mathrm{CNS}^-]^2)$

and $v = (P^{-1}[\mathrm{CNS}^-]^{-1} + P[\mathrm{CNS}^-])$. Equation (10) was solved by the method of least squares for the eight experimental points of series A and the nine experimental points of series B, and the results are given in Table III.

TABLE III.

	Series A.	Series B.	Series B, calc. by Bjerrum's theory.
P	1·68	3·365 ± 0·005	—
a	$(1{\cdot}39 \pm 0{\cdot}144) \times 10^{-5}$	$(3{\cdot}352 \pm 0{\cdot}16) \times 10^{-5}$	—
b	$(4{\cdot}69 \pm 0{\cdot}59) \times 10^{-2}$	$(2{\cdot}054 \pm 0{\cdot}10) \times 10^{-2}$	—
c	$(-\ 4{\cdot}03 \pm 15{\cdot}1) \times 10^{-3}$	$(-\ 1{\cdot}008 \pm 2{\cdot}07) \times 10^{-3}$	—
nk_0	$2{\cdot}93 \times 10^{-6}$	$0{\cdot}879 \times 10^{-6}$	$1{\cdot}045 \times 10^{-6}$
nk_1	$2{\cdot}665 \times 10^{-4}$	$1{\cdot}077 \times 10^{-4}$	$1{\cdot}28 \times 10^{-4}$
nk_2	$2{\cdot}79 \times 10^{-2}$	$6{\cdot}09 \times 10^{-3}$	$3{\cdot}92 \times 10^{-3}$
nk_3	$<11{\cdot}1 \times 10^{-3}$	$<1 \times 10^{-3}$	$3{\cdot}005 \times 10^{-2}$
nk_4	$7{\cdot}87 \times 10^{-2}$	$6{\cdot}90 \times 10^{-2}$	$5{\cdot}76 \times 10^{-2}$
nk_5	$2{\cdot}12 \times 10^{-3}$	$1{\cdot}38 \times 10^{-2}$	$2{\cdot}77 \times 10^{-2}$
nk_6	$6{\cdot}59 \times 10^{-5}$	$1{\cdot}28 \times 10^{-3}$	$3{\cdot}34 \times 10^{-3}$
K_1	91 ± 0·9	122·5 ± 1·0	(122·5)
K_2	105·4 ± 17	56·5 ± 3·7	30·65
K_3	<0·39	<0·184	7·67
K_4	>0·717	>62·8	1·92
K_5	0·027 ± 0·004	0·200 ± 0·013	0·481
K_6	0·031 ± 0·005	0·0926 ± 0·006	0·1205

It is unfortunate that in each case the value of nk_3 is less than its experimental error. It must be positive, since $k_3 = 1$ and n is the partition coefficient, and the best that can be done is to indicate a " maximum " value, obtained by adding the standard error to the observed figure.

We must now consider why the two series do not give identical results. There are two possible reasons. The first is that in spite of Rabinowitch and Stockmayer's evidence (*loc. cit.*), a complex may be formed between the ferric and the nitrate ions. The second is that the activity coefficients of the reacting substances may change even at constant ionic strength when one salt is substituted for another. The activity coefficients of ammonium thiocyanate and of sodium perchorate at high concentration do not appear to be accurately known, but both are probably about 0·54 at 1·8M. It is reasonable to assume that the activity of a small amount of a third substance dissolved in a mixture of these two will not be greatly affected by the proportions of the two salts in the mixture. This is borne out by the symmetry in Curve B, which could scarcely survive any marked change in activity coefficient.

In contrast with the above, the activity coefficient of potassium thiocyanate and potassium nitrate are respectively 0·56 and 0·34 at 1·8M., and it is probable that the activity of a third substance will be considerably affected by the proportions of the two salts, so that a rather large systematic error will be introduced. We cannot be certain that even series B is quite free from this error, but it is clearly much more reliable than series A.

In order to obtain more evidence on the magnitude of the effects likely to result from changing from one salt to another, some measurements were made of the value of K_1 by the optical method, lithium nitrate being used instead of potassium nitrate. The results of these experiments, and also some at lower salt concentrations, are given in Table II. It can be seen that the variations in K_1 are of the same order as the variations in the activity coefficients of various salts as determined by their solubilities. There is no evidence of specific interaction with the nitrate ion.

The various complexes, being differently charged, will have different activity coefficients, and without a knowledge of these individual values, it is not possible to predict accurately what the effect on the extraction ratio will be of changing these by altering the base salt. An approximate calculation can be made if we assume that each of the activity coefficients, except that of the neutral complex, which will remain unity, is changed in the same ratio, f_R, when the change of salt is made. f_R for the complexes in 1·8M-potassium nitrate solution (as compared with 1·8M-ammonium thiocyanate) is given by the ratio of K_1 in the two salts (=91·0/122·5 = 0·742), and the values for mixtures of these two salts can be found by assuming that log f_R varies linearly with the concentration of nitrate in the mixture. It is then found that

$$k_0{}^A = k_0{}^B/f_R{}^4;\ k_1{}^A = k_1{}^B/f_R{}^2;\ k_2{}^A = k_2{}^B/f_R{}^2;\ k_3{}^A = k_3{}^B;$$
$$k_4{}^A = k_4{}^B;\ k_5{}^A = k_5{}^B f_R \text{ and } k_6{}^A = k_6{}^B \,.\, f_R{}^2$$

[where $k_x{}^A$ and $k_x{}^B$ are the constants of equation (8) in series A and series B, respectively], so it is possible from equation (8) to calculate $(Fe)_W/(Fe)_E$ for solutions of series A by using the constants found experimentally from series B. The resulting graph (Curve *C*, Fig. 3) shows that this approximate calculation partly accounts for the difference between the two series. We cannot tell whether a correction based on accurately known activity coefficients would bring about exact coincidence or not, but it is significant that the greatest relative divergence between Curves *A* and *C* lies in the region where we know least about the activity coefficients, that is, where negative complexes are present in large proportion.

Bjerrum (*Z. physikal. Chem.*, 1923, **106**, 219) suggested that in the case of symmetrical weak acids, the dissociation constants were connected by the relationship

$$K_1/K_2 = K_2/K_3 = \ldots = Q \qquad (11)$$

This relationship follows if we assume that the free energies of the different complexes differ from one another only in the electrostatic work required to remove the thiocyanate ion to infinity, a quantity which will increase in regular increments from one complex to the next. Though this is undoubtedly an over-simplification, Bjerrum's relationship seems to give reasonable results in a number of cases. The uncertainty in the value of k_3 (which affects both K_3 and K_4) makes a direct test of this hypothesis impossible with the figures obtained in this work, but the theory may be tested in another way. By combining equations (8) and (11), we find

$$(Fe)_W/(Fe)_E = k_0[CNS^-]^{-3} + k_0K_1[CNS^-]^{-2} + k_0K_1{}^2Q[CNS^-]^{-1} + k_0K_1{}^3Q^3$$
$$+ k_0K_1{}^4Q^6[CNS^-] + k_0K_1{}^5Q^{10}[CNS^-]^2 + k_0K_1{}^6Q^{15}[CNS^-]^3 \quad . \quad (12)$$

Q is most easily found by assuming the logarithmic curve to be symmetrical, and by equating, for example, the coefficient of $[CNS^-]^{-3}$ to that of $[CNS^-]^3$ after shifting the origin to that used in the solution of equation (9), thus : $k_0/P^{-3} = k_0K_1{}^6Q^{15}P^{-3}$, P and K_1 being known. Equation (12) is then solved for any one experimental point to obtain k_0, and the other constants follow. Since, however, there is a possibility that a systematic error has been caused by substituting ammonium thiocyanate for sodium perchlorate progressively throughout the series, and since K_1 is measured in excess of perchlorate, it is probably sounder not to assume that the point of symmetry is the same as that found experimentally, but to solve equation (12) for the two experimental points where the perchlorate concentration was highest. This may be done graphically. The results are given in Table III, column 4, and the values of log $(Fe)_E/(Fe)_W$ worked out from these are plotted in Fig. 3, Curve *D*.

Curves *B* and *D* are in only approximate agreement, but they show a very marked similarity, and the agreement may possibly be within the limits of a systematic error caused by changing activity coefficients. This seems to show that the complexes differ in stability from one another mainly in the electrostatic strength of their bonds. There must be a considerable covalent contribution to the bond strength, since even the negative complexes are fairly stable; but either this contribution is about the same for all complexes, or it also varies in regular steps with the charge. There are other factors contributing to the stability, such as the symmetry of the complex, and also the heat of hydration caused by the orientation of the solvent dipoles round the charged ions, which cannot be expected to vary in equal steps through the series. The accuracy of the experiments is not sufficient to enable us to gauge even approximately the importance of these factors, except to say that they are evidently not predominating.

The ferric ion forms complexes with many other anions, and its seems probable that the partition method could be used to determine the stability constants in many cases where one of the complexes is a neutral molecule. It is noteworthy that the ability of ethers to extract ferric chloride (Dodson, Forney, and Swift, *J. Amer. Chem. Soc.*, 1936, **58**, 2573; Nachtrieb and Conway, *ibid.*, 1948, **70**, 3547) passes through a maximum similar to the maximum found in the present work, at a chloride concentration of about 6—10M. This seems to indicate that negative complexes of the type $FeCl_4^-$ to $FeCl_6^{3-}$ predominate at these concentrations, and migration experiments in 11M-acid, carried out in the apparatus described above, though not very definite, seemed to bear out this conclusion. (In their spectroscopic study, Rabinowitch and Stockmayer detected the presence of the lower complexes $FeCl^{2+}$ to $FeCl_3$, and found some evidence of negative complexes at chloride-ion concentrations of about 10M.)

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