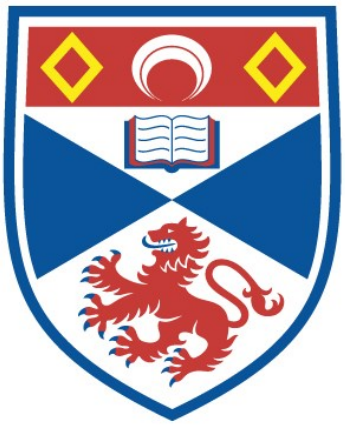
THE NATURE OF THE FERRIC THIOCYANATE COMPLEXES

Kenneth McLean Mitchell

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE NATURE OF THE FERRIC THIOCYANATE COMPLEXES

A Thesis by

KENNETH McLEAN MITCHELL

presented to the

UNIVERSITY of St.ANDREWS

in application for the degree

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RESEARCH TRAINING AND EXPERIENCE

I first matriculated at the University of St.Andrews in October 1942 and graduated Bachelor of Science in June 1945, being subsequently awarded first class Honours in Chemistry in June 1946. In October of that year, I was enrolled as a Research Student under the direction of Dr.J.Y.Macdonald. During session 1948-9, I worked on a problem in kinetics at the School of Chemistry in the University of Alabama, U.S.A., and was awarded the degree of Master of Science of that University. Thereafter, I returned to the University of St.Andrews and completed the research work, herein described, by January 1950.

D E C L A R A T I O N

I hereby declare that the following dissertation is a record of work carried out by me, that it is my own composition, and that it has not been accept-ed in any previous application for a higher degree. The work was carried out in the Chemical Research Laboratory of the United College in the University of St.Andrews under the direction of Dr.J.Y.Macdonald.

16:4:51

C E R T I F I C A T E

I certify that Kenneth Mc.Lean Mitchell has spent nine terms at research work under my supervision, that he has fulfilled the conditions of Ordinance No.16 (St.Andrews) and that he is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

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INTRODUCTION

The red colour produced when thiocyanate is added to a solution of a ferric salt is well known as a sensitive test for iron. Yet, despite its wide application in this respect, it is surprising that attempts to define the exact nature of the markedly coloured compound have been confined to the last two decades. On the other hand, the concepts generally accepted in the earlier part of this century that ferric thiocyanate belonged to the class of co-ordination compounds described by Werner, and that its formula was $Fe.Fe(CNS)_6$ were not unreasonable in the light of work on ferricyanides to which ferric thiocyanate would naturally appear analogous and allied. Had it not been for the increased availability of optical methods of chemical analyses, it is possible that the hexathiocyanic compound might yet be accepted. For it is both notable, and unfortunate, that the first attempts to identify the exact nature of the compound seemed to indicate the existence of an iron-thiocyanate complex of the type $Fe(CNS)_6^{3-}$ and it is interesting that this concept has been used as

recently as 1949(3). However, the observations of a number of workers based on optical experiments made it quite clear that a simple ion of the type $FeCNS^{2+}$ existed in aqueous iron-thiocyanate solutions, and not only was it coloured, but formed almost to the exclusion of all other possible ions when iron and thiocyanate ions were mixed under conditions of dilution. At present, the probability is entertained, with some conviction, that the addition of thiocyanate to an aqueous solution containing ferric ions results, not in the formation of a single complex ion, but of a whole series of such ions in which the number of thiocyanate groups attached to a single iron ion may range from one to six, the proportions of the various complexes depending upon the concentration of thiocyanate employed. Moreover, depending on the number of thiocyanate groups attached to an iron ion, the electrostatic charge born by the various complexes will be positive or negative, or zero in the particular case of the neutral molecule $Fe(CNS)_3$. In addition, it must be remembered that, under conditions of high thiocyanate concentration required for the formation of the negative complexes $Fe(CNS)_4^-$, $Fe(CNS)_5^{2-}$, and $Fe(CNS)_6^{3-}$, the concentration of free ferric ions becomes negligible, and that these

negative ions are in equilibrium with the cations of the thiocyanate donating salt and are, consequently, anions of salts of the type $K_3Fe(CNS)_6$ (say) rather than $Fe.Fe(CNS)_6$, as might be expected.* It is not easy to predict which iron-thiocyanate complex will predominate in any particular solution, except under conditions of high dilution; moreover, with the exception of the simplest complex $FeCNS^{2+}$, it has not been possible until now to establish with certainty, the individual identity of any of the complexes postulated. Furthermore, care must be exercised in any claim concerning the nature of the ferric thiocyanate complexes present in a solution based on observations made on solutions under remotely different conditions of concentration.

Before an account is given concerning the development of these ideas, and concerning contemporary researches, mention should be made that ferric thiocyanate cannot readily be obtained, if at all, in a state of crystalline purity, and this would

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* Crystalline salts corresponding to the formula $R_3Fe(CNS)_6$, where R = Na^+, K^+, or NH_4^+, have been prepared, and analysed by Rosenheim and Cohn[25].

perhaps be anticipated in consideration of the apparent extreme solubility of ferric thiocyanate in water, its deliquescence, and its tendency to decompose either chemically, or by the agency of light. Repeated attempts to prepare the compound have been unsuccessful, the product being contaminated with divalent iron and sulphur-containing compounds. Success has, indeed, been claimed for the preparation of crystalline ferric thiocyanate but, though the validity of such a preparation cannot be denied, it cannot be accepted without reserve.

In 1931 Schlesinger and Van Valkenburgh[27] reported the preparation of crystalline ferric thiocyanate which they found to be soluble in ether and in benzene. The molecular weight of ferric thiocyanate calculated from the elevation in boiling point and depression of freezing point of solutions in these solvents was shown to correspond to that of double molecules $Fe_2(CNS)_6$. In aqueous solution, the red colour moved towards the anode when subjected to an electric potential, and it seemed evident that the formula of ferric thiocyanate could be given with certainty as $Fe.Fe(CNS)_6$ in view of the negatively charged coloured ion.

It is notable that, in 1937, Möller[19] postulated ions of the type $FeCNS^{2+}$, $Fe(CNS)_2^+$ and $Fe(CNS)_4^-$ as a result of conductivity measurements, but not until 1941 was the ion $FeCNS^{2+}$ firmly established as a result of optical experiments by Bent and French[4]. Colour experiments by these workers designed to determine the dissociation constant of $Fe(CNS)_6^{3-}$ indicated the absence of this complex and that the colour denoting compound produced under the conditions of their experiments consisted of a single iron ion attached to only one thiocyanate ion - $FeCNS^{2+}$. Furthermore, the compound was shown to carry a positive charge since it migrated towards the cathode when subjected to an electric potential. The existence of this simple complex was further substantiated by similar optical experiments by Edmonds and Birnbaum[8], Gould and Vosburgh[11], and by the independent observations of at least one other worker at an early date*. Moreover, Ricco and Faraone[24] recently obtained evidence for the complex $FeCNS^{2+}$ and the possible existence of $Fe(CNS)_2^+$ based on the reduction in conductivity noted when iron and

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* J.Y.Macdonald, The University of St. Andrews, 1944.

thiocyanate solutions are mixed, and, to them, these ions appeared analagous to ferric azide, $Fe(N_3)^{2+}$, a coloured ion with similar electron distribution.(24)

It became evident that, below a limiting thiocyanate concentration, the red colour of ferric thiocyanate solutions is contributed almost wholly by the simple ion $FeCNS^{2+}$. Consequently it is possible to obtain a value for the dissociation constant of this complex since it may be assumed that light absorption in the visible region is due to $FeCNS^{2+}$ alone, and that any measure of light absorption is a measure of the concentration of that ion. As the thiocyanate concentration increases the proportions of the higher complexes become involved, and optical density measurements cease to be of value as a measure of concentration. Values of the dissociation constant of $FeCNS^{2+}$ have been obtained in this way by the above mentioned workers(4, 8) and it has been shown that variation in the numerical value of the constant associated with change in ionic strength is in harmony with the current theories.

Much information relating to the iron thiocyanate complexes has been published during the course of the researches shortly to be described.

Babko(1), 1946, and Frank and Ostwalt(9), 1947,

have substantiated the work of Bent and French by furnishing similar evidence for the complex $FeCNS^{2+}$ and have obtained values for its dissociation constant; these workers also indicate concentrations of thiocyanate above which complexes other than $FeCNS^{2+}$ would be expected to form in more than negligible amounts.

The nature of ferric thiocyanate in organic solvents has aroused some interest. Uri[30], 1947, claims a double molecule in 96% alcohol based on measurements of conductivity and consideration of the dimer postulated by Schlesinger and Van Valkenburgh[27]. Baldwin and Svirbely[3], 1949, also favour the dimer and negative complexes in aqueous organic solvents - acetone, ethanol, methanol, glycerol, and others - as a result of optical measurements on solutions in iso-dielectric solvents. Finally, Ferrari and Cavalca[10], 1948, have emphasised the frequency of co-ordination number 4 in thiocyanate complexes, e.g. $Cu(CNS)_4^{3-}$, $Ag(CNS)_4^{3-}$, and Babko[2] has given some attention to the stability of $Fe(CNS)_4^{-}$ on theoretical rather than practical grounds.

In view of what has been said, it will be realised that, of all the postulated iron thiocyanate complexes, only the simplest one $FeCNS^{2+}$, has been identified with certainty. For, apart from this complex, the identity

of the higher complexes has been rather uncertain, evidence for their formation being based to a large extent upon discrepancies in observation anticipated with $FeCNS^{2+}$ in mind and tending in a direction supported by the postulation of such higher complexes as have been mentioned. It seemed advisable to proceed with further researches on the subject with a view to elucidating the nature of the ferric thiocyanate complexes, and, to this end certain justification was lent in consequence of the early discovery of the $FeCNS^{2+}$ ion in the laboratory at St. Andrews.

AIMS OF RESEARCH ON FERRIC THIOCYANATE

We may thus accept, from the work of other authors, that a series of complexes ranging from $FeCNS^{2+}$ to $Fe(CNS^{-})_6^{3-}$ may be formed; that, in dilute solution, the simplest complex $FeCNS^{2+}$ is the only one to be formed, and that the stability constant of this complex, which varies with ionic strength, is of the order 100. It is also known that ferric ions form complexes with other anions, such as hydroxide and chloride ions, which will interfere by competing with the thiocyanate ions for the iron. It is generally assumed that nitrate and perchlorate ions do not form such complexes, but there seems to be no proof for this, at least in the rather high concentrations used in this work.

The main objective of this work has been to apply the partition law to an elucidation of the ferric thiocyanate equilibria. It was first shown that the only complex which is extracted by ether when it is shaken with aqueous solutions of ferric thiocyanate is the neutral molecule $Fe(CNS)_3$, with no measureable polymerisation or dissociation. Estimation of the concentration of ferric iron in the ether phase thus gives a measure of this

particular species in the aqueous phase, and, by conducting these experiments over a range of thiocyanate concentrations, it has been possible to establish values of the stability constants of all the postulated species. The theory is as follows.

The amount of ferric thiocyanate extracted by ether from an aqueous solution of ferric thiocyanate is determined by the partition coefficient n, where

$$\left[Fe(CNS)_3\right]_W = n\left[Fe(CNS)_3\right]_E$$

$\left[Fe(CNS)_3\right]_W$ is the concentration of undissociated ferric thiocyanate molecules in the aqueous phase and $\left[Fe(CNS)_3\right]_E$ is the total concentration of ferric thiocyanate (or iron) in the ether phase hereafter denoted, for brevity, by Fe_E. The advantages to be gained by the study of partition experiments arise from the fact that the product of Fe_E x n gives, at once, the concentration of one of the seven postulated iron thiocyanate complexes to which the concentration of all the other complexes must be related by means of equilibrium constants. The various equilibria in the aqueous phase are denoted by the following equations:-

Equilibrium	Equilibrium Constant
$Fe(CNS)_3 \rightleftharpoons Fe^{3+} + 3CNS^-$	k_0
$\rightleftharpoons Fe(CNS)^{2+} + 2CNS^-$	k_1
$\rightleftharpoons Fe(CNS)_2^+ + CNS^-$	k_2
$CNS^- + Fe(CNS)_3 \rightleftharpoons Fe(CNS)_4^-$	k_4
$2CNS^- + Fe(CNS)_3 \rightleftharpoons Fe(CNS)_5^{2-}$	k_5
$3CNS^- + Fe(CNS)_3 \rightleftharpoons Fe(CNS)_6^{3-}$	k_6

The general equilibrium constant appertaining to the above equilibria takes the form

$$k_x = \frac{\left[Fe(CNS)_x^{3-x}\right]\left[CNS^-\right]^{3-x}}{n\ Fe_E}$$

where x has the values 0 - 6. In the particular case when $x = 3$, k_x will, of course be equal to unity. The above constants are related to the usual stability constants of the complexes as follows:-

$$\frac{k_1}{k_0} = K_1 = \frac{\left[FeCNS^{2+}\right]}{\left[Fe\right]\left[CNS^-\right]}$$

$$\frac{k_2}{k_1} = K_2 = \frac{\left[Fe(CNS)_2^+\right]}{\left[FeCNS^{2+}\right]\left[CNS^-\right]} \qquad \text{etc.}$$

From the general equilibrium constant, k_x, it follows that the concentration of any complex in the aqueous phase may be given by

$$\frac{Fe_E}{[CNS^-]^{3-x}} \cdot nk_x$$

where x is the number of the thiocyanate groups attached to the iron atom in the particular complex. It also follows that the total concentration of iron, free and combined, in the aqueous phase, Fe_W, must be equal to

$$\sum_{x=0}^{x=6} \frac{Fe_E}{[CNS^-]^{3-x}} \cdot nk_x = Fe_W$$

whence

$$\sum_{x=0}^{x=6} nk_x [CNS^-]^x = \frac{Fe_W}{Fe_E} \cdot [CNS^-]^3$$

On expansion this becomes

$$nk_0 + nk_1[CNS^-] + nk_2[CNS^-]^2 + nk_3[CNS^-]^3 + nk_4[CNS^-]^4 + nk_5[CNS^-]^5 + nk_6[CNS^-]^6 = \frac{Fe_W}{Fe_E} \cdot [CNS^-]^3$$

This equation correlates the experimentally obtainable values Fe_W, Fe_E and (CNS^-) - the thiocyanate ion concentration in the aqueous phase - with all six equilibrium constants and n, the partition coefficient

which are the desired unknowns. These constants may then be obtained in theory, at least, by any mathematical manipulation whereby an equation of the above type may be solved (i.e. a homogeneous equation in ascending powers of a known variable - in this case thiocyanate concentration).

The relative proportions of the complexes in any solution will be given by

$$Fe^{3+} : FeCNS^{2+} : FeCNS_2^{+} \quad \ldots\ldots\ldots \quad FeCNS_5^{2-} : FeCNS_6^{3-}$$

$$= k_0[CNS^-]^{-3} : k_1[CNS^-]^{-2} : k_2[CNS^-]^{-1} \quad \ldots\ldots\ldots \quad k_5[CNS^-]^{2} : k_6[CNS^-]^{3}$$

$$= k_0 : k_1[CNS^-] : k_2[CNS^-]^{2} \quad \ldots\ldots\ldots \quad k_5[CNS^-]^{5} : k_6[CNS^-]^{6}$$

One very interesting conclusion from this theoretical study is that the relative proportions of the various complexes, though dependent on the thiocyanate concentration and on activity coefficient, 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. This has been proved by light absorption experiments in an interesting way. It follows that, although ferric iron can be determined colorimetrically keeping the thiocyanate concentration and activity

constant, it is not possible to use this reaction for the quantitative estimation of thiocyanate colorimetrically, for, even if the iron concentration were kept the same, the varying thiocyanate concentration would bring about a variation in the proportions of the complexes with consequent variation in both the tint and the intensity of colour absorption.

The distribution experiments described above have enabled fairly accurate estimates of the stability constants of all species to be determined. From these, a nomogram has been prepared from which the proportions of each complex at different thiocyanate concentrations may be read off. It has been found that the absorption spectra of the mixed species varies both in intensity and wavelength of maximum absorption with variation in thiocyanate concentration and it is now possible, using the nomogram above, to set up a series of simultaneous equations from which at least rough values of the absorption coefficients of each species might be determined at various wavelengths. Light absorption measurements have also been used to simplify the calculation of the various stability constants mentioned above, for, in low concentrations of thiocyanate, only

the simplest complex is formed and its stability constant may be calculated from optical measurements at two suitable concentrations. This reduces the number of parameters to be calculated in solving the partition equation given above.

The equilibria being studied are sensitive to the activity coefficient and thus to the ionic strength of the solution. For this reason, the ionic strength of solutions studied was usually kept constant at a high value corresponding to that of the highest thiocyanate concentration used, by additions of potassium nitrate or sodium perchlorate. Addition of these (and other) salts to an iron-thiocyanate mixture results in a reduction in the intensity of the colour, and whereas this may be due simply to the increase in ionic strength with consequent reduction in the activity coefficient of the reacting ions, there was no certainty that competing complexes of the type $FeNO_3^{2+}$ (say) were not being formed. By keeping the nitrate concentration constant and altering the activity coefficient (by substituting lithium nitrate for potassium nitrate) and conversely by keeping the activity coefficient constant and altering the nitrate concentration, it has been possible to show that the

effect is at least mainly due to the change in ionic strength. No reliable evidence for the formation of complexes with nitrate ions was found.

The distribution measurements indicated that above a certain thiocyanate ion concentration, the total concentration of negatively charged ferric thiocyanate complexes exceeds that of the positive ones. Moving boundary migration experiments have been carried out and confirmed this prediction.

PART 1

PART 1

PREPARATION OF SOLUTIONS AND SOLVENTS

All aqueous solutions of ferric thiocyanate employed in this work were prepared by mixing solutions of ferric and thiocyanate salts. The choice of ferric salts is limited since it is known that ferric ions form complexes with certain cations. It is generally believed that neither nitrate nor perchlorate ions form such complexes; Rabinowitch and Stockmayer[23] found no evidence of complex formation up to 3M ClO_4^-. Consequently, salts of these ions were used.

Since the ferric thiocyanate equilibria are sensitive to activity coefficient, and thus to ionic strength, this was kept constant by the addition of suitable salts - potassium nitrate and sodium perchlorate. A high value of ionic strength was chosen so as to allow of the study of equilibria in fairly high thiocyanate concentrations. The acidity of ferric thiocyanate solutions was also kept constant in the majority of cases, and sufficiently high to repress hydrolysis. Bray and Hershey[6] and Lamb and Jacques[16] found that, in the absence of acids,

the ferric ion concentration is reduced by the reaction

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$$

which has a hydrolysis constant

$$K_h = 6 \times 10^{-3} \quad \text{(B. and H.)}$$
$$2.5 \times 10^{-3} \quad \text{(L. and J.)}$$

Using the latter,

$$\frac{[Fe(OH)^{2+}]}{[Fe^{3+}]} = \frac{2.5 \times 10^{-3}}{[H^+]}$$

$$= 2.5 \times 10^{-2} \quad \text{(when } [H^+] = 0.1$$

Thus, in 0.1N acid, the hydrolysis error is about 2.5 percent. In 0.18N acid, the error is about 1.4 percent. In most of the subsequent experiments, the ferric thiocyanate solutions were about 0.18N with respect to acid, and the hydrolysis error ignored.

The stock solutions were prepared as follows:-

<u>0.03M Ferric Perchlorate</u> was prepared by dissolving freshly precipitated ferric hydroxide in perchloric acid. The ferric hydroxide was precipitated from ferric alum (Analar grade) by addition of aqueous sodium hydroxide, washed several times with hot water, and dissolved in perchloric to an acidity of 0.9N.

0.03M Ferric Nitrate in 0.9N nitric acid was prepared in like manner.

2M Potassium Thiocyanate. Analar potassium thiocyanate was recrystallised twice from methyl alcohol and dried by heating to 60°C. The product so obtained was non-hygroscopic and could be easily weighed.

2M Ammonium Thiocyanate. The salt was purified in like manner.

Potassium Nitrate, (laboratory grade) was recrystallised twice from hot water.

Sodium Perchlorate. Recrystallised Hopkins-Williams sodium perchlorate was used.

The iron solutions were standardised by titanous sulphate, the perchlorate solutions by precipitation of the potassium salt, and the thiocyanate solutions by precipitation of the silver salt. All solutions used in optical work were filtered prior to standardisation and allowed to stand in the dark for some time to allow dust and filter particles to settle.

Appropriate solutions containing thiocyanate concentrations up to 1.6M could be prepared from these stock solutions, in which the ionic strength was maintained at 1.78 and the acid concentration at 0.18N.

PART 2

PART 2.

THE MOLECULAR STATE OF FERRIC THIOCYANATE IN ORGANIC SOLVENTS.

Ebullioscopic Methods - Ether and Alcohol

Conductivity Method - Ether

Solubility in Benzene

Ferric thiocyanate is soluble in a limited number of organic solvents, notably the lower alcohols, ethers, and in acetone and glycol. The solubility diminishes with increasing length of carbon chain. Despite this marked solubility in organic solvents, the nature of ferric thiocyanate in such solvents is not well defined. Before proceeding with the partition experiments, it was necessary that some understanding should be reached concerning the molecular state of ferric thiocyanate in ether, since the state of aggregation in the extracting solvent would have a profound bearing on any calculation concomitant with these essays.

It has generally been accepted that ferric thiocyanate exists as a dimer, $Fe.Fe(CNS)_6$, in organic solvents. Schlesinger and Van Valkenburgh[27]

determined the molecular weight of ferric thiocyanate in benzene and in ether by cryoscopic and ebullioscopic methods, and concluded that ferric thiocyanate was dimeric in these solvents. It will be recalled that a crystalline preparation was employed for these experiments and, as will be shown, such a preparation, and any data accumulated as a result of its use for experimental purposes, are best treated with reserve. On the other hand, Uri[30] has shown conclusively by conductivity measurements on iron-thiocyanate solutions in 96% alcohol that the iron thiocyanate ratio is 1 : 3. On the basis of the previous work, Uri assumed a dimer exists in 96% alcohol as does in ether and in benzene. These findings have, in turn, led Baldwin and Svirbely[3] to assume that in iso-dielectric aqueous-non-aqueous solvent pairs, there exists an equilibrium of the type

$$Fe^{3+} + Fe(CNS)_6^{3-} = Fe.Fe(CNS)_6$$

since such an equilibrium offers a plausible explanation for the variation in colour intensity of solutions of ferric thiocyanate in such solvents. The intense colours in solvent pairs which are poor electron donors is attributed to the complex

$Fe.Fe(CNS)_6$, while the less intense colour of solutions in solvents which are more freely electron donating is due to the formation of the less intensely coloured $Fe(CNS)_6^{3-}$ ions.

Since the work of Schlesinger and Van Valkenburgh is associated with some uncertainty, and since their conclusions have, to some extent, influenced the findings of subsequent workers, it was desirable that the molecular state of ferric thiocyanate in organic solvents should be clarified, particularly in the case of ether as solvent. Determinations of molecular weight by the boiling point method have shown that ferric thiocyanate exists as a monomer in both ether and alcohol. Furthermore, conductivity measurements on ethereal solutions indicate that all the iron in the ether is in the molecular and not the ionic form. Attempts to prepare solutions of ferric thiocyanate in benzene have failed, and it has been concluded that ferric thiocyanate is not soluble in pure benzene.

Boiling point measurements were made with the aid of a differential ebulliometer specially constructed for the purpose. The design and calibration of this apparatus are described in some detail in subsequent pages.

APPARATUS.

The molecular weight of ferric thiocyanate in ether and in alcohol has been calculated from measurements of boiling point of such solutions determined with the aid of a differential ebulliometer of the Swietoslawski type,[29,32] specially constructed for this work* (fig.1). Essentially, the apparatus is a modified form of the Washburn ebulliometer and may be used to determine, directly, the elevation in boiling point of a solution, thus eliminating any error (or necessary correction) resulting from possible fluctuations of the atmospheric pressure.

The solution, contained in the bulb "X" is heated to boiling by an externally wound coil, while ebullition is promoted by a small internal coil in series with the outer windings. The vapour, unable to escape, rises up the narrow outlet tube carrying with it solution which is finally ejected on to the first thermometer cup. The hot solution trickles down the helicoidal spiral sealed

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* Apparatus constructed by Dr. J.Y.Macdonald.

round the thermometer cup and returns to the bulb containing the boiling solution. The hot vapour, on the other hand, passes over the second thermometer cup, and, after condensation by a double-spiral water-cooled condenser returns to the boiler by way of the drop counter "Y".

When equilibrium has been attained, the first thermometer, "B", registers the boiling point of the solution and the second thermometer, "A", records the boiling point of the solvent. In practice, thermometers with arbitrary scales are used, and the scales are standardised before elevations in boiling point can be determined.

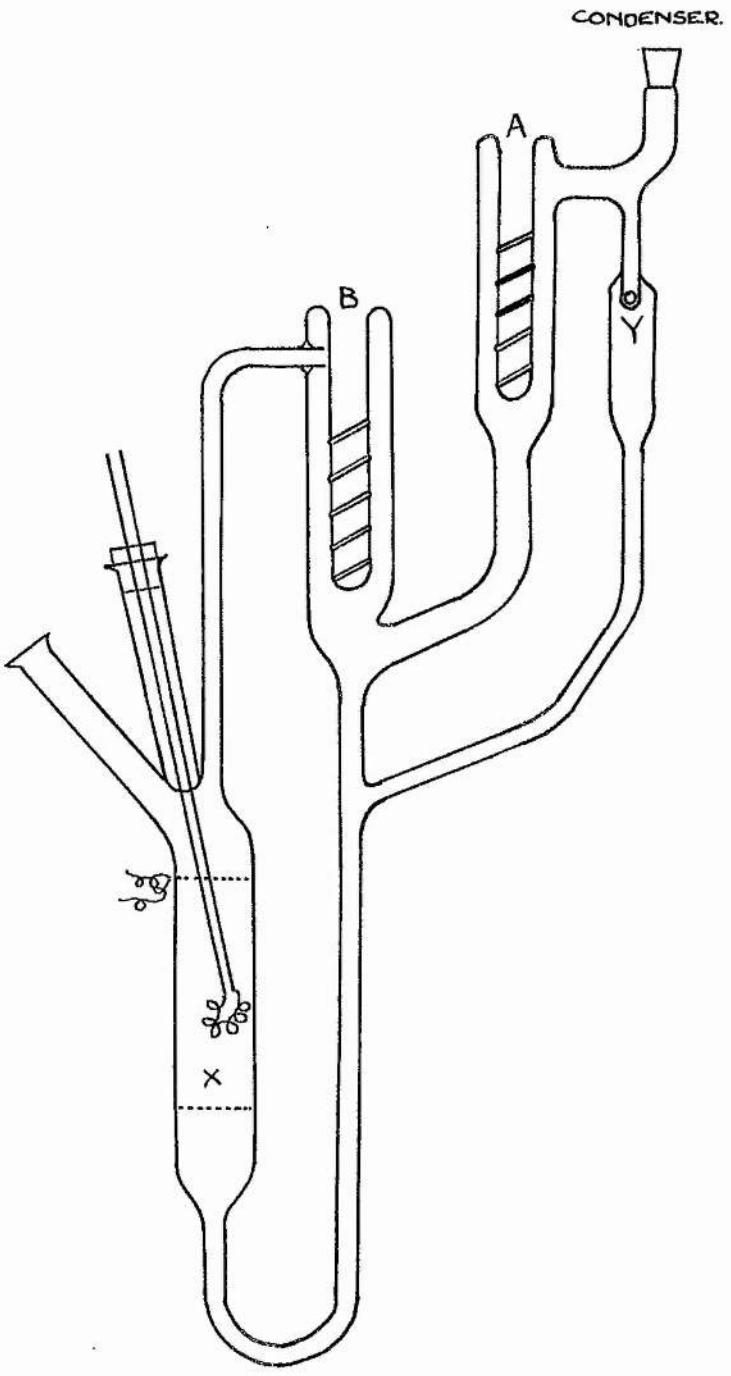


FIG. 1

STANDARDISATION OF THE EBULLIOMETER

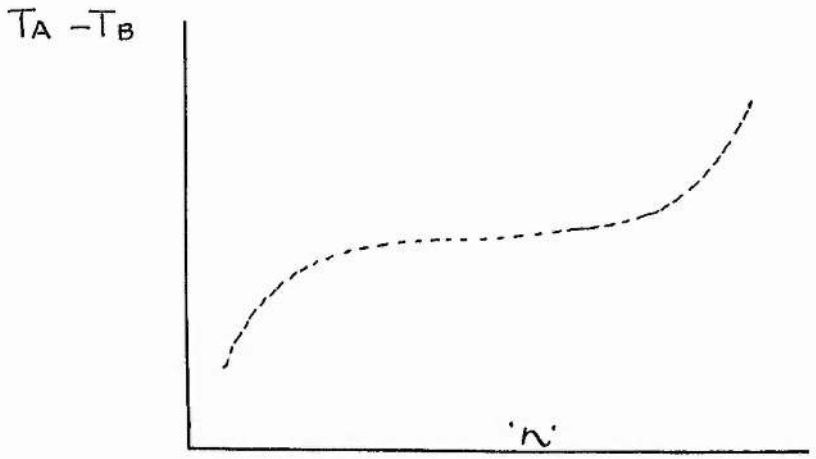
AND THE PROCEDURE FOR ITS USE

1. Rate of Ebullition (Regulation of heating).

Over-heating of the solution may result in superheating to such an extent that equilibrium between solution and vapour is not attained at the instant when the solution is ejected on to the first thermometer cup. Insufficient heating results in similar sources of error. It is, therefore, essential to regulate the heating within appropriate limits and the drop counter is incorporated to facilitate doing so. When pure solvent is boiling in the apparatus, each thermometer registers the true boiling point, T_A and T_B, measured on similar scales with arbitrary "fixed points": that is, provided no superheating occurs, a constant value should be obtained for the difference in the readings on the two thermometers, $T_A - T_B$; such will not, however, be the case when the solution is over or under-heated, and, if the amount of heat applied to the solution is varied, it is possible to plot the values of $T_A - T_B$ thus obtained against the number of drops, "n", falling from the drop counter. An S-shaped curve is obtained

from which can be read an optimum value of "n" for the particular solvent. Should the number of drops be maintained at this value in subsequent experimentations with that particular solvent, that is, by regulation of the heating current, a sufficient heating will be ensured without superheating.

A typical curve is shown.



2. Calibration of the Thermometers. Beckmann thermometers were used and these were calibrated in the apparatus using the solvent in the same condition as it is to be used in the final experiment, and it has been assumed that when moist solvent is used, the degree of fractionation occurring in both cases would be approximately the same. When solvent is boiling in the apparatus and the rate of boiling is at its optimum, the constant value of (T_A-T_B) is recorded

(variation $\pm$ 0.004°C).

When solution is boiling in the apparatus, T'_B will be the boiling point of the solution and T'_A that of the solvent: ($T_A = T'_A$ provided there is no change in pressure). Hence, $T'_A - T'_B$ will be less than $T_A - T_B$ by an amount equal to the elevation in boiling point of the solution. Consequently, the elevation in boiling point of any solution may be rapidly determined by subtracting the experimental value of $T'_A - T'_B$ from the value of $T_A - T_B$ previously determined for the solvent (and always provided that the same thermometers with similar arbitrary scales be used).

3. Summary of Procedure. The procedure to be adopted for the determination of molecular weights may be summarised.

   a) Determination of the constant numerical difference in the readings on the arbitrary scales of the thermometers, $T_A - T_B$ (solvent in ebulliometer).

   b) Determination of elevation in boiling point of solutions of a solute, the molecular weight of which is known, in the solvent. From this datum, the elevation constant for the solvent may be calculated. (Alternatively, a theoretical value of the elevation constant may be used instead of an experimental value).

c) Determination of elevation in boiling point of solution and subsequent calculation of the molecular weight of any solute, by means of the elevation constant.

4. Heat Loss. The apparatus was lagged with cotton wool to diminish loss of heat and to ensure more rapid attainment of equilibrium. This measure was considered desirable in view of possible decomposition in the ferric thiocyanate at the temperatures of the boiling solutions. The whole apparatus was contained in a glass cupboard which afforded protection from draughts.

5. Analysis of Solutions. The solutions were analysed at the end of the experiment. The current was switched off, and the solution allowed to cool, in order to reduce loss by vaporisation: two samples of solution were then drawn off for analysis. The samples were weighed and analysed quantitatively by titrametric methods.

EXPERIMENTAL

The molecular weights of ferric thiocyanate in alcohol and in ether have been determined.

The preparation of solutions of ferric thiocyanate in these solvents is attended by considerable difficulty since, as will be shown, solid ferric thiocyanate cannot be obtained in a state of purity. A solution in dry alcohol can be prepared, indirectly, by the interaction of alcoholic solutions of ferric sulphate and barium thiocyanate, both of which are soluble in alcohol to a considerable extent while barium sulphate is not soluble. The comparatively low solubilities of these substances in ether render this method impracticable for preparing solutions of ferric thiocyanate in ether and these had to be prepared by extraction of an aqueous solution with AnalaR ether. The ethereal solutions, thus prepared, were saturated with water and attempts to remove the water were not successful. Anhydrous sodium sulphate decolourised the solutions while sodium, phosphorus pentoxide and other desiccating agents result in the formation of deleterious by-products. In consequence, the molecular weight of ferric thiocyanate was determined in ether saturated with water: a certain amount of

fractionation occurred between the two thermometers, giving rise (in the case of ether saturated with water) to a difference in temperature of 0.023°C. The extent of this fractionation was assumed to be the same for all solutions though this will not be quite correct, since the solution of water in ether, and, hence its vapour pressure, are not independent of other solutes.

Experiments to Test the Ebulliometer.

A. Salicylic Acid in Dry Ether. Figures are given for experimentally determined values of the molecular elevation for dry ether, K, calculated as being the elevation in boiling point of 1000 gm of ether in which is dissolved one gm mol of salicylic acid. Values of K calculated from the data in the International Critical Tables, are shown for purposes of comparison.

Table 1

Conc. gm mol / 1000 gm	K I.C.T.	K Obs.
0.0767	-	2.065 a)
0.100	2.16	-
0.200	2.18	-
0.237	-	2.16 b)
0.300	2.22	-
0.441	-	2.20 b)

Notes: a) The concentration of salicylic acid was estimated by evaporation of the ether from a known weight of solution: the ether was removed with the aid of a fan followed by heating in an oven for two hours at 40°C.

b) The concentration of salicylic acid estimated by titration with standard alkali.

The figures show good agreement and are indicative of the reliability which may be placed on the ebulliometer.

B. Benzoic Acid in Dry Alcohol. Similar experiments were performed, as a check on the procedure adopted, employing alcohol as the solvent. Benzoic acid was selected as solute since the molecular elevation calculated over a wide range of concentration is reasonably constant. The acid used in these experiments was not recrystallised or further purified in any way: its estimation was effected by titration of the diluted alcoholic solution with aqueous alkali (dilution with water). The results are tabulated and comparison can be made with values of the molecular elevation derived from the International Critical Tables.

Table 2

Conc. gm mol / 1000	K I.C.T.	K Obs.
0.10	1.15	-
0.20	1.15	-
0.273	-	1.17
0.326	-	1.117
0.33	-	1.11
0.50	1.14	-
0.70	1.135	-

Once again, agreement between the figures served as a check on the apparatus.

EBULLIOSCOPIC CONSTANTS FOR MOIST ETHER AND DRY ALCOHOL

The thermodynamic ebullioscopic constant for dry ether is calculated to be 2.10°C so that the constant for moist ether will have a value numerically less than this. In order to determine this value, ebullioscopic observations were made on a solution of salicylic acid in ether previously saturated with water, and, also, on ethereal solutions of ~~hydro~~thiocyanic acid obtained by extraction of an aqueous solution. The values of K thus determined for moist ether are compared, in the tables, with the values obtained for dry ether, taken from the previous experiments in the case of salicylic acid, and from the International Critical Tables in the case of thiocyanic acid.

Table 3

Salicylic acid		Thiocyanic acid		
Conc. gm mol / 1000 gm	K Obs.	Conc. gm mol / 1000 gm	K I.C.T.	K Obs.
0.237	2.16	0.10	-	2.075*
0.287	2.12*	0.20	1.917	
0.441	2.20	0.35	-	2.08*
-	-	0.50	1.925	

* wet ether

A value of 2.09°C was chosen as the ebullioscopic constant for moist ether.

It should be observed that the figures also serve to show that the thiocyanic acid has its normal molecular weight in (moist) ether.

The ebullioscopic constant for dry alcohol was taken as 1.19°C, a reliable value calculated by Hoyt and Fink.(14)

PREPARATION OF SOLUTIONS OF FERRIC THIOCYANATE IN MOIST ETHER AND IN ALCOHOL

Repeated attempts were made to prepare pure crystalline ferric thiocyanate after the manner described by Schlessinger,[27] that is, by slow evaporation of a solution prepared from barium thiocyanate and ferric sulphate, or from thiocyanic acid and ferric hydroxide. In no instance was a pure product obtainable, the iron being very largely in the ferrous condition, free sulphur and poly-sulphides being produced. A typical analysis of three crops of crystals from the same batch is given.

Table 4

Crop	Thiocyanate	Ferric	Ferrous
First (large)	10.1 %	2.25 %	
Second	16.5 %	2.68 %	
Third (small)	29.3 %	2.57 %	23.6 %
Theoretical (anhydrous)	75.8 %	24.2 %	0.0 %

It is evident that an internal oxidation-reduction was taking place: the evaporation was carried out in the dark and extended over several weeks.

Evaporation of an ethereal extract did not prove to be satisfactory as difficulty was experienced in drying the extract. On adding the ethereal extract to a large volume of benzene, droplets of water separated out and could be removed by filtration through several thicknesses of paper, and, when the ether was removed under diminished pressure, a solid separated and this was found to have the composition : $CNS^{'}$ = 23.6%, Fe^{3+} = 5.48% and Fe^{2+} = 19.0%.

In view, therefore, of these results, attempts to prepare a crystalline solid were abandoned and solutions were prepared as follows.

1. In Ether. An aqueous solution of potassium thiocyanate, ferric sulphate and sulphuric acid was extracted with AnalaR ether and the wet extract used directly in the ebulliometer, its composition being determined by titrametric analysis. The extract was found to contain thiocyanic acid to a considerable extent, but to be free from sulphate, showing that no extraction had occurred of complexes analogous to those extracted by ether from solutions of ferric chloride in hydrochloric acid. Every effort was made to ensure complete separation of the ethereal and aqueous layers after extraction.

2. In Alcohol. An alcoholic solution of ferric thiocyanate was prepared indirectly by shaking a solution of anhydrous ferric chloride in alcohol for some hours with silver sulphate. The solution contained exactly equivalent amounts of ferric and sulphate ions. The resultant solution was then shaken for four hours with the exact equivalent of anhydrous barium thiocyanate. A gelatinous precipitate was formed, and, while this could be removed by filtration only with the greatest difficulty, it was readily separated in a centrifuge. The solution, again, contained thiocyanic acid but no sulphate and only a trace of barium could be detected.

EXPERIMENTAL RESULTS.

The following tables record the results obtained using solutions prepared as above. In calculating the results, the elevation due to the thiocyanic acid is worked out and deducted from the total elevation. The difference is assumed to be due solely to ferric thiocyanate, the molecular weight of which is to be determined.

The theoretical molecular weight for single molecules is 230.

Table 5

Moist Ether. K = 2.09

Conc. $Fe(CNS)_3$ (gm/1000 gm)	Conc HCNS (gm/1000gm)	Total elevation °C	Mol.Wt.
7.876	1.04	0.112	219
35.75	7.06	0.569	234

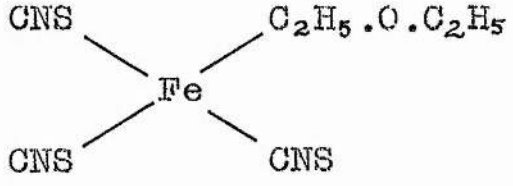
Dry Alcohol. K = 1.19

Conc. $Fe(CNS)_3$ gm/1000 gm	Conc HCNS (gm/1000gm)	Total elevation °C	Mol.Wt.
22.1	1.244	0.144	221
36.7	0.466	0.221	206

It has been concluded from the above results that ferric thiocyanate exists in solution in ether, alcohol and similar polar solvents, only in the form of single molecules, and it is to be noted, in this respect, that, according to the International Critical Tables, ferric chloride, which might be expected to be similar, does also exist as single molecules in ether solution. This has been shown to be the case also for ferric chloride dissolved in alcohol.

Notes on the Alternative Calculation of Results.

Account must be taken of the possible co-ordination by ferric thiocyanate in ether, of molecules either of ether or of water co-ordinated by the iron atom before extraction. Should this be the case, a certain proportion of the weight of the ethereal solution is assumed to be free solvent, when, in fact, it may represent combined ether or even water molecules attached to the ferric ion, and which have been extracted from the aqueous solution. By analogy to ferric chloride, it was assumed that one ether molecule is attached to each iron atom in the molecule giving a molecule of the type



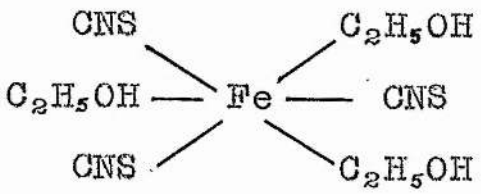
The solution must, therefore, be more concentrated than previously assumed. The experiments were recalculated on this basis and the following results obtained.

Table 6

Conc. $Fe(CNS)_3$ (gm/1000gm)	Conc HCNS (gm/1000gm)	Total elevation °C	Mol.Wt.
7.90	1.042	0.112	220
36.18	7.15	0.569	239.5

The effect of such a correction on the final value of the molecular weight is very small. The weight of one molecule of ether is 74, and this is almost equivalent to the weight of four molecules of water. Consequently, the effect of four co-ordinated water molecules would be similar: since, however, the number of co-ordinated water molecules is not likely to be greater than 3, an intermediate value for the molecular weight would be found.

Thus, also, if it is assumed that a symmetrical molecule is formed by the co-ordination of three alcohol molecules in alcoholic solution, as suggested by the following diagram,



the molecular weight of ferric thiocyanate in alcohol is found to be 221 and 206.

Conclusion

Ferric thiocyanate exists as single molecules in alcohol and ether solutions, and, although this has been demonstrated conclusively by ebullioscopic determinations, these measurements afford no indication of the extent to which ferric thiocyanate forms complex compounds with these solvents.

A NOTE ON THE ELECTRICAL CONDUCTIVITY OF ETHEREAL SOLUTIONS

The validity of the partition method depends upon the assumption that the only substances extracted from the aqueous layers are the molecules $Fe(CNS)_3$ and HCNS. This has been shown to be the case by ebullioscopic experiments and has, in large measure, been confirmed by conductivity measurements which should detect the presence of any ions of the type $FeCNS^{2+}$ (say).

Conductivities were measured in a large Washburn cell - cell constant 0.0161. The following values of resistance and specific conductivity were obtained.

Solution	Resistance ohms	Specific Conductivity mhos
1. Ether, saturated with water	$> 999{,}000$	$< 1.6 \times 10^{-8}$
2. Ether, shaken with KCNS solution	$> 999{,}000$	$< 1.6 \times 10^{-8}$
3. Ether, shaken with aqueous ferric thiocyanate	47,100	3.4×10^{-7}

(that is, an ethereal solution of ferric thiocyanate and HCNS).

Quantities were not accurately measured, and room temperature was employed. It seems probable that most of the conductance in No.3 might be due to HCNS. Even if it were all due to ferric ions this would only account for one percent of the iron in the ether.

The ether solution was found to be 0.0118N with respect to iron. Taking the equivalent conductivity at infinite dilution for ferric thiocyanate in water as being about 100 mhos, the value in ether would be about 500 mhos since the viscosity of water is about five times that of ether.

Whence

$$\lambda_v = (1000 \times 3.4 \times 10^{-7}) \div 0.0118$$
$$= 0.0289 \text{ mhos}$$

and

$$\alpha = \frac{\lambda_v}{\lambda_\infty} = 5.8 \times 10^{-5}$$
$$= 0.058\%$$

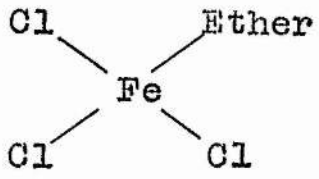
It thus appears that all the iron in the ether is in the molecular form, and the only possibilities besides $Fe(CNS)_3$ are molecules of the type $Fe(CNS)_3.xHCNS$ or $Fe(CNS)_4.H$. But, as the boiling point elevations previously given are not sufficiently low to account for such compound formation, it must be concluded that these are not formed to any appreciable extent.

A NOTE ON THE SOLUBILITY OF FERRIC THIOCYANATE IN BENZENE.

The failure of benzene to extract the red colour from an aqueous solution of ferric thiocyanate seemed to indicate that ferric thiocyanate was not soluble in this solvent. It will be recalled that Schlesinger and Van Valkenburgh[27] dissolved crystalline ferric thiocyanate and, from the lowering of freezing point, assumed that a dimer was formed. The preparation of a solution of ferric thiocyanate in benzene proved to be a matter of some difficulty. The insolubility of ferric and thiocyanate salts in benzene rendered the usual methods void, nor can ferric thiocyanate be extracted from an aqueous solution by benzene. A solution, however, was prepared in a mixed ether benzene solvent. An aqueous solution of ferric thiocyanate was extracted with peroxide free ether and the separated ether phase mixed with pure distilled benzene. The resultant dark coloured solution had a decided purple tint. It was anticipated that removal of ether from a solution prepared in this manner would yield a solution of

ferric thiocyanate in benzene. On removing the ether by distillation at reduced pressure, the colour gradually diminished, and a dark deposit settled on the walls of the distilling flask. On cooling the residual faint purple solution to 0°C a further small precipitate came out, leaving the benzene colourless. The black residue was dry, and had the appearance of soot. It was very soluble in water and in ether but quite insoluble in benzene. However, a purple solution was obtained by addition of benzene to the ether solution. The solutions in water and ether were red in colour, the colour of the aqueous solution being extractable by ether. The aqueous solution was shown to contain ferric and thiocyanate ions, but also a considerable amount of ferrous ions.

It is apparent that ferric thiocyanate is insoluble in pure dry benzene, but may be soluble in the presence of a little ether, due to the formation of a soluble compound, analogous to that obtained with ferric chloride in ether



Removal of the co-ordinated ether molecule as a result of the treatment described, may lead to precipitation and decomposition of the apparently insoluble salt.

PART 3

Part 3

THE PARTITION OF FERRIC THIOCYANATE BETWEEN WATER AND ETHER

The main object of this work has been to elucidate the nature of the ferric thiocyanate equilibria by application of the partition law. It has been possible in this way to establish the identity of all the ferric thiocyanate complexes, to obtain values of the stability constants of each, and to deduce the manner in which ferric iron will distribute itself amongst the various complexes when thiocyanate is added to the solution of a ferric salt.

It has been assumed that a series of ferric thiocyanate complexes ranging from $FeCNS^{2+}$ to $Fe(CNS)_6^{3-}$ is formed. Migration experiments - e.g. Schlesinger and Van Valkenburgh (27), Bent and French (4) - show that, under suitable conditions, either positively or negatively charged complexes may exist. The existence of the simple complex $FeCNS^{2+}$ in dilute solutions is well known. The possibility of a complex $Fe(CNS)_6^{3-}$ is suggested both by analogy to the ferricyanides, and by the existence of crystalline compounds $M_3Fe(CNS)_6$ (25). Apart from the simplest complex and the

neutral complex, $Fe(CNS)_3$ - Part 3 - the identity of no other ferric thiocyanate complex has, till now, been established, nor has there been any concrete evidence of their individuality.

The stability constant of the simple complex has been determined from observations on the optical density of solutions in which the thiocyanate concentration is small since, under such conditions, the complex $FeCNS^{2+}$ is, virtually, the only complex formed. If the thiocyan--ate concentration is increased so as to promote the formation of higher complexes, difficulties arise in the interpretation of optical data since the optical densities of such solutions depend on both the concentrations and extinction coefficients of the various complexes present, a total of, at least, twelve parameters. When, however, an aqueous solution of ferric thiocyanate is extracted with ether, there is obtained, at once, a measure of the concentration of one of the complexes - the neutral molecule - to which the concentrations of all the other complexes in the aqueous phase must be related by means of equilibrium constants. In this way, the number of parameters is greatly reduced. By conducting a series of experiments in which the thiocyanate concentration in the extracted aqueous solution is varied, sufficient data may be accumulated to permit the calculation of stability

constants. Qualitative examination of such data has indicated the existence of all ferric thiocyanate complexes previously assumed to exist. Quantitative analysis of such data has led to real positive values of stability constants which have established the identity of all the ferric thiocyanate complexes.(see Part 4)

In 1901, Hantsch and Vagt (12) examined the distrib-
-ution of ferric thiocyanate between water and ether, measuring only the thiocyanate concentration in both phases. Considering that much thiocyanic acid is extract-
-ed simultaneously, the data have little value. The extract-
-ion of ferric thiocyanate by ether is quite remarkable. When 250 ml of an aqueous solution (Fe^{3+} = 0.006 M., CNS^- = 0.4 M.) is shaken with 150 ml of ethyl ether, approximately ninety percent of the iron passes into the ether layer as $Fe(CNS)_3$. On the other hand, the extraction of colour from a golden brown solution in which the thiocyan-
-ate concentration is very small, is exceedingly slight, as a result of the limited extent to which the neutral molecule is formed. Despite such striking effects, no further quantitative treatment of the distribution has been reported.

THEORY

It has been shown that when an aqueous solution of ferric thiocyanate is extracted with ether, the only complex extracted is the neutral molecule $Fe(CNS)_3$, and that the concentrations of the various ferric thiocyanate complexes in the aqueous phase may be related to the concentration of the ferric thiocyanate in the ether phase by means of equilibrium constants. (see page 12). These constants take the general form

$$k_x = \frac{\left[Fe(CNS)_x^{3-x}\right]\left[CNS^-\right]^{3-x}}{n.Fe_E}$$

where 'n' is the partition coefficient of $Fe(CNS)_3$ between water and ether, Fe_E is the concentration of $Fe(CNS)_3$ in the ether phase, and $\left[CNS^-\right]$ is the concentrat--ion of thiocyanate ions in the aqueous phase.

Under conditions in which one complex is formed almost to the exclusion of the others, it is possible to determine 'x' by reducing the above equation to logarith--mic form.

$$\log.k_x = \log.\frac{\left[Fe(CNS)_x^{3-x}\right]}{Fe_E} + (3-x)\log.(CNS^-) - \log.n$$

Replacing $\left[Fe(CNS)_x^{3-x+}\right]$ by the total aqueous iron concentration, denoted by Fe_W, the equation becomes

$$\log.(Fe_E + Fe_W) = (3-x)\log.(CNS^-) - \log.k_x - \log.n$$

and by plotting the variation in $\log.(Fe_E + Fe_W)$ against $\log.(CNS^-)$, a line is obtained, the slope of which, at any point, will be given by $\underline{3-x}$. If the proportions of the various complexes formed vary with thiocyanate concentration, the value of $\underline{x}$ will vary and consequently the slope will vary, as will, of course, the intercept. The table below lists the slopes of a plot of $\log.(Fe_E + Fe_W)$ against $\log.(CNS^-)$ corresponding to fictitious complete formation of the various complexes.

Complex	$\underline{x}$	Slope
Fe^{3+}	0	+3
$FeCNS^{2+}$	1	+2
$Fe(CNS)_2^+$	2	+1
$Fe(CNS)_3$	3	0
$Fe(CNS)_4^-$	4	-1
$Fe(CNS)_5^{2-}$	5	-2
$Fe(CNS)_6^{3-}$	6	-3

Fig.I shows the form of curve obtained by plotting preliminary experimental results for $\log.(Fe_E \div Fe_W)$ against $\log.(CNS^-)$. The change from positive to negative gradients is quite marked. It is obvious that the iron in the aqueous phase, Fe_W, at points where the slope is equal in value to any of the integrals given above, is not wholly in the form of the corresponding complexes, but the value represents a mean of the various complexes in solution. Use is made of this in determining the concentration of free thiocyanate ions in the aqueous phase. This may not vary appreciably from the total measured value of the thiocyan-ate concentration in cases where the thiocyanate concentrat-ion is large, but when the total concentration of thiocyan-ate is small, the proportion of thiocyanate combined in complexes is considerable. The free thiocyanate concentrat-ion in the aqueous phase may therefore be determined by plotting $\log.(Fe_E \div Fe_W)$ against the logarithm of the total aqueous thiocyanate concentration. From the slopes at the various experimental points of such a curve, it is possible to ascertain approximately the extent to which thiocyanate is united to iron. The process may then be repeated using the first approximate values of the free thiocyanate ion concentration, and then, by succesive approx-imations, values of the uncombined thiocyanate concentrat-ion are obtained which may be regarded as reliable.

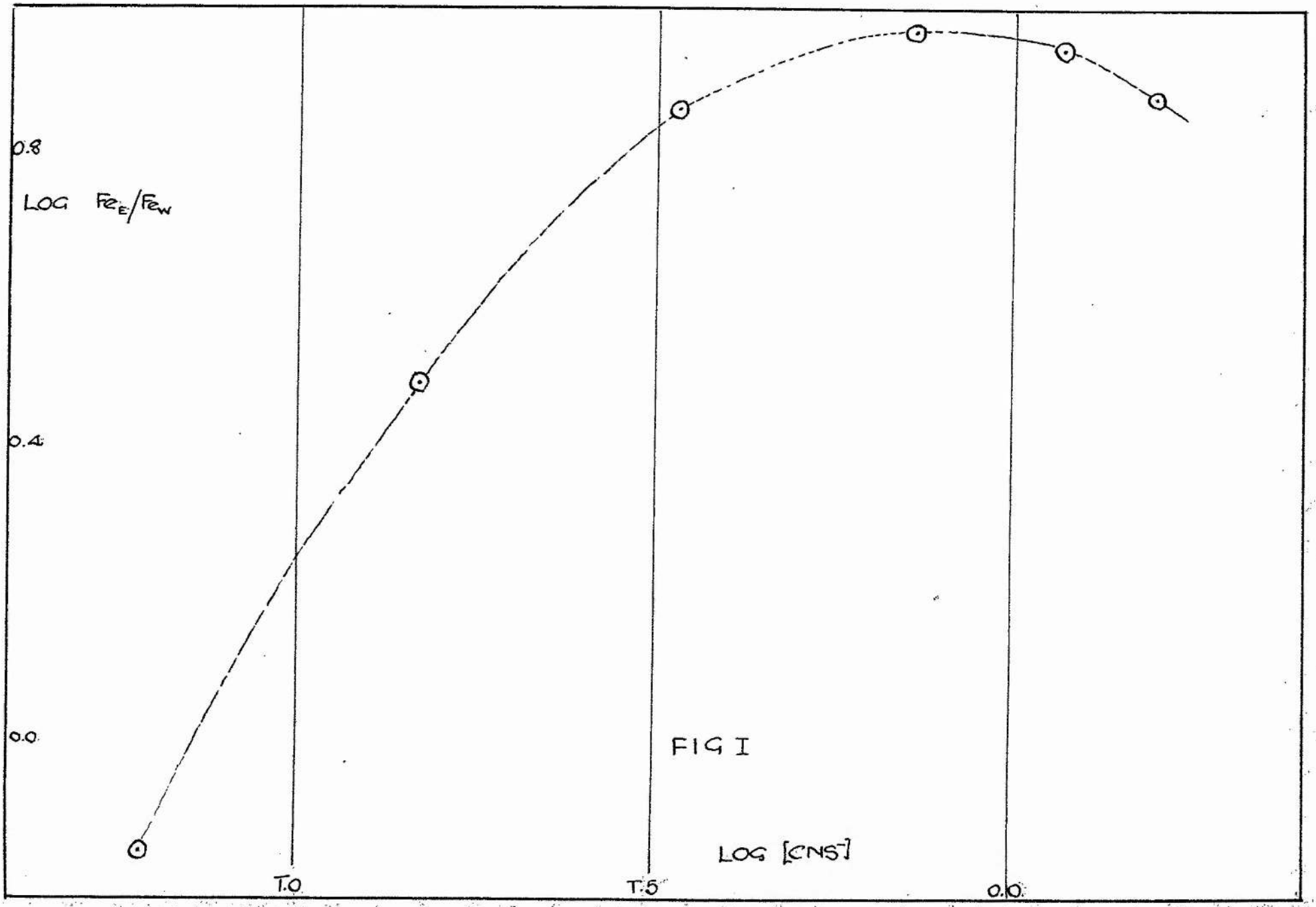


FIG I

EXPERIMENTAL

Two series of experiments were performed in which aqueous solutions containing fixed amounts of iron and acid, and varying amounts of thiocyanate were extracted with ethyl ether. It was, however, first shown that no ferric complexes are extracted from aqueous solutions containing ferric nitrate and nitric acid in the same concentrations as were to be used in the partition experiments. The same was shown to apply to ferric perchlorate in perchloric acid solution. This should be contrasted with ferric chloride which is known to form stable complexes, e.g. $FeCl^{2+}$ (23) and $FeCl_3.HCl$ which is formed in strongly acid solutions and is extractable by ether. (7/20)

It was then shown that, when aqueous solutions containing thiocyanate salts and acid, but no ferric salt, are shaken with ether, thiocyanate is extracted in the form of thiocyanic acid. The thiocyanate and hydrogen ion concentrations in the ether phase were equivalent, and no metallic cations were found. The amount of thiocyanic acid extracted increases both with the acidity and with the thiocyanate concentration of the original aqueous phase as shown by the following data.

Extraction of Thiocyanic Acid by Ether

Aqueous phase = 100 ml

Ether phase = 100 ml

Original Solution		Ether Phase
H_2SO_4 m/l	KCNS m/l	HCNS m/l
0.011	0.089	0.008
0.022	0.089	0.013
0.033	0.089	0.016
0.044	0.089	0.018
0.229	0.202	0.090
0.229	0.404	0.147
0.229	0.606	0.180
0.229	0.808	0.222

It may be concluded that when aqueous solutions of ferric salts (nitrate and perchlorate), containing acid to prevent hydrolysis, and to which thiocyanate has been added, are shaken with ether, the only compounds extract-ed are $Fe(CNS)_3$ and HCNS. These are in the monomeric form and are not ionised to any significant extent. (Part 2) Due to the extraction of HCNS, and to variation in the amount extracted depending upon the thiocyanate concentration, difficulty arises in maintaining the ionic strength

of the aqueous phase constant after extraction.

Two series of partition experiments were performed. In each series, 250 ml. of solutions containing fixed amounts of iron and varying amounts of thiocyanate were extracted with 150 ml. of ether. The acidity of the original aqueous phase was also constant at 0.18N. (see page 17) The series differed in the choice of salts employed. Also, in series A, the ionic strength of the initial aqueous phase was maintained at 1.78 by addition of neutral salt, whereas, in series B, the ionic strength of the extracted aqueous phase was kept sensibly constant at 1.78 , additional salt being added to the original aqueous solution to compensate for the extraction of HCNS; the amount of extra salt required was calculated from the amounts of thiocyanate extracted in series A. The compositions of the solutions extracted are summarised in the following table.

SERIES	A	B
Iron Salt	$Fe(NO_3)_3$ 0.0061 M	$Fe(ClO_4)_3$ 0.006 M
Acid	HNO_3 0.182 M	$HClO_4$ 0.182M
Neutral Salt	KNO_3 0.00 - 1.56 M	$NaClO_4$ 0.12 - 1.56 M
Thiocyanate Salt	KCNS 0,04 - 1.60 M	NH_4CNS 0.04 - 1.60 M
Ionic Strength	1.78 before extraction	1.78 after extraction
Volume, aqueous phase	250 ml	250 ml
Volume, extracting ether	150 ml	150 ml
Temperature	18*.1°C	18±.1°C

The choice of extracting solvents was limited, ethyl ether and iso-propyl ether being considered the most suitable. Iso-propyl ether is advantageous in that its capacity to dissolve water and ferric thiocyanate is much less than that of ethyl ether, but this, in consequence, renders the estimation of extracted iron more difficult. Colorimetric estimation of ferric thiocyanate in iso-propyl ether proved to be less satisfactory than the estimation of ferric thiocyanate in ordinary ether by titrametric methods. Ethyl ether was therefore used as extracting solvent.

The ether was freed from peroxides by shaking with acidulated ferrous sulphate, and then with water. It was then stored over clean copper wire, and portions distilled as required. In this way, reliable and reproducible values of ethereal iron concentration could be obtained by reduction titration. The iron could thus be measured with accuracy in both ether and aqueous phases by titration with 0.02N titanous sulphate solution. The thiocyanate concentration in both phases was determined by silver titration.

The partitions for each thiocyanate concentration were carried out individually in order to minimise time of procedure and thus any decomposition that might occur prior to analysis of the partition phases. The procedure was simple. The partition mixtures, with the exception of the iron, were pipetted into a dark bottle, which was stoppered, shaken, and placed in a thermostat at $18\pm0.1^{\circ}C$ for one hour. After that time, the fixed volume of iron solution, which contained all the acid and was, also, preheated to 18°, was introduced into the bottle which was then shaken and returned to the thermostat, shaking being repeated over a period of ten minutes. Experiment had shown that equilibrium was quickly established, and that distribution was complete in this time. The two

phases were then separated as carefully as possible, and suitable portions of each titrated directly with titanous sulphate. The thiocyanate estimation could be carried out directly, or after dilution of appropriate volumes.

The experimental results are given in Tables I and II, the concentrations of iron and thiocyanate in the original and final phases being given. The free thiocyanate ion concentration in the final aqueous phase has been obtained in the manner already described. Any thiocyanate in the ether layer in excess of three times the iron concentration has been assumed to be thiocyanic acid.

The relative volumes of ether and water are signif-icantly changed by the solubility of the two liquids in one another. This does not affect the figures for the concentrations which were measured directly, but it was desirable to know the volume change so that the total amounts extracted could be calculated and compared with the original amounts taken, as a check on the analysis. The solubility of ether in water was determined by shaking known volumes of ether with water in a flask with a long graduated neck, and noting the volume changes in the layers. In this manner, it has been shown that, at 18°C, 200ml of water dissolve 19.6 ml of ether to yield 217.25 ml of

Table I Experiment A

Index	INITIAL CONCENTRATIONS			FINAL CONCENTRATIONS					
	AQUEOUS PHASE			AQUEOUS PHASE			ETHER PHASE		
	Fe^{3+}	KCNS	KNO_3	Total CNS^-	Free CNS^-	Iron	Total CNS	$Fe(CNS)_3$	HCNS
1	0.00611	0.04	1.56	26.73	20.6	4.752	22.48	2.026	16.4
2	0.00611	0.08	1.52	57.36	51.5	3.614	48.75	5.393	32.5_7
3	0.00611	0.16	1.44	106.50	102.4	2.408	85.78	8.047	61.6_6
4	0.00611	0.40	1.20	294.0	291.6	1.140	156.54	9.173	129.0
5	0.00611	0.60	1.00	467.2	464.5	0.901_6	198.0	9.730	168.8
6	0.00611	0.80	0.80	641.6	639.0	0.897	222.0	9.980	192.0
7	0.00611	1.20	0.40	1006.4	1002.8	1.004	257.2	9.547	228.7
8	0.00611	1.60	0.00	1369.6	1365.0	1.142	287.3	9.360	259.2

HNO_3 - 0.182 M
ionic strength 1.78
concentrations: gm.mol/l.

concentrations: 10^{-3} gm.mols./litre

Table II Experiment B

Index	INITIAL CONCENTRATIONS			FINAL CONCENTRATIONS					
	AQUEOUS PHASE			AQUEOUS PHASE			ETHER PHASE		
	Fe^{3+}	NH_4CNS	$NaClO_4$	Total CNS^-	Free CNS^-	Iron	Total CNS^-	$Fe(CNS)_3$	HCNS
1	0.00599	0.04	1.560	21.47	17.95	3.667	33.90	4.121	21.5_4
2	0.00599	0.08	1.535	42.46	39.67	1.861	70.20	8.134	45.8_0
3	0.00599	0.16	1.475	92.87	91.13	0.896	116.90	10.07	86.7
3a	0.00599	0.24	1.402	150.0	148.7	0.437_9	210.8_7	10.87_7	126.1
4	0.00599	0.40	1.270	278.9	277.6	0.568_5	157.9	10.61	178.2
5	0.00599	0.60	1.092	453.1	451.3	0.5094	239.7	10.85	207.2
6	0.00599	0.80	0.900	633.9	631.5	0.6334	256.4	10.74	224.2
7	0.00599	1.20	0.538	994.5	990.9	0.8945	284.0	10.02	254.0
8	0.00599	1.60	0.120	1341.0	1337.0	1.184	293.3	9.45_9	264.9
	$HClO_4$		0.182 M	concentrations			10^{-3} gm.mols./litre		
	ionic strength		1.78						
	concentrations		gm.mol/l						

of solution, and this agrees with the value calculated from the International Critical Tables, at 19.4 ml of ether per 200 ml of water. This value would indicate a probable change of the partition volumes on shaking from 150 ml ether and 250 ml water to 125.5 ml ether and 271.5 ml water. Assuming this to be correct, and also assuming that solutes play no part in altering the respect-ive volumes, it is possible to estimate the total amounts of iron and thiocyanate distributed between the two phases and, thereby, obtain an estimate of the possible error involved in titration. These are tabulated below for series B, the 'possible error' being the percentage of each ion originally taken which is unaccounted for, or in excess of the original amount, in the final analysis.

Index	'Possible Error' (percent)	
	Thiocyanate	Iron
1	1.0	0.85
2	1.6	1.68
3	-0.8	0.38
3a	1.0	-0.37
4	1.5	-0.75
5	2.0	-0.12
6	2.0	1.30
7	1.8	0.01
8	2.0	0.71
mean	1.4	0.66

The error involved in estimating the iron is apparently small when determined by this method. Greater discrepencies appear to exist in the determin--ation of thiocyanate, and that is to be expected since difficulty was experienced in estimating thiocyanate in ether by silver titration. The accuracy of that determination has, however, no direct bearing on the application of the partition law.

DISCUSSION

Examination of the data given in Tables I and II shows that the amount of iron extracted by ether from an aqueous solution containing iron and thiocyanate ions increases as the thiocyanate concentration increases, indicating that the proportion of the neutral molecule, $Fe(CNS)_3$, increases as the thiocyanate concentration increases. But, when the thiocyanate concentration is increased beyond a certain limit, the amount of iron extract-ed becomes less and less, showing that the amount of $Fe(CNS)_3$ molecules in the aqueous phase is likewise dimin-ishing, due to the formation of still higher complexes at the expense of the lower ones. The critical thiocyanate concentration corresponding to optimum formation of the neutral molecule is not, however, the same in both experimental series, and this is clearly revealed in the curves - Fig.II - in which $\log.(Fe_E \div Fe_W)$ is plotted against the logarithm of the free thiocyanate ion concentrat-ion in the aqueous phase. The maxima of these curves lie at quite distinct positions. The curves themselves are smooth and exhibit symmetry which is quite remarkable. In both, the gradients change gradually from a positive value of about +3, through zero, to a negative value tending towards -3, and this is in harmony with the previous

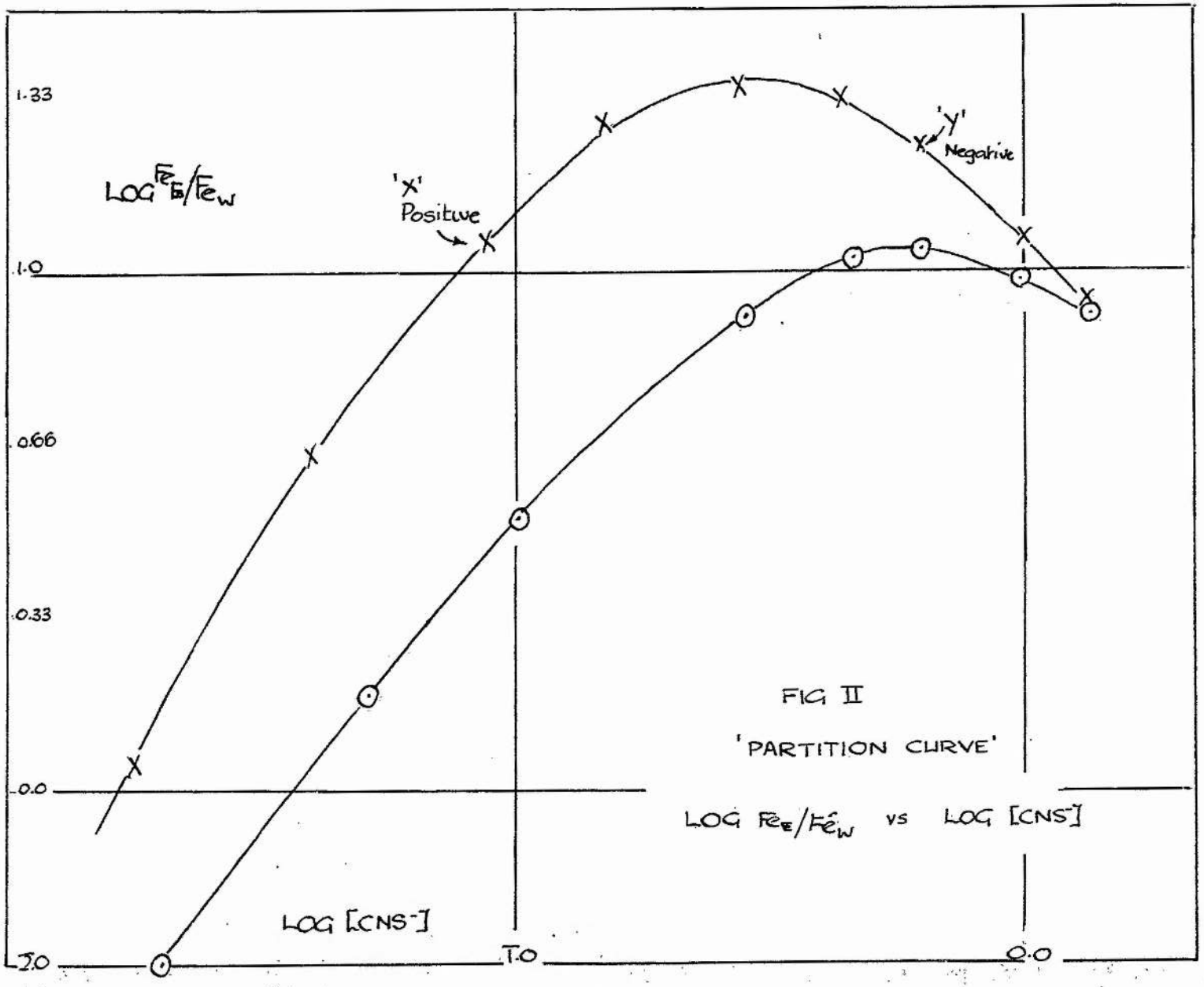


FIG II

'PARTITION CURVE'

LOG Fe_E/Fe_W vs LOG [CNS⁻]

theoretical discussion. It may be concluded that all the postulated complexes are formed, that the proportions of the various complexes vary with thiocyanate concentration, and that there is a change from lower to higher complexes as the thiocyanate concentration changes from low to high values. Despite the symmetry of the curves, the transition from simple to more elaborate complexes may not be interpretated as being a uniform function of the thiocyanate ion concentration. As the complexity of the complexes increases, so they become relatively more difficult to form, and ever greater amounts of thiocyanate must be added in order to pass from one complex to the next.

Two explanations may be given to account for the displacement of the partition curves. KNO_3 was used as neutral salt in series A. Therefore it may be thought that complex formation between ferric and nitrate ions occured to such an extent that it would be wrong to take the total aqueous iron concentration as a measure of the total concentration of iron thiocyanate complexes and free ferric ions, Fe_W . The partition ratios would therefore be too small at high KNO_3 concentrations, but, as the KNO_3 was replaced by KCNS, the error would become less, and the partition ratios would gradually approach the values obtained in series B. The overall result would be that the series A curve would be displaced downwards from the series B curve, the difference

between the curves being greatest at low thiocyanate concentrations, and least at high thiocyanate concentrations. Further, the series A curve would have a false maximum, displaced towards higher thiocyanate concentrations. This explanation seems unlikely in view of any evidence for such complex formation not having been obtained.

Alternatively, it may be thought that, if $\log.(Fe_E + Fe_W)$ were plotted against the logarithm of the thiocyanate activity - a_{CNS^-} - instead of the concentration - c_{CNS^-} - a better agreement might be found. 'a_{CNS^-}' is the thiocyanate activity which would be found by multiplying the thiocyanate concentration 'c_{CNS^-}' by a suitable activity coefficient 'f'. The maintenance of ionic strength at a constant value is a well known device for keeping the activity coefficient, f, constant, but, in this case, it can only have been partly effective since the process involved the substition of one salt for another. Thus, in series A, KCNS was gradually substituted for KNO_3 , and it is known that the activity coefficient of 1.6M KCNS is about 0.55 whereas that of 1.6M KNO_3 is about 0.37. The activity coefficients of ions dissolved in these two salt solutions are not likely to be the same in each solution.

The two partition curves diverge to the greatest extent

when the neutral salt concentration is greatest, and the thiocyanate concentration is small. Should the two curves agree better by plotting log.(Fe_E + Fe_W) against log.a_{CNS^-} instead of log.c_{CNS^-} , this would result from the activity coefficient of small amounts of thiocyanate ions in KNO_3 solution being less than that in $NaClO_4$ solution. This would, in fact, be the case were it assumed that these activity coefficients are similar in magnitude to those of the salt solutions themselves. In Fig.III, the activity coefficients of KNO_3 and $NaClO_4$ are plotted against a range of concentrations on a logarithmic scale, and, it will be seen, that, at the maximum salt concentrations used in these experiments (1.6M), the activity coefficient of KNO_3 is less than that of $NaClO_4$. On the other hand, the activity coefficient of 1.6M KCNS, the maximum concentration used, is approximately the same as that of 1.6M NH_4CNS. The curve for NH_4CNS follows closely that of $NaClO_4$. At this concentration, therefore, it would be expected that the partition curves might concur, which, in fact, they do.

The calculation of activity coefficients in mixtures of electrolytes is at present very uncertain, but approximate values may be obtained from a study of the distribution of HCNS in the same salt mixtures.

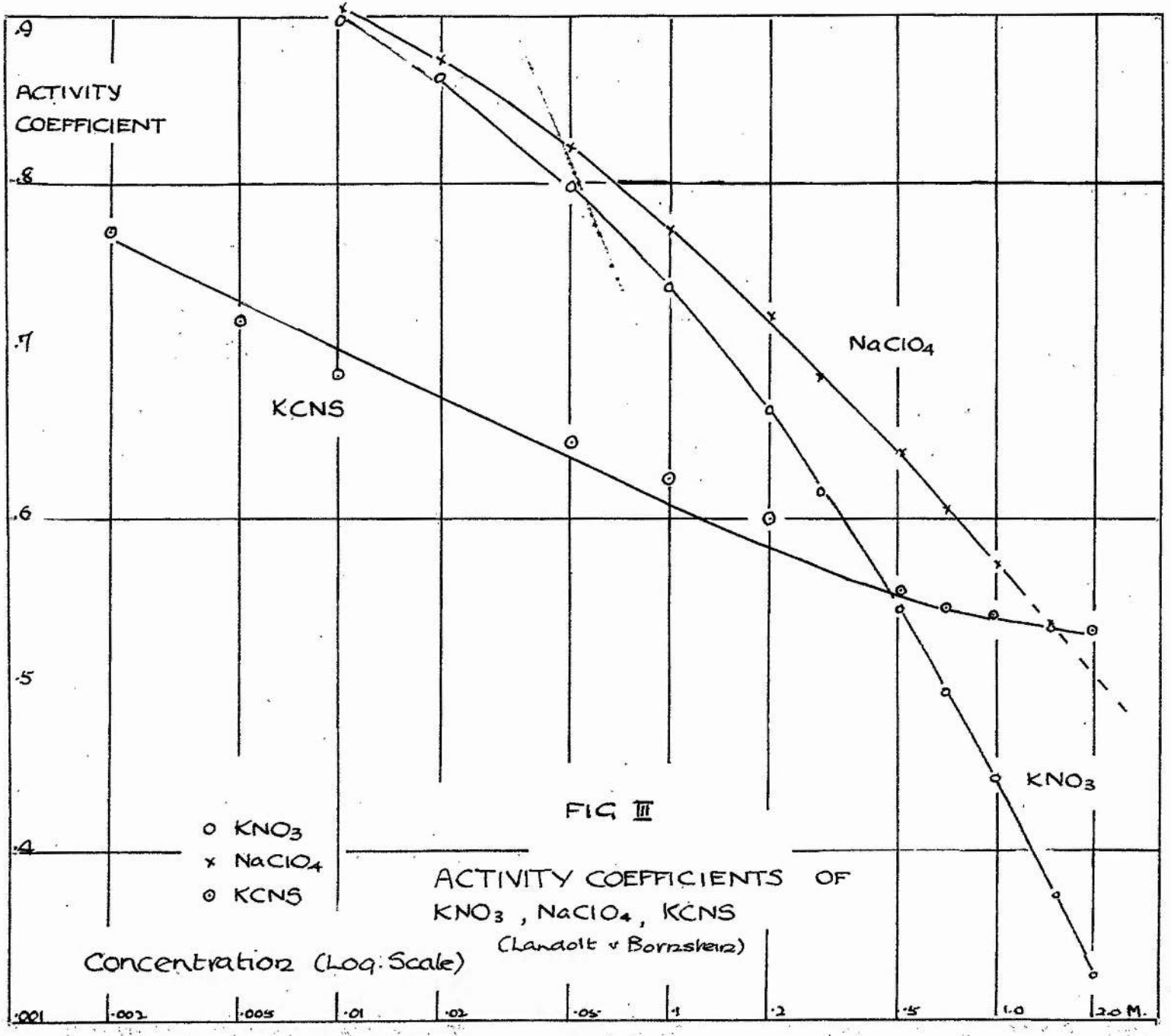


FIG III

ACTIVITY COEFFICIENTS OF
KNO_3, $NaClO_4$, KCNS
(Landolt v Bornstein)

$$H^+ + CNS^- \rightleftharpoons HCNS$$

water ether

For this, the relationship holds

$$\frac{a_{H^+} \times a_{CNS^-}}{a_{HCNS}} = \frac{[H^+][CNS^-]}{[HCNS]_E} \times \frac{f_+ \times f_-}{f_O} = K'_{HCNS} = K_{HCNS} \times f_\pm^2$$

If, therefore, we can find factors which will make K_{HCNS} constant, in both experiments, we will have some measure, at least, of activity factors which may apply, approximately, to the ferric thiocyanate equilibria under consideration.

Suitable factors which make the partition curves coincide have been obtained in the following manner. Values of K_{HCNS} were calculated from the partition data. The methods of obtaining $[HCNS]_E$ and $[CNS^-]_W$ have been described. $[H^+]_W$ is taken as the original aqueous hydrogen ion concentration, less that extracted as HCNS, correction being made for changes in volume of the ether and aqueous phases. These values of K_{HCNS} are given in Table III. In experiments, index 1-3, the neutral salt concentration is approximately 1.6M and the activity coefficients of these salts are

A	1.6M KNO_3	$f_\pm = .37$
B	1.6M $NaClO_4$	$f_\pm = .55$

It was then assumed that, in these experiments, the activity of the relatively small amounts of thiocyanate ion in the aqueous phase would be given by $[CNS^-] \times f_\pm$ where $f_\pm$ has the values given above. Values of K'_{HCNS} in which these thiocyanate activities are substituted for the corresponding concentrations in K_{HCNS} are given below.

Values of K'_{HCNS}

$(K_{HCNS} \times f_\pm)$

Index	Series A	Series B
1	74.5	72.7
2	89.7	70.5
3	78.4	74.5
3a	-	71.0

The similarity between those values underscored, compared with the original 'uncorrected values', (Table III) led to a mean value of 72.7 being taken as the 'true' value of K_{HCNS}. It remained then to divide the 'true' value of K_{HCNS} by the calculated values in order to obtain the corresponding values of the corresponding factors f_{CNS^-} by which the thiocyanate concentrations should be multiplied in each case to obtain the 'true' value of K_{HCNS}. The values of K used in these calculations were taken from a plot of the calculated values against the logarithm of the

Table III

Values of $K_{HCNS} = \frac{[H^+][CNS^-]}{[HCNS]_E}$

Index	Series A	Series B
	$\times 10^3$	$\times 10^3$
1	202	132.4
2	243	127.8
3	212	135.0
3a	-	129.5
4	246	134.2
5	248	158.1
6	267	181.1
7	279	198.0
8	256	229.5

Table IV

Values of $f_{CNS^-} - 72.7^o \div K^{\times}_{HCNS}$

	Series A		Series B	
Index	$K^{\times}_{HCNS}$	f_{CNS^-}	$K^{\times}_{HCNS}$	f_{CNS^-}
	$\times 10^3$		$\times 10^3$	
1	202	0.360	121.5	0.60
2	208	.350	122.5	.59
3	215	.338	128.0	.57
3a	-	-	132.0	.55
4	244	.298	142.0	.51
5	258	.282	158.0	.46
6	267	.272	172.0	.42
7	279	.260	210.0	.345
8	256	.283	229.5	.316

× Values obtained by interpolation as described

o $\times 10^{-3}$

thiocyanate ion concentration. These more reliable values, along with the activity factors, f_{CNS^-} , calculated from them, are given in Table IV.

Remarkable agreement is obtained by applying these activity factors to the partition curves. Fig.IV shows a plot of $\log.(Fe_E + Fe_W)$ vs $\log.[CNS^-] \times f_{CNS^-}$. It will be seen that the curves for series A and B now exhibit maxima at the same values of thiocyanate 'activity' where, formerly, the maxima occured at quite different thiocyanate concentrations. On the other hand, the values of $\log.(Fe_E + Fe_W)$ is still greater than the corresponding values in curve A , in curve B. Since Fe_W represents the sum of very small concentrations of ferric ions and ferric complexes, contiguous with the same salt solutions, as have been discussed it seemed likely that the same activity factors might apply to these ions as did apply to the thiocyanate ions. Fig.V shows plots of $\log.(Fe_E + Fe_W \times f_{CNS^-})$ vs $\log.[CNS^-] \times f_{CNS^-}$ for both partition series. It will be noticed that almost complete coincidence of the curves has resulted. The appropriate data are given in Table V. It is concluded that differences observed between the partition data obtained by using solutions in which the ionic strength is maintained constant by $NaClO_4$ and KNO_3 can be accounted for by variation in activity coefficients brought about by these salts (see also Part 5).

Table V

Modified Partition Data

Index	$[CNS^-]_{m/l}$	$[CNS^-]_{m/l} \times f_{CNS^-}$	$Fe_E \div Fe_W$	$Fe_E \div Fe_W \cdot f_{CNS^-}$
	$\times 10^3$	$\times 10^3$		
		Series A		
1	20.6	7.4	0.444	1.23
2	51.5	18.0	1.495	4.27
3	102.4	34.6	3.340	9.85
4	291.6	87.0	8.050	27.00
5	464.5	131.0	10.80	38.20
6	639.0	167.0	11.00	40.50
7	1002.8	261.0	9.50	36.60
8	1365.0	386.0	8.20	29.05
		Series B		
1	17.95	10.8	1.121	1.87
2	39.67	23.4	4.370	7.41
3	91.13	52.0	11.210	19.70
3a	148.7	81.9	18.70	34.00
4	277.6	142.5	22.95	44.70
5	451.3	208.0	21.30	46.25
6	631.5	268.0	16.95	40.00
7	990.9	342.0	11.22	32.50
8	1337.0	422.0	8.00	25.20

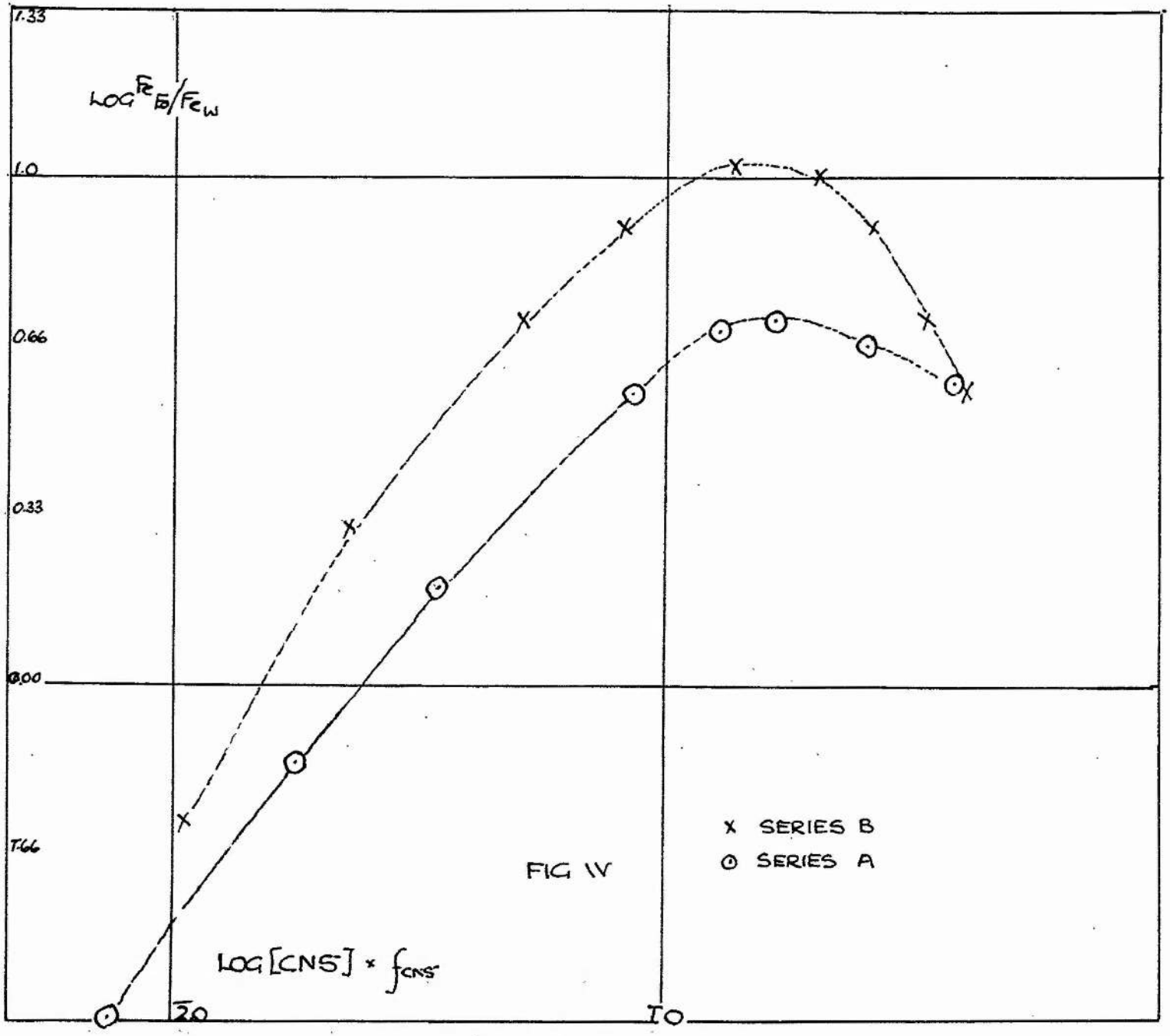

1.33
LOG Fe Eb/Fe w
1.0
0.66
0.33
0.00
T.66
20
10
LOG [CNS] × f CNS
X SERIES B
⊙ SERIES A

FIG IV

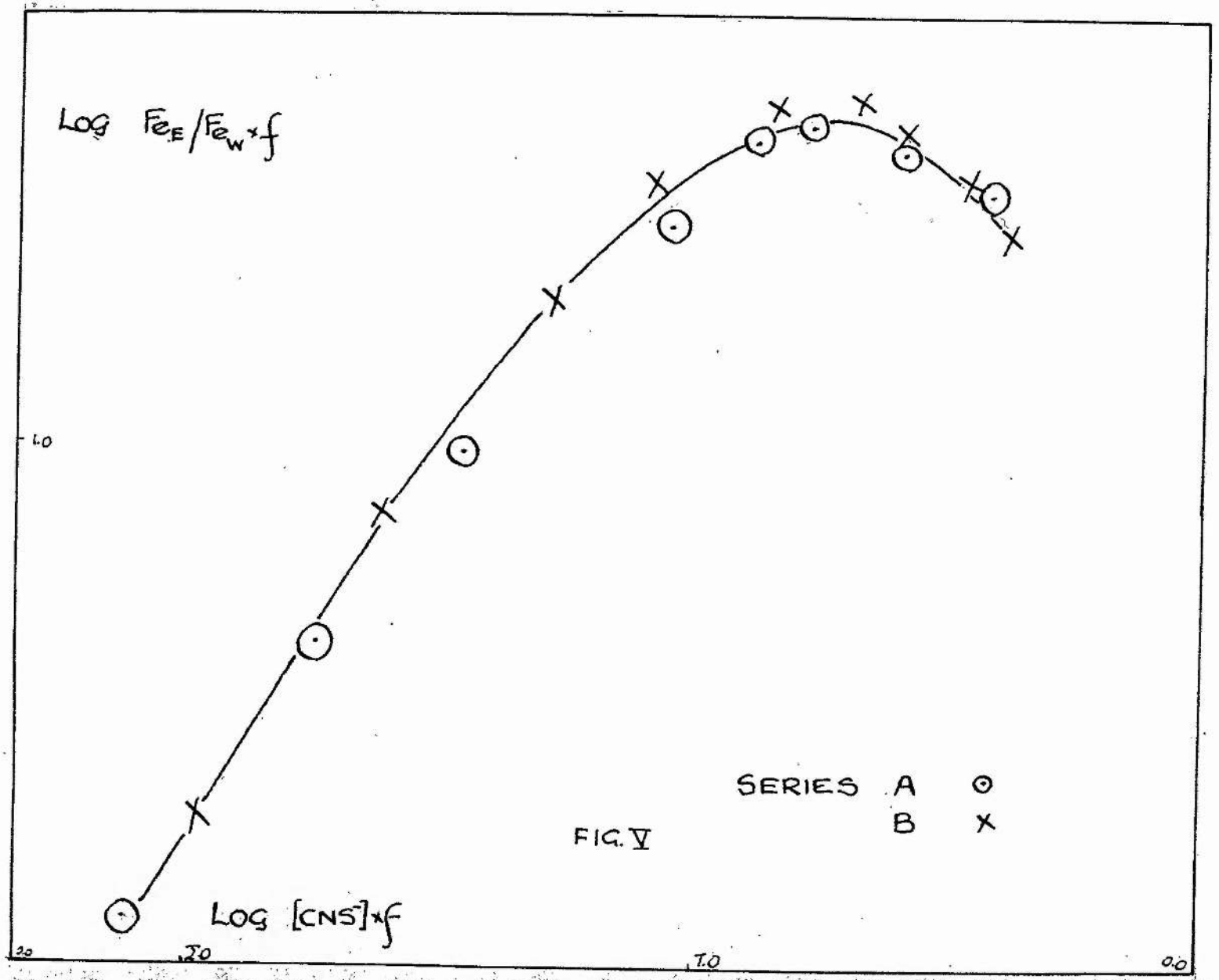


FIG. V

PART 4

PART 4

THE STABILITY CONSTANTS OF THE FERRIC THIOCYANATE COMPLEXES

The main object of this work has been to establish values of the stability constants, K_x, of each of the ferric thiocyanate complexes.

It will be recalled that the partition ratio may be related to the free thiocyanate concentration in the aqueous phase by the equation

$$Fe_W/Fe_E = ax^{-3} + bx^{-2} + cx^{-1} + d + ex + fx^2 + gx^3 \quad . . (1)$$

where $a = nk_0$, $b = nk_1$, $c = nk_2$, ... $g = nk_6$

$$k_x = \frac{\left[Fe(CNS)_x^{3-x+}\right]\left[CNS^-\right]^{3-x}}{\left[Fe(CNS)_3\right]}$$

and where 'x' in equation (1) is the free thiocyanate ion concentration in the aqueous phase.

By making a sufficient number of accurate measure-ments of the partition ratio at different thiocyanate concentrations, it is possible, in theory, to determine all the values of 'nk_x' and 'n', and, hence, values of the

stability constants, K_x, which are connected to them by the relationship

$$K_x = k_x + k_{x-1}$$

The number of parameters in equation (1) 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 (9) have shown that the value of K_1 can be found from measurements of the optical density of solutions of low thiocyanate concentration. Thirdly, an empirical relationship has been found, as will be described, 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 a manageable number of three.

Equation (1) has been derived 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.

The relationship between k_0 and k_6, k_1 and k_5, k_2 and k_4

In Fig.II, Part 3, log Fe_E/Fe_W is plotted against log x, and it has been noted that the curve derived from the series B experimental data shows remarkable symmetry. Assuming this curve to be symmetrical about a line log.x = log.P it follows that the values of log Fe_E/Fe_W should be equal at all pairs of thiocyanate concentrations x_1 and x_2 where $x_1 = P \times x$ and consequently

$$x_2 = P \div x$$

Applying this to equation (1)

$$a(P/x)^{-3} + b(P/x)^{-2} + c(P/x)^{-1} + d + e(P/x) + f(P/x)^2 + g(P/x)^3$$
$$= a(Px)^{-3} + b(Px)^{-2} + c(Px)^{-1} + d + e(Px) + f(Px)^2 + g(Px)^3$$

From which

$$(aP^{-3} - gP^3)(x^3 - x^{-3}) + (bP^{-2} - fP^2)(x^2 - x^{-2}) + (cP^{-1} - eP)(x - x^{-1}) = 0$$

This equation is valid only if

$$aP^{-3} = gP^3 , \quad bP^{-2} = fP^2 , \text{ and } \quad cP^{-1} = eP$$

Substituting the values of a, b, c, etc.,

$$k_0 = k_6.P^6 \qquad k_1 = k_5.P^4 \qquad k_2 = k_4.P^2$$

On applying this simplification to equation (1) and remembering that $K_1 = k_1 + k_0$, we may write it in the form

$$Fe_W/n.Fe_E = u.k_0.P^3 + v.k_2.P + k_3 \quad . \quad . \quad . \quad . \quad (3)$$

where

$$u = (P^3x^3 + P^{-3}x^{-3} + K_1.P^{-3}x^{-2} + K_1.Px^2)$$

and

$$v = (Px + P^{-1}x^{-1})$$

Simplification of the Partition Equation by the Theory Postulated by Bjerrum

Bjerrum (5) suggested that in the case of symmetrical weak acids, the dissociation constants are connected by the following relationship.

$$K_1 + K_2 = K_2 + K_3 = \ldots\ldots\ldots = Q' = 1 + Q \qquad (4)$$

This relationship follows if we assume that the free energy 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 another. The theory is most likely to be correct (or applicable) in cases where the character of the bond is largely electrostatic, which is probably the case with these complex thiocyanates. Thus, applying this theory

$$K_2 = QK_1 \ , \ K_3 = Q^2K_1 \ , \ K_4 = Q^3K_1 \ . \ . \ . \ K_6 = Q^5K_1$$

But, $k_1 = k_0K_1$, $k_2 = k_1K_2 = k_0K_1QK_1$ . . . . . etc.

Combining this with equation (1)

$$Fe_W/(Fe_E.n.k_0) = x^{-5} + K_1x^{-2} + K_1^2.Q.x^{-1} + K_1^3.Q^3 + K_1^4.Q^6.x +$$

$$+ K_1^5.Q^{10}.x^2 + K_1^6.Q^{15}.x^3 \quad . . (5)$$

This equation contains only two unknowns, nk_0 , and 'Q', the value of K_1 being known. The equation may be solved employing the results of two partition experiments. nk_0 is first eliminated, and the resulting equation in the fifteenth power of 'Q' may be solved graphically, but not without difficulty.

If the symmetry of the partition curve is assumed once again,

$$P^{-3} = P^3.K_1^6.Q^{15}$$

or $$Q^{15} = P^{-6}.K_1^6$$

where 'P' has the value already described. 'P' and K_1 both being known, a value of 'Q' is readily computed. nk_0 is found by substituting 'Q' in equation (5) and from that, in turn, are found all the values of nk_x and the stability constants K_x

Algebraic Solution of the Partition Equation

Equation (1) may be regarded as a simple equation of the first degree containing seven unknowns, evaluation of which should be possible by simple simultaneous solution of seven equations. Alternatively, it may be regarded as

a homogeneous equation of the seventh order of 'x', the coefficients of which are not known but which may be obtained by a method of interpolation, for example, Gregory's method. (33)

EVALUATION OF THE CONSTANTS k_x AND K_x

Values of the constants k_x and K_x were computed by three methods.

I Algebraic Method - solution of equation (1)

II Symmetry Method - solution of equation (3)

III Bjerrum Method - solution of equation (5)

Method I No satisfactory values of k_x could be obtained by algebraic solution of the partition equation (1) either by simultaneous solution, or by the application of Gregory's interpolation formula. Negative values always appeared. This is not unexpected in view of the wide range of thiocyanate concentrations employed, i.e. the 'x' terms, the magnification of experimental errors by such terms as x^a (a = -3 to +3) and the cumulative effect of such errors in the various mathematical processes which such methods of solution demand.

Method II

$$Fe_W/n.Fe_E = uk_0P^3 + vk_2P + k_3 \quad \ldots\ldots \quad (3)$$

where

$$u = fn(P,K_1,x) \ ,$$

$$v = fn(P,x) \ ,$$

and 'P' is given by $\log.x = \log.P$, the axis of symmetry of the partition curve $\log.Fe_E/Fe_W$ vs $\log.x$

Values of 'P' for both series were obtained from the partition curves, a mean of ten or so pairs of readings being taken. K_1, the stability constant of th e complex $FeCNS^{2+}$ was found experimentally (see Part 5).

Series A	P = 0.595	K_1 = 91.0	(μ = 1.8 KNO_3)
Series B	P = 0.297	K_1 =122.5	(μ = 1.8 $NaClO_4$)

Solution of equation (3) led to positive values of all constants nk_x and K_x for both series. These are tabulated in Table I under the heading AII and BII for series A and B respectively.

It will be recalled that values of 'x', the free thiocyanate ion concentration in the aqueous phase were obtained by a method of approximations. Alternative values may be obtained by calculation using the above determined constants, and employing them in turn to calculate 'revised constants'. It is doubtful whether the accuracy of the original constants permit of such a

calculation. In series A, the revised constants differed to a negligible extent from the original values. Those in series B differed slightly and are therefore given for comparison (column BIIa, Table I)

Method III Equation (5) has been completely solved using both the 'revised' and original values of 'x'. (columns BIII a,b) Values of nk_x and K_x have also been obtained by the simplified solution of equation (5) in which the symmetry of the partition curve is assumed. These values are given in column BIIIc.

Series	A	B	B*	B*	B	B*
Method	II (1)	II (2)	IIa (3)	IIIa (4)	IIIb (5)	IIIc (6)
P	0.595	0.295	0.295			0.295
nk_0	2.93×10^{-6}	1.016×10^{-6}	0.879×10^{-6}	1.104×10^{-6}	1.14×10^{-6}	0.874×10^{-6}
nk_1	2.66×10^{-4}	1.252×10^{-4}	1.077×10^{-4}	1.349×10^{-4}	1.401×10^{-4}	1.08×10^{-4}
nk_2	2.79×10^{-2}	5.728×10^{-3}	6.09×10^{-3}	4.052×10^{-3}		3.14×10^{-2}
nk_3	$<1.11\times10^{-2}$	2.228×10^{-4}	-1.01×10^{-3}	3.035×10^{-2}		2.16×10^{-2}
nk_4	7.87×10^{-2}	6.483×10^{-2}	6.90×10^{-2}	5.666×10^{-2}		3.55×10^{-2}
nk_5	2.12×10^{-3}	1.607×10^{-2}	1.38×10^{-2}	2.638×10^{-2}	1.79×10^{-2}	1.38×10^{-2}
nk_6	6.59×10^{-5}	1.474×10^{-3}	1.28×10^{-3}	3.063×10^{-3}	1.66×10^{-2}	1.28×10^{-3}

Note: In those columns in which a value of 'P' is given, "symmetry" was assumed in the calculation. In those marked with an *, revised values of 'x' were used.

Table I Calculated Values of 'nk_x'

Series	A^o	B^o	$B^{o}*$	B^*	B	$B^{o}*$
Method	II (1)	II (2)	IIa (3)	IIIa (4)	IIIb (5)	IIIc (6)
K_1	91±0.9	122.5±1.0	122.5	122.5		122.5
K_2	105.4±17	45.6	56.5±3.7	30.04	not	29.0
K_3	< 0.39	0.04	< 0.18	7.49		6.9
K_4	> 0.717	290.0	> 62.7	1.867	computed	1.65
K_5	0.027±.4	0.25	0.20±.013	0.465		0.39
K_6	0.031±.005	0.092	0.092±.006	0.116		0.092

Note: In those columns marked with a *, revised values of 'x' were used. In those marked 'o', symmetry was assumed in the calculation of the values of nk_x

Table I (continued) Values of 'K_x'

DISCUSSION

In view of the discussion in Part 3, it was not anticipated that the values of nk_x obtained from series A and B would be the same. These values are, however, remarkably similar, and show the same trends. The partition curves indicated, it will be recalled, that greater concentrations of thiocyanate are required for the formation of higher complexes in solutions containing KNO_3 than in solutions containing equivalent amounts of $NaClO_4$. The data in columns (1) and (2) bear this out. The values of nk_x for series A are greater than those for series B for values of $x = 0 - 2$, and smaller when $x = 4 - 6$. In the case of series B it is not possible to say that any advantage is gained by employing revised values of thiocyanate ion concentration, the accuracy of the revised constants, column (3), depending upon the accuracy of the original values, column (2). (Compare also columns (4) and (5)).

More interesting are the values of nk_x obtained by Method III - Bjerrum's method - in which a regular relationship between stability constants is assumed. Note, for example the close similarity between the values of nk_x in columns (2) and (4) or (5). Whereas in column (2) a wholly justifiable relationship between constants k_x existed, -

- $k_0 = f(k_6)$, $k_1 = f(k_5)$, etc. - the whole range of constants in columns (4) and (5) are computed from the one constant k_0. Only in the terms nk_3 does any discrepency occur.

Consider next the values of K_x, the stability constants of the complexes. Method III assumes the relationship $K_x \cdot K_{x-1} =, Q$ to be valid for all values of 'x'. Consequently the values of K_x computed by this method exhibit such a property. The values of K_x calculated by method II seem to indicate that such a relationship does not hold for the following reason.

$$K_x = \left[Fe(CNS)_x^{3-\dot{x}}\right] \div \left[Fe(CNS)_{x-1}^{4-\dot{x}}\right]\left[CNS^-\right]$$

Therefore

$$K_x \cdot K_{x-1} = Q_{x-1} = \left[Fe(CNS)_x^{3-\dot{x}}\right]\left[Fe(CNS)_{x-2}^{5-\dot{x}}\right] \div \left[Fe(CNS)_{x-1}^{4-\dot{x}}\right]^2$$

$$= K'_{x-1}$$

That is, $Q_{x-1} = K'_{x-1}$ is the constant corresponding to the equilibrium

$$2\ Fe(CNS)_{x-1}^{4-\dot{x}} \rightleftharpoons Fe(CNS)_x^{3-\dot{x}} + Fe(CNS)_{x-2}^{5-\dot{x}} \quad \ldots(6)$$

Method III assumes, therefore, that values of K'_x are the same for all values of x, ie. for all complexes. Values of K'_x for series A and B are therefore compared in the following table.

Table II

Values of K'_x

Complex	AII	BII	BIIa	BIIIa
$FeCNS^{2+}$	1.16	0.37	0.46	0.236
$Fe(CNS)_2^+$	$< 4 \times 10^{-3}$	9×10^{-4}	$<3 \times 10^{-3}$	0.236
$Fe(CNS)_3$	$\gg 2$	7×10^3	$>4 \times 10^2$	0.236
$Fe(CNS)_4^-$	$<4 \times 10^{-3}$	9×10^{-4}	$<3 \times 10^{-3}$	0.236
$Fe(CNS)_5^{2-}$	1.16	0.37	0.46	0.236

It would seem, from this data, that it is not entirely correct to assume a regular relationship between values of K_x. In fact, the most stable ferric thiocyanate complexes appear to be $Fe(CNS)_2^+$ and $Fe(CNS)_4^-$. It is interesting, in this respect, that consideration has been given to the stability of other tetra-thiocyanate complexes, e.g. $Cu(CNS)_4^{3-}$, $Ag(CNS)_4^{3-}$.(10)

On the other hand, the neutral complex, $Fe(CNS)_3$, is apparently unstable. The ferric thiocyanate reaction is not one of addition but, rather, one of substitution, or replacement of co-ordinated water molecules by thiocyanate groups. For example

$$Fe(H_2O)^{3+} + CNS^- \rightleftharpoons FeCNS(H_2O)_5^{2+} + H_2O$$

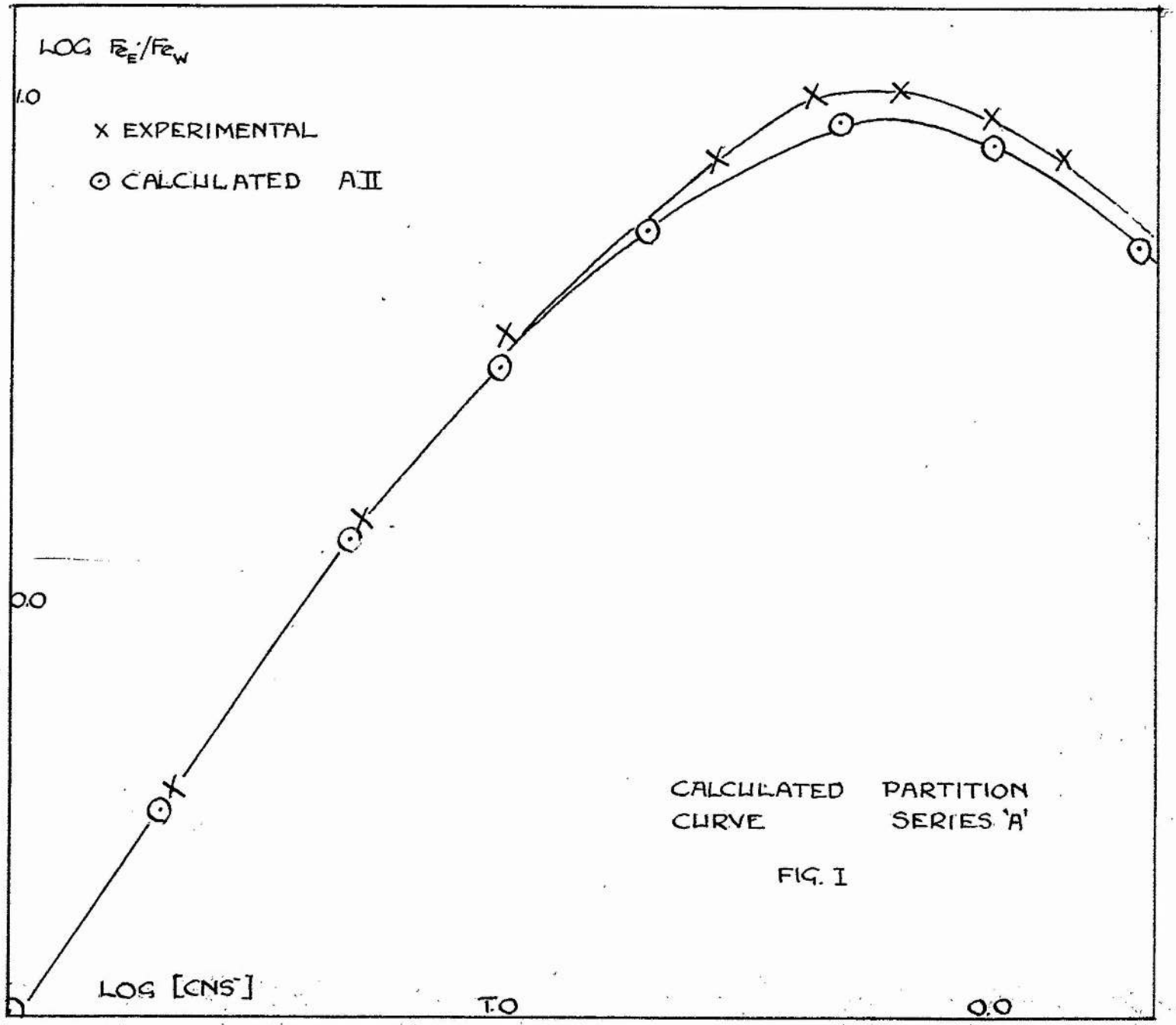
The molecules of water are dipoles, and these orient about the ferric ion, their orientation depending upon the central charge It seems likely that, when the charge is zero, the water molecules will be much less strongly held so that the neutral molecule will be much less stable than the other complexes and the following reaction may readily occur.

$$Fe(CNS)_2(H_2O)_4^+ \longleftarrow Fe(CNS)_3(H_2O)_3 \longrightarrow Fe(CNS)_4(H_2O)_2^-$$

Likewise, the more symmetrical complexes $Fe(CNS)_2(H_2O)_4^+$ and $Fe(CNS)_4(H_2O)_2^-$ may well exhibit greater stability than the asymmetrical complexes $Fe(CNS)(H_2O)_5^{2+}$ and $Fe(CNS)_5(H_2O)^{2-}$. This at least might be suggested by the data in Table II.

It would appear, therefore, that Method III is not truly applicable, though the error involved may appear greater than it actually is.

Fig.I and II show curves $\log.Fe_E/Fe_W$ vs $\log.(CNS^-)$. Fig.I shows the experimental curve for series A and given with it are plots calculated from the values of nk_x (AII) in conjunction with equation (1). Similarly, Fig.II represents experimental and computed data for series B (BII and $BIII_a$). The agreement between calculated and experimental curves is excellent in both cases where calculation was done with the Method II constants. However, the



CALCULATED PARTITION CURVE SERIES 'A'

FIG. I

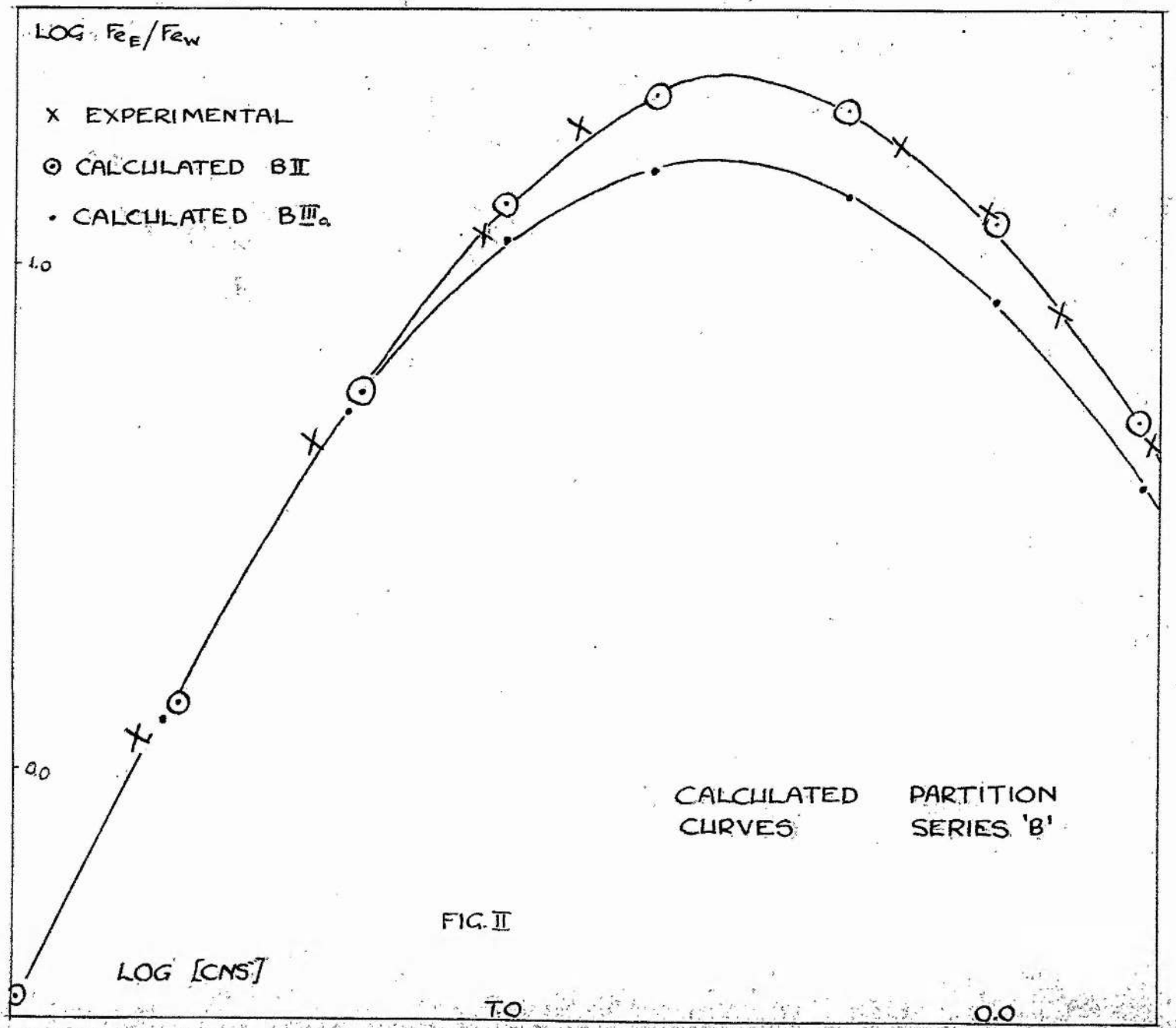

LOG Fe_E/Fe_W
X EXPERIMENTAL
⊙ CALCULATED BII
• CALCULATED BIIIa
1.0
0.0
CALCULATED PARTITION CURVES SERIES 'B'
LOG [CNS]
1.0
0.0

FIG. II

curve computed from the Bjerrum data (BIIIa) is lower than the experimental curve, indicating that less of the neutral molecule is extracted. This follows naturally from the above discussion. By assuming that Bjerrum's theory is applicable, the neutral complex is assumed to have greater stability than, in fact, it has. Hence the calculated partition ratio $[Fe(CNS)_3]_W + [Fe(CNS)_3]_E = nk_3$ is greater, and, consequently, the calculated values of $\log.Fe_E/Fe_W$ are less than the experimental values. It has been noted earlier that the values of $nk_3 = n$ calculated by Methods II and III are not compatible.

The calculated values of nk_x have been used to construct nomograms from which may be read off the proportions of the different ferric thiocyanate complexes in solutions containing a wide range of thiocyanate concentrations. These nomograms are shown in Fig.III and IV. The former is calculated from the series A constants, and applies, therefore, to ferric thiocyanate solutions in which the ionic strength is maintained at 1.8 with KNO_3. The nomogram in Fig.IV is calculated from the series B data (symmetry method II) and, consequently applies to solutions of ionic strength 1.8 and containing $NaClO_4$. These nomograms apply strictly in cases where the iron concentration is small compared with the thiocyanate

concentrations, though it is possible, with their aid, to to estimate the complex concentrations in any solution containing quite a range of iron and thiocyanate concentrations by a method of approximations. So, also, it should be possible with their aid to prepare solutions containing predetermined complex concentrations.

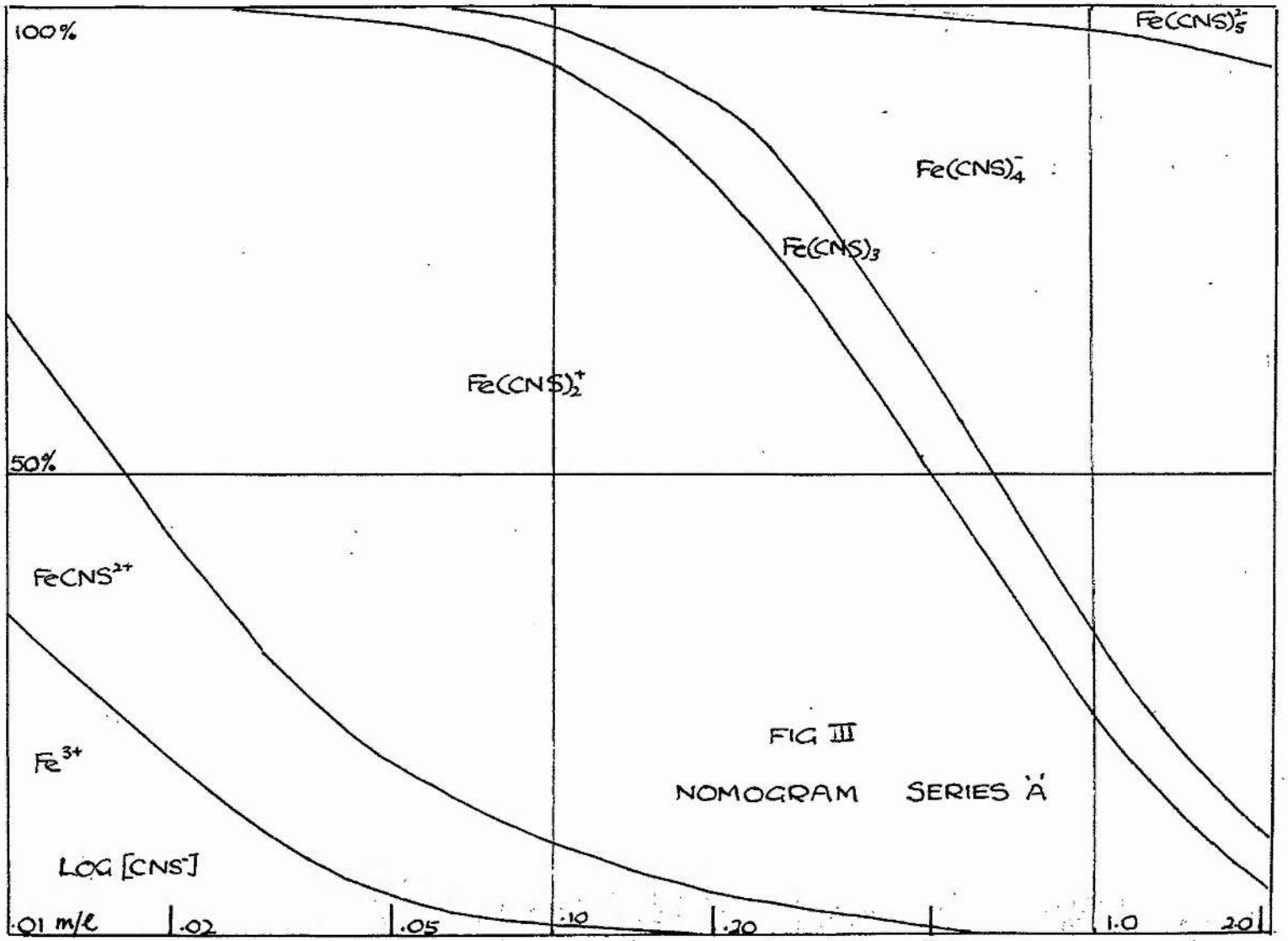


FIG III

NOMOGRAM SERIES 'A'

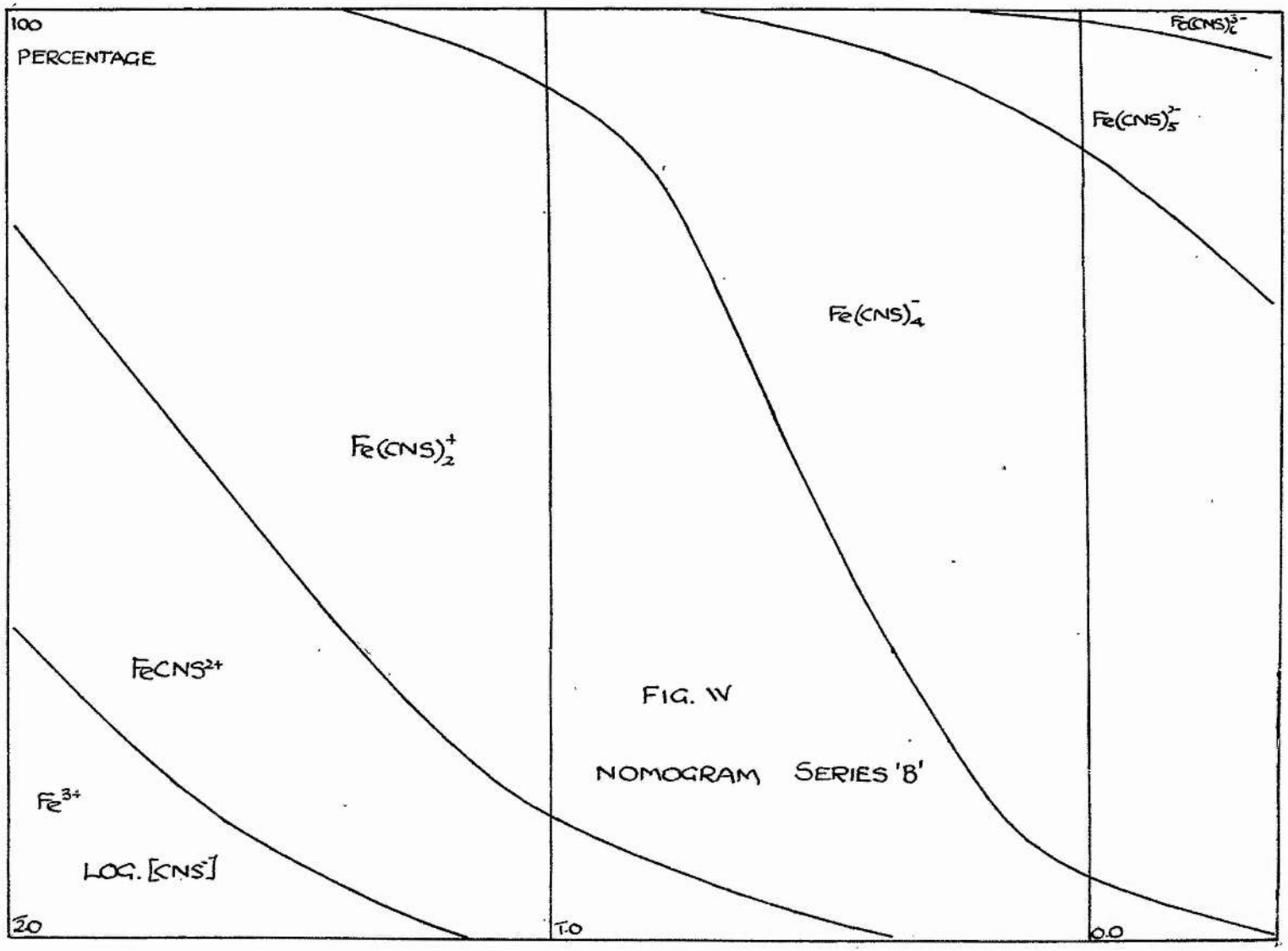


FIG. IV

NOMOGRAM SERIES 'B'

PART 5

APPLICATION of SPECTROCHEMICAL ANALYSIS to the STUDY of the FERRIC THIOCYANATE COMPLEXES.

No study of ferric thiocyanate would be complete without an attempt being made to measure, on a quantitative basis, the extent to which the markedly coloured solutions of ferric thiocyanate complexes absorb light in the visible region of the spectrum. It is realised, however, that such an attempt must be associated with considerable difficulty, since all but the simplest of these solutions contain a number of coloured species, the capacity of which to absorb light will be expected to vary from one complex to another. However, with a knowledge of the various equilibrium constants interrelating the individual complexes, the concentrations of the different ionic species in any particular solution may be calculated. In turn, it should be possible, by mathematical analyses, to separate, from the absorption spectra of such solutions, the individual absorption spectra characteristic of the constituent ions.

Moreover, since the colour of solutions in which the thiocyanate concentration is small is due entirely to the simplest complex $Fe(CNS)^{2+}$, any measure of the light absorption of such solutions is itself a measure of the

extent to which thiocyanate ion is united with ferric ion, and such a measure may be used to advantage in obtaining a value of the stability constant of the simplest complex $Fe(CNS)^{2+}$. And in turn, such a method may be utilised in determining the effect which added ions may have in diminishing the colour of ferric thiocyanate solutions, either by the formation of complexes, or by their capacity to alter ionic strength.

The following pages are devoted to an account of:-

(a) the construction, and calibration of a photoelectric spectrophotometer, employed in this work, and the theory of spectrochemical analysis.

(b) the determination of the stability constant of the simplest complex $Fe(CNS)^{2+}$ (absorption spectra of ferric thiocyanate solutions containing a small concentration of thiocyanate and varying concentrations of iron).

(c) the absorption spectra of ferric solutions containing fixed amounts of ferric ion, and varying amounts of thiocyanate ion.

(d) the absorption spectra of ferric thiocyanate solutions in various organic solvents.

(e) the absorption measurements on ferric thiocyanate solutions of different ionic strengths (activity coefficients).

THEORY OF SPECTROCHEMICAL ANALYSIS

The colour of a solution arises from the capacity of the solute to absorb light of specific wavelengths; the intensity of colour is a measure of the extent to which the solution is capable of absorbing light of these specific wavelengths. When a beam of monochromatic light enters an absorbing medium, the intensity of light decreases exponentially as it passes through the medium, the intensity of the emergent beam being given by

$$I = Io\,e^{-D_\lambda}$$

where I and Io are the intensities of the transmitted and incident monochromatic light, measured on some appropriate scale. A convenient measure of the light absorbed may be given by the function extinction where

$$\text{"extinction"} = \log_{10} Io/I = D_\lambda{}^{*} = ecd \quad \text{(Beer's Law)}$$

Obviously, extinction must be a function of concentration c, the thickness of the absorption medium, d, as well as the nature of the absorbing substance. (Since d was maintained at unity, in all experiments reported, it may be disregarded). The relative

---

* D_λ is used in preference to the usual symbol "K" as this latter symbol is reserved for use in another respect.

capacities of various substances to absorb particular wavelengths may then be given by

$$e = D_\lambda / c$$

where *e* is the molecular extinction coefficient for the particular species, and is simply a measure of the extinction of a solution containing one gram mole per litre of coloured substance. A measure of the relative colours of solutions of different coloured solutes is obtained by comparison of their absorption curves, constructed by plotting extinction against wavelength for solutions of similar concentration, or by plotting molecular extinction (extinction ÷ concentration) against corresponding wavelengths.

The colour of solutions containing two coloured species will now be considered. Provided the solutes obey Beer's Law (that is, their capacity to absorb light in a particular solvent is dependent only on concentration), and provided the concentration of such solutions be known, it should be possible to determine the specific extinction coefficients of each solute for any wavelengths, by measurements of the overall extinction of only two such solutions in which the concentration of at least one solute is varied. On the other hand, should the molecular extinction coefficients of both solutes be known for a number of wavelengths, it should

be possible to determine the concentrations of the solutes in any solution containing both, by measurement of the extinction of such a solution at, at least, two wavelengths for which the molecular extinctions are known. Solutions of ferric thiocyanate may be considered as containing a number of coloured species, each complex having a unique ionic extinction curve, the whole observed curve being the synthesis of a number of these individual extinction curves. The problem of separating such spectra, however, is complicated unless the true ionic extinction coefficients, and the relative amounts of the different species (governed by equilibrium constants) are known. Until such time as they are known, use may be made in constructing absorption curves, of the <u>apparent molecular extinction coefficient</u>, 'α'; α may be defined as log Io/I ÷ x where <u>x</u> is the concentration of iron when thiocyanate is in excess, and where <u>x</u> is the concentration of thiocyanate when the iron is in excess. It is assumed, thereby, that, when thiocyanate is in excess, all the iron is in the form of coloured complexes $Fe(CNS)_z^{3-z}$, (z = 1-6) and that α is, as it were, a mean molecular extinction coefficient of all the coloured species formed. On the other hand, when iron is in excess, all the thiocyanate is assumed

to be in the form of lower complexes, for which α in turn, is a molecular mean extinction coefficient. By plotting α against wavelength, an apparent molecular absorption spectrum is obtained for the multiple solution in question.

CONSTRUCTION, CALIBRATION, AND PROCEDURE FOR USE OF THE PHOTOELECTRIC SPECTROPHOTOMETER.

INTRODUCTION

A photoelectric spectrophotometer was constructed which was of simple design, yet which was capable of detecting low levels of light intensity over the entire visible range, and of employing small slit widths. Essentially, the instrument consisted of two parts, (a) an optical system, and (b) a photoelectric multiplier cell with accompanying potentiometer and power pack (see fig. I).

A source of white light is focussed on the entrance slit of the monochromator which was adapted from a Hilger constant deviation spectrometer by substituting a variable slit for the eyepiece. By turning the wavelength drum, the diffracting prism is slowly rotated in such a way that the spectrum formed moves across the exit slit into which it is focussed by a lens. The second slit, therefore, transmits a narrow band of approximately monochromatic light, the centre wavelength of which is given by the reading on the wavelength drum. The cells containing solvent and solution are rigidly mounted on

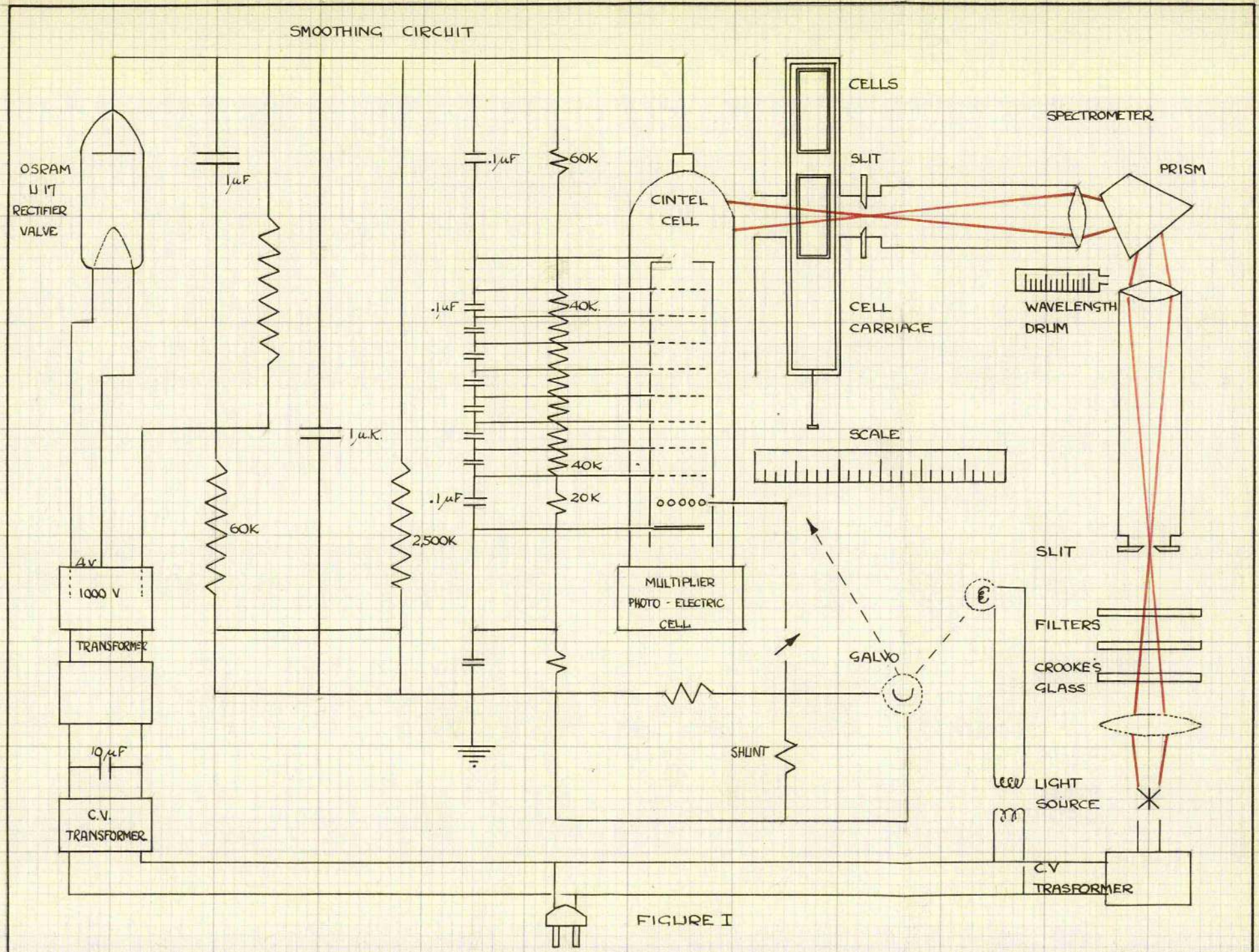

SMOOTHING CIRCUIT
OSRAM U 17 RECTIFIER VALVE
1 μF
.1 μF
60K
CINTEL CELL
CELLS
SLIT
SPECTROMETER
PRISM
CELL CARRIAGE
WAVELENGTH DRUM
.1 μF
40K.
1 μ.K.
40K
SCALE
.1 μF
20K
60K
2,500K
4 V.
1000 V
TRANSFORMER
MULTIPLIER PHOTO - ELECTRIC CELL
SLIT
FILTERS
GALVO
CROOKE'S GLASS
10 μF
C.V. TRANSFORMER
SHUNT
LIGHT SOURCE
C.V TRASFORMER

FIGURE I

a smooth sliding carriage, so that either cell may be placed in the path of the monochromatic ray falling on to the sensitive surface of the multiplier cell. After amplification, the photoelectric current is detected by a sensitive mirror galvanometer and measured by readings of the spot on a centimetre scale. The ratio of successive readings for solution and solvent gives a measure of the transmission (I/I_o) of the solution.

It is advantageous to have the optical cells situated at the exit slit of the monochromator, since the low intensity of light passed by the monochromator is insufficient to cause appreciable photo-chemical decomposition of the solutes. In contrast to this, the photo-chemical decomposition of ferric thiocyanate was marked when solutions of ferric thiocyanate were placed before the entrance slit of the monochromator, despite the use of suitable filters, and of heat absorbing glass.

Light Source. The source of white light was a 500 watt Osram projection lamp, run from a 230 volt constant voltage transformer. A plate of Crookes heat absorbing glass (N 119) was positioned between the lamp and the

monochromator to prevent the passage of heat to the solutions and optical system while suitable filters (Ilford H 558 Set and others) were placed behind the heat absorbing glass to diminish the effect of stray light from the prism.

Monochromator. Both entrance and exit slits of the monochromator were calibrated to be set at any desired width, and optimum settings were determined for various band widths isolated. Incorporated in the entrance slit was a variable wedge for regulating the intensities of the beam of light entering or leaving the monochromator. This could otherwise be done with the aid of neutral density filters placed before the entrance slit.

Optical Cells and Cell Carriage. The optical cells were fused U-bends (Tintometer - CLF 24, SCL 4), and were one centimetre in width. These were held in a sliding carriage to which they were firmly attached by means of a springy brass clip. The carriage could easily be moved to one or other of two fixed positions, bringing each of the cells, in turn, directly into the path of the monochromatic beam. Mechanical perfection of the cell mounting was ensured, and thus, also, reproducibility and equivalence of the cell positions.

Photoelectric Cell. The photoelectric cell was a 9-stage "Cintel" multiplier cell (MA 20, Serial No. A 363) in which the primary current is amplified by secondary emission. The overall voltage was supplied by a main's rectifying unit giving an output voltage of 1000 volts. Fig. I illustrates both this power unit and the potentiometer providing the potentials for the individual stages in the cell. The characteristics of the photocell are given as

30 - 80 μa/ℓ Cathode Sensitivity

1000 - 5000 total multiplication when 1000 volts overall.

The spectral sensitivity curve provided by the makers is sketched, fig. II. The photocell was contained in a dark metal box and mounted on a bakelite base which afforded complete insulation to the electrical leads passing through. The potentiometer was mounted in a bakelite container where it had access to circulating air.

Galvanometer. A sensitive mirror galvanometer (Cambridge D'arsonal approximately 440 ohms resistance) detected the small photocurrent, used in conjunction with a scale graduated in centimetres.

The monochromator, cell carriage and photocell were all joined in one lightproof unit firmly fixed to an optical bench. The positions of the other components of the optical system could be adjusted to give finer focussing on the entrance slit.

A similar spectrophotometer was constructed at an earlier date in which the spectral region was isolated by means of a Bellingham & Stanely monochromator. This instrument was found to be useful in work of a preliminary nature but was less satisfactory than the instrument just described in several respects, being less refined and, in particular, since it had an arbitrary wavelength scale. In consequence it was set aside in preference to the present instrument which was used in obtaining all the data to be given.

CALIBRATION OF THE SPECTROPHOTOMETER

PHOTOELECTRIC CELL

Wavelength - Sensitivity Curve. The sensitivity curve provided by the makers of the cell shows a maximum sensitivity in the region of 4600Å. This is approximately the region of maximum absorption by the ferric thiocyanate complexes, and, therefore, the cell is admirably suited for use in the study of their absorption spectra. Fig. III shows experimental curves for the relative sensitivity of the Cintel photoelectric cell, and an EEL selenium-iron barrier layer photocell. The Cintel cell is approximately ten times as sensitive as the barrier cell.

The curves in Figs. II and III are not entirely comparable. The curve in Fig. II denotes the sensitivity of the photocell in absolute energy units, whereas Fig. III depicts the variation of deflection with wavelength when monochromatic light from the light source falls on the photocell; this, therefore, gives a very useful combined measure of the photocell sensitivity and the wavelength energy distribution of the light source.

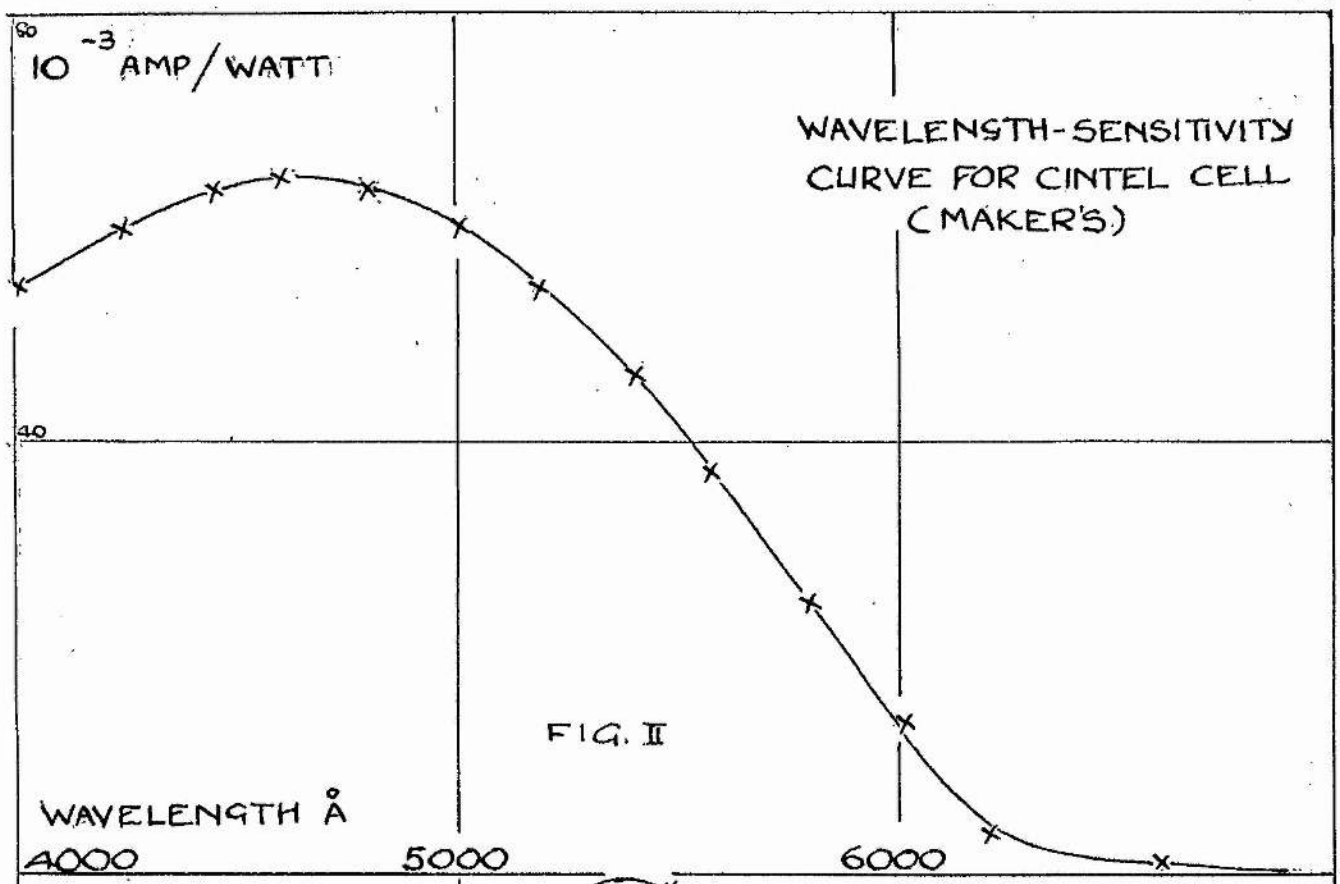


FIG. II

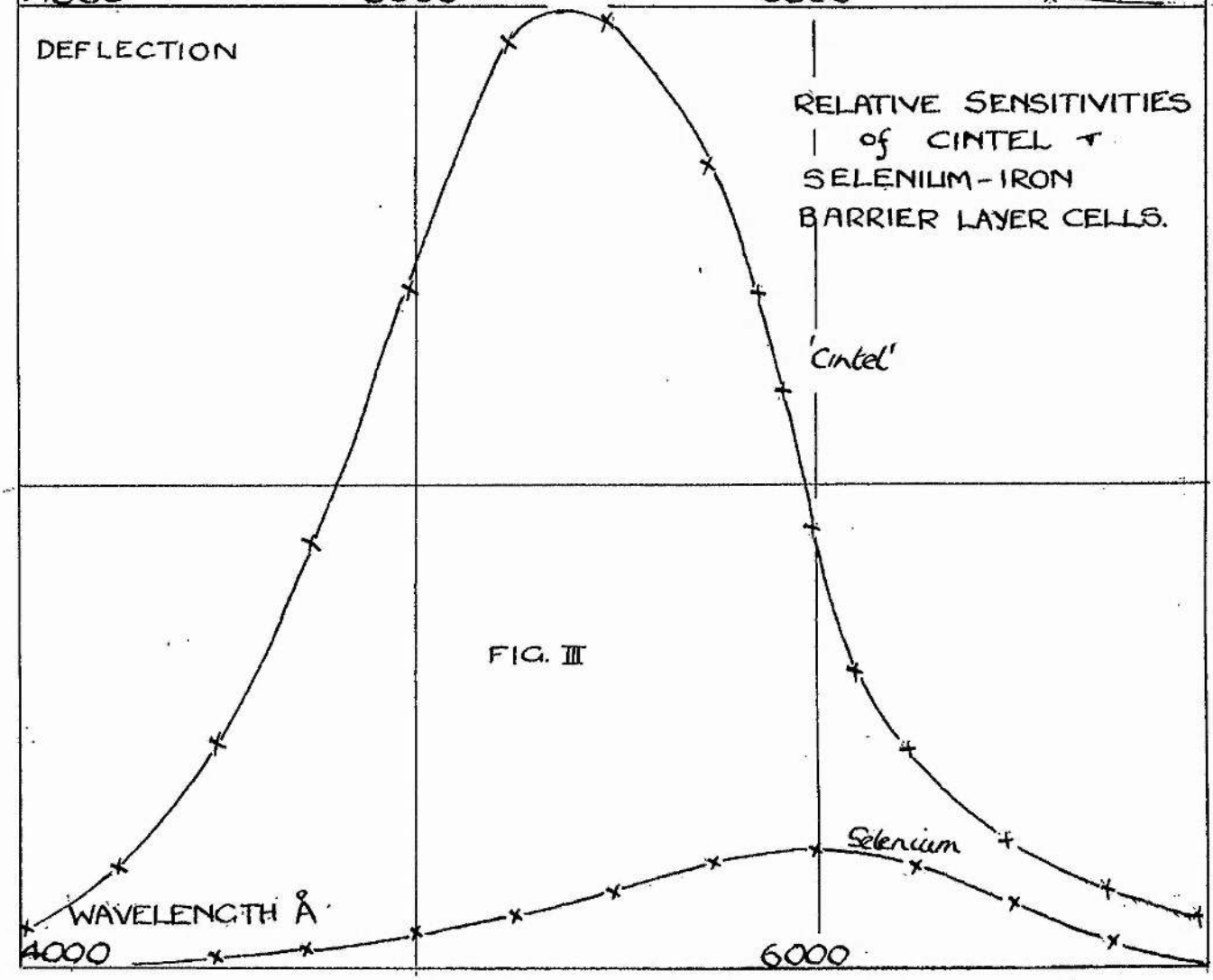


FIG. III

Linearity of Response. This may best be demonstrated by measuring the extinction (log I_o/I) at various wavelengths using calibrated screens, that is, by estimation of the extinction at various wavelengths of screens taken singly and in pairs, and subsequent comparison of the numerical values obtained. Neutral density gray filters were used, and use may also be made of coloured solutions of varying concentration and contained in cells of varying depth. Both methods were used at a particular wavelength (mercury green - 5461Å) while density filters were used over the whole range of wavelengths.

An essential preliminary was to determine the consistency of values obtained for a particular absorption. The figures in the following table were obtained by employing dilute potassium permanganate solution.

Solution. 4.1×10^{-5} M $KMnO_4$ in a 1 cm. cell

Wavelength 5461 Å

Band width 80 Å (a calibrated Bellingham and Stanley monochromator used)

Table I

$Log.I_0/I$	$Log.I_0/I$	
0.4758	0.4775	
0.4755	0.4745	Mean
0.4748	0.4740	0.4748
0.4740	0.4740	±.0012

Probable error ± 0.25 percent

These figures suggest that the mean of three readings of any extinction would be sufficiently accurate.

In the above experiments, I_0 was constant, but similar close agreement is obtained when I_0 is varied. Table II records the values obtained for extinction ~~by using~~ of a neutral density filter, ~~but by~~ varying the amount of light incident upon the photo-cell, by means of the wedges at the monochromator slits.

Band width 80 Å

Wavelength 5461 Å

Table II

I_0 = 40 units	I_0 = 30	I_0 = 17	I_0 = 7
Extinction	Extinction	Extinction	Extinction
0.298	0.300	0.2995	0.294
.2985	.2985	.300	.298
.2975	.298	.298	.294
.2975	.2965	.299	.2975
.298	.298	$.297_3$	.2965
mean 0.2979 $\pm$.0004	0.2982 $\pm$.0011	0.298 8 $\pm$.0010	0.2960 $\pm$.0017

The mean of all four is 0.2977 and each is within its probable error of this figure. These figures show marked consistency, and give a measure of the linearity of response of the photo-cell. In order to verify this, it is necessary to show that the sum of the extinctions of individual density screens (as measured by the cell) is equal to the extinction of the screens taken together. The figures given on the next page show that such is the case when density filters are used with mercury green light and similar band width.

Table III

Density filter A	Filter B	Filter A + B
Extinction	Extinction	Extinction
0.283	0.481	0.775
0.281	0.4855	0.768
0.284	0.484	0.776
0.2825	0.482	0.760
0.2855	0.4875	0.771
Mean 0.283	0.484	0.770
Extinction A + Extinction B = 0.767		
Extinction (A+B) = 0.770		

That linearity of response was a property of the cell for all wavelengths was shown to be the case by repeating the above experiment over the entire range of visible wavelengths. The values of extinction were not consistent for all wavelengths but that was interpretated as being due to the filters which were not strictly neutral. However, when the filters were taken in pairs, it was found that the extinction was, within experimental error, equal to the sum of the extinctions found for the filters taken individually.

MONOCHROMATOR

In all optical systems, a certain amount of light is scattered by reflection at lens and prism surfaces, and this scattered white light may, in certain circumstances, cause serious errors in absorption measurements. The ideal solution is to use a double monochromator. In its absence, it becomes necessary to incorporate suitable colour filters into the optical system to minimise the amount of stray light in the 'monochromatic' beam ultimately passing through the coloured solutions. The choice of such suitable filters and the width of the spectrometer slits are of some importance in determining the nature of the light leaving the monochromator, and the determination of these controlling factors will now be discussed.

Colour Filters The need for filtering in this case is well shown by the following experiments. Cobalt blue glass transmits light at both blue and red wavelengths. The following table indicates the measured transmission (I_0/I) at two long wavelengths (red) in cases where the cobalt glass was used alone, and where a additional red filter was inserted to remove stray blue light passing through th e monochromator.

Wavelength Å	Percent Transmission of Co-blue Glass	
	no filter used	red filter used
7200	15.4	27.9
7300	13.6	20.0

Distinction should be drawn with the case in which the solution or filter transmits green light, since the scattered light (green) increases the apparent transmission at the red end. But when, as in the case of cobalt blue glass, and of ferric thiocyanate solutions, green light is absorbed strongly, the scattered blue or green light affects the blank reading more strongly (i.e. I_0). Therefore the apparent transmission is too low. Correction may, in either case, be made by the use of a red filter to eliminate stray wavelengths. This is further illustrated by the following

Filter Tested	Hg Yellow	Hg Yellow	T.C.Red (Tricolour Red)	T.C.Red	T.C.Red
Added Filter	nil	T.C.Red	nil	Hg Yellow	Ilford 608
Wavelength Å	Percent Transmission				
7000	62.3	86.2	-	71.0	71.1
7500	39.5	84.6	28.1	58.5	50.7
8000	26.9	83.4	15.96	46.2	22.0

The transmission of a number of suitable colour filters was determined using the spectrometer in conjunction

with the photo-cell. As in the case of subsequent optical experiments, the wavelength of the spectrometer was carefully standardised with sodium light, and the setting of the wavelength drum checked by mercury green lines. Arbitrary slit widths were used for these measurements, but were the same for all the filters. The nature of the transmission curves for various filters are indicated in Fig.V. Noted on each curve are the respective band widths, defined as the width of the transmission band in Angstrom units at half its maximum height. From consideration of these curves, various filters are chosen as appropriate for use when extinction measurements were made at specific wavelengths. The choice of filters are given below.

Wavelength-Å	Filter	Wavelength-Å	Filter
3850	U.V.Glass	5000	Ilford 603
3900	U.V.Glass	5300	Hg Green
4000	Blue Glass	5500	Ilford 605
4300	Ilford 601	5750	Ilford 606
4500	Hg Violet	6000	Ilford 607
4600	Hg Violet	6500	Ilford 608
4700	Ilford 602	7000	Ilford 608
4800	Ilford 602	7500	Ferric thiocyan-
4900	Ilford 603	8000	-ate solution

At the ends of the spectrum, a piece of ultra violet transmitting glass was used at λ = 3850Å (the limit of the instrument) while, in the range 6500 - 8000 Å, use was made of a solution of ferric thiocyanate freshly made from stock solution. Such a solution, sufficiently dense that

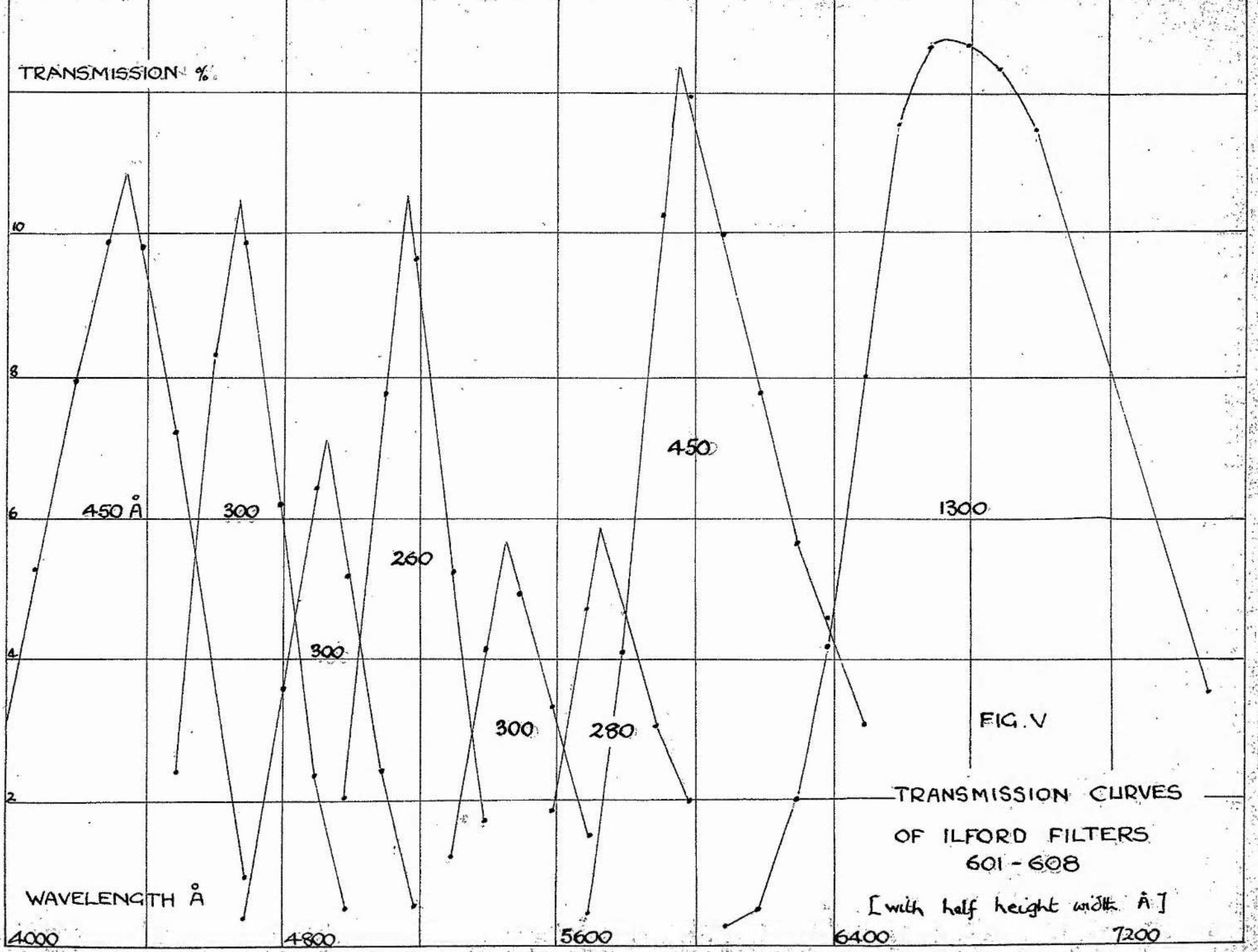


FIG. V

TRANSMISSION CURVES
OF ILFORD FILTERS
601 - 608
[with half height width Å]

the filament of a lamp can just be seen through it, is extremely transparent to red and infra red light, and opaque to other visible wavelengths.

The effect of using suitable filters is shown by Fig.VI which shows the extinction curve for a stable solution of cobaltous nitrate, in cases where no filter and a suitable filter is used. It will be seen that the values of extinction for unfiltered light are high at extreme wavelengths, and low at intermediate wavelengths. The effect of filters in reducing extinction (increasing transmission) is very marked at the red end of the spectrum, and this would be expected since cobalt nitrate absorbs green wavelengths strongly Though 0.25 mm slits were used in the above run, the same results were obtained for runs using 0.5 mm slits, and using the barrier layer cell.

Slit width and band width The range of wavelengths transmitted by a spectrometer is dependent on the prism, the dimensions of the instrument, and on the width of the entrance and exit slits. The slits alone are variable and, consequently, a knowledge of the variation of band width with slit width is desirable. An approximate estimation of the band widths transmitted by the spectrometer, and of optimum slit widths was obtained by determination of the widths of bands transmitted for mercury spectral lines.

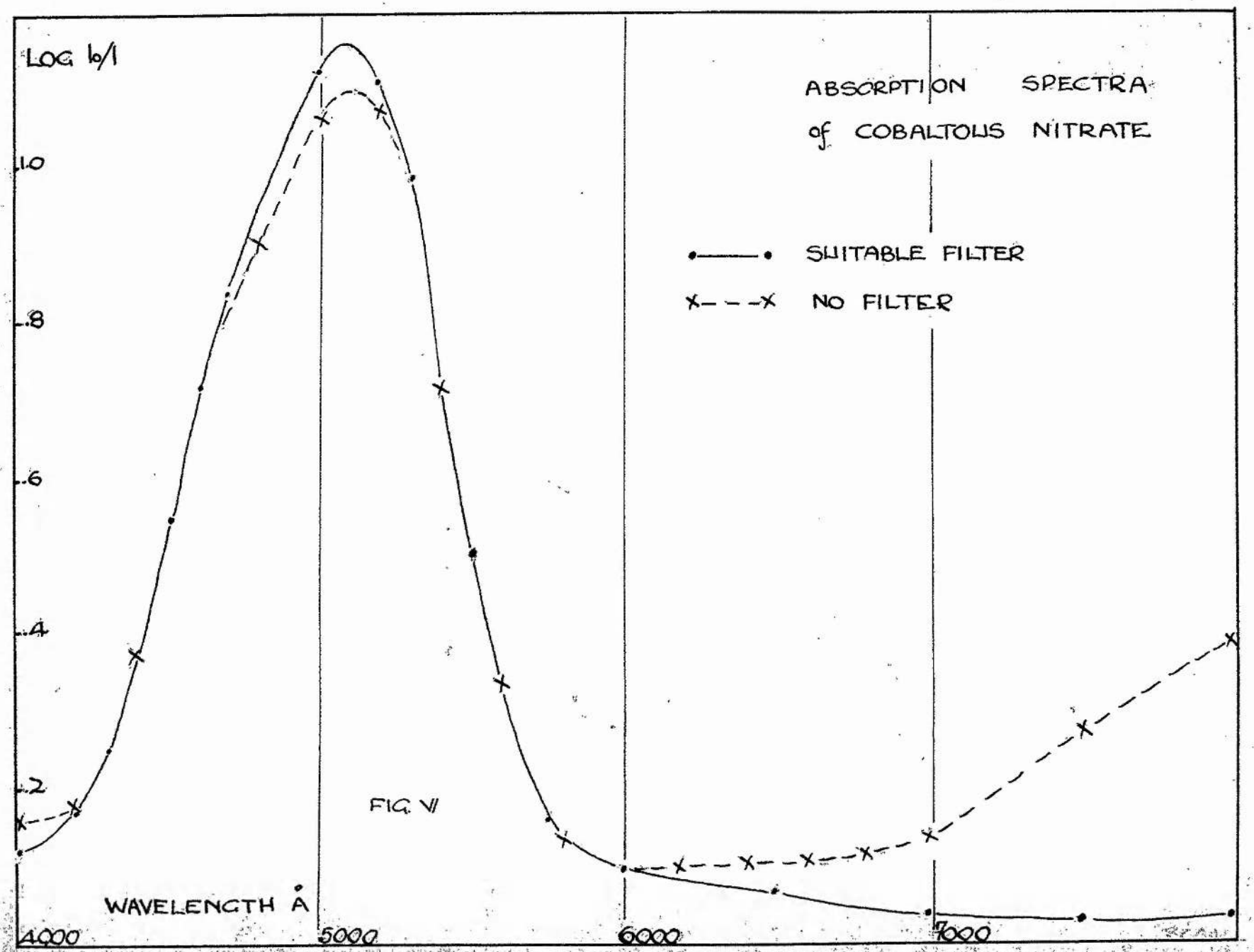

LOG I0/I
1.0
.8
.6
.4
.2
ABSORPTION SPECTRA
of COBALTOUS NITRATE
SUITABLE FILTER
NO FILTER
WAVELENGTH Å
4000
5000
6000
7000

FIG. VI

Best results were obtained when both slits were of the same width. Using an Osira H P mercury vapour lamp as light source, the wavelength drum was rotated, and readings of deflection recorded as the spectral lines moved across the exit slit. Fig.VII shows typical plots of deflection against wavelength for equal slit widths of 0.25 and 0.5 mm. From such graphs as these, values of the band widths transmitted at specific wavelengths were obtained, and these are tabulated below. Band width is a measure of the range of wavelengths transmitted by the spectrometer for any particular settings of slit widths and the wavelength drum, and this is taken as being the width of the band transmitted at half the maximum intensity, and is measured in wavelength units.

Variation in band width with slit width

Wavelength Å	slit width 0.25 mm	slit width 0.5 mm
	Band Width Å	
4047	17	38
4365	21	47
4900	30	60
5475	50	104
5785	63	130

Most of the experimental measurements were made with 0.25 mm slits opened to 0.5 mm at extreme ends of

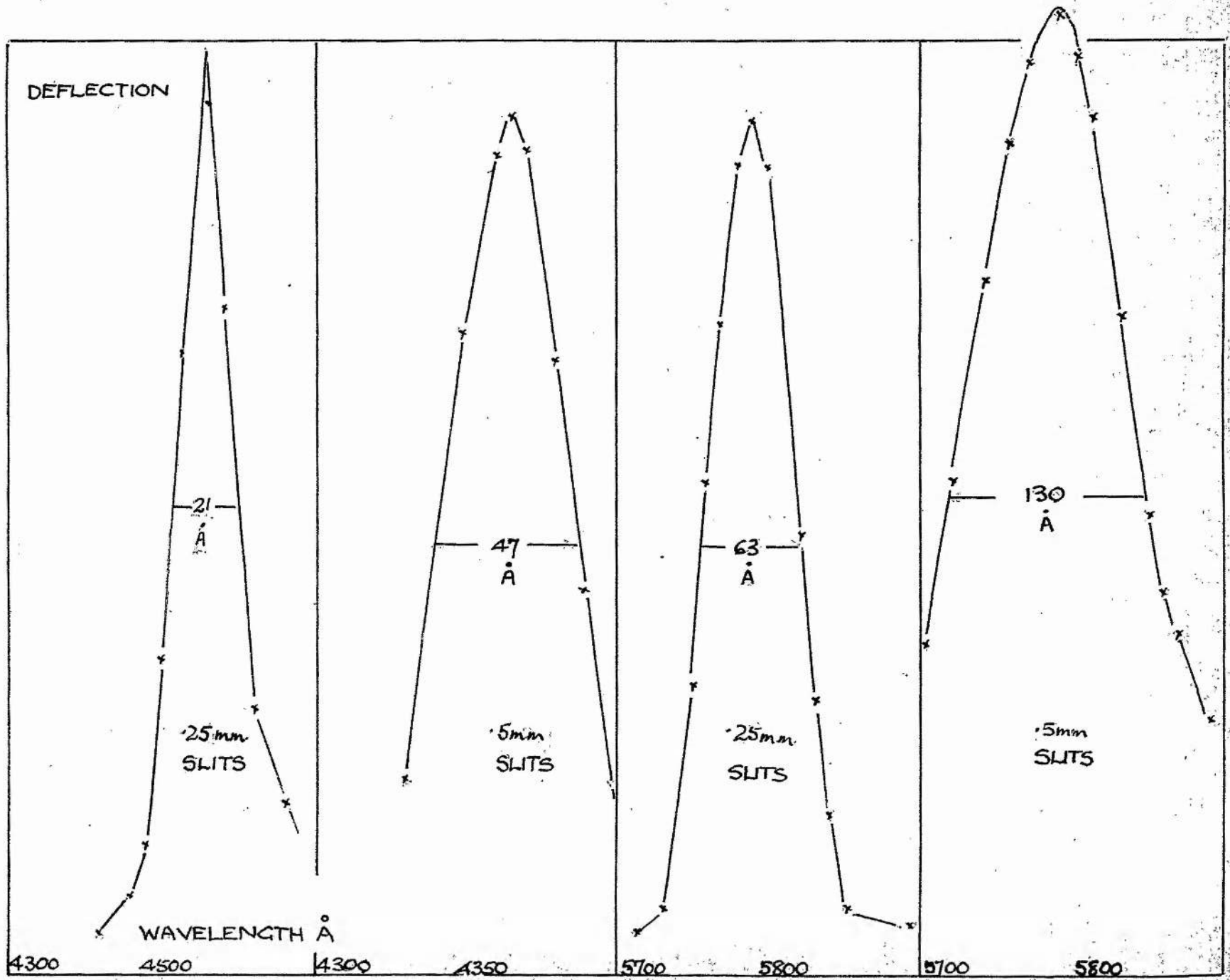


FIG III VARIATION IN BAND WIDTH WITH SLIT WIDTH

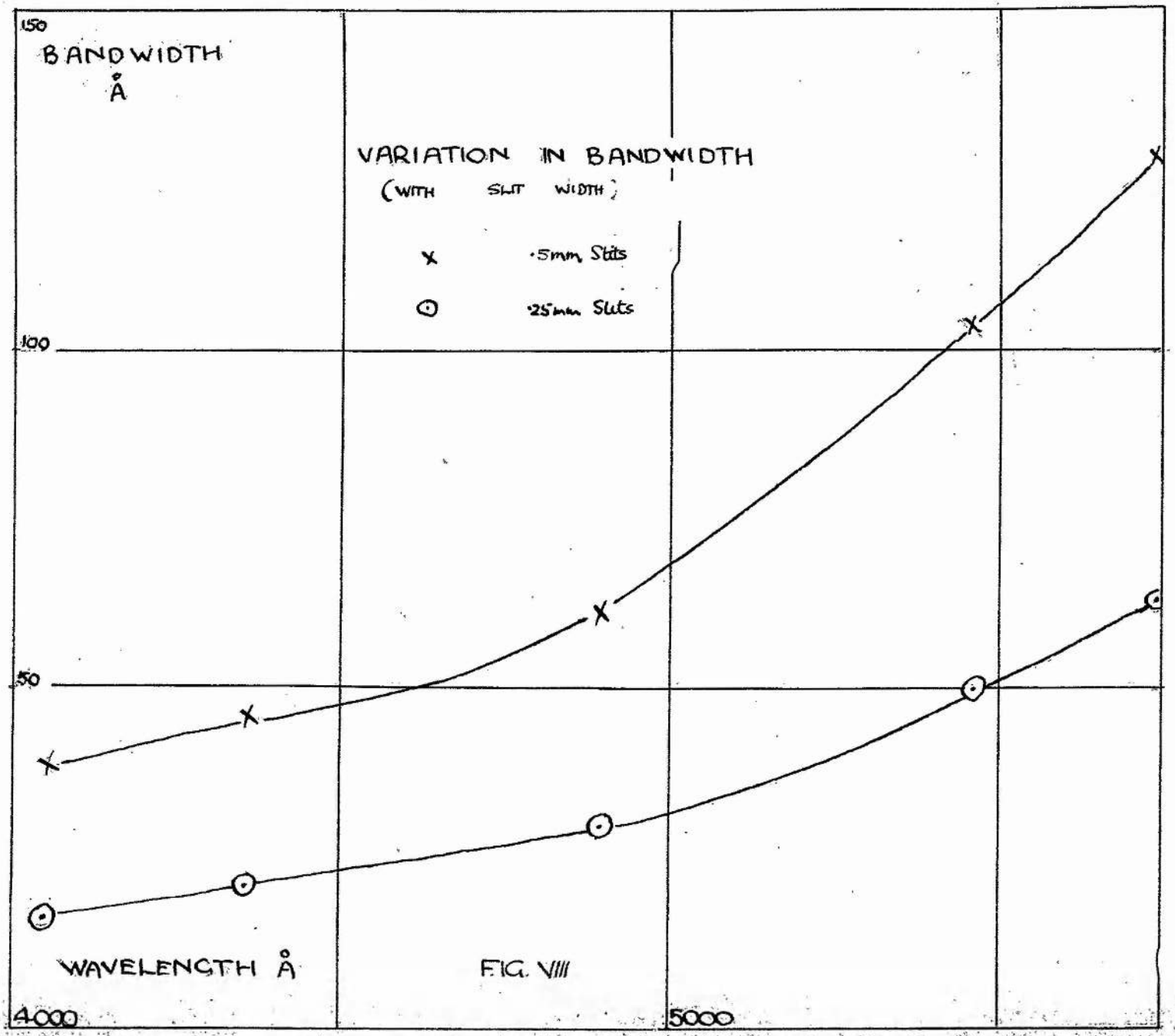

150
BANDWIDTH
Å
VARIATION IN BANDWIDTH
(WITH SLIT WIDTH)
X ·5mm Slits
⊙ ·25mm Slits
100
50
WAVELENGTH Å
4000
5000

FIG. VIII

the spectrum where the sensitivity of the photo-cell was diminished. It will be noticed that the band width is almost proportional to the slit width. The variation in band width with wavelength is shown in Fig.VIII.

PROCEDURE

The optical cells were kept scrupulously clean. Immediately prior to use, they were thoroughly cleaned with concentrated nitric acid and rinsed successively with water and alcohol. No difficulty was experienced in drying and polishing them with a clean white cloth. One cell was strictly reserved for use with solvent, and the other for solution. In most cases, the colour-less solution ('solvent') was of similar concentration to the coloured solution save that one of the ions required for the production of colour was omitted, usually the iron. Thereby, error arising from the presence of that ion as impurity in the other stock solutions could be eliminated. The solutions were filtered to free them from dust, and in certain instances thermostated before use.

No measurements were made until the light source had been illuminated for some minutes, in order that it might reach a steady state.

The coloured solutions, themselves, were protected from light in so far as that was possible. Once in the instrument, the solutions were completely isolated from any light other than that transmitted by the spectrometer. That decomposition was negligible was shown by repetition of earlier readings at the completion of a run. A minimum of four extinction measurements were made at each wavelength and a mean value taken. The order in which $\underline{I}$ and $\underline{I}_0$ are measured are not relevant, but $\underline{I}$ was measured alternatively first and second in actual practice. This led to a slight economy of time and a complete spectral analysis of a single solution could be made in about one hour.

THE STABILITY CONSTANT OF THE COMPLEX $FeCNS^{2+}$

$$FeCNS^{2+} \rightleftharpoons Fe^{3+} + CNS^{-}$$

$$K_I = \frac{[FeCNS^{2+}]}{[Fe^{3+}][CNS^{-}]}$$

= Stability Constant

The complex $FeCNS^{2+}$ differs from the others in that it is possible to obtain a solution in which it is formed almost exclusively. On the other hand any attempt to obtain a solution in which any of the other complexes is in a state of virtual isolation must fail in as much as each of these complexes must at all times be in equilibrium with other complexes in such proportions that do not allow of isolation. It is generally accepted that the simple ion $FeCNS^{2+}$ is the only complex formed to any measurable extent when the thiocyanate concentration is small. Provided the thiocyanate concentration is maintained at a sufficiently low level, it may be assumed that the red colour of such solutions is due, essentially, to the complex $FeCNS^{2+}$ and, consequently, that any estimation of the colour of such solutions serves as a measure of the concentration of the simple complex. If the total concentrations of iron and thiocyanate in the coloured solutions are known, it is

possible to derive a value for the stability constant of the complex. A variety of such values have been obtained by various workers e.g. Frank and Ostwalt (9), Edmonds and Birnbaum (8), Bent and French (4), and Babko (1). In no case did these workers employ values of ionic strength greater than unity and it is significant that none of them performed their experiments at constant temperature, even though the colour of ferric thiocyanate solutions is believed to be sensitive to changes in temperature. The object of the experiments about to be reported was to obtain, at 18°C, a value of K_1 for solut-ions in which the ionic strength was maintained at 1.78 with NH_4ClO_4 and with KNO_3. The values so obtained have been employed in the partition calculations previously described.

Theory

Although a number of methods have been devised for the determination of K_1, all are substantially the same, being developed from the assumption that, under conditions of dilution, no complex, other than $FeCNS^{2+}$, is formed in appreciable amounts. The method adopted was essentially that described by Frank and Ostwalt (loc.cit.).

The optical densities of solutions containing a small fixed amount of thiocyanate and varying amounts of iron are measured over a range of wavelengths, the acid content and ionic strength of all the solutions being the same. If the original concentrations of iron and thiocyanate are 'a' and 'b', and if the concentration of $FeCNS^{2+}$ is 'x', then

$$K_1 = \frac{x}{(a-x)(b-x)}$$

for any particular ionic strength, and assuming for the moment that no hydrolysis of the ferric ions occurs. It follows that

$$x^2 - (a + b + K).x + ab = 0 \qquad K = 1 + K_1$$

i.e.
$$x = \frac{ab}{a + b + K} + \frac{(ab)^2}{a + b + K}$$

Since 'a' and 'b' are small, the second term on the right hand side may be ignored. Hence

$$x = \frac{ab}{a + b + K}$$

But, since it is assumed that all the colour is due to $FeCNS^{2+}$

$$\log I_o/I = \varepsilon .x.d$$

for any particular wavelength, $\log I_o/I$ being the extinction D_λ, ε the molecular or ionic extinction coefficient for the same wavelength, and 'd' the thickness of the optical cell, in this case unity. By combining the last two equations one obtains

$$D_\lambda = \frac{\varepsilon . ab}{a + b + K}$$

whence

$$\frac{ab}{D_\lambda} = \frac{1}{\varepsilon}(a+b) + \frac{K}{\varepsilon} \qquad \ldots\ldots (1)$$

Equation (1) represents a straight line, the slope of which is equal to the reciprocal of the extinction coefficient for any particular wavelength and the intercept of which is equal to the quotient $1 + \varepsilon K_1$. If sufficient experimental data is available, the equation may be solved by the method of least squares. On the other hand, should optical measurements be made on two specific solutions only in which the iron concentrations are $\underline{a}$ and $\underline{a}'$, ε the extinction coefficient for any wavelength, is given by

$$\varepsilon = \Delta a \div \Delta\left(\frac{ab}{D\lambda}\right) \qquad \ldots\ldots (2)$$

Knowing values of $\underline{\varepsilon}$, values of K, and hence K_1, may readily be found. This latter method was chosen for obtaining values of K_1. At the same time a series of extinction curves were obtained for ferric thiocyanate solutions in which the thiocyanate concentration was small and the iron concentration varied over the largest possible range set by the instrument.

EXPERIMENTAL

The experiments are divided into two sections

A The effect upon the absorption spectra of ferric thiocyanate solutions of varying the iron concentration,

and B The determination of K_1.

A The absorption spectra of ferric thiocyanate solutions containing a range of iron concentrations.

The solutions analysed photometrically had the following compositions.

NH_4CNS	3×10^{-4} M
$Fe(ClO_4)_3$	5.786×10^{-4} M $\times$ x
	x = 1-15
$HClO_4$	0.182 M
Ionic strength	1.78 with $NaClO_4$

The thiocyanate concentration was small and sufficient only to permit of the formation of $FeCNS^{2+}$. The various solutions from which the coloured solutions were prepared were preheated to 18±.1°C in a thermostat. Measurements of extinction were made immediately on mixing. A complete analysis from 3850Å to 7000Å, with four readings at each wavelength, took about an hour. That no decomposition or

change in the depth of colour occured in that time could be shown by repetition of certain earlier extinction measurements at the end of that time.

The experimental data are given in table I. A number of representative curves obtained by plotting extinction ($= D_\lambda = \log I_o/I$) against wavelength for these solutions are shown in Fig.I These curves have maxima at the same wavelength, 4560Å. Since change in the wavelength of maximum absorption is probably indicative of the formation of higher complexes, it would appear that no such complexes are formed, and this would be in harmony with the theory postulated earlier.

Table I

The extinction of ferric thiocyanate solutions containing varying amounts of iron

Wavelength Å	x = 1	2	3	4
3850	.0004	-	.0233	.1262
3900	.0414	.0772	.1179	.1587
4000	.0503	.0941	.1309	.2357
4200	.0730	.1364	.1911	.2711
4300	.0809	.1553	.2180	.2963
4400	.0906	.1694	.2380	.3071
4450	.0930	.1722	.2452	.3111
4500	.0950	.1783	.2511	.3143
4550	.0950	.1804	.2536	.3143
4600	.0930	.1793	.2534	.3133
4700	.0909	.1738	.2445	.3029
4800	.0835	.1638	.2304	.2844
4900	.0763	.1483	.2084	.2585
5000	.0682	.1319	.1847	.2282
5250	.0422	.0845	.1196	.1461
5500	.0140	.0453	.0672	.0838
5750	-	.0203	.0327	.0391
6000	-	.0094	.0149	.0191

Table I ctd.

The extinction of ferric thiocyanate solutions containing varying amounts of iron

Wavelength Å	x = 6	10	12	15
3850	-	.2214	-	.2455
3900	.1923	.2407	.2834	.3104
4000	.2243	.3014	.3395	.3870
4200	.3228	.4445	.4983	.5623
4300	.3736	.5083	.5694	.6420
4400	.4116	.5584	.6235	.6993
4450	.4236	.5682	.6382	.7204
4500	.4264	.5860	.6578	.7390
4550	.4298	.5915	.6712	.7490
4600	.4293	.5907	.6717	.7446
4700	.4231	.5709	.6425	.7294
4800	.3979	.5379	.6033	.6900
4900	.3617	.4899	.5491	.6215
5000	.3236	.4348	.4929	.5511
5250	-	.2810	.3238	.3653
5500	-	.1584	-	.2098
5750	-	.0391	-	.1093
6000	-	-	-	-

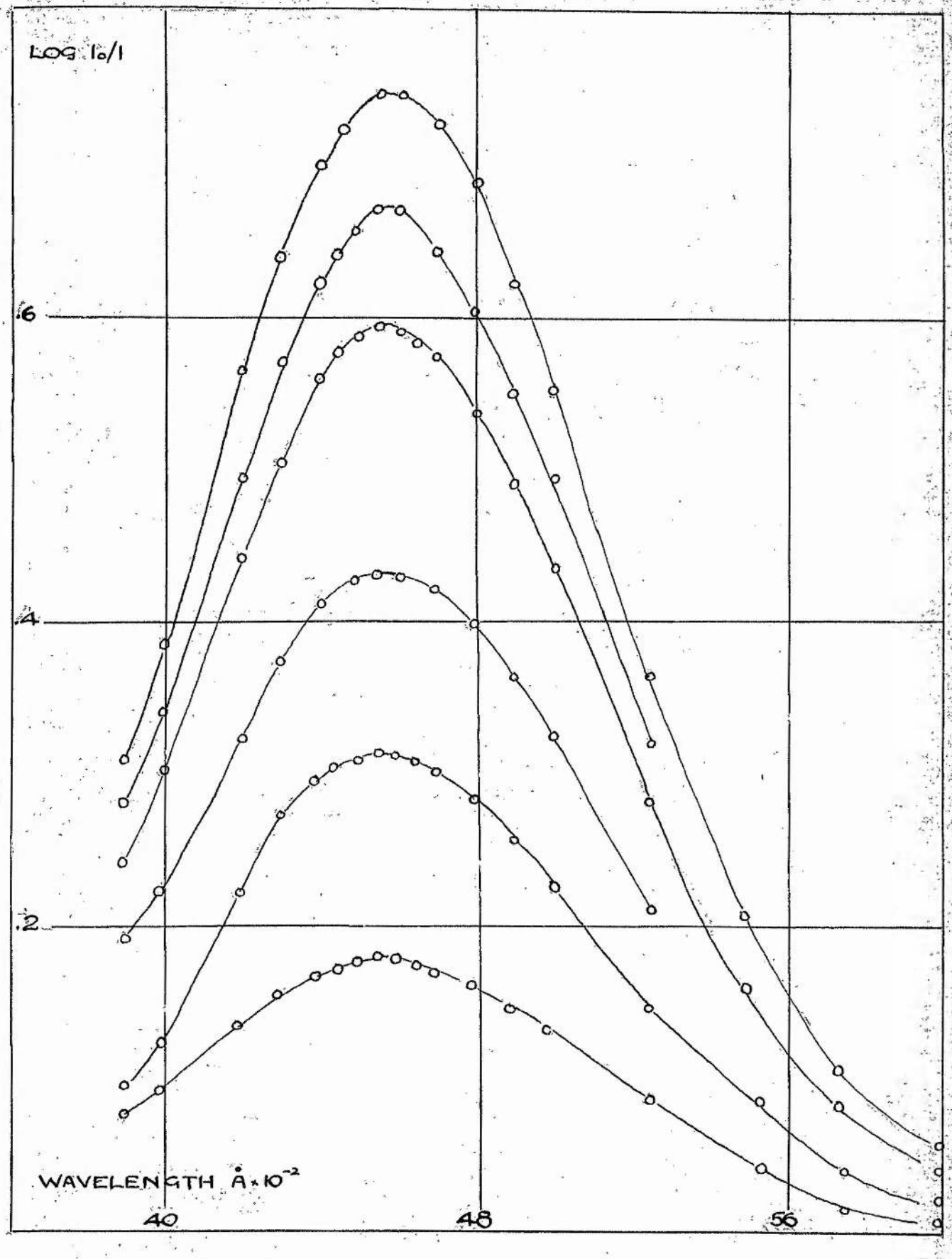


FIG. I

B The determination of K_1, the stability constant of $FeCNS^{2+}$

Values of K_1 have been obtained for the complex $FeCNS^{2+}$ in solutions in which the ionic strength is maintained at 1.78 with (1) $NaClO_4$ and (2) KNO_3. Two solutions were examined for each salt base in which the thiocyanate concentration was constant and small, and in which the iron concentration was varied fourfold. The experimental procedure was the same as in experiment A. The solutions analysed had the following composition.

Experiment B_1 ($NaClO_4$ base)

$NaClO_4$	1.6 M
$HClO_4$	0.18M
NH_4CNS	.0002M = b
$Fe(ClO_4)_3$	.002 M = a_1
	.008 M = a_4

Experiment B_2 (KNO_3 base)

Similar concentrations, but the following electrolytes were used.

KNO_3, HNO_3, KCNS, and $Fe(NO_3)_3$.

Table II

Wavelength Å	Experiment B_1		Experiment B_2	
	D_1	D_4	D_1	D_4
3900	0.078	0.197	0.063	0.163
4000	.101	.261	.082	.216
4100	.126	.321		
4200	.150	.379	.119	.321
4300	.172	.435	.136	.370
4400	.187[5]	.475	.150	.402
4500	.195	.495	.155	.417
4600	.195	.494	.155	.416
4700	.188	.474	.150	.399
4800	.174[5]	.443	.140	.371
4900	.157[5]	.401		
5000	.138	.350	.108	.287
5500	.051	.130	.040	.107
6000	.014	.034	.130	.245

Note The values of 'D' given for Expt.B_1 are the mean of five runs. The variation between runs was of the order one percent.

Table II lists values of the extinction, 'D', of these solutions at various wavelengths, these being a mean of five separate experimental values in the case of Expt.B_1 ($NaClO_4$), and of two concordant experiments in the case of Expt.B_2.

From these, and the values of 'a' and 'b', the original iron and thiocyanate concentrations, were calculated with the aid of equation two given earlier, the molecular extinction coefficients of $FeCNS^{2+}$ for a whole range of wavelengths. These were used, in turn, with equation one to calculate values of K_1. The values of ε and K_1 calculated from both series of experimental data are given in Table III.

From these experiments, mean values of K_1, the stability constant of the simple complex $FeCNS^{2+}$, were chosen as follows.

K_1 = 123.2 ± 0.5	ionic strength = 1.78	$NaClO_4$
K_1 = 100.2 ± 1.1	ionic strength = 1.78	KNO_3

It should be noted that a one percent error in 'D' leads to an error of three to four percent in ε and K_1, so the ~~so the~~ probable error of ε and K_1 is about ± 5 percent.

Table III

Molecular Extinction Coefficients of $FeCNS^{2+}$

Values of K_1 (Calculated)

Wavelength Å	Experiment B_1		Experiment B_2	
	ε	K_1	ε	K_1
3900	2005	(123.5)	1733	(113.7)
4000	2770	(113.9)	2380	106.3
4100	3050	125.0		
4200	3840	125.0	3703	98.1
4300	4425	124.0	4350	94.4
4400	4835	123.5	4560	100.4
4500	5060	122.5	4745	100.7
4600	5040	123.0	4760	99.1
4700	4780	125.8	4460	103.1
4800	4530	122.3	4120	104.7
4900	4140	120.4		
5000	3590	122.0	3220	103.1
5500	1335	121.7	1225	99.8
6000	325	(141.0)	1887	(141.)
	Mean[×]	123.2 ± 0.5		100.2 ± 1.1

[×] Values of K_1 in brackets not included in mean

Molecular Absorption Spectrum of the Complex $FeCNS^{2+}$

Fig.II shows the molecular absorption curve of the simple complex $FeCNS^{2+}$. Values of ε, the molecular extinction coefficients of $FeCNS^{2+}$, obtained in experiment B_2 are plotted against wavelength. The absorption is general, and it will be noted that the maximum absorption is in the region of 4550Å. The maximum value of extinction coefficient at this wavelength is of the order 4900. These important observations are referred to later in connection with the absorption spectra of the other ferric thiocyanate complexes.

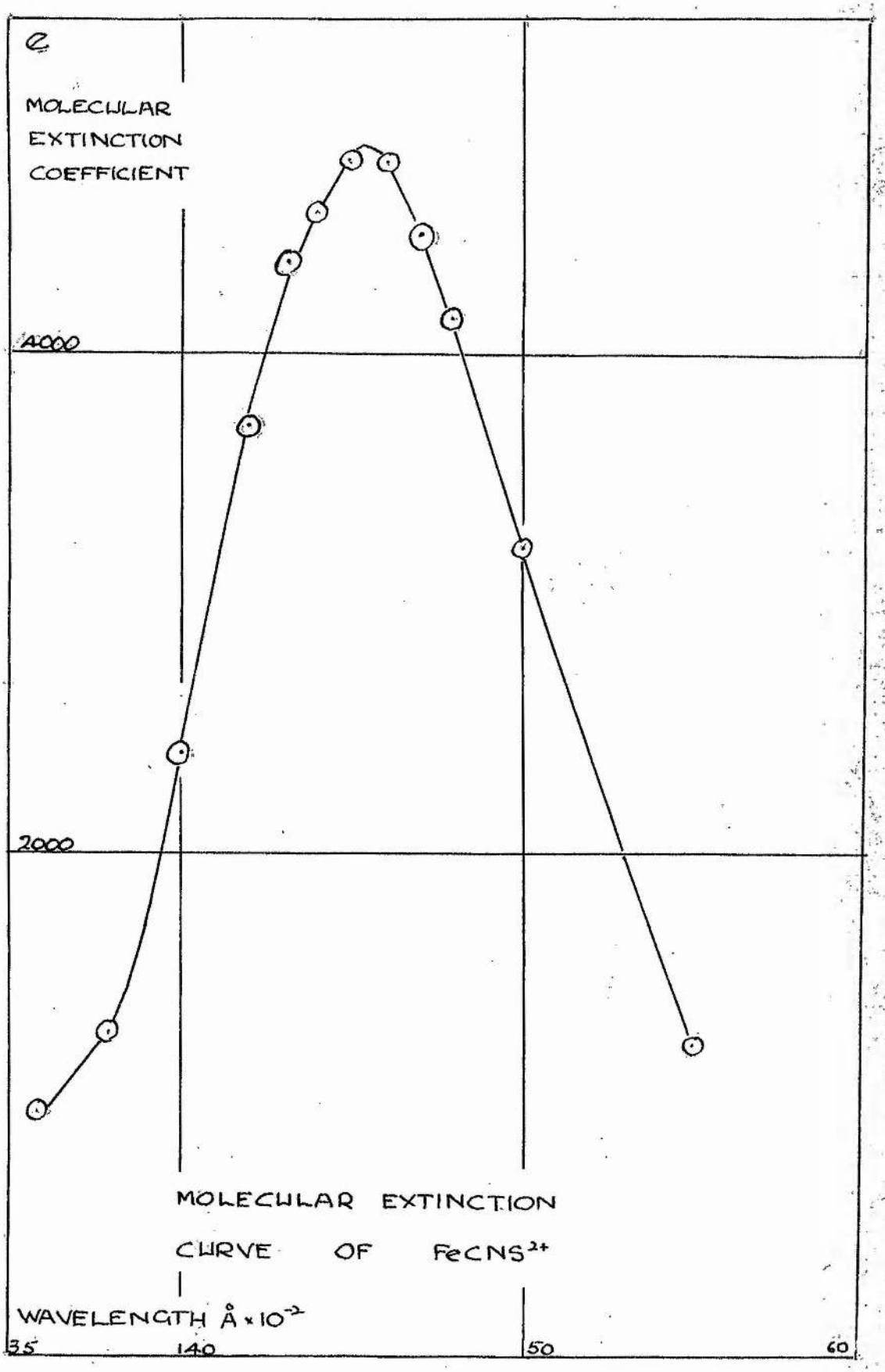

ε
MOLECULAR
EXTINCTION
COEFFICIENT
4000
2000
MOLECULAR EXTINCTION
CURVE OF FeCNS2+
WAVELENGTH Å × 10-2
35
40
50
60

FIG. II

Note on the effect of Hydrolysis

The hydrolysis constant of the ferric ion has been determined by Bray and Hershey (6), and by Lamb and Jacques (16).

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$$

$$K_h = 6 \times 10^{-3} \quad \text{(B and H)}$$

$$= 2.5 \times 10^{-3} \quad \text{(L and J)}$$

Unless the acidity of an iron solution is very large, account must be taken of hydrolysis in quantitative methods employing iron concentrations. Approximate correction in the value of K_1 may be made as follows.

$$K_h = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}]}$$

The true value of K_1 is given by K_1'.

Putting

$$K = 1 + K_1$$

and, consequently

$$K' = 1 + K_1'$$

then

$$K' = \frac{[Fe^{3+}][CNS^-]}{[FeCNS^{2+}]}$$

and the apparent value obtained from the above experiments

$$K = \frac{[Fe^{3+} + FeOH^{2+}][CNS^-]}{[FeCNS^{2+}]}$$

Therefore, the ratio of true and apparent constants is given by

$$K' \div K = \frac{[Fe^{3+}]}{[Fe^{3+}] + [FeOH^{2+}]} = \frac{1}{1 + \frac{[FeOH^{2+}]}{[Fe^{3+}]}}$$

By making use of the hydrolysis constant, the value of the true dissociation constant is found to be

$$K' = K \div (1 + K_h/[H^+])$$

Taking 4×10^{-3} as a value of K_h and 0.18 as the hydrogen ion concentration, the following corrected values of the stability constant of $FeCNS^{2+}$ were calculated for an ionic strength of 1.78.

$K_1' = 126.0$ ($NaClO_4$)

$K_1' = 102.5$ (KNO_3)

These values are compared with the values of other workers.

	K_1'	ionic strength	electrolyte
Frank, Ostwalt (9)	236.5	0.128	$HClO_4$
	138.0	0.50	$HClO_4$
Edmonds, Birnbaum (8)	127.3	1.0	
Present work	126.0	1.78	$NaClO_4$, ~~HNO_3~~ $HClO_4$
	102.5	1.78	~~$NaClO_4$~~ KNO_3, HNO_3

These values are of interest in connection with the effect of activity and added electrolytes on the Fe^{3+} - CNS^- equilibria.

APPARENT ABSORPTION SPECTRA of FERRIC THIOCYANATE SOLUTIONS CONTAINING a WIDE RANGE of THIOCYANATE CONCENTRATION

Apparent absorption spectra have been obtained for ferric thiocyanate solutions containing varying amounts of thiocyanate. Ferric nitrate and potassium thiocyanate were chosen as reactants to avoid formation of complexes other than those desired. The stock ferric nitrate solution was standardised with titanous sulphate and diluted as required; the thiocyanate solution was standardised with silver nitrate. All coloured solutions analysed spectrophotometrically were kept at constant ionic strength (1.78) - see page 58 - with potassium nitrate, except in a few instances mentioned later. The pH was kept sufficiently low to suppress hydrolysis by addition of nitric acid. Extinction measurements were made with the specially constructed photoelectric spectrophotometer already described.

The theory has been postulated (page 13) that the proportions of the various complexes in a ferric thiocyanate solution are dependent on the thiocyanate concentration and independent of variations in the iron concentration. Consequently, provided the

thiocyanate concentration is constant, so also will be the distribution of the iron present amongst the various complex forms. Should the total iron concentration be doubled, the concentration of each complex will be doubled, and apparent extinction measurements on such solutions in which the thiocyanate concentration is constant, and the iron concentration varied, should obey Beer's Law. Therefore, for each thiocyanate concentration, a number of absorption runs were made using various iron concentrations. In the main, Beer's Law was found to apply; any variations that occurred were random and not reproducible.

The compositions of the solutions analysed are given in Table I. All solutions were 0.18M with respect to nitric acid; with the exception of numbers 11 - 13, the ionic strength of the solutions was 1.78. Since thiocyanate was in excess in all these solutions, the apparent molecular extinction coefficient, α, was taken as extinction divided by the total iron concentration (see page 104). In the case of experiments Nos. 11, 12, in which the thiocyanate concentration was very small, α is taken as log Io/I divided by the total thiocyanate concentration. Various iron concentrations were employed, and for any wavelength, and any

thiocyanate concentration, the calculated apparent molecular extinction coefficients were found to agree. Mean values were taken. Table II contains values of the apparent molecular extinction coefficients of ferric thiocyanate solutions for the visible range of wavelengths, and for varying thiocyanate concentrations. Fig.I shows the apparent absorption curves of these solutions obtained by plotting values of $\underline{a}$ against wavelength for different thiocyanate concentrations.

Table I

Index	KCNS m/l	KNO_3 m/l	$Fe(NO_3)_3$ m/l
1	0.008	1.592	With the exception of nos. 1 and 2 four runs were made with iron concentrations 0.191, 0.382, 0.764, 1.528, or 3.056 mol.× 10^{-4}/l. At the ends of the wavelength scale, a few readings made with 6.110 and 30.6 mol.× 10^{-4}/l
2	.016	1.548	
3	.040	1.560	
4	.080	1.520	
5	.160	1.440	
6	.400	1.200	
7	.600	1.000	
8	.800	0.800	
9	1.200	0.400	
10	1.600	nil	
μ = 1.78		[H⁺]= 0.18M	
11	9.5×10^{-5}		0.481N
12	1.82×10^{-4}		0.218N
13	5.35		as 1 - 10

Table II Apparent Molecular Extinction Coefficients $\alpha \times 10^{-4}$

Index	1	2	3	4	5	6
CNS^- m/l	.008	.016	.040	.08	.16	.4
wavelength Å						
3850	.091[6]	.127	.205	.209	.264	.313 . . .
3900	.111[3]	.158	.218	.250	.298	.358 . . .
4000	.170	.225	.265	.336	.407	.464 . . .
4300	.281	.380	.431	.591	.643	.746 . . .
4500	.322	.445	.501	.648	.770	.939 . . .
4600	.325	.456	.514	.679	.820	1.010 . . .
4700	.325	.458	.525	.701	.858	1.071 . . .
4800	.315	.446	.515	.709	.873	1.088 . . .
4900	.289	.419	.493	.691	.877	1.075 . . .
5000	.271	.389	.462	.650	.825	1.038 . . .
5300	.175	.259	.320	.468	.604	.767. . . .
5500	.122	.183	.220	.338	.442	.578 . . .
5750	.068	.099[5]	.125	.194	.249	.346 . . .
6000	.039[3]	.052[4]	.065	.102	.132	.191 . . .
6500	.007[8]	.009[2]	.013[6]	.021[6]	.026[7]	.032 . . .
7000	- -	- -	.025[9]	.004[4]	.005[4]	.007[1]. . .
7250	- -	- -	- -	- -	.002[0]	.003[5]. . .
7500	- -	- -	.013	.003[6]	.0013	.0017. . .
7750	- -	- -	- -	- -	.0008	.0003 . .
8000	- -	- -	.013[4]	- -	.0001	.0026 . .

Table II ctd. Apparent Molecular Extinction Coefficients $\alpha \times 10^{-4}$

7	8	9	10	11	12	13
.6	.8	1.2	1.6	9.5×10^{-5}	18.2×10^{-5}	5.35
.318	.357	.398	- -	- -	- -	.761
.371	.405	.440	- -	- -	.137	1.034
.488	.495	.522	.563	.368	.215	.975
.785	.813	.861	.903	.331	.367	1.690
1.001	1.027	1.118	1.173	.435	.438	2.425
1.090	1.111	1.234	1.295	.460	.453	2.600
1.126	1.194	1.314	1.346	.447	.449	2.675
1.152	1.216	1.317	1.353	.455	.431	2.770
1.118	1.189	1.307	1.333	.424	.401	2.615
1.071	1.136	1.240	1.291	.399	.366	2.555
o.865	0.865	0.911	0.963	.257	.227	1.970
.608	.654	.691	.725	.181	$.150^{5}$	1.330
.368	.402	.427	.462	.102	$.080^{7}$	.76L
.200	.218	.245	.259	$.051^{6}$	$.044^{5}$	.690
.042	.043	.053	.057	.0126	.0077	.273
.0088	.0095	.0109	.0148	- - -	.0022	.155
$.0038^{5}$	$.0047^{7}$	- - -	- - -	- - -	- - -	.202
$.0026^{5}$	$.0031^{6}$	$.0032^{7}$	.0046			
$.0007^{2}$	$.0016^{0}$	$.0020^{6}$	- - -			
$.0015^{4}$	$.0012^{5}$	.0091	.0033			

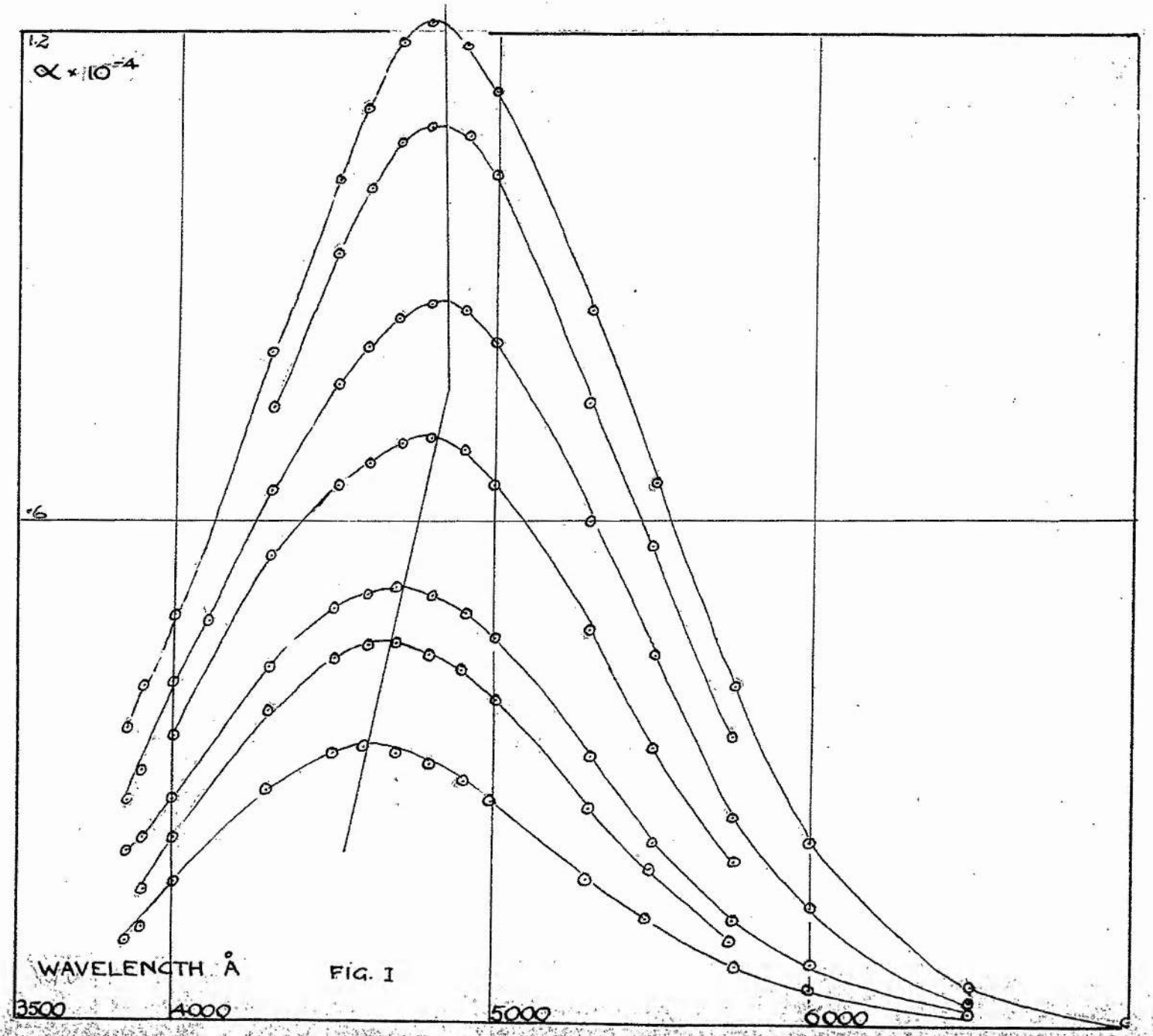


FIG. I

DISCUSSION

The curves in Fig.I form a complete family of comparable apparent absorption spectra of ferric thiocyanate solutions, with the exception of numbers 11, 12, 13, in which the ionic strengths were different. It is apparent that ferric thiocyanate solutions exhibit general absorption in the visible region of the spectrum. The most striking feature of the curves is the marked movement of the wavelength of maximum absorption to longer values, as the thiocyanate concentration is increased, until a maximum value is reached. The position of the maxima are given in the following table, though it is not easy to ascertain the exact value in certain cases owing to the flatness of the curves. (See Table III)

It appears that the position of the maxima reaches a steady state at thiocyanate concentrations less than 0.001M and greater than 0.4M. It will be seen that values of $\underline{\alpha}$ in expts. 11 and 12 are much greater than the corresponding values in expt.1 though the thiocyanate concentration is much less. This can be attributed to the fact that the stability constant of $FeCNS^{2+}$ (the only complex likely to be formed under the conditions of these experiments) is given by

$$\frac{[FeCNS^{2+}]}{[Fe^{3+}][CNS^{-}]} = 125$$

Table III

Position of Maxima

Free [CNS⁻] conc.m/l	Wavelength Å	Free [CNS⁻] conc.m/l	Wavelength Å
$.16\times10^{-5}$	4650	0.6	4810
$.6\times10^{-5}$	4650	0.8	4810
0.008	4650	1.2	4800
0.016	4670	1.6	4780
0.040	4700	5.35	4800
0.080	4780	6.86	4800
0.160	4840	8.34	4900
0.400	4800	-	-

and is such that, in no.1, an appreciable amount of iron is not combined. This is found to be the case for the first five experiments.

Index	1	2	3	4	5
Percent iron as $FeCNS^{2+}$	50	68.5	83.2	91	95.5

Making correction for this, much closer agreement is obtained between values of apparent molecular extinction below a free thiocyanate concentration of about 0.05M.

Index	$\underline{\alpha}$ 4500Å	$\underline{\alpha}$ 5000Å	Free [CNS-] m/l
11	0.435	0.399	0.16×10^{-5}
12	0.438	0.366	0.6×10^{-5}
1	0.644	0.542	0.008
2	0.650	0.567	0.016
3	0.602	0.508	0.040
4	0.713	0.715	0.080
5	0.806	0.864	0.160
	(values of $\underline{\alpha} \times 10^{-4}$)		

The shift in wavelength of maximum absorption with increasing thiocyanate concentration is attributed to the formation of higher ferric thiocyanate complexes, and it interesting to note that not only does the colour of the ferric thiocyanate complexes alter slightly with increasing complexity, but so also does the intensity of their colour increase rapidly with increasing complexity.

Note on the APPLICATION of BEER'S LAW and CORRECTION for 'BLANK' ERROR

The apparent molecular absorption curves given in the immediately preceeding section were obtained from measurements of apparent extinction, $\underset{x}{\log} I_o/I$, at various wavelengths for small iron concentrations x. Those values of α, so obtained, were consistent with Beer's Law in most cases, but discrepencies were noted at the extreme ends of the wavelength scale, in cases where the the thiocyanate concentration was high. This was traced to the value of I_o in the estimation of which water was used as blank liquid instead of the same H^+- K^+- NO_3^- - CNS^- mixture as was in the coloured solution. Since the nitric acid used contained traces of iron, the proper blank was slightly coloured. As was to be expected, the error was particularly great at high thiocyanate concentrations. This was also the case at extreme ends of the wavelength scale where the values of I_o and I tend to be similar in magnitude. Correction may be made on the assumption that the observed extinction'x' = true extinction'D' + blank error'y' and that 'D' is proportional to the iron concentration for a fixed thiocyanate concentration. Since all solutions were 0.18M with respect to nitric acid, it follows that,

for any wavelength, and any thiocyanate concentration, the blank error will be independent of the concentration of iron added. The blank error 'y' may be evaluated from the results of two experiments employing different iron concentrations.

Suppose that the observed extinctions are x_1 and x_2 when the iron concentrations are in the ratio 1.2, then

$$x_1 = D_1 + y$$
$$x_2 = D_2 + y \quad = 2D_1 + y$$

whence $$y = 2x_1 - x_2$$

In the previously described experiments for which true apparent molecular extinction coefficients are given, the values of 'D' were obtained in the manner just described in instances in which Beer's Law was not obeyed. Such was the case for thiocyanate concentrations greater than 0.16M (no 7).

Experiment 10A was a repeat of experiment no 10 using freshly prepared iron solution. The solutions were made acid by the addition of freshly prepared nitric acid (0.18M) and it will be noted from the data in Table IV that Beer's Law is not obeyed in this case owing to the presence of coloured material independent of the iron added. The error is particularly pronounced at low iron concentrations,

Table IV

Experiment 10A. Measured values of Extinction 'x' and Apparent Molecular Extinction Coefficients 'α'

Index	$10A_3$		$10A_2$		$10A_1$	
Iron Conc m/l	0.191×10^{-4}		0.382×10^{-4}		1.528×10^{-4}	
Wavelength	x_3	α'_3	x_2	α'_2	x_1	α'_1
4000	0.138	0.722	0.225	0.589	0.818	0.536
4300	.201	1.085	.370	.968	1.338	.875
4500	.261	1.364	.464	1.215	1.788	1.170
4700	.293	1.535	.527	1.380	2.043	1.340
4800	.296	1.550	.533	1.397	2.051	1.342
5000	.276	1.442	.496	1.300	1.927	1.262
5300	.203	1.060	-	-	1.468	0.960
5500	.160	0.838	.283	.741	1.104	.723
6000	.058	.303	.100	.262	.394	.258
6500	.016	.084	.026	.068	.092	.060
7000	-	-	.008	.021	$.028_5$	.018

$$\alpha' = \alpha \times 10^{-4}$$

since the concentration of coloured impurity is proportion-ately greater. Correction may be made as outlined in the previous discussion.

Suppose once more that the observed extinction is 'x', the true extinction 'D', and the variable blank error a uniform function of 'y', then the following holds,

Iron conc. m/l	True Extinction	Observed Extinction
1.528×10^{-4}	D_1	x_1
0.382×10^{-4}	$D_2 = D_1 + 4$	x_2
0.191×10^{-4}	$D_3 = D_1 + 8$	x_3

Whence

$$8x_3 = 8(D_3 + y) = D_1 + 8y \quad . \ . \ . \ (1)$$

$$4x_2 = 4(D_2 + y) = D_1 + 4y \quad . \ . \ . \ (2)$$

$$x_1 = D_1 + y \quad . \ . \ . \ (3)$$

Values of 'y', the blank error, may be obtained by simultaneous solution of any two of these equations. Equation (2) and (3) were chosen since the iron concentration was larger in these cases, and systematic error in estimating extinction probably smaller. In the following table (V) are given values of 'y' obtained as above, and values of $\underline{\alpha}$ in which correction is made for blank error. Also tabulated for comparison are the values of apparent molecular extinction coefficients ($\underline{\alpha}$) obtained in experiment 10 in which the correction described has

Table V

Experiment 10A. Blank Error and corrected values of Apparent Molecular Extinction Coefficient

Wavelength	Experiment 10A					10
A	y	α_3	α_2	α_1	mean α	α
4000	.027	.548	.518	.526	.531	.563
4300	(.047)	(.807)	(.846)	(.845)	(.833)	.903
	.025×	.922	.903	.859	.895	
4500	.023	1.247	1.155	1.155	1.186	1.173
4700	.022	1.420	1.322	1.335	1.356	1.346
4800	.027	1.410	1.322	1.330	1.354	1.353
5000	.019	1.399	1.250	1.250	1.300	1.291
5300	.015	.985	-	.952	.969	.963
5500	.009	.791	.717	.717	.742	.725
6000	.002	.293	.257	.252	.234	.259
6500	.012	$.020^{9}$	$.036^{7}$	$.036^{7}$	$.031^{4}$	.057
7000	.012	-	$.018^{3}$	$.017^{7}$	$.018^{0}$	.015

(Values of $\alpha \times 10^{-4}$)

× Interpolated value

been applied. The latter should be identical to the corrected values in experiment 10A.

The values at 4300Å seemed unreasonably high and for this wavelength and 5300Å (where a reading is missing) the values of 'y' were interpolated. ~~by guess-work~~.

Experiment 10B was a second repeat of experiment no.10, this time using water instead of nitric acid in order to eliminate the error due to impurities. Water was again used as blank. The values of α are consequently slightly low due to the lower ionic strength and hydrolysis effect. On the other hand, divergence from Beer's law is completely eliminated as the figures in Table VI will show. Note that the iron concentrations used were quite apart. The excellent agreement between α, the apparent molecular extinction coefficients, in $10B_1$ and $10B_2$ shows that extinction is proportional to iron concentration, or, otherwise, that Beer's Law is obeyed at constant thiocyanate concentrations, provided variation in the iron concentration is within such limits as not to alter the ionic strength and the free thiocyanate ion concentration appreciabley. This shows, further, that the distribution of iron amongst the various complexes is independent of the iron concentration within the same limits.

Table VI

Experiment 10B. Values of Extinction and Apparent Molecular Extinction Coefficient

Index	Experiment $10B_1$		Experiment $10B_2$	
Iron Conc	0.191×10^{-4}m 1		1.528×10^{-4}m 1	
Wavelength	$\log I_o/I$	$\alpha\times10^{-4}$	$\log I_o/I$	$\alpha\times10^{-4}$
3900	.076	.398	.616	.399
4000	.096	.502[5]	.756	.495
4300	.162	.848	1.283	.841
4500	.206[5]	1.082	1.673	1.095
4700	.234	1.225	1.904	1.247
4800	.235	1.230	1.908	1.249
4900	.228	1.193	1.865	1.220
5000	.291	1.094	1.794	1.173
5300	.162	.848	1.340	.878
5500	.126	.660	1.025	.671
6000	.042	.222	.348	.228

Thiocyanate concentration = 1.6M

ABSORPTION SPECTRA OF FERRIC THIOCYANATE IN NON - AQUEOUS SOLVENTS

Absorption spectra of ferric thiocyanate in a limited number of organic solvents have been constructed with a view to comparing the colour of such solutions. It is quite noticable that the colour of ferric thiocyanate in organic solvents tends tobe more magenta than red, and, in the particular case of an ether solution to which benzene is added, quite purple. The curves in the following figure were obtained by plotting extinction against wave-length for solutions of ferric thiocyanate in alcohol, iso-propyl ether, ethyl ether, and an ether-benzene mixture. No measurement of concentration was made, and consequently the absorption curves are qualitative rather than quantitative. They should be compared with other curves given in other sections of this part. It is significant that the wavelength of maximum absorption is approximately 5040Å for all three solutions in the pure solvents, whereas the addition of benzene to the ether solution causes the maximum to shift to even longer wavelengths. These values should be compared with the maximal and minimal values for aqueous ferric thiocyanate solutions. (4550Å, 4800Å)

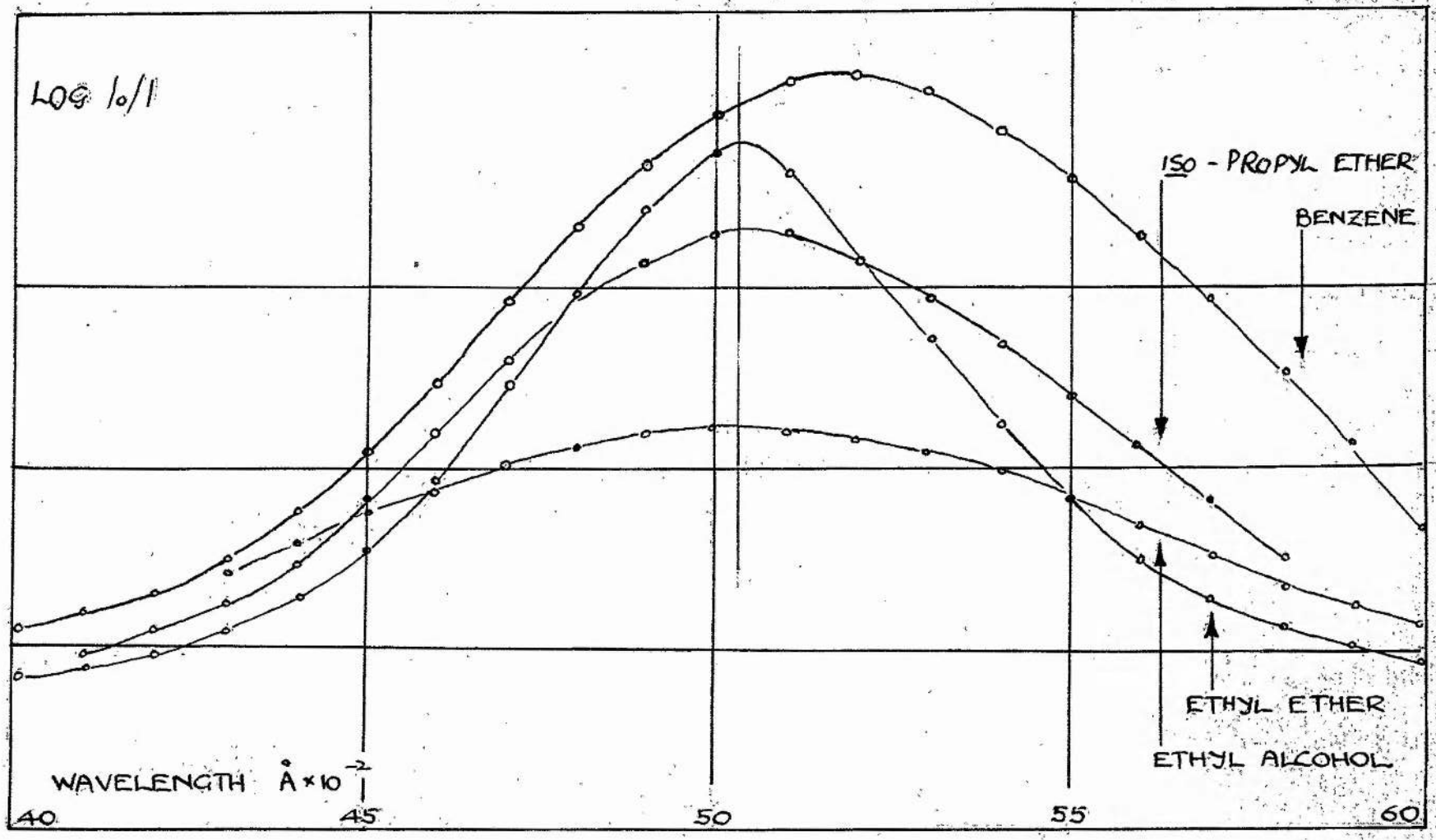


FIG. I ABSORPTION SPECTRA of FERRIC THIOCYANATE IN NON-AQUEOUS SOLVENTS.

The EFFECT of ELECTROLYTES on the FERRIC THIOCYANATE EQUILIBRIA

The addition of electrolytes to ferric thiocyanate solutions is known to have a marked effect in diminishing the colour of such solutions. In certain instances, it is concluded that colourless complexes are formed between ferric ions and the added anion. Thus, the added anion competes with the thiocyanate ions, thereby reducing the effective ferric thiocyanate concentration. The effect is best studied by addition of such electrolytes to ferric thiocyan-ate solutions in which the thiocyanate concentration is small. In such solutions, $FeCNS^{2+}$ is virtually the only complex formed. Thus removal of Fe^{3+} ions from the equilibrium

$$Fe^{3+} + CNS^{-} \rightleftharpoons FeCNS^{2+}$$

will displace the equilibrium towards the left, with accompanying reduction in colour intensity. This is brought about by such reactions as

$$Fe^{3+} + OH^{-} \rightleftharpoons FeOH^{2+}$$

and, in part, by

$$Fe^{3+} + Cl^{-} \rightleftharpoons FeCl^{2+} \qquad (23)$$

$$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^{+}$$

and the analogous reaction,

$$Hg^{2+} + CNS^{-} \rightleftharpoons HgCNS^{+}$$

in which the thiocyanate ion is removed.

In other instances, the possibility of complex formation cannot be entertained, for instance, when $NaClO_4$ is added, it being known that the ClO_4^- ion forms no comparable complex with ferric ions.

The addition of acid to such ferric thiocyanate solutions is interesting. Small amounts of acid increase the colour intensity, while subsequent addition of further amounts of acid decreases the depth of colour. Small quantities of acid reduce hydrolysis thus increasing the ferric ion concentration

$$FeOH^{2+} + H_3O^{+} = Fe^{3+} + 2H_2O$$

The subsequent reduction in colour is less readily explained particularly in cases where the acids addéd contain non-complex-forming anions.

It can only be assumed that addition of such electrolytes reduce the activities of the interacting ferric and thiocyanate ions and of their complexes to such an extent that displacement of the equilibrium occurs with accompanying reduction in colour, and that, in cases where complexes are formed, both the competitive and activity effects play a part.

In solutions in which the thiocyanate concentration is small, the equilibrium

$$Fe^{3+} + CNS^{-} \rightleftharpoons FeCNS^{2+}$$

alone, will be of importance. Whence,

$$\frac{[FeCNS^{2+}]}{[Fe^{3+}][CNS^{-}]} = \underline{K}_1 \cdot \frac{f_1 \times f_2}{f_3}$$

where $\underline{K}_1$ is the true activity constant, f_1 the activity coefficient of the ferric ions, f_2 that of the thiocyanate, and f_3 that of the complex ion. The presence of neutral salt will alter these activity coefficients, and, in turn, will alter the equilibrium. Decrease in the activity will result in a diminishing of the colour intensity, and vice versa. If conditions are chosen so that the concentration of $FeCNS^{2+}$ is small in comparison with that of Fe^{3+} and CNS^{-} the intensity of colour will be proportional to the ratio of the activity coefficients. If $f_1 = f_2 = f_3 = f$ (say) the colour will be proportional to 'f'. Experiments have been carried out on these lines. The true values of f_x are of course not readily accessible, and in these experiments extinction is plotted against the 'activity coefficient' of the solutions, the latter being interpolated from the tables in Landolt and Bornstein. In this interpolation, the concentrations of all electrolytes present were added together and treated as if they were the diluting salt. Such a procedure may introduce some error, especially when the salt concentration was small, but seemed to be the only course open.

EXPERIMENTAL

These experiments were of an exploratory nature and, as such, are described briefly below.

The effect of electrolytes on the ferric thiocyanate equilibria has been demonstrated in two ways,

A by comparison of the extinctions of solutions
  (a) containing small amounts of Fe^{3+} and CNS^- and varying amounts of added electrolyte,
  (b) in which the ionic strength was the same, but in which the addéd salts were different

and

B by determining values of K_1 in different salt solutions with
  (a) the same ionic strength and different salts
  (b) different ionic strength and the same salt.

A The effect of salts and acids upon the Fe^{3+} - CNS^- - $FeCNS^{2+}$ equilibrium.

Experiment 1. The method has been outlined in the above preamble. The solutions had the following composition

Fe^{3+}	0.0027 M	CNS^-	0.0027 M
HNO_3, HCl	0.00455 M - 1.825 M		

The percentage of iron in these solutions combined as $FeCNS^{2+}$ did not exceed 5 percent. The extinctions of these solutions were measured at 4550Å. Fig.1 shows the effect of varying the concentration of acid upon the extinction of these solutions, ie. upon the ferric thiocyanate equilibrium. It will be noted that the addition of small amounts of acid increases the colour due to supression of hydrolysis and that subsequent addition decreases the colour intensity considerably. That this is not a function of the acid activity coefficients is also shown by Fig.I in which extinction is plotted against activity coefficients obtained in the manner described above. The curves do not coincide, even at low acid concentrations, but this is accounted for by the fact that the ferric solutions contained acid, the concentration of which was not known.

The effect of activity is better illustrated by the use of salt in place of acid.

Experiment 2. The effect of KNO_3 and NaCl was shown by examination of solutions with the following compositions.

Fe^{3+}	0.0027 M	CNS^-	0.0027 M
KNO_3, NaCl	0.00455 M - 1.825 M		

The plot of extinction against concentration of salt is quite irregular, but, when extinction is plotted against the 'activity coefficient' of the solution, remarkable linearity is obtained. (see Fig.II)

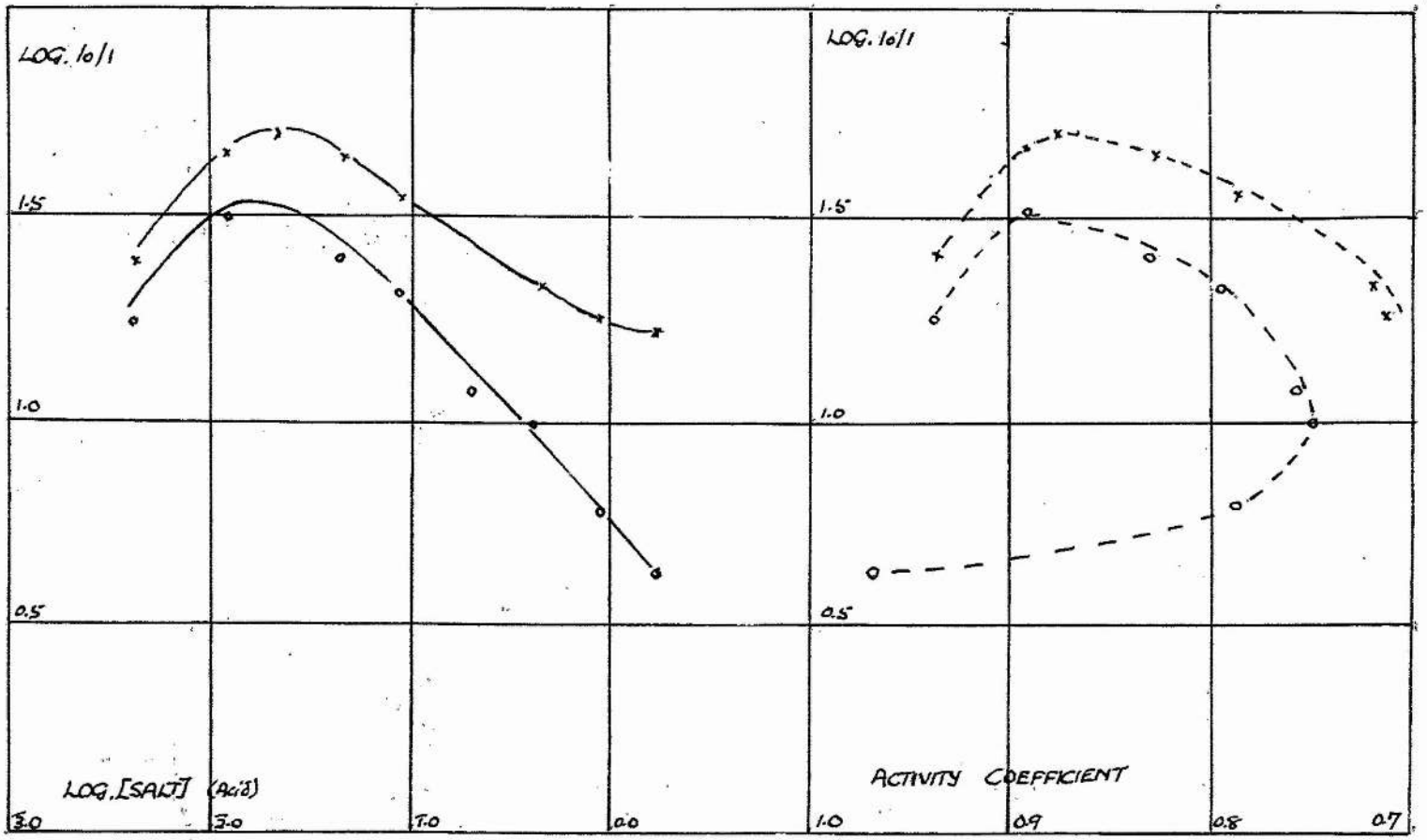
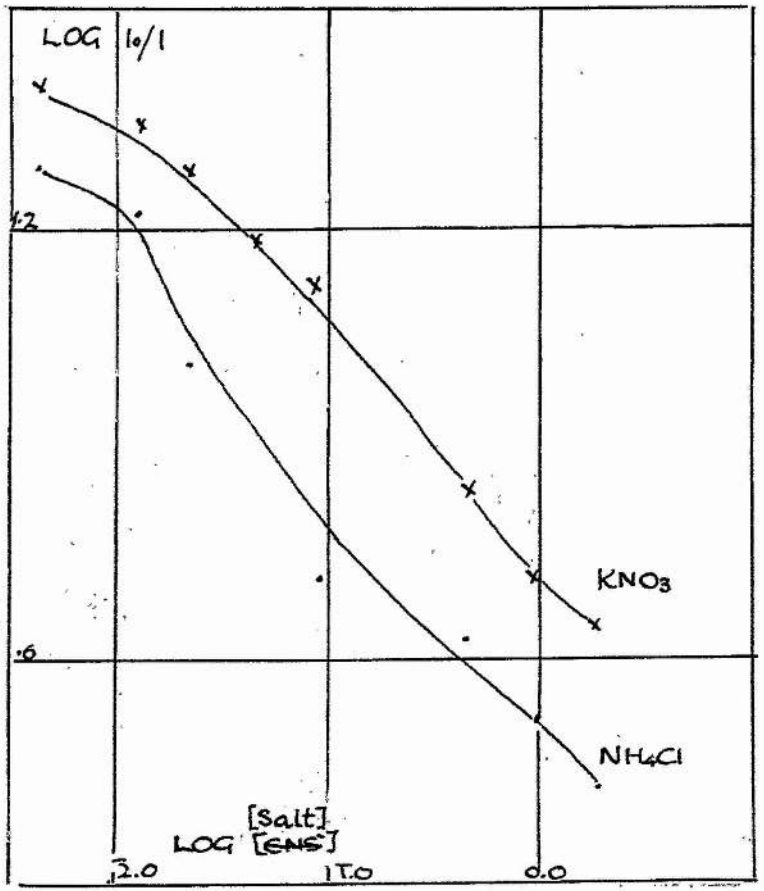

LOG. 1o/1
1.5
1.0
0.5
LOG. [SALT] (Acid)
3.0
3.0
2.0
1.0
LOG. 1o/1
1.5
1.0
0.5
ACTIVITY COEFFICIENT
1.0
0.9
0.8
0.7

FIG I


LOG Io/I
1.2
.6
KNO3
NH4Cl
[salt]
LOG [ENS]
2.0
1.0
0.0

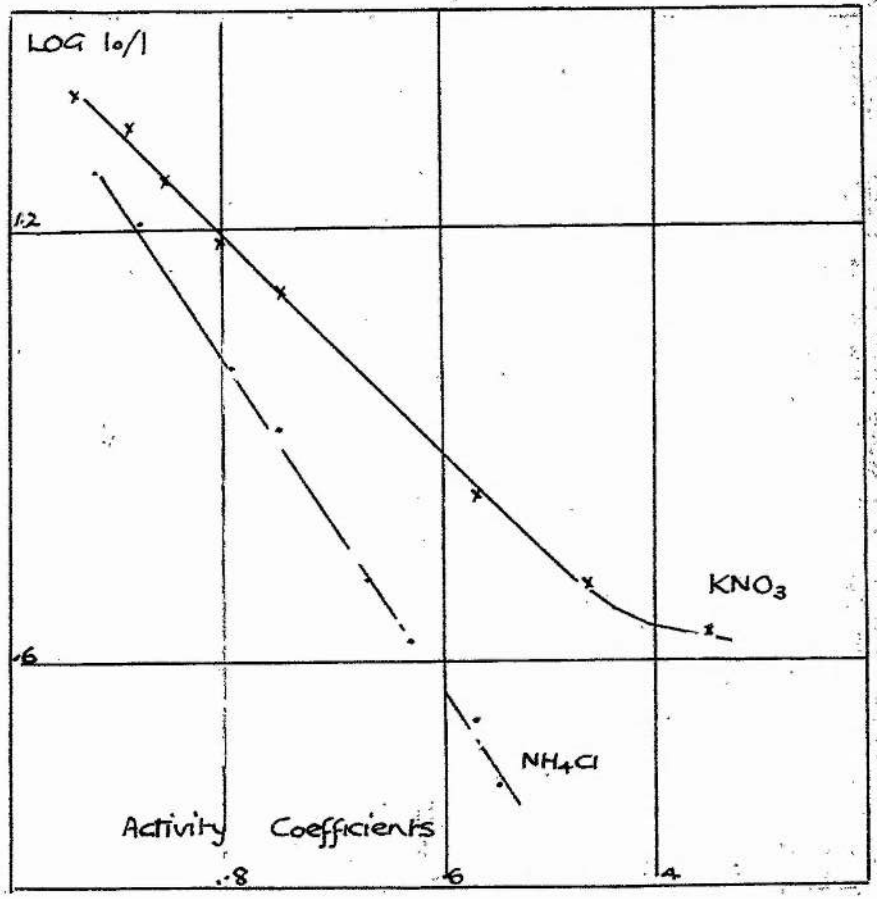

LOG Io/I
1.2
.6
KNO3
NH4Cl
Activity Coefficients
.8
.6
.4

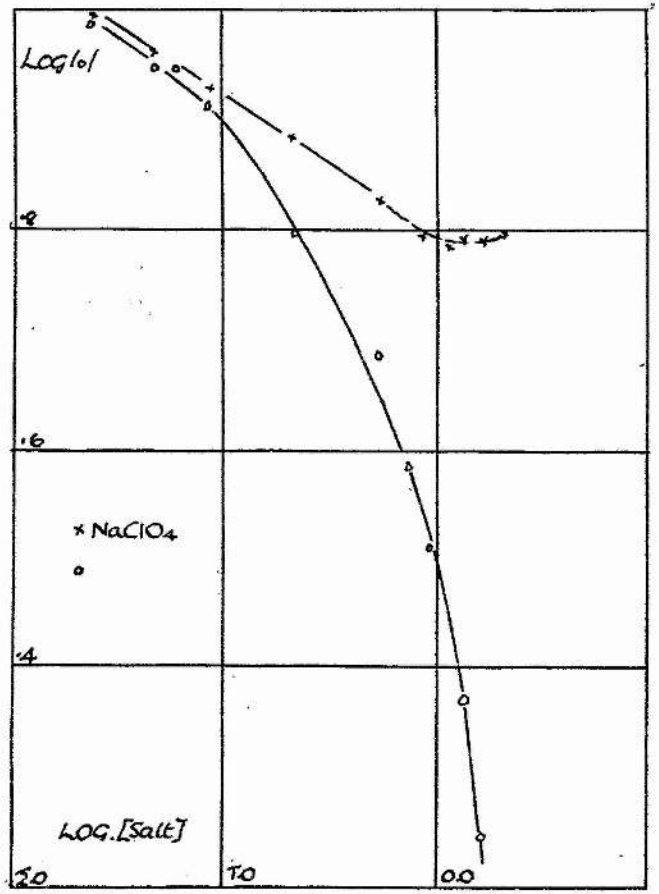
FIG. II

It would seem from this experiment that the extent of the ferric thiocyanate equilibrium is largely determined by the activity coefficient of the neutral salt present in the same solution. The slope of the NaCl curve is greater than that of the corresponding KNO_3 curve, but this is attributed to the competitive effect of the chloride ion, chloride ions being known to form stable complexes with ferric ions, for example, $FeCl^{2+}$. (23)

Experiment 3. was similar to experiment 2, but was designed to compare the effects of KNO_3 and $NaClO_4$ since the effect of these salts is of some importance in connection with the partition experiments previously described. The extinction coefficients of the following solutions were measured.

Fe^{3+}	0.00119 M	CNS^-	0.00119 M
H^+	0.0216 M		
KNO_3 , $NaClO_4$	0.00951 M - 1.905 M		

Fig.III shows a plot of extinction against concentration measured on a logarithmic scale. It is at once apparent that the capacity of KNO_3 to reduce the colour of ferric thiocyanate solutions is considerabley greater than that of $NaClO_4$. The resemblance between this curve and a plot of the activity coefficients of these salts against the same base is very marked. (See Fig.III, Part 3 ,page 71)


LOG I₀/I
.8
.6
× NaClO₄
o
.4
LOG. [Salt]
2.0
1.0
0.0

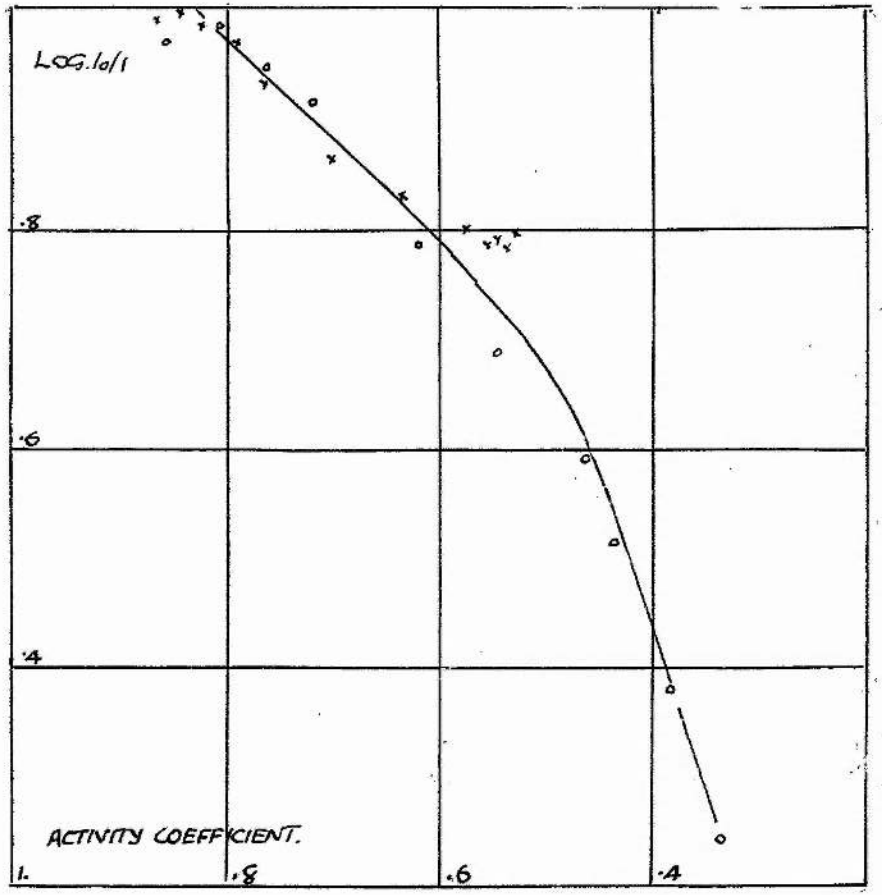

LOG. I₀/I
.8
.6
.4
ACTIVITY COEFFICIENT.
1.
.8
.6
.4

FIG. III

On plotting extinction against the 'activity coefficient' of the solutions, much closer agreement is reached, and the curves themselves tend more towards linearity. The slight curving of the KNO_3 curve at its lower extremity might suggest that competitive complex formation was occuring to a slight extent at salt concentrations of about 1.0 M.

Experiment 4 was likewise designed to compare the effects of KNO_3 and $NaClO_4$. In this simple experiment, the ionic strength was maintained constant at a high value. The salt and iron concentrations were constant and the thiocyanate concentration was varied between two small values.

Fe^{3+} 0.00445 M Salt 1.815 M

Fig.IV shows the effect of adding to 22ml of such a solution 0.1 - 1.5 ml of 0.01 M KCNS, extinction measured at 5500 Å being plotted against the number of ml thiocyanate solution added. Given for comparison is the corresponding plot for the case in which no salt was present. The slopes of the three lines (taken as an approximate measure of K_1) are tabulated below and compared with the 'activity coefficients' of the solutions

	Slope	f	
Water	1	1	(assumed value)
$NaClO_4$	.719	~~.513~~ .619	
KNO_3	.513	.408	

(Relative values off slopes given)

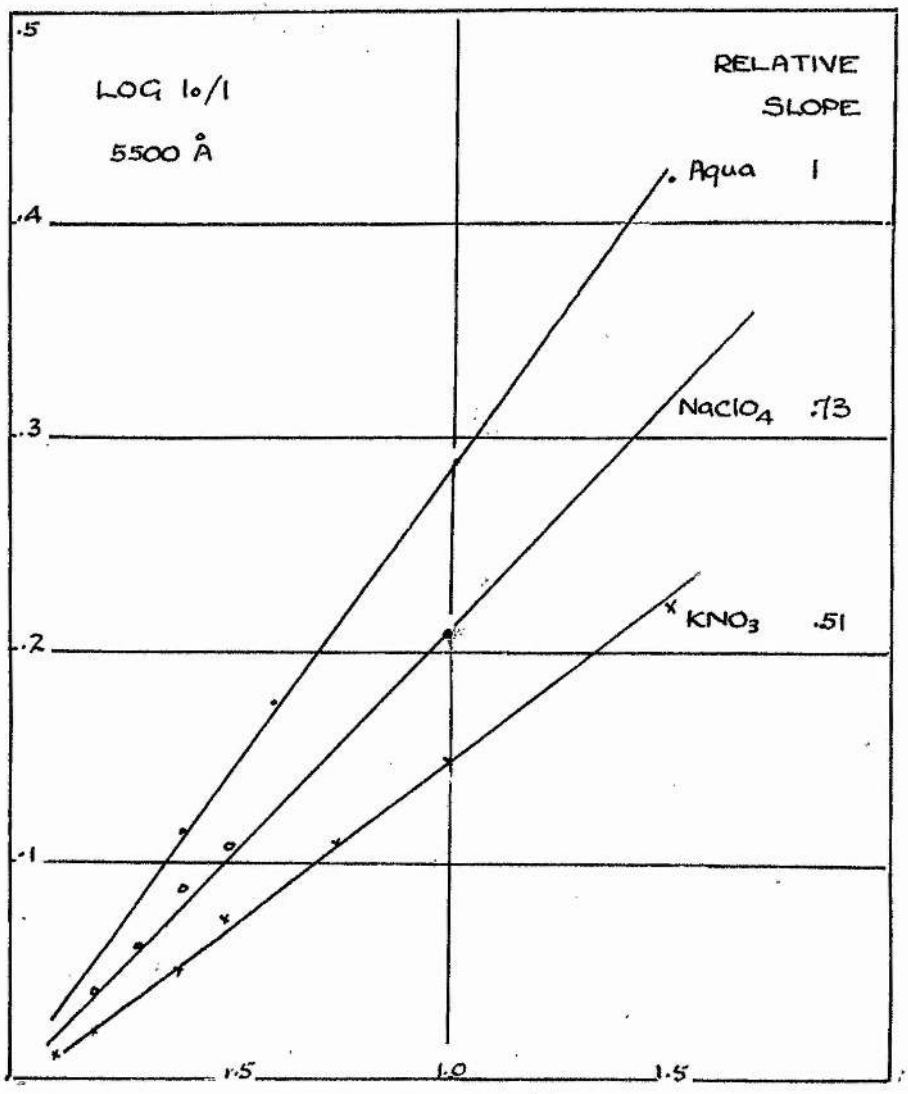

.5
LOG Io/I
5500 Å
RELATIVE
SLOPE
Aqua 1
.4
NaClO4 .73
.3
KNO3 .51
.2
.1
1.5
1.0
1.5
CNS⁻ m.l added.

FIG. IV

In view of the approximate nature of the experiment, these values are in remarkable agreement, and it would appear that no complex was formed between ferric and nitrate ions.

It may be concluded, so far, that the ferric thiocyan--ate equilibrium is sensitive to the presence of neutral salt, that, in the case of nitrate and perchlorate, the effect is one of activity rather than competition, and that the extent to which salts of these anions affect the equilibrium is approximately proportional to the activity coefficient of the added salt.

B Determination of K_1 - the stability constant of $FeCNS^{2+}$ - in solutions of $NaClO_4$, KNO_3, and $LiNO_3$.

The experimental method and procedure have already been described in detail. The solutions analysed had the undernoted compositions

	Fe^{3+}	0.002 M and 0.008 M
HNO_3 or	$HClO_4$	0.18 M
	KCNS	0.0002M
	Salt	1.6 M and 0.8 M

The solutions were examined spectrophotometrically over the entire visible wavelength scale. A total of 24 runs were

made, including 11 in the case of the perchlorate and 6 in the case of nitrate. These led in turn to values of ε, the molecular extinction coefficient of $FeCNS^{2+}$, which were averaged for each wavelength, and then used, in turn, in the computation of values of K_1 in the manner described earlier. In the case of $NaClO_4$, for instance 220 values were obtained from 11 runs and reliable measurements at 20 odd wavelengths.

The experimental values of K_1 are tabulated below, these being mean values for any salt concentration.

Index	Salt	Ionic Strength	K_1	f
a	1.6M $NaClO_4$	1.78	122.5×	.56
b	1.6M KNO_3	1.78	91.0×	.346
c	1.6M $LiNO_3$	1.78	114.4	>.77
d	0.8M $NaClO_4$	0.98	127.9	.576
e	0.8M KNO_3	0.98	98.8	.439
f	0.8M $LiNO_3$	0.98	109.5	.765

(Values of 'f' were again calculated on the assumption that all electrolytes present were neutral salt which was in excess in each case)

× These reliable values of K_1 were employed in the partition calculations in preference to those described earlier.

Interesting conclusions may be drawn from these experiments. It is at once apparent that uniform values of K_1 do not necessarily result in cases where the ionic strength is maintained at a constant figure with different salts, since the salts themselves have a profound effect. In the case of $NaClO_4$ and KNO_3 , the effect is directly proportional to the activity coefficients of the salts. Taking values of K_1 with subscripts corresponding to the indices of the salt concentrations employed, the following relationships hold

i) Constant ionic strength - different salts

ionic strength 1.78

$$K_a + K_b = 1.345 \qquad 1.62 = f_a + f_b$$

ionic strength 0.98

$$K_d + K_e = 1.295 \qquad 1.31 = f_d + f_e$$

ii) Different ionic strengths - same salt

$NaClO_4$

$$K_a + K_d = 0.965 \qquad 0.97 = f_a + f_d$$

KNO_3

$$K_b + K_e = 0.92 \qquad 0.77 = f_b + f_e$$

It would appear from these results that in dilute solutions at least K_1 is a function of the activity coefficients of added electrolyte and that complex formation between ferric

and nitrate ions does not occur.

The effect of $LiNO_3$ is uncertain as the values of K_1 obtained in this salt solution do not fit in with the above scheme.

Summarising, it seems likely that variations in K_1, and consequently in the partition experiments, can be explained entirely in terms of differences in activity coefficient and that no complex with nitrate ions is formed.

PART 6

Part 6

ABSORPTION SPECTRA OF THE FERRIC THIOCYANATE COMPLEX IONS

The apparent absorption spectra of ferric thiocyanate solutions described in a previous part appear to indicate that the higher complexes are more intensely coloured than is the simple complex $FeCNS^{2+}$ for which a true absorption spectrum is readily obtained. Further, it seems that the wavelengths of maximum absorption for the higher complexes are longer than that of the simple complex. True absorption spectra have been obtained for all the charged complexes, except $Fe(CNS)_6^{3-}$, by analysis of the apparent absorption spectra, and it has been shown that the intensity of colour increases with the complexity of the complexes, and that the wavelengths of maximum absorption are interrelated in an interesting way.

METHOD

It will be recalled that the apparent absorption spectra, described on page 153 were obtained by measuring the extinction coefficients at various wavelengths of solutions containing small amounts of ferric nitrate, and in which the thiocyanate concentrations ranged from

0.008 - 1.600 N. The ionic strength was maintained at 1.8 with KNO_3. The values of extinction coefficient were then divided by the iron concentration, thus giving apparent molecular extinction curves. Since the relative concentrations of any complex in these solutions are given by $k_x.(CNS^-)^{x-3}$ (see page 13) and since the thiocyanate concentrations were, at all times, much in excess of the iron concentrations, it is possible readily to calculate the percentage of iron represented by each curve which is present in each complex form. The values of k_x given in Table I , column AII, page 88, were employed since these were obtained from experiments also employing ferric nitrate and potassium nitrate. Knowing the distribution of iron amongst the various complexes for each thiocyanate concentration, it is a simple matter to compute the molal extinction coefficients of the various complexes at various wavelengths

RESULTS

In Table I below are listed the concentrations of the various ferric thiocyanate complexes in aqueous solutions containing thiocyanate concentrations equal to those used in determining the apparent molal absorption spectra. The concentrations of the complexes are given as a percentage of the total iron concentration, ~~namely one mole~~.

Table I

	CNS^- conc. Mol per l.	Fe^{3+}	FeA^{2+}	FeA_2^+	FeA_3	FeA_4^-	FeA_5^{2-}	FeA_6^{3-}
1.	0.016	20.5	29.7	49.77	-	-	-	-
2.	0.04	5.0	18.2	76.5	-	0.3	-	-
3.	0.08	1.4	10.3	86.5	0.28	1.56	-	-
4.	0.16	-	5.2	87.5	0.56	6.30	-	-
5.	0.40	-	1.6	66.85	1.06	30.20	0.30	-
6.	0.60	-	0.8	48.45	1.16	49.26	0.40	-
7.	0.80	-	0.4	34.62	0.11	62.50	1.35	-
8.	1.20	-	-	19.20	-	78.20	2.50	0.10
9.	1.60	-	-	11.70	-	84.40	3.65	0.18

'A' denotes a CNS^- group

It will be noted that the percentage of the neutral molecule $Fe(CNS)_3$ is negligibly small and that the highest complex formed in appreciable amounts in 1.6N KCNS is $Fe(CNS)_5^{2-}$ though the amount is small. The extinction coefficients of $Fe(CNS)_2^+$ and $Fe(CNS)_4^-$ were obtained with the aid of data in lines 5-8. For purposes of calculation, the small amounts of $FeCNS^{2+}$ and $Fe(CNS)_3$ noted in lines 5-8 were assumed to be $Fe(CNS)_2^+$, and $Fe(CNS)_5^{2-}$ was assumed to be $Fe(CNS)_4^-$. It can then be deduced that

$$\varepsilon_2 = (1.8A - B) \div 1.615$$

and

$$\varepsilon_4 = (B - 0.5433\,\varepsilon_2) \div 1.4465$$

where ε_2 = molecular extinction coefficient of $Fe(CNS)_2^+$

and ε_4 = molecular extinction coefficient of $Fe(CNS)_4^-$

for any wavelength.

A is the sum of the apparent molecular extinction coefficients for series 5 and 6 for any wavelength and B the corresponding sum for series 7 and 8 for the same wavelength. True molecular extinction curves have been calculated for the complexes $Fe(CNS)_2^+$ and $Fe(CNS)_4^-$ by solution of the above equations in conjunction with the corresponding apparent extinction curves.

These extinction values were used, in turn, with series 9 to compute the molecular extinction curve for

$Fe(CNS)_5^{2-}$. These last values are open to error partly because the percentage of $Fe(CNS)_5^{2-}$ was too small to allow of accurate calculation.

The molecular extinction coefficients of these complexes are given in Table II, those of $FeCNS^{2+}$, previously obtained, being given for comparison.

Table II

Wavelength Å	$FeCNS^{2+}$	$Fe(CNS)_2^+$	$Fe(CNS)_4^-$	$Fe(CNS)_5^{2-}$
	ε_1	ε_2	ε_4	ε_5
3900	1733	2890	4760	
4000	2380	4310	5411	14750
4300	4350	6715	9050	15800
4500	4745	8340	11670	27200
4600	4760×	8900	12900	26400×
4700	4460	8970	13980	18500
4800	4120	9255×	14020×	16900
4900		8945	13900	14700
5000	3220	8815	13100	(21200)
5300		6660	9800	(17000)
5500	1225	4885	6910	(21900)

× denotes maximum

DISCUSSION

The calculated true molecular extinction curves of $Fe(CNS)_2^+$ and $Fe(CNS)_4^-$ are shown in Fig. I. That of $FeCNS^{2+}$, described earlier, is given for comparison. In Fig.II, these curves are shown along with that of $Fe(CNS)_5^{2-}$ Owing to the instability of $Fe(CNS)_3$, calculation of the appropriate curve was not possible. However, a probable rough estimate of its form is given by the molecular extinction of $Fe(CNS)_3$ in ether which is given for comparison.× Difficulty is experienced in obtaining such a curve owing to the volatility of the ether, and the actual values may be approximate only. It serves to indicate the wavelength of maximum absorption.

Examination of these curves show interesting relationships between the maximum values of extinction coefficients of the complexes and between their wavelengths of maximum absorption. It is at once apparent that the

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× This curve was obtained by Dr. J.Y.Macdonald with whose permission it is given here. It should be compared with the extinction curves of $Fe(CNS)_3$ in ether, alcohol, and iso-propyl ether given on page 164 which, it should be noted, all have the same wavelength of maximum absorption.

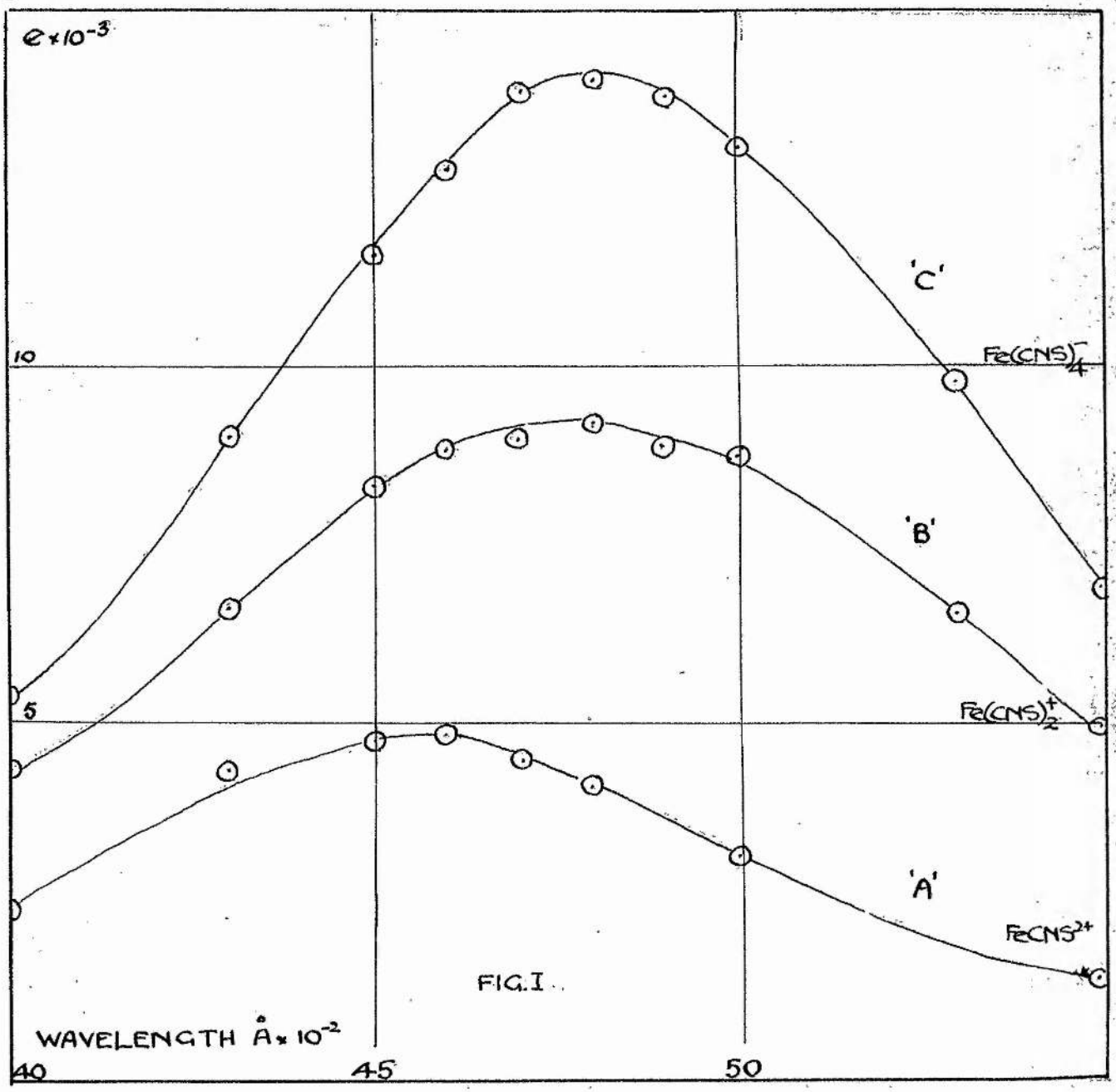


FIG.I

MOLECULAR EXTINCTION CURVES

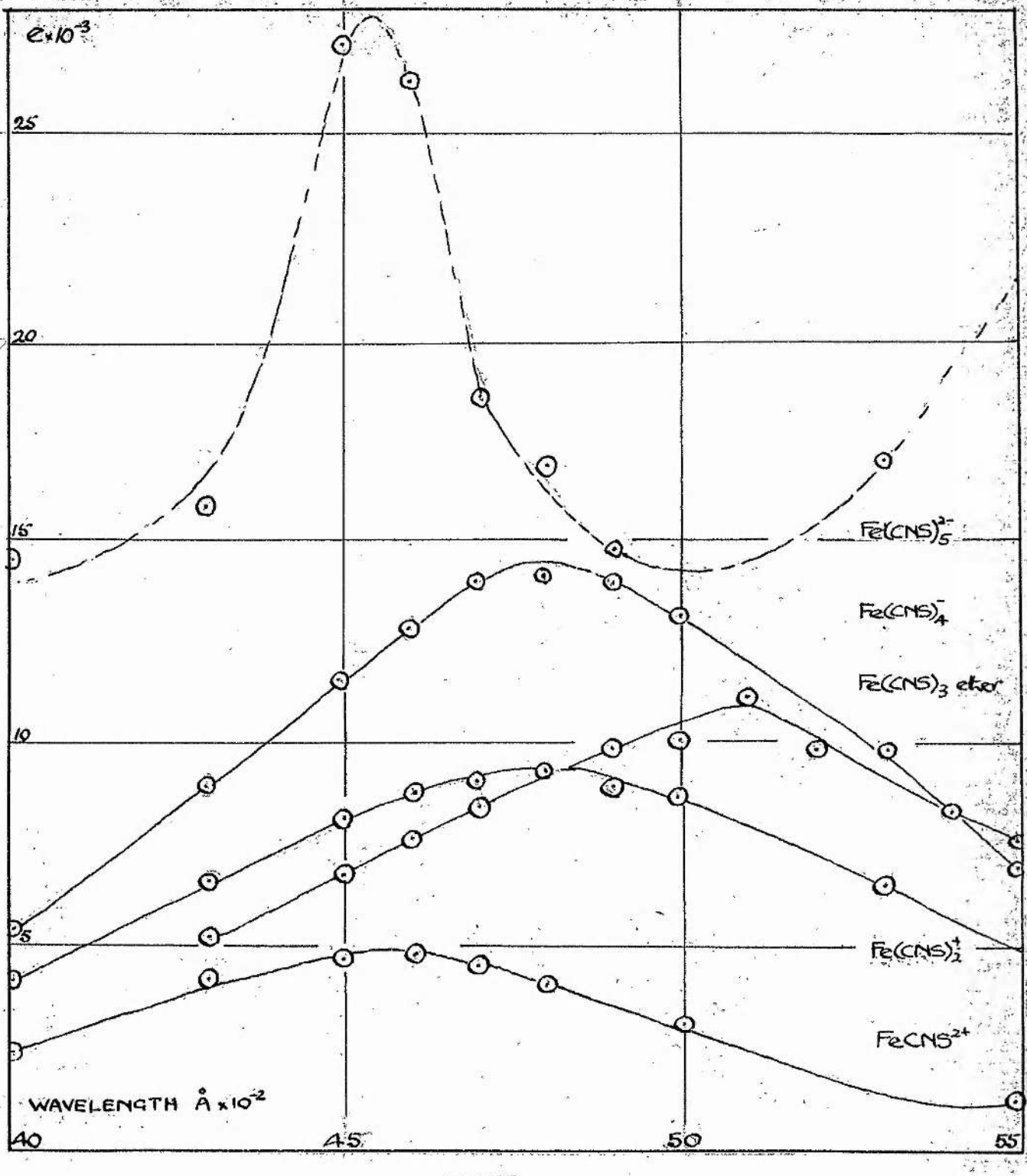


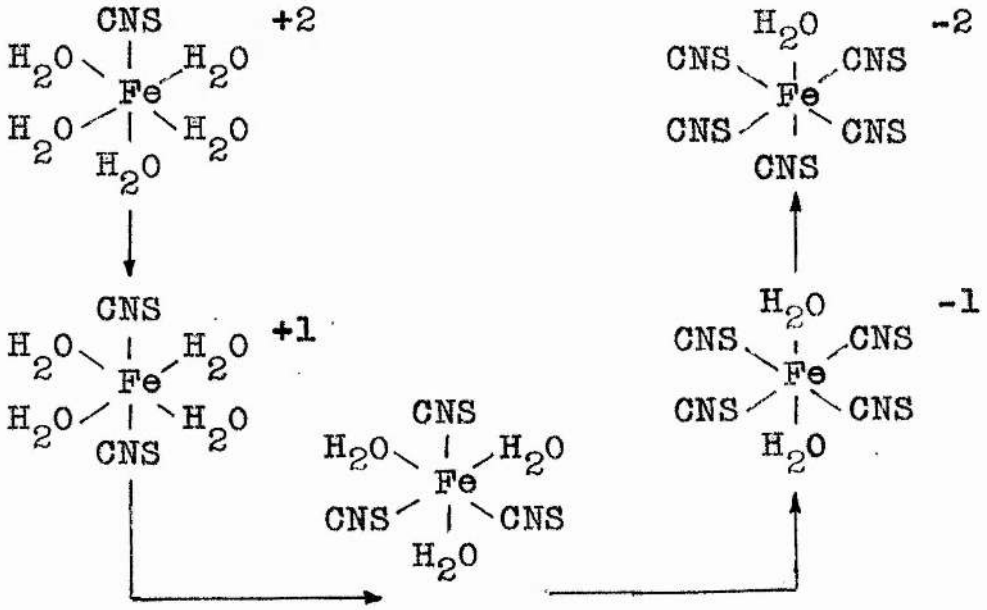
FIG. II

MOLECULAR EXTINCTION CURVES OF FERRIC THIOCYANATE COMPLEXES

complexes become progressively more intensely coloured with the addition of each CNS^- group. Further, the wavelengths of maximum absorption increase with increasing symmetry and decreasing numerical charge, and those complex ions with the same symmetry and numerical charge have the same maximum wavelength. The wavelengths of maximum absorption are given below.

	Complex	Charge	Wavelength
I	$FeCNS^{2+}$	+2	4550 Å
	$Fe(CNS)_5^{2-}$	-2	
II	$Fe(CNS)_2^+$	+1	4800 Å
	$Fe(CNS)_4^-$	-1	
III	$Fe(CNS)_3$	0	5100 Å

This interesting relationship is not altogether unexpected in consideration of the similarity and symmetry of the following ion pairs.



The maximum values of the extinction coefficients of the complexes also exhibit a curious relationship, which may not at once be apparent. The values of ε_{max} are given below. Their relative magnitudes are indicated in the last column.

	Complex	ε_{max}	rel.vals.
1	$FeCNS^{2+}$	4900	0.53
2	$Fe(CNS)_2^+$	9250	1.00
3	$Fe(CNS)_3$	11000	1.19
4	$Fe(CNS)_4^-$	14020	1.52
5	$Fe(CNS)_5^{2-}$	28000	3,03

If ε_2 is the maximum extinction coefficient of the complex $Fe(CNS)_2^+$, etc., the following relationship seems to hold, thus showing further an ordered relationship between the ferric thiocyanate complexes.

$$\varepsilon_1 + \varepsilon_2 = \underline{0.53} \qquad \varepsilon_4 + \varepsilon_5 = \underline{0.50}$$

$$\varepsilon_2 + \varepsilon_3 = \underline{0.84} \qquad \varepsilon_3 + \varepsilon_4 = \underline{0.78}$$

PART 7

PART 7

ELECTRICAL MIGRATION EXPERIMENTS.

In the previous parts, experiments have been described which have shown that a series of ferric thiocyanate complexes exist. Furthermore, the nature of the complexes which most predominate in any solution depends on the thiocyanate concentration and is independent of the iron concentration - at least, when this is small. When the thiocyanate ion concentration is large, negatively charged complexes are formed in greater amounts than are the positively charged complexes. On the other hand, when the thiocyanate ion concentration is small, positively charged complexes predominate. Electrical migration experiments in which the coloured complexes have been allowed to move under the influence of an electric potential, have further demonstrated this change in complex formation in a simple way.

Similar experiments have already been reported. Those of Schlesinger and Van Valkenburgh[27] indicated negatively charged complexes and were used

to support the postulated molecule $Fe.Fe(CNS)_6$. On the other hand, Bent and French[4] found that the coloured ions bore a positive charge which was in harmony with the ion $FeCNS^{2+}$ put forward by them. This apparent discrepancy is clarified when it is considered that the former workers employed thiocyanate concentrations which were large and very much greater than those used by the latter.

In measuring the migration of an ion which is in equilibrium with other ions, it is important that the medium into which movement is taking place should be as nearly as possible the same as that from which the ion is passing, otherwise the equilibrium will change and, with it, the ionic type which is being measured. Thus a complex $FeCNS^{2+}$ migrating into pure water would dissociate,

$$FeCNS^{2+} \longrightarrow Fe^{3+} + CNS^{-}$$

the colour would be discharged and the boundary would be stationary. Again, if a solution containing free thiocyanate ions were migrating into one containing free ferric ions, the negative thiocyanate ions moving to the anode would react with the ferric ions to give a coloured complex, and, if this complex moved less

rapidly to the cathode, the boundary would move, as a whole, to the anode, and give a fictitious result.

In the ideal case, the solutions would be identical, for instance - N KCNS with a trace of ferric iron added migrating into N KCNS, or N $Fe(NO_3)_3$ with a trace of thiocyanate migrating into N $Fe(NO_3)_3$. In such a case, however, the specific gravities of the two solutions are identical, the boundary unstable, and easily destroyed by convection. In the first series of experiments, therefore, the upper solution was made somewhat more dilute than the lower, but in the second series described, the same thiocyanate concentration was used in both layers, though in several attempts the boundary became lost by convection.

These considerations do not seem always to have been taken into account by other workers.

EXPERIMENTAL

Two series of experiments are reported here.

Series 1. The apparatus consisted of a U-tube about 25 cm. long. The colourless solution was poured in at the top, while the more dense coloured solution was introduced through a side limb at the foot. A potential gradient of about one volt per centimetre was applied through platinum electrodes immersed to a depth of one centimetre in the upper solution. In none of the experiments in this series was the movement of the boundary large. The end levels were checked to determine whether migration of the coloured layer had occurred as a whole.

The compositions of the solutions employed in four typical experiments are given.

Index	Coloured Solution			Colourless Solution		
	KCNS m/l	$Fe(NO_3)_3$ m/l	HNO_3 m/l	KCNS m/l	$Fe(NO_3)_3$ m/l	HNO_3 m/l
1	0.50	1.5×10^{-5}	-	0.1	-	-
2	4.00	0.1	0.1	2.0	-	0.1
3	0.50	0.2	0.5	-	0.2	0.1
4	0.01	0.6	0.5	-	0.13	0.5

Experiments 1 and 2 are characterised by a large excess of thiocyanate. In No.1 a faintly coloured boundary moved 2 mm. towards the anode indicating the formation of an excess of negatively charged complexes under such conditions. Similarly, in No.2 the coloured zone moved 2.5 mm. towards the anode and this was verified by an identical experiment carried out in series.

On the other hand, in experiment 4 the colour boundary advanced 4 mm. towards the cathode in sixty minutes and receded 2 mm. from the anode in the same time. These observations suggest that, when the thiocyanate concentration is small, positively charged complexes predominate. This is in harmony with the previous discussions.

In experiment No.3, the colour boundary moved 4 mm. towards the cathode in half an hour. This is interesting because, whereas negative complexes predominated in experiment No.1 in which the total thiocyanate was the same, positive complexes existed in greater amount in this case. This can be explained on the assumption that the iron concentration is sufficiently great to reduce by combination the free thiocyanate ion concentration

below the limiting amount above which the net charge on the negative ions is greater than that of the positive ions.

Series 2. It is seen from the nomogram on page 98,99 that the concentration of negative complexes exceeds that of the positive complexes when the free thiocyanate ion concentration is greater than 0.28M. This is also signified by the partition curve given on page 67 . Solutions corresponding in composition to the aqueous phase at points marked "X" and "Y" were subjected to an electric potential and it was found that the solution containing less than 0.28 M thiocyanate contained an excess of positive complexes whereas, at point "Y", where the thiocyanate concentration exceeded 0.28 M, negative complexes predominated.

A modified apparatus was used. It consisted of a large U-tube about 20 cm. deep and 1 cm. diameter; large wide bored taps were inserted about 10 cm. from the top of each limb. The coloured solution was poured in till the levels were just above the taps; these were then closed and any coloured solutions above the taps washed out. The colourless solution was then poured in at the

top of each limb; on opening the taps good boundaries were obtained. The voltage applied through platinum electrodes was not greater than 0.2 volts per centimetre, and the current passing 25 milliamperes. The whole apparatus was maintained at 18°C to reduce heating effects. The stock solutions were also kept in the same thermostat.

Index	Coloured Solution			
	NH_4CNS m/l	$NaClO_4$ m/l	$Fe(ClO_4)_3$ m/l	$HClO_4$ m/l
5	0.0928	1.370	0.00090	0.127
6	0.6339	0.830	0.00063	0.064

The upper colourless solutions had the same concentrations as the lower coloured solutions except that no iron salt was added.

In experiment 5 (point marked "X") the colour boundary advanced 3 mm. towards the cathode and receded 2 mm. in the anode limb in one hour. After a further period of one hour, the boundary had advanced 6 mm. to the cathode and receded 4.5 mm. from the anode. There seems to be little doubt that the net charge carried by the complexes was positive, and that the enhanced migration can be attributed to the fact that the movement of the boundary was into a medium not too different from that in which the coloured complexes were originally formed.

In the case of experiment 6 (point "Y"), the colour migrated in the opposite direction, though the movement of the boundaries was only half as great as in the previous case.

Some preliminary experiments in which convection was prevented by using agar solutions as employed by Bent and French[4] gave results which were in general agreement with the above, but as they were not entirely satisfactory, they were abandoned in favour of the direct method reported above.

THE STABILITIES OF COMPLEX COMPOUNDS

Burkin has recently reviewed those factors affecting the stability of complexes and the nature of the forces between the metallic ion and the co-ordinated groups. (Quarterly Reviews, 5, 1, 1951.)

Bjerrum's theory, to which reference has been made, is currently accepted. According to this theory, the relative values of succesive stability constants of co-ordination complexes may be represented by

$$\log.K_x - \log.K_{x+1} = T_{x,x+1}$$

$$= {}_{x,x+1}^{S} + {}_{x,x+1}^{L}$$

Statistical Effect Ligand (Co-ordinated Gp) Effect

The Statistical Effect takes into account the chances of attachment of a co-ordinated group to an ion of co-ordinating valency 'N' and to which 'n' ligands are already attached, and is given by

$${}_{x,x+1}^{S} = \log.\frac{(N - x + 1)(x + 1)}{(N - x).x}$$

The Ligand Effect, on the other hand, represents the electrostatic effect on $\log.K_x - \log.K_{x+1}$ of any ionic charge on the ligand (CNS^-) and the effect which attached ligands may have in modifying the ability of further groups to attach

themselves to lower complexes already formed. Owing to the unavoidable uncertainties encountered when trying to calcul-ate the electrostatic effect, it is elected to choose, for $T_{x,x+1}$, a constant value, Q', referred to in Part 4, page 82.

To what extent the ligand effect plays a part in determining the relative values of K_x may be readily ascer-tained by consrasting actual values of $\log.K_x - \log.Kx+1$ with the corresponding values of $_xS_{x+1}$. On the assumption that this latter alone determines theerelative values of K_x, $\log.K_x - \log.K_{x+1} = {}_xS_{x+1}$. These values are compared for the Series B experiment, in which activity played the least role.

x	$\log.K_x - \log.K_{x+1}$	$_xS_{x+1}$
1	0.43	0.38
2	3.05	0.27
3	-3.20	0.25
4	3.05	0.27
5	0.43	0.38

The comparable values of $\log.K_x - \log.K_{x+1}$ for values of $x = 1,5$ result, of course, from the symmetry of the partition curve, which would, in itself, follow, were the assumption made above to be approximately true.

This much, at least, may be concluded, that the entry of thiocyanate groups into the formation of the higher complexes is not impaired to any marked degree. The extreme instability of the neutral molecule is, at the same time, apparent.

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