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# OXIDATION - REDUCTION POTENTIALS OF COMPLEX IONS - THE TRIS-(PYRIDINE 2-ALDOXIME) IRON(III)-IRON(II) SYSTEM

BY

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# ABSTRACT

The redox potential of the tris-(pyridine 2-aldoxime)-iron(III)/iron(II) system has been determined by two independent methods, and the relevant thermodynamic data have been evaluated.

Potentiometrically, the redox potential, E, referring to the half-cell $P(III)^0 + e^- = P(II)^-$, where $P(III)^0$ and $P(II)^-$ stand for the iron(III) and iron(II) complexes respectively, was measured with a rhodium electrode against a saturated calomel electrode using an agar-KCl bridge. The measurements were extended over a range of concentrations, pH, ionic strength, and temperature. The variation of E with pH was consistent with the assumption that the iron(II) complex is in equilibrium with its conjugate acid: $HP(II)^0 = P(II)^- + H^+$, an ionization which has been studied spectrophotometrically by Hanania and Irvine (ref.2). At 25° and I = 0, the pH independent redox potential $E_T^0 = 0.341$ volt and the corresponding enthalpy and entropy changes are: $\Delta H^0 = -23.5$ kcal/mole and $\Delta S^0 = -52.6$ e.u.

The redox potential E was also obtained from spectrophotometric measurements of the equilibrium constant, K, for the reaction:

$$C(III)^{3-} + P(II)^- = C(II)^{4-} + P(III)^0$$

where $C(III)^{3-}$ and $C(II)^{4-}$ stand for the hexacyanoferrate(III) and (II) ions respectively. K was measured over a range of pH, ionic strength and temperature. The pH independent value at 25° and I = 0, $K_T^0 = 0.48$. From this value and the known thermodynamics of the $C(III)^{3-}/C(II)^{4-}$ couple (ref. 7) the redox potential of the $P(III)^0/P(II)^-$ couple was found to be $E_T^0 = 0.381$ volt, and the corresponding enthalpy and entropy changes were $\Delta H^0 = -23.3$ kcal/mole and $\Delta S^0 = -48.6$ e.u.

These results and their significance are discussed in relation to similar data for other complex ions.

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## SYMBOLS

$E$ : Redox potential at 50% reduction at given I, pH, and T.
$E^o$ : Redox potential at I = 0.
$E_T$ : pH independent redox potential (50% reduction) at given I & T.
$E_T^o$ : pH independent redox potential at I = 0.
$E_{cal}$ : E.m.f. of cell with respect to saturated calomel electrode.
$E_h$ : E.m.f. of cell with respect to standard hydrogen electrode.
$K$ : Measured equilibrium constant.
$K_T$ ; pH independent equilibrium constant at given I & T.
$K_T^o$ : pH independent equilibrium constant at I = 0.
$I$ : Ionic strength (moles/l).
$A$ : Absorbancy.
$f$ : Activity coefficient.
fn : A function of.
PAL : Pyridine 2-aldoxime.
P(II) : Tris-(pyridine 2-aldoxime)-iron(II) complex.
$P(II)^-$ : Triply ionized P(II), also $Fe(PAO)_3^-$ .
$HP(II)^o$: Conjugate acid of $P(II)^-$, also $Fe(PAO)_3H^o$.
Red := $P(II) = HP(II)^o + P(II)^-$.
P(III) : Tris-(pyridine 2-aldoxime)iron(III) complex.
$P(III)^o$: Triply ionized P(III).
$C(III)^{3-}$: $Fe(CN)_6^{3-}$.
$C(II)^{4-}$: $Fe(CN)_6^{4-}$ .

# INTRODUCTION

The work described in this thesis is a thermodynamic study of an oxidation-reduction equilibrium involving the tris-(pyridine 2-aldoxime)-iron(III)/iron(II) complex ion system in dilute aqueous solution. The purpose of such work is to obtain and examine the relevant thermodynamic parameters ($E^o$, $\Delta H^o$, $\Delta S^o$) in relation to similar data on other complex ions.

The significance of the work may be viewed from the following consideration:

Firstly, few redox complex ion systems have been similarly treated. In the vast majority of cases, redox potentials and their variation with pH and/or ionic strength are reported, but not their variations with temperature. As such, very few $\Delta H^o$ and $\Delta S^o$ values are available for cell reactions involving complex ions. It is important that much more experimental work be done on a variety of systems before the interpretation of redox potentials can develop further.

Secondly, as knowledge about the structure of complex ions and the nature of aqueous solutions increases, so does the need for a more fundamental understanding of the entropies of complex ions and their role in aqueous solution. George, Hanania and Irvine[1] have shown that the partial molal entropy of a complex ion with the metal in a given oxidation state can differ considerably from that of the conjugate acid of the corresponding complex ion with the metal in its reduced oxidation state although their charges are identical. Since many types of reactions, including acid-base catalysis, involve protenated transition states, it is clear that the interpretation of kinetic data requires a more thorough understanding of entropies and their changes in reactions involving ions. Similarly, almost all aquo ions are protonated complexes and their equilibria may also involve spurious entropy changes which need further examination.

Thirdly, the present work has biological implications. Recent interest in biological chemistry is well known: it is known that hemoproteins are iron complexes, vitamin $B_{12}$ is a cobalt complex, and enzymes are usually metalloprotein complexes. The study of the biochemical role of these substances obviously involves coordination chemistry. It is important that as much thermodynamic data as possible be available for the interpretation of the stability and reactivity of biological molecules.

Fourthly, since so many biological substances are coordination compounds, the "simple" complex ions may be used as "models" for their analogous macromolecules. In particular, the tris-(pyridine 2-aldoxime)-iron(III)/iron(II) system is a model for the study of metal-linked ionizations, namely the influence of the metal on the ionization of the oxime acid group. Hanania and Irvine[2] have shown that coordination of pyridine 2-aldoxime to ferrous iron increases the acid strength of the oxime group from $pK^0 = 10.22$ in the free ligand to $pK^0 = 7.13$ in the complex, and that this change is reflected mainly in enthalpy, $\Delta H^0$ changing from 6.8 to 0.75 kcalmole$^{-1}$, rather than in entropy, the corresponding change in $\Delta S^0$ being from -24 to -30 calmole$^{-1}$ deg$^{-1}$. A knowledge of such effects can be used in the interpretation of similar linked ionization phenomena in metalloproteins where one cannot directly measure the ionization in a free ligand or group.

Furthermore, by comparing two model systems which have similar structures but different overall charges (e.g. complexes of pyridine 2-aldoxime vs. complexes of 2, 6-pyridine dialdoxime), one may be able to get a measure of the influence of charge on a linked ionization.

Interest in redox potentials of complex ions is quite recent. It started with the measurement of redox potentials of organic dyes, for their importance as redox indicators in industry, and of metalloporphyrins because of their biological significance. Conant, Michaelis, and Walden worked much on redox indicators, while Clark and his coworkers concentrated on the study of metalloporphyrins. This type of work started about 1930, and was mostly concerned with measuring redox potentials and their variation with pH. Analysis of results gave pK values of acid-base ionizations in the systems studied. The effect of coordination and polymerization on redox potential was also studied by Clark and coworkers. An excellent detailed review of the work is given in Clark's recent book on oxidation-reduction potentials of organic systems[3].

The development of the Debye-Huckel theory encouraged several workers to measure redox potentials as a function of ionic strength in order to test the validity of the principle of ionic strength and the applicability of the Debye-Huckel limiting law. Complex ions enabled work at lew ionic strength, this being difficult with simple ions which show extensive hydrolysis and change of species with pH. Ionic strength studies were also used to get redox potentials at zero ionic strength and to examine the effect of various neutral salts on the redox potentials of complex ions. Kolthoff and Tomsicek's study of the hexacyanoferrate(III)-hexacyansferrate(II) system[4] is an example of such work.

More recently, Dwyer and his coworkers have published a series of papers on the redox potentials of such systems as tris-(2,2'-dipyridyl)-osmium(III)/osmium(II)[5] with special reference to the effect of neutral salts. They and others have observed deviations of experimental data from the simple Debye-Huckel relation, and the suggestion has been made that the electrostatic treatment of the Debye-Huckel theory may not apply to complex ions.

Several workers[3] have also observed that measured redox potentials for metal ions in strongly acidic solutions vary depending on the acid used. It is probable that the complex ion species which occur in such solutions contain the anion of the acid and consequently vary from one medium to another. Moreover, such results are usually obtained at high ionic strengths and are not thermodynamically significant.

Latimer has collected available thermodynamic data (heats and free energies of formation and entropies) for the elements and their compounds, including some complex ions. The free energies tabulated were in many cases calculated from estimated entropy values. The work was first published in 1938 and was revised in 1952[6]. It is very useful as it enables one to get approximate thermodynamic data for many reactions.

During the past few years, George, Hanania and Irvine have started the measurement of redox potentials and enthalpies of cell reactions for complex ions and have compiled data on $\Delta H^0$ and $\Delta S^0$ for a number of systems such as the hexacyanoferrate(III)/(II), tetracyanodipyridyl-iron(III)/iron(II), tris-(2,2'-dipyridyl)-iron(III)/iron(II), hexa-chloroiridate-(IV)/(III) etc.[7,8] They have also proposed an empirical equation which enables one to estimate the partial molal entropy of a complex ion and have used it to interpret differences in the entropies of complex ions having the same charge where one is the conjugate acid of the other complex ion with the metal in the next lower oxidation state (see Discussion below).

From the above brief review it can be seen that work in this field is far from complete. There remains a real need for reliable thermodynamic data on all types of redox systems in aqueous solution, especially those of complex ions. The present work may be regarded as an attempt to provide some useful data in this field.

## THEORY - POTENTIOMETRY

The analysis of redox potential data for the tris-(pyridine 2-aldoxime)-iron(III)/iron(II) system is based in part on the equilibrium studies of Hanania and Irvine.[2,9] The relevant physico-chemical information on these complex ions may be summarized as follows:

(i) The iron(II) and the iron(III) complexes contain 3 moles of ligand to 1 mole of the ion, and in both cases, the bonding is through the two nitrogen atoms of the ligand.

(ii) The formation of the iron(II) complex

$$Fe^{2+} + 3PAOH = Fe(PAOH)_3{}^{2+} \qquad (K) \qquad (1)$$

is accompanied by three successive acid ionizations of the oxime group in the complex ion:

$$Fe(PAOH)_3{}^{2+} = Fe(PAO)_3H_2{}^{+} + H^{+} \qquad (K_1) \qquad (2)$$

$$Fe(PAO)_3H_2{}^{+} = Fe(PAO)_3H^{0} + H^{+} \qquad (K_2) \qquad (3)$$

$$Fe(PAO)_3H^{0} = Fe(PAO)_3{}^{-} + H^{+} \qquad (K_3) \qquad (4)$$

where $pK_1 \ll 3$, $pK_2 \sim 3.5$ and $pK_3 \sim 7$.

Accordingly, the formation constant, K, is a function of pH. The measured value of K is $3 \times 10^{11}$ at pH $\sim 5$, $3 \times 10^{13}$ at pH $\sim 5.9$ and $10^{25}$ at pH $> 8$. The last value is the pH independent value referring to the formation of the completely ionized species.

(iii) The formation of the iron(III) complex

$$Fe^{3+} + 3PAOH = Fe(PAOH)_3{}^{3+} \qquad (5)$$

is also accompanied by three successive ionizations of the oxime group which correspond to the above equilibria of the iron(II) complex with one extra positive charge. In this case, as expected,

$pK_1$ and $pK_2$ are very small and $pK_3 \sim 3.5$. Here again, the formation constant is a function of pH, the pH independent value at pH $>$ 6 being about $10^8$. The complex is unstable (as described in the experimental chapter below).

(iv) Since the present redox work is confined to the pH range 6-8, it is clear that only the third ionization of the iron(II) complex, i.e. the equilibrium between the uncharged species and the negatively charged species, need be considered. The iron(III) complex is uncharged in this pH range.

On the above basis we may write the redox reaction as

$$\begin{tikzcd} Fe(PAO)_3^{0} + \tfrac{1}{2}H_2 = Fe(PAO)_3^{-} + H^+ \arrow[d, leftrightarrow] \\ Fe(PAO)_3H^{0} \end{tikzcd} \qquad (6)$$

Rewriting eqation 6 in terms of symbols (see table of symbols), we get

$$\begin{tikzcd} P(III)^{0} + \tfrac{1}{2}H_2 = P(II)^{-} + H^+ \arrow[d, leftrightarrow] \\ HP(II)^{0} \end{tikzcd} \qquad (6')$$

for which

$$E_h = E^0 + \frac{RT}{F} \ln \frac{(P(III)^0)}{(Red)} \qquad (7)$$

where $E_h$ is the measured emf with respect to the standard hydrogen electrode, $E^0$ is the redox potential at I = 0 and given pH and T. Unless otherwise stated, E values are the redox potentials at 50% reduction. Red stands for total reductant (i.e. $P(II)^- + HP(II)^0$) and brackets indicate activities. R, T and F have their usual meaning.

When concentrations, indicated by square brackets, and molar activity coefficients, represented by f, are substituted for activities, equation (7) becomes

$$E_h = E^o + (RT/F)\ln \frac{f_o}{f_{Red}} + (RT/F)\ln \left[P(III)^o\right]/\left[Red\right] \qquad (8)$$

Dependence of E on pH (at constant T and I)

The above equation (8) may be rewritten in the form

$$E_h = E + (RT/F)\ln \left[P(III)^o\right]/\left[Red\right] \qquad (9)$$

where

$$E = E^o + (RT/F)\ln f_o/f_{Red} \qquad (9')$$

that is, E is the redox potential at finite ionic strength and is identical with $E_h$ at 50% reduction, and $E^o$ is the redox potential at $I = 0$. The pH dependence arises from the acid-base equilibrium involving the reductant

$$HP(II)^o = H^+ + P(II)^- \qquad (4')$$

for which the thermodynamic acid ionization constant is given in terms of activities:

$$K_3^o = \frac{(P(II)^-)}{(HP(II)^o)} \times h \qquad (10)$$

whereas the measured ionization constant , $K_3$, is given by

$$K_3 = \frac{\left[P(II)^-\right]}{\left[HP(II)^o\right]} \cdot h \qquad (10')$$

The ratio of molar concentrations in equation (10') is obtained spectrophotometrically and the hydrogen ion activity, h, is obtained from pH measurements using the definition $pH = -\log(h)$. $K_3$, as expected, will be a function of ionic strength and becomes equal to $K_3^o$ at $I = 0$.

Now, from equation (10')

$$\left[HP(II)^o\right] = \left[P(II)^-\right] \cdot h/K_3 \qquad (11)$$

The total concentration of reductant is

$$[\mathrm{Red}] = [\mathrm{P(II)}^-] + [\mathrm{HP(II)}^0] \qquad (12)$$

From equations (11) and (12), we get

$$\begin{aligned}[\mathrm{Red}] &= [\mathrm{P(II)}^-] + [\mathrm{P(II)}^-] \cdot h/K_3 \\ &= [\mathrm{P(II)}^-]\ (K_3 + h)/K_3 \qquad (12')\end{aligned}$$

so that

$$[\mathrm{P(II)}^-] = [\mathrm{Red}] \cdot K_3/(K_3 + h) \qquad (13)$$

Now, the true pH independent redox potential at given I, $E_T$, referring to the reaction (6') with the reductant as the conjugate base only, is given by

$$E_h = E_T + (RT/F)\ln\ (\mathrm{P(III)}^0 \ /\ \mathrm{P(II)}^-\ ) \qquad (14)$$

Substituting for $[\mathrm{P(II)}^-]$ from equation (13), we get

$$E_h = E_T + (RT/F)\ln\ \frac{[\mathrm{P(III)}^0]}{[\mathrm{Red}]} \cdot \frac{K_3 + h}{K_3} \qquad (15)$$

Consequently, from equations (15) and (9), we get (at 50% reduction)

$$E = E_h = E_T + (RT/F)\ln \frac{K_3 + h}{K_3} \qquad (16)$$

which gives the variation of E with h (i.e. measured pH) at given I and T.

### Dependence of E on I (at constant pH and T)

Equation (15) may now be rewritten as

$$E_h = E_T^0 + (RT/F)\ln \frac{K_3 + h}{K_3} + (RT/F)\ln \frac{[\mathrm{P(III)}^0]}{[\mathrm{Red}]} + (RT/F)\ln \frac{f_0}{f_{\mathrm{Red}}} \qquad (17)$$

which at 50% reduction reduces to

$$E = Eh = \left(E_T^0 + (RT/F)\ln \frac{K_3 + h}{K_3}\right) + (RT/F)\ln \frac{f_0}{f_{\mathrm{Red}}} \qquad (17')$$

$K_3$ varies with I, and as this variation is known, the variation of Eh with the last term of equation (17') can be evaluated. The above equation (17') may be rewritten as

$$E = \text{constant} + (RT/F)\ln \frac{f_O}{f_{Red}} \qquad (17'')$$

bearing in mind that ~~the~~ by constant is meant a known value at each ionic strength. It is to be noted that when $K_3 \gg h$, the above constant reduces to $E_T^0$ which is the pH independent redox potential at $I = 0$.

In sufficiently dilute solutions, one may use a Debye-Huckel type of equation for activity coefficients

$$-\log f = AZ^2 \, fn(I)$$

where A is a constant and Z is the charge on the ion; then

$$E = \text{constant} - (RT/F) \; A \, fn(I)(Z_O^2 - Z_{Red}^2) \qquad (18)$$

Assuming charges on basis of complete ionization, one gets

$$E = \text{constant} + A(RT/F)fn(I) \qquad (18')$$

which shows the variation of the measured redox potential with ionic strength. It was decided, in this work, to use the Davies[10] equation

$$fn(I) = \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.30I$$

for ionic strength studies.

Dependence of E on T (at constant pH and I)

The variation of E with temperature is important as it enables one to get the enthalpy and entropy changes for the cell reaction.

Assuming that over the temperature range investigated, 15-30°C, the activities of the ions are independent of T, one can write

$$dE_T/dT = dE_T^0/dT$$

where $dE_T/dT$ is the change of $E_T$ with T at finite low ionic strength. The above assumption also implies that over this small temperature range, heat capacities are constant, that is, $\Delta H$ is independent of T. This is a reasonable approximation for our purposes. Then

$$\Delta H^0 = nF(T dE_T^0/dT - E_T^0) \tag{19}$$

and

$$\Delta S^0 = nF\, dE_T^0/dT \tag{20}$$

from which we evaluate $\Delta H^0$ and $\Delta S^0$. It is to be noted that the reference state is chosen at $pH > 8$, not the standard state of $h = 1$.

## THEORY - EQUILIBRIUM CONSTANT

The reversible reaction between ferricyanide ion and the tris-(pyridine 2-aldoxime)-iron(II) complex is an oxidation - reduction reaction involving the transfer of one electron. In the pH range 6-8, the tris(pyridine 2-aldoxime)-iron(III) complex is completely ionized and uncharged, ferricyanide has the charge -3, the ferrocyanide ion is present completely in its form $Fe(CN)_6^{4-}$, the acid-base equilibrium:

$$HFe(CN)_6^{3-} = H^+ + Fe(CN)_6^{4-} \qquad (21)$$

having $pK^0 = 4.16$ at 25.0°C [7]. The PAL- iron(II) complex involves the acid-base equilibrium in equation (4) above, so that the reaction is really

$$\begin{array}{l} Fe(PAO)_3^- + Fe(CN)_6^{3-} = Fe(PAO)_3^0 + Fe(CN)_6^{4-} \\ \Big\downarrow \\ Fe(PAO)_3H^0 \end{array} \qquad (22)$$

which may be rewritten as

$$\begin{array}{l} P(II)^- + C(III)^{3-} = P(III)^0 + C(II)^{4-} \\ \Big\downarrow \\ HP(II)^0 \end{array} \qquad (22')$$

for which the thermodynamic equilibrium constant is given in terms of activities

$$K^0 = (P(III)^0)(C(II)^{4-})/(Red)(C(III)^{3-}) \qquad (23)$$

and the measured equilibrium constant at finite I will be given in terms of concentrations

$$K = [P(III)^0]\,[C(II)^{4-}]/[Red]\,[C(III)^{3-}] \qquad (23')$$

where $[Red] = [P(II)^-] + [HP(II)^0]$.

### Dependence of K on pH (at constant T and I)

At finite ionic strength, the true pH independent equilibrium constant, $K_T$, referring to reaction in equation (22') with the iron(II) complex as the conjugate base only, is given by

$$K_T = [P(III)^0]\,[C(II)^{4-}]/[P(II)^-]\,[C(III)^{3-}] \qquad (24)$$

Substituting for $[P(II)^-]$ its value from equation (13), we get

$$K_T = \frac{[P(III)^0]\,[C(II)^{4-}]}{[Red]\,[C(III)^{3-}]} \cdot \frac{K_3 + h}{K_3} \qquad (24')$$

From equations (23') and (24'), we get

$$K = K_T \cdot \frac{K_3}{K_3 + h} \qquad (25)$$

which gives the variation of K with h (i.e. measured pH) at given I and T.

### Dependence of K on I (at constant T and pH)

From the charges appearing on the reactants and products in equation (22) it is expected that the dependence of K on I will be appreciable.

Rewrite equation (25) as

$$\log K = \log K_T + \log(K_3/(K_3 + h)) \qquad (25')$$

From equation (24)

$$K_T = K_T^0 \cdot f_1\, f_3/f_0\, f_4 \qquad (26)$$

where $K_T^0$ is the pH independent equilibrium constant at I = 0, and f values are molar activity coefficients with subscripts indicating species with corresponding charges. Rewriting above equation as

$$\log K_T = \log K_T^0 - (\log f_0 + \log f_4 - \log f_1 - \log f_3) \qquad (26')$$

and substituting values of log f from a Debye-Huckel type of equation, the above equation becomes

$$\log K_T = \log K_T^0 + 6A\, fn(I) \qquad (26'')$$

Substituting for $\log K_T$ from equation (26'') into equation (25') we get

$$\log K = \log K_T^0 + \log K_3/(K_3 + h) + 6A\ \mathrm{fn}(I) \qquad (27)$$

which gives the variation of K with I, the value of $\log K_3/(K_3 + h)$ being known at each ionic strength. Here also,

$$\mathrm{fn}(I) = (I^{\frac{1}{2}}/1 + I^{\frac{1}{2}}) - 0.30I$$

was used.

### Dependence of K on Temperature (at given I and pH)

Considering the pH independent equilibrium constant at I = 0, $K_T^0$, we have the following relations for the thermodynamic properties of the above reaction:

$$\Delta G^0 = -RT \ln K_T^0 \qquad (28)$$

and

$$\Delta H^0 = RT^2 (d \ln K_T^0/dT) \qquad (29)$$

which in its integrated form, assuming constancy of $\Delta H$(as in potentiometry), gives

$$\ln K_T^0 = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \text{constant} \qquad (29')$$

Also,

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \qquad (30)$$

The reference state is also chosen at $pH > 8$, rather than $h = 1$.

### Evaluation of $E_T^0$ from $K_T^0$

Consider the two half-cell reactions

$$C(III)^{3-} + \tfrac{1}{2}H_2 = C(II)^{4-} + H^+ \qquad \Delta G_1^0 \qquad (31)$$

$$P(III)^{o} + \tfrac{1}{2}H_2 = P(II)^{-} + H^{+} \qquad \Delta G^{o}_{2} \qquad (32)$$

Subtracting equation (32) from equation (31) we get

$$C(III)^{3-} + P(II)^{-} = C(II)^{4-} + P(III)^{o} \qquad \Delta G^{o} \qquad (33)$$

for which the free energy change is

$$\Delta G^{o} = \Delta G^{o}_{1} - \Delta G^{o}_{2} \qquad (34)$$

Also, from the pH independent equilibrium constant at $I = 0$, we have

$$\Delta G^{o} = -RT \ln K^{o}_{T} \qquad (35)$$

In this work, $\Delta G^{o}$ is obtained from the equilibrium measurements and $\Delta G^{o}_{1}$ is known [7]. Hence $\Delta G^{o}_{2}$ can be calculated (equation (34)), and from it one gets $E^{o}_{T}$ using the relation

$$\Delta G^{o}_{2} = -nFE^{o}_{T} \qquad (36)$$

which is the measured value (from potentiometry) for the cell reaction in equation (32).

## EXPERIMENTAL - POTENTIOMETRY

The potentiometric work involved the following steps:

I. Investigations of conditions of experiment.

II. Preparation of stock solutions.

III. Measurement of redox potentials.

### I. Investigations of Conditions of Experiment:

### (A) Purity of salts:

### (1) Standardization of ferrous ammonium sulfate:

The iron(II) complex was prepared using the same sample of this salt throughout. The purity of the salt was determined by titration against standard $KMnO_4$ solution. It was found to be 99.9% pure. Consequently, a 0.1% increase in the weight of samples was applied as a correction factor.

### (2) Standardization of ferric ammonium sulfate:

The iron(III) complex was prepared using the same sample of this salt throughout. The purity of the salt was determined by titration against standard $SnCl_2$ solution. It was found to be 98.6% pure. Consequently, a 1.4% increase in the weight of samples was applied as a correction factor.

### (B) Formation and stability of complexes:

### (1) Tris-(pyridine 2-aldoxime)-iron(II) complex:

The iron(II) complex with pyridine 2-aldoxime forms rapidly, and if more than 40 seconds are given for the reaction in water before addition of buffer ($pH > 6$), the product is quite stable as judged by constancy of absorbancy at 515mμ, the absorption band maximum of the complex. Since the formation constant for the complex is very high, the

PAL/Fe ratio of 36x which was used was enough for complete formation. Also, since the complex undergoes acid-base ionization with pK $\sim$7, the extinction coefficient at 515 mμ varied with pH in accordance with the titration curve (figure 1).

(2) Tris-(pyridine 2-aldoxime)- iron(III) complex:

The ferric complex formed much more slowly than the corresponding ferrous complex and was much less stable. The formation constant is also much smaller as can be seen in figure 2 which gives experimental results at pH $\sim$7 for both complexes. From the curves, it can be seen the Fe(III) complex is about 75% formed at PAL/Fe = 36. Since potentiometric measurements were mostly done on solutions where PAL/Fe = 36, a correction factor was needed.

Theoretically, if the effective molar concentration of the complex is only 75%, the redox potential will have been about 7.5 m.v. too low. Therefore a correction term of 7.5 m.v. should be added to the measured value of E. However, because uncomplexed ferric ions could also introduce other complications in the system, it was decided to check this by direct experiment. Using PAL/Fe = 100, experiments were made at pH $\sim$ 7 and pH $\sim$ 6.4, and in both cases, the E values were found to be 18.0 m.v. higher than those usually obtained at PAL/Fe = 36. The discrepancy is probably due to complication in the system with free ferric ions. It was therefore decided to add 18.0 m.v. as (the correction term) to all the results obtained in the pH range 6-7.5, and at PAL/Fe = 36. Furthermore, since at PAL/Fe = 100 the ferric complex is only 95% formed, a further correction term of 1.3 m.v. was applied making a total additional term of 19.3 m.v. to be added to the measured E values.

The ferric complex was also difficult to keep because of

Figure 1

Absorbance of Tris-(Pyridine 2-Aldoxime)-Iron(II) Complex vs.pH.

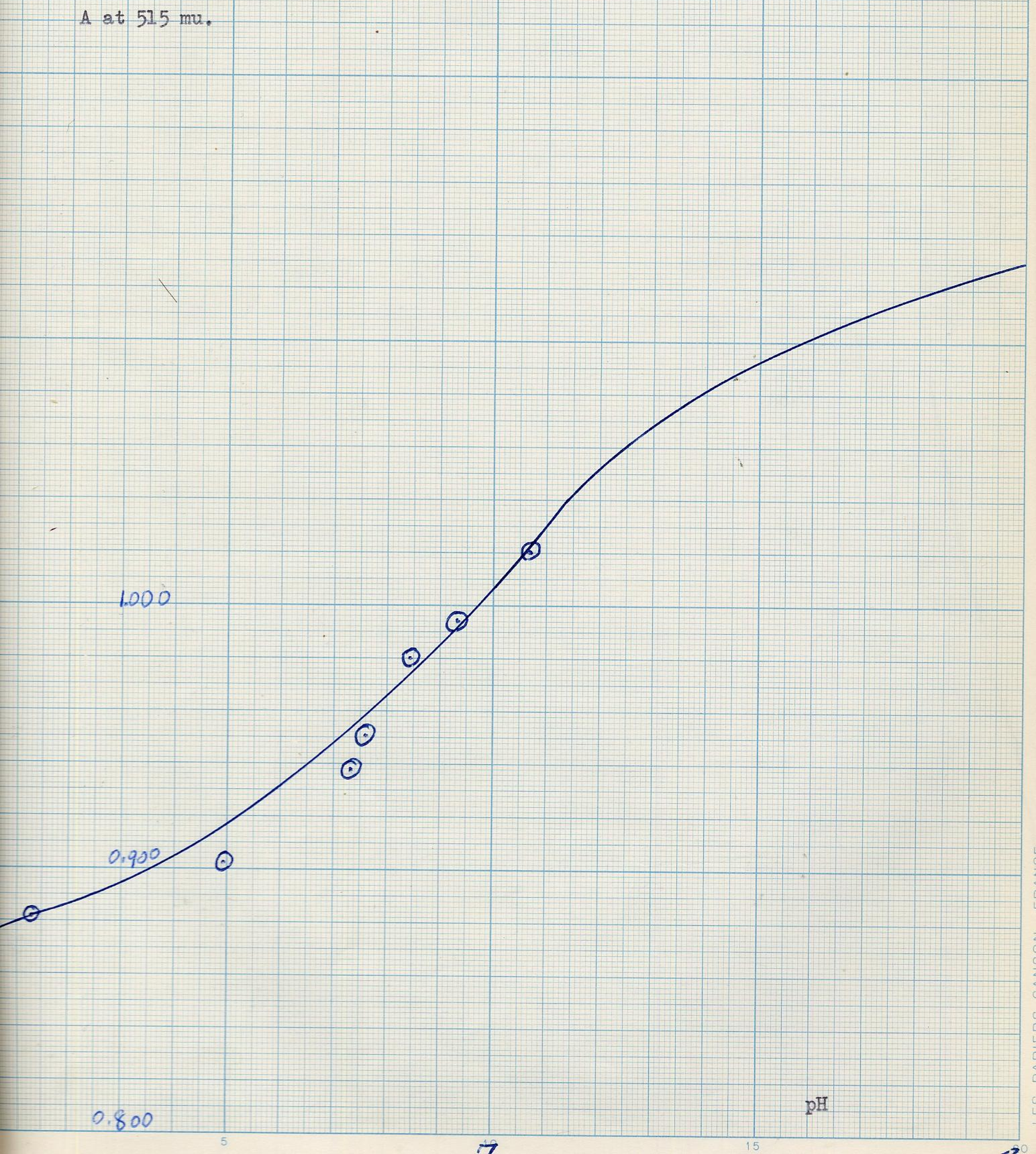
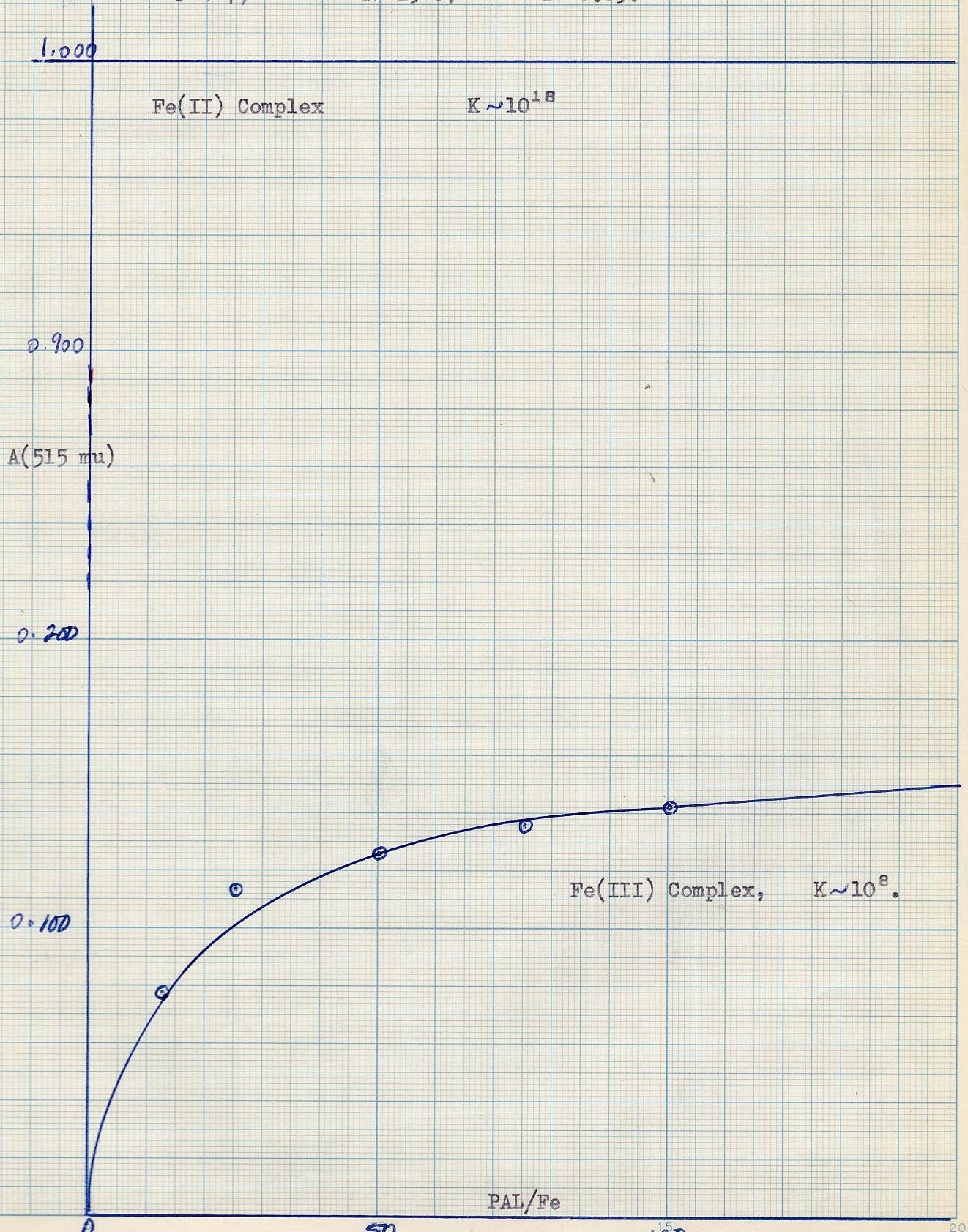


Figure 2

Formation of Fe(II) and Fe(III) Complexes of PAL

pH ~7, T~ 25°C, I~ 0.05.



(i) its rapid autoreduction to the Fe(II) complex; (ii) its rapid dissociation; and (iii) its slow coming out of solution.

(C) Stability of potential:

(1) Effect of stirring and time:

As the ferric complex is unstable, it is expected that the redox potential would change with time. This has been observed and E values were obtained by extrapolating to $t = 0$.

The table below shows the effect of stirring on E. In the absence of stirring, the potential dropped fairly rapidly, and readings were affected by vibrations. Under the same conditions, when the mixture was stirred, E values were more reasonable and were not affected by vibrations. Also, the table shows the change in potential when stirring was stopped.

It was concluded that stirring was essential to get reasonably steady potentials and to eliminate outside sources of error.

Table

Effect of stirring on redox potential

$T = 25.0 \pm 0.1$, $I = 0.047M$, $pH = 6.96$, PAL/Fe = 36

| Time(min.) | With stirring $E_{cal}$(m.v.) | | Without stirring $E_{cal}$(m.v.) |
|---|---|---|---|
| 3 | 85.6 | | 79.1 |
| 4 | 86.6 | | 78.1 |
| 5 | 87.1 | | vibrations |
| 6 | 87.2 | | 78.0 |
| 7 | 87.3 | | 77.1 |
| 8 | 87.3 | | 76.5 |
| 9 | 83.1* | stirring stopped | 76.0 |
| 10 | 81.3* | | 75.5 |
| 11 | 80.1* | | 75.1 |

### (2) Effect of diffusion of KCl from bridge:

The above tests show that diffusion from the agar-KCl bridge could not have been significant. A direct determination of the amount of KCl diffusion from conductivity measurements is described below:

One end of the bridge was dipped in 20 ml of deionized and redistilled water for ten minutes, with stirring. The conductance of this solution was measured using a conductivity bridge (Model RC 16B2, Idustrial Instruments inc.). The measured conductance was $2.25 \times 10^{-3}$ mhos, compared to the measured conductance of deionized and redistilled water which was about $1.6 \times 10^{-5}$ mhos. In 14ml of solution (the volume of redox solutions), this corresponded to about $3 \times 10^{-3}$ M KCl solution.

In the course of experiments, an average of 0.002M was added to ionic strength to correct for the diffusion of KCl.

## (D) Reproducibility of Measurements:

### (1) Comparison of electrodes:

Three rhodium and two platimum electrodes were used to measure the potential of the iron(III)/ iron(II), the hexacyanoferrate(III)/ hexacyanoferrate(II), and the tris-(pyridine 2-aldoxime)-iron(III)/ iron(II) systems against a saturated calomel electrode. For the first two systems, the five electrodes agreed to within less than 0.5 mv. In the third system, the Rh electrodes agreed among themselves, and so did the Pt electrodes, but compared to each other, the Pt electrodes gave consistently higher readings than Rh electrodes by 30-40 mv, and had a slower response (12 minutes). In this work, it was decided to use Rh rather than Pt electrodes.

Two calomel electrodes were checked against each other, and they agreed to within less than 0.5 mv.

All through, redox measurements were taken using the same calomel and Rh electrodes.

### (2) The agar-KCl bridge:

A number of agar-KCl bridges were always kept in saturated KCl solution. When tested by changing the bridge, the emf reading was found to vary by ± 0.2 mv or less.

### (3) Reversibility of the system:

Using varying proportions of oxidant and reductant, the reversibility of this one-electron transfer system was tested. The experiment was done using PAL/Fe = 100 at T = 25.0° C and I = 0.05 M. The results are summarized in the following table:

| $P(III)^{o}$ / P(II) | $E_h$(mv) | -(.059 log $P(III)^{o}$/ P(II))mv | Correction term (see I.B.2 above) | $E_T$(mv) |
|---|---|---|---|---|
| 1:4 | 296.9 | + 35.6 | - 1.3 | 331.1 |
| 1:2 | 314.6 | + 17.8 | - 1.3 | 331.1 |
| 1:1 | 330.6 | 0 | + 1.3 | 331.9 |
| 2:1 | 349.1 | - 17.8 | +1.3 | 332.6 |
| 4:1 | 366.0 | - 35.6 | + 1.3 | 331.8 |

### (4) Effect of concentration of complex ions on redox potential:

The redox potential was also measured using a range of concentrations from $1.0 \times 10^{-4}$M to $9.0 \times 10^{-4}$M. The results in the table below show that the redox potential is independent of final concentration of the mixture. However, some difficulty at high concentrations ($9.0 \times 10^{-4}$M) was encountered as the iron(III) complex tended to get out of solution.

| Concentration of Oxidant and of Reductant (M) | $E_T$(mv) |
|---|---|
| $1.0 \times 10^{-4}$ | 331.4 ± 0.9 |
| $3.0 \times 10^{-4}$ | 331.6 ± 0.6 |
| $5.0 \times 10^{-4}$ | 331.1 ± 0.7 |
| $9.0 \times 10^{-4}$ | 330.7 ± 1.2 |

(5) Repeats:

Every run under a certain set of conditions was repeated at least once. Measurements usually reproduced each other within 0.25-1.2 mv, and repeats presented no problem in the vast majority of cases.

(E) Stability of pH:

An equimolar mixture of the iron(III) and iron(II) complexes was prepared and its pH (6.76) was followed with time for ten minutes. No change in pH was observed. After an hour, the pH of the mixture was still the same. It was concluded that, within the pH range of the experiments (6-7.5), there is no problem of pH changes.

(F) Charge Types of the Complexes:

Electrophoretic mobility on paper was checked for the Fe(III) and Fe(II) complexes in the pH range of the experiments. The results, tabulated below, fitted the expected pattern, namely that the Fe(II) complex has an equilibrium between/un-charged and negatively charged species (see equation 4), while the iron(III) complex is uncharged.

| pH range | Fe(II) complex | Fe(III) complex |
|---|---|---|
| 6.2 - 6.5 | Mainly 0, with tendency towards negative. | 0 |
| 6.9 - 7.2 | Negative, with same 0. | 0 |
| 7.7 - 8.0 | Negative. | Diffuse ~ 0 |

## II. Preparation of Stock Solutions:

Except for buffers, all solutions were treshly prepared and were kept only for few hours. The complexes were prepared just before use. In all cases, deionized and glass redistilled water was used in making solutions.

### (A) Buffers:

A series of phosphate buffers, over the range of pH 6.0-7.8 and at the required ionic strength, were prepared by adding NaOH to $NaH_2PO_4 \cdot H_2O$ in the appropriate ratios and making up to the total volume with $CO_2$-free deionized redistilled water. In some cases, NaCl was used to adjust ionic strength.

All the chemicals used were of the A.R. grade, and were not further purified before use.

### (B) Ferrous Ammonium Sulfate Solutions:

A.R. grade $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was used. Solutions were prepared by weighing 100.1% of the required amount of the salt (see I.A.1.), dissolving it in water, adding $HClO_4$, and making up to total volume with water. The final concentration of such solutions was usually $2.5 \times 10^{-2}$M, and in a few cases $1.25 \times 10^{-2}$M. The quantity of acid added was such as to give $[H^+]/[Fe(II)] = 0.8$.

(C) Ferric Ammonium Sulfate Solutions:

A.R. grade $Fe(NH_4)(SO_4)_2.12H_2O$ was used. Solutions were prepared by weighing 101.4% of the required amount of the salt (see I.A.2), dissolving in water, adding $HClO_4$, and making up to total volume with water. The final concentration was $2.5 \times 10^{-2}M$ and in a few cases $1.25 \times 10^{-2}M$. The acid added was such that $[H^+]/[Fe(III)] = 3.2$. Such solutions were filtered as there was a tiny insoluble residue.

(D) Pyridine 2-Aldoxime Solutions:

A sample of pyridine 2-aldoxime was purchased from Light & Co., England, and was used without further purification. 0.1M and 0.125 M solutions were prepared by dissolving the correct amount of the compound in water. This is about the limit of solubility at room temperature.

(E) Tris-(Pyridine 2-Aldoxime)-Iron(II) Complex:

The complex was formed by adding PAL solution to the ferrous solution (usually 1.0 ml) such that PAl/Fe = 36, (and in later experiments 100). The mixture was shaken for about 40 seconds and buffer solution was then added. Usually, the concentration of this stock complex was $1.0 \times 10^{-3}M$. The solution is bright red in color and is fairly stable.

(F) Tris-(Pyridine 2-Aldoxime)-Iron(III) Complex:

The iron(III) complex was formed by adding PAL solution to the ferric solution (usually 1.0 ml) such that PAL/Fe = 36, (and in later experiments 100). After 4 minutes, buffer solution was added. Usually the concentration of this stock complex was $1.0 \times 10^{-3}M$. The solution was brown, but its stability presented a problem (see I.B.2.).

## III. Measurement of Redox Potential:

### (A) Apparatus:

A cell with liquid junction was set up. It consisted of two small glass cylinders about 7 cm long and 3 cm in diameter across which the agar-KCl bridge could sit and dip in the two half-cells. The bridge was made by dissolving 4 grams agar-agar powder plus 35 grams KCl in 100 ml of hot water, and after boiling for a few minutes, the liquid was sucked into a U tube bridge. The liquid in the bridge was allowed to cool and solidify into a gel. Several bridges were always kept equilibrating in saturated KCl solution, and a fresh bridge was used for every experiment.

The reference half-cell was a saturated calomel electrode dipping in saturated KCl.

The other half-cell contained an equimolar mixture of the iron(III) and iron(II) complexes with pyridine 2-aldoxime at given conditions, and in which dipped a mechanical stirrer and a Rh electrode.

The cell was suspended in a water bath whose temperature was controlled by a "WACO" tempunit (Wilkens-Anderson Co., U.S.A.), the temperature control in the cell being within ± 0.1°C. The thermometer was calibrated against a standard calibrated thermometer (National Physical Laboratory, England, 1961).

Potential measurements were directly read on the potentiometer (Radiometer, pH Meter 4, type PHM4c No. 39535), which read to 0.1 mv.

All pH measurements were taken on a pH meter (Radiometer, pH Meter 4, type PHM 4c No. 39538) which read to within 0.001 pH unit. The pH of a mixture was usually measured directly after the redox measurement. Water from a thermostat was circulated around the vessel in which pH measurement was made, and temperature control was within ± 0.2°C. The pH meter was standardized against 0.05 M KHphthalate standard buffer, and sometimes rechecked with standard phosphate and/or standard borax. The pH values of the standard buffers as given by the National Bureau of Standards are given below.[11] These standards were selected because of their stability with respect to changes of concentration or slight contamination, the errors being less than ± 0.01 pH unit.

pHs of NBS Standards

| Standard Buffer | 15.0°C | 20.0°C | 25.0°C | 30.0°C |
|---|---|---|---|---|
| 0.05 M KHphthalate | 4.00 | 4.01 | 4.01 | 4.01 |
| 0.025 M $KH_2PO_4$<br>0.025 M $Na_2HPO_4$ | 6.90 | 6.88 | 6.86 | 6.85 |
| 0.01 M borax | 9.27 | 9.22 | 9.18 | 9.14 |

(B) Solutions:

Redox potentials were measured using 14 ml of solution. To 7.0 ml of the freshly prepared iron(II) complex already transferred to the reaction half-cell, 7.0 ml of fresh iron(III) complex were added directly after the complex was prepared. Immediately, timing was started, the stirrer was set on, and the agar-KCl bridge inserted.

The potential was followed with time. Usually, it rose for about 5 minutes, probably due to equilibration of temperature and to mixing, then it dropped with time at a rate which increased with increasing acidity of solution. Usually, every measurement was followed at 1 minute intervals up to 10 minutes. Values of E were obtained by extrapolating to t = 0, which is the time of mixing.

### (C) Estimation of Ionic Strength (I):

The total molar ionic strength of the mixture was contributed by the buffer, the salts, the acid and the agar-KCl bridge. For details, see sample run below.

#### (1) Contribution of buffer to I:

The pH of the mixture was always lower than the pH of the stock buffer. This is due to the effect of $H^+$ ions from the $HClO_4$ in the ferrous and especially ferric solutions. So, as $HPO_4^{2-} + H^+ = H_2PO_4^-$, a dicrease in ionic strength would be expected. Buffers prepared by adding 0.04 N NaOH to 50 ml 0.04 M $NaH_2PO_4.H_2O$, and making to 200 ml with $CO_2$-free water would have the ionic strengths which have been calculated and are given in the table below:

| pH | Calculated I(M) | pH | Calculated I(M) |
|---|---|---|---|
| 6.0 | .0122 | 6.9 | .0206 |
| 6.2 | .0134 | 7.0 | .0218 |
| 6.3 | .0142 | 7.1 | .0229 |
| 6.4 | .0150 | 7.2 | .0240 |
| 6.5 | .0161 | 7.3 | .0248 |
| 6.6 | .0171 | 7.4 | .0257 |
| 6.7 | .0183 | 7.6 | .0271 |
| 6.8 | .0194 | 7.8 | .0280 |

The change in I which results from the change in pH was estimated from the above table. Also, changes due to dilution were considered. Then the resultant contribution of buffer to I was estimated in every case.

(2)

(2) Contribution of salts and acid to I:

On the assumption of 100% ionization, the effect of the ions: Fe(II), Fe(III), $NH_4^+$, $SO_4^{2-}$, $H^+$ and $ClO_4^-$, on the ionic strength was considered.

(i) Fe(II) and Fe(III): both ions go into complexes. The ferric complex is uncharged and does not contribute to I. Although, as discussed above, the ferric complex was only 75% formed in the experiments where PAL/Fe = 36, the net contribution to I can be shown to be negligible.

Ferrous ions go conpletely into the Fe(II) complex, and are involved in the equilibrium: $HP(II)^0 = P(II)^- + H^+$. It can be shown that the contribution to I here is also insignificant.

(ii) $NH_4^+$, $SO_4^{2-}$ and $ClO_4^-$: these ions are still present and their contribution to I was estimated.

(iii) $H^+$: from pH values, it is evident that the concentration of hydrogen ions is very small ($10^{-6}$M), and negligible.

(3) Contribution of bridge to I:

This was estimated to be 0.002 M (see I.C.2).

(D) Sample Run: Measurement of Redox Potential:

A sample run was chosen and is presented below as representative of the type of work done:

Date: July 17, 1962.

Experimental Conditions:

$T = 25.0 \pm 0.1^\circ C$; $pH = 6.79_0$ ; $I = 0.047$ M.

Total concentration of Fe(II) complex = Total concentration of Fe(III) complex = $5.0 \times 10^{-4}$M.

### Stock Solutions:

Distilled deionized water was used.

(1) Phosphate buffer, pH 7.2, I = 0.072 M.

(2) $2.50 \times 10^{-2}$M $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution: 0.4906 grms salt + 1.0 ml $HClO_4$(0.98 N), diluted to 50 ml with water.

(3) $2.50 \times 10^{-2}$M $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ solution: 0.6118 grms salt + 4.0 ml $HClO_4$(0.98 N), diluted to 50 ml with water.

(4) 0.10 M PAL solution: 1.220 grms PAL dissolved in water to 100 ml.

(5) $1.0 \times 10^{-3}$M iron(II) complex: 1.0 ml Fe(II)-($2.5 \times 10^{-2}$M) + 9.0 ml PAL(0.1 M) + 15.0 ml buffer (I = 0.072 M)

(6) $1.0 \times 10^{-3}$M iron(III) complex: 1.0 ml Fe(III)-($2.5 \times 10^{-2}$M) + 9.0 ml PAL (0.1 M) + 15.0 ml buffer (I = 0.072 M).

### Mixture:

7.0 ml of each complex (fresh) were mixed in the reaction cell, and stirring was immediately started, and bridge was set in place.

### Experimental Results:

The redox potential was read as described above. The values of E were recorded as they changed with time. The data for three such runs have been plotted in figure 3 which shows the extrapolation to t = 0.

The average value of $E_{cal}$ at time of mixing = 94.4 ± 0.4 mv.

Therefore, Eh = 94.4 ± 0.4 + 244.4 + 19.3* = 358.1 ± 0.4 mv.

From equation (16), the pH independent value is, using $^{2}pK_3$ = 7.02,

$E_T$ = (358.1 ± 0.4) - (25.5 ± 0.7) = 332.6 ± 1.1 mv.

### Measurement of pH:

The pH of each solution was measured as described above directly

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* Correction term for incomplete formation of Fe(III) complex (see I.B.2).

after the measurement of E. The pH meter was standardized against 0.05 M KHphthalate whose pH is 4.01 at 25.0°C. The pH was found to be 7.90.

Estimation of Ionic Strength:

The contribution of every species to I was estimated as follows:

(1) Contribution of buffer: Due to dilution, the ionic strength of buffer = 0.072 x 15/25 = 0.0432 M. Subtracting the change resulting from the change of pH from 7.2 to 6.8, which amounts to 0.0240 - 0.0194 = 0.0046 M (see table in (III) C), then the ionic strength of buffer is 0.0432 - 0.0046 = 0.0386  0.039 M.

(2) Contribution of salts and acid to I:

(a) Fe(III): contribution of uncomplexed ion (25%) in final mixture is: $\frac{1}{2}(5 \times 10^{-4} \times 3^2) \times 25\% = 0.0005$ M which is negligible, expecially because free Fe(III) ions probably form other complexes with lower positive charge.

(b) Fe(II) complex: From the equilibrium in equation (4), the concentration of the charged species is:

$$P(II)^- = (K_3/K_3 + h) \times 5 \times 10^{-4} = 1.85 \times 10^{-4} \text{ M},$$

where $pK_3 = 7.02$ at I = 0.047, and so contribution to I is:

$$I = \frac{1}{2}(1.85 \times 10^{-4} \times 1^2) = 9.2 \times 10^{-5}\text{M},$$

which is negligible.

(c) $NH_4^+$ : 3 ions come from both the Fe(II) and Fe(III) salts, and contribution to I is:

$$I = \frac{1}{2}(3 \times 5 \times 10^{-4} \times 1^2) = 7.5 \times 10^{-4}\text{M}.$$

(d) $SO_4^{2-}$ : 2 ions come from each salt, the contribution to I amounting to: $\frac{1}{2}(4 \times 5.0 \times 10^{-4} \times 2^2) = 40 \times 10^{-4}$M.

(e) $H^+$: Negligible contribution.

(f) $ClO_4^-$ : The concentration of this ion in the final mixture is: (1 x 0.98 x 1/50 x 1/25 x 7/14) + (4 x .98 x 1/50 x 1/25 x 7/14) = 19.6 x $10^{-4}$M, and the contribution to I is therefore: $\frac{1}{2}(19.6 \times 10^{-4} \times 1^2) = 9.8 \times 10^{-4}$M.

Therefore total contribution of ions to I = 0.006 M.

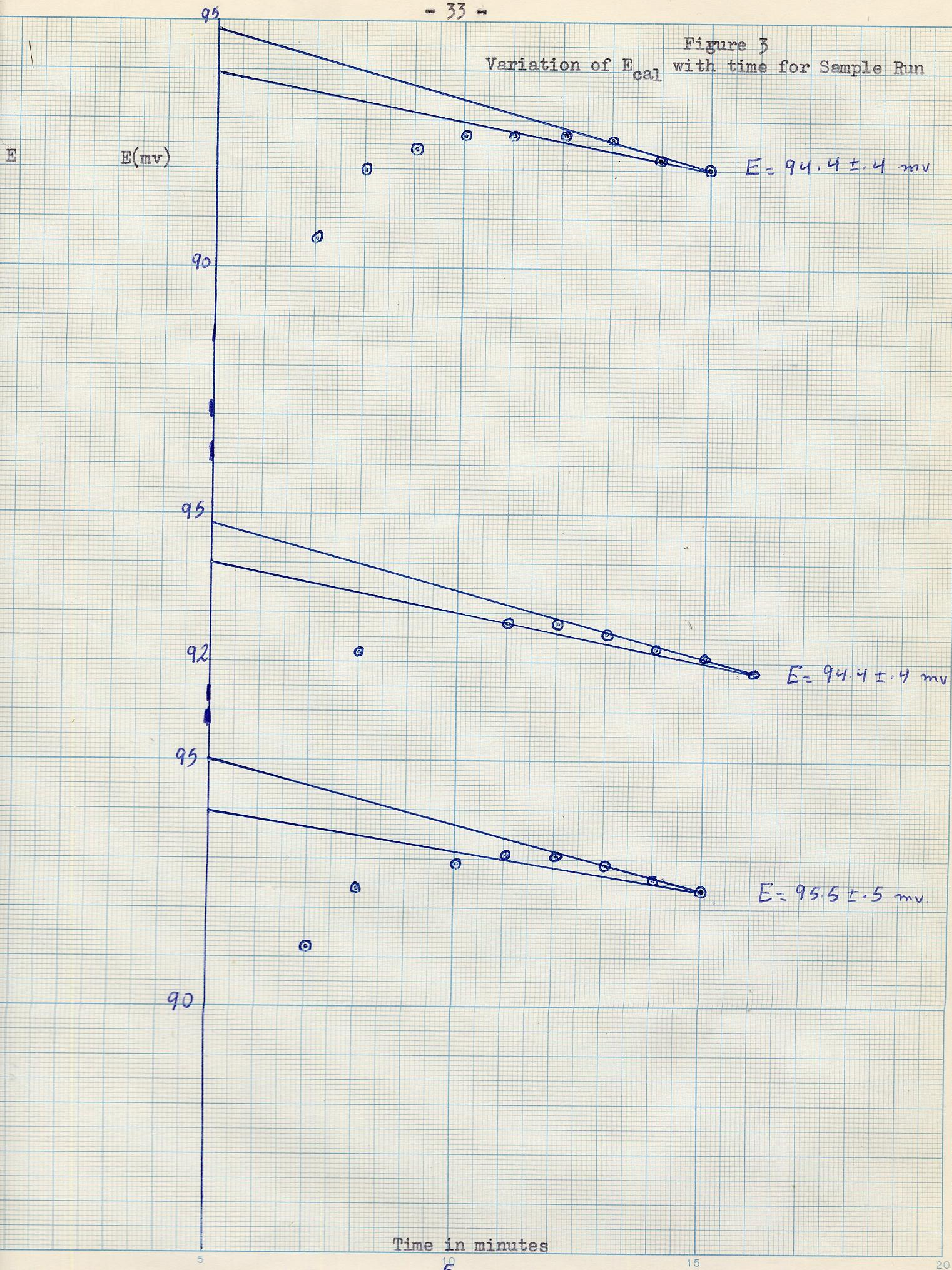
(3) Contribution of bridge: KCl diffusion contributes 0.002 M to I.

So,

Total I = 0.039 + 0.006 + 0.002 = 0.047 M.

Figure 3

Variation of $E_{cal}$ with time for Sample Run



LES PAPIERS CANSON _ FRANCE

## EXPERIMENTAL - EQUILIBRIUM CONSTANT

As in potentiometry, equilibrium work involved three steps:

I. Investigation of the conditions of experiment.

II. Preparation of stock solutions.

III. Measurement of equilibrium constants.

### I. Investigation of Conditions of Experiment:

#### A. Purity of Salts:

Standardization of Fe(II) and Fe(III) salts is as described above.

#### B. Equilibrium Mixture:

The method of formation of the tris-(pyridine 2-aldoxime)-iron(II) complex was described above. Once the complex was formed, it was put in buffer (pH 6-7) where it is stable for some time. $Fe(CN)_6^{3-}$ is also stable under these conditions. Usually, $K_3Fe(CN)_6$ solution was added to the buffer and the iron(II) complex was then added. When the order was reversed, i.e. when iron(II) complex was first added to the buffer and the ferricyanide solution was then added, there was no difference in the results.

As a test for reversibility, it was thought that the reverse reaction mixture (ferrocyanide and the iron (III) complex) should also be tried. Experimentally, however, this proved to be complicated possibly because of the instability and difficulty of formation of the iron(III) complex, and the test was abandoned.

#### C. Optical absorption of the four species involved:

The wavelength 515 mμ was chosen for measurements of absorbancy, A, since the iron(II) complex has a strong absorption maximum at this wavelength while the iron(III) complex has a much smaller A. As figure 2 shows, $10^{-4}$ iron(II) complex has A = 1.000 at pH 7, the value varying with pH in accordance with the ionization in equation (4), also shown in figure 1, while $10^{-4}$M iron(III) complex has A = 0.150 (which is constant in the pH range 6-7). Ferrocyanide of the same concentration has negligible absorbancy at 515 mμ.

$2.5 \times 10^{-4}$M ferricyanide has A = 0.004. The contribution was considered significant when $3.6 \times 10^{-4}$M ferricyanide was used, and in this case, 0.003 was subtracted from measured A values.

## II. Preparation of Stock Solutions:

### A. Buffers:

Prepared as described above.

### B. Ferrous Ammonium Sulfate Solutions:

Same salt used as in potentiometry. $H_2SO_4$ rather than $HClO_4$ was used in most solutions, and $H^+/Fe \sim 1$. Solutions were always $1.0 \times 10^{-3}$M.

### C. Ferric Ammonium Sulfate Solutions:

Same salt used as in potentiometry, and same procedure was followed. Concentration of solutions was $1.0 \times 10^{-3}$M.

### D. PAL Solutions:

A recrystallized sample was used for most optic experiments, and solutions of 0.05 M and 0.1 M in water were made.

### E. Potassium Ferricyanide Solutions:

$K_3Fe(CN)_6 \cdot 3H_2O$ of A.R. grade was used without further treatment. Four solutions were usually prepared to cover the range of concentration $0.5 - 4.0 \times 10^{-3}$M. The most concentrated solution was prepared by dissolving the required weight in the appropriate volume of water. ~~The~~

The other three solutions were prepared by dilution, and were kept in brown bottles. Fresh solutions were made daily.

### F. Tris-(pyridine 2-aldoxime)-Iron(II) Complex:

Same procedure was used as in potentiometry. PAL/Fe = 10 for most experiments, and in some cases PAL/Fe = 110.

### G. Tris-(Pyridine 2-Aldoxime)-Iron(III) Complex:

Same procedure and precautions as in potentiometry. PAL/Fe 110.

## III. Measurement of the Equilibrium Constant:

### A. Apparatus:

All absorbancy measurements were made on a Unicam S.P.500 spectrophotometer using glass cells. Water was circulated in the cell compartment from a water bath whose temperature was controlled by using a WACO tempunit to within ±0.1°C.

pH was usually measured on a mixture of the solutions used in a given run. The pH meter has been described above.

### B. Solutions:

Fresh stock solutions were prepared for each set of measurements. 8.0 ml buffer were transferred to each of a number of dry test tubes (usually six) which had been already cleaned and rinsed with redistilled deionized water. These test tubes were transferred to the thermostat and left to attain the constant temperature of the bath.

In one tube, 1.0 ml water + 1.0 ml freshly prepared 1.0 x $10^{-3}$M iron(II) complex solution are mixed, and the absorbance is read at 515 mμ. In another tube, 1.0 ml water + 1.0 ml freshly prepared iron(III) complex solution are mixed and A read. To each of the other four test tubes, 1 ml $Fe(CN)_6^{3-}$ of the specified concentration was added. Then 1 ml of the iron(II) complex was added, and A was read over a period of time.

The ionic strength was estimated from the ionic strength of the stock buffer taking its dilution into account. Contributions from the salts and acids can be shown to total about 0.002 M (see sample run below).

## C. Calculation of the Equilibrium Constant:

For the reaction given by equation (22), the equilibrium constant as given by equation $(23)'$ is:

$$K = [P(III)^0]\,[C(II)^{4-}] / [P(II)]\,[C(III)^{3-}]$$

Let A(II) and A(III) be the absorbancies of $1.0 \times 10^{-4}$M iron(II) and iron(III) complexes respectively, and let $C \times 10^{-4}$M stand for the initial concentration of $C(III)^{3-}$. Then, in any solution with absorbancy A, the concentrations of the species are:

$$[P(II)] = [HP(II)^0] + [P(II)^-] = \left\{(A - A(III))/(A(II) - A(III))\right\} \times 10^{-4} M.$$

$$[P(III)^0] = [C(II)^{4-}] = 10^{-4} \times (A(II) - A)/(A(II) - A(III))M$$

$$[C(III)^{3-}] = \frac{(C - A(II) - A)}{A(II) - A(III)} \times 10^{-4}$$

$$= \frac{C(A(II) - A(III)) - (A(II) - A)}{A(II) - A(III)} \times 10^{-4}M$$

Inserting these values in expression for K (equation 23'), we get:

$$K = \frac{(A(II) - A)^2}{(A - A(III))\,\{C(A(II) - A(III)) - (A(II) - A)\}} \qquad (37)$$

## D. Sample Run: Meaurement of Equilibrium Constant:

A sample run was chosen and is now discussed as representative of equilibrium constant measurements. All stock solutions, except the buffer, were freshly prepared. The following data were reported:

Date : September 6, 1961.

Conditions:

$T = 25.4 \pm 0.1^{\circ}C$, $I = 0.075$ M,

pH = 6.76, $\lambda = 515$ mμ.

Stock Solutions:

(1) Phosphate buffer: pH = 6.8, I = 0.084 M.

(2) Ferrous ammonium sulfate solution - 0.01 M: 0.3960 grms salt + 1 ml $H_2SO_4$(1N)/100 ml of solution.

(3) Ferric ammonium sulfate solution - 0.01 M: 0.4822 grms + 4 ml $H_2SO_4$(1N)/100 ml of solution.

(4) PAL solution - 0.05 M: 0.611 grms/100 ml of solution.

(5) Potassium ferricyanide solutions:

(a) $3.558 \times 10^{-3}$M: 0.1176 grms $K_3Fe(CN)_6.3H_2O$/100 ml of solution.

(b) $2.372 \times 10^{-3}$M: 66.6 ml of (a) diluted to 100 ml.

(c) $1.186 \times 10^{-3}$M: 50 ml of (b) diluted to 100 ml.

(d) $0.593 \times 10^{-3}$M: 50 ml of (c) diluted to 100 ml.

(6) Tris-(pyridine 2-aldoxime)-iron(II) complex- $1.0 \times 10^{-3}$M: 1.0 ml Fe(II)(0.01M) + 2.0 ml PAL(0.05 M) + 7.0 ml buffer.

(7) Tris-(pyridine 2-aldoxime)-iron(III) complex - $1.0 \times 10^{-3}$M: 1.0 ml Fe(III)(0.010M) + excess PAL + 9.0 ml buffer.

Solutions:

1. 1.0 ml Fe(II) complex + 8.0 ml buffer + 1.0 ml $H_2O$.
2. 1.0 ml Fe(III) complex + 8.0 ml buffer + 1.0 ml $H_2O$ .
3. 1.0 ml Fe(II) complex + 8.0 ml buffer + 1.0 ml ferricyanide (d).
4. 1.0 ml Fe(II) complex + 8.0 ml buffer + 1.0 ml ferricyanide (c).
5. 1.0 ml Fe(II) complex + 8.0 ml buffer + 1.0 ml ferricyanide (b).
6. 1.0 ml Fe(II) complex + 8.0 ml buffer + 1.0 ml ferricyanide (a).

Experimental Results:

The absorbancy (A) of each of the above solutions was read at 515 mu. A for solutions 3, 4, 5 and 6 was followed with time and extrapolated to t = 0 as shown in figure 4. In case of solution 6, 0.003 was subtracted from A as has been explained above. The results are:

| Solution | A | K (equation 23') |
|---|---|---|
| 1 | 0.950 | - |
| 2 | 0.150 | - |
| 3 | 0.690 | 0.585 |
| 4 | 0.566 | 0.624 |
| 5 | 0.448 | 0.606 |
| 6 | 0.384 | 0.629 |
| | | Mean K = 0.611 ± 0.015 |

Here, K was calculated using equation (23'), A(II) = 0.950, A(III) = 0.150, and A = 0.690, 0.566, 0.448 and 0.384 for solutions 3, 4, 5, and 6 respectively. The pH of a mixture of the above solutions was measured on pH meter standardized against 0.05 M KHphthalate at 25.4°C.

Estimation of I:

1. Buffer: 10 ml equilibrium mixture contains 8 ml buffer and 1 ml Fe Fe(II) complex which was made with 7 ml buffer in 10 ml solution. Hence, for buffer of original I = 0.084 M, net contribution to $I = (0.084 \times 7/10 \times (1/10) + (0.084 \times 8/10) = 0.073$ M.
2. Ions: $NH_4^+$ and $SO_4^{2-}$, net contribution estimated as described under potentiometry is 0.001 M.
3. Contribution of ferro- and ferricyanides:

   For $1.0 \times 10^{-4}$M $K_3Fe(CN)_6$, $I = \frac{1}{2}(3 \times 1^2 + 1 \times 3^2) \times 10^{-4} = 0.0006$ M.

For $1.0 \times 10^{-4}$M $K_4Fe(CN)_6$, $I = \frac{1}{2}(4 \times 1^2 + 1 \times 4^2) \times 10^{-4} = 0.001$ M.

In the reaction mixture, both are present to a different extent. I = 0.001 M was taken as an average contribution.

So,

Total I = 0.073 + 0.001 + 0.001 = 0.075 M.

Calculation of $K_T$:

At the conditions of this experiment $pK_3 = 6.99^2$ (equation 10'), then using equation (25), the pH independent value for the equilibrium constant is

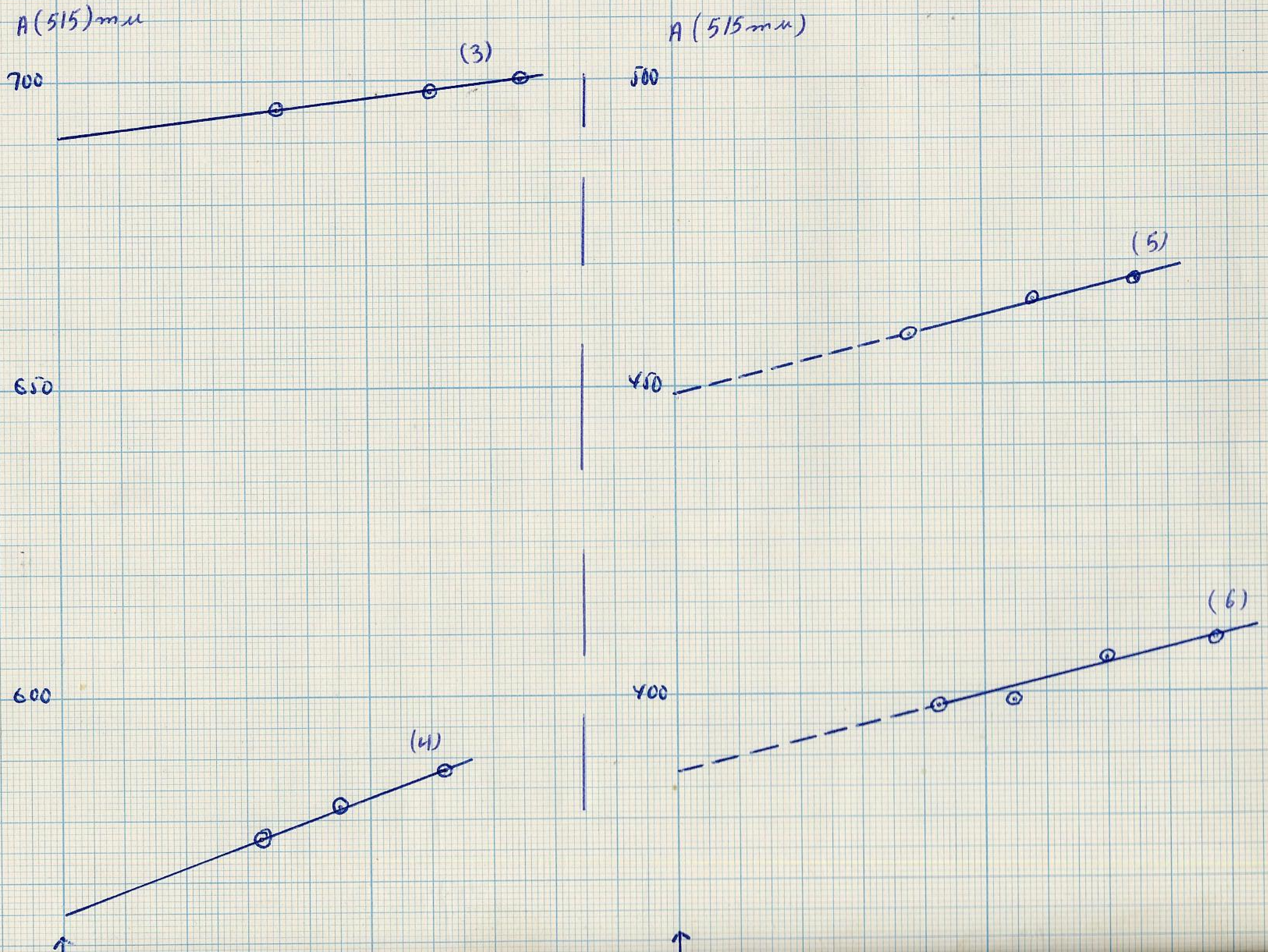
$$K_T = K . \frac{K_3 + h}{K_3}$$

$$= 0.611 \times \frac{(10.23 + 17.4) \times 10^{-8}}{(10.23) \times 10^{-8}} = 1.65 \pm 0.045$$

Figure 4

Variation of A with Time for Sample Run

(equilibrium measurements)



## RESULTS - POTENTIOMETRY

Following the procedure described above, the redox potential for the tris-(pyridine 2-aldoxime)-iron(III)/iron(II) system was measured over a range of pH, ionic strength, and temperature.*

The variation of E with pH (pH range 6.0-7.5) at 25°C and I = 0.047 M is sammarized in table 1, with the pH independent redox potential, $E_T$, calculated in each case using equation (16). The results are also illustrated in figure 5 where the E values are plotted vs. pH. The figure shows that at pH 8, the value of E approaches the pH independent value $E_T$ (0.332 v. at 25° and I = 0.047 M), and that at pH 6 the variation of E with pH becomes linear with a slope approaching the theoretical slope of -0.0592.

The variation of E with ionic strength (I = 0.08 - I = 0.004 M) at 25°C is summarized in table 2 which also gives the calculated values of $E_T$ (equation 16). A plot of $E_T$ vs. $fn(I) = ((I^{\frac{1}{2}}/1 + I^{\frac{1}{2}}) - 0.30\ I)$. is shown in figure 6. Linear extrapolation of the results to zero ionic strength gives the value of the thermodynamic pH independent redox potential $E_T^0 = 0.341 \pm 0.002$ v. at 25°C.

It is to be noted that the above slope is about +0.055 whereas the expected theoretical limiting slope should be +0.0296 (equation 18'). As shown in figure 6, it is possible to draw a smooth curve through the experimental points with the theoretical limiting slope yielding a

---

* Values for the standard potential of the saturated calomel electrode, as well as for RT/F, were taken from Bates[11]. Values of $K_3$ (equation 10') at various ionic strengths and temperatures were obtained from the work of Hanania and Irvine[2].

value of $E^0_T$ about 0.334 v. instead of 0.341 v. This anomaly is commented on in the Discussion.

The variation of redox potential E with temperature was measured within the range 15° to 30°C, at I = 0.047 M and pH values between 6.78 and 6.83. The results are given in table 3 which also gives the calculated values of the pH independent redox potential $E_T$ (equation 16). In figure 7, the four values of $E_T$ are plotted against temperature and it can be seen that the variation is linear with a slope $dE/dT = -(2.28 \pm 0.16) \times 10^{-3}$ volt/deg. which may be assumed to be the value of $dE^0_T/dT$ (see page 10).

The thermodynamic quantities (at 25° and I = 0) for the cell reaction (equation 6) may now be summarized as follows:

$E^0_T$ = 0.341 (± 0.002) volt.

$\Delta G^0 = -nFE^0_T = -7.86$ (± 0.02) kcal/mole.

$\Delta H^0$ (equation 19) = −23.5 (± 1.1)kcal/mole.

$\Delta S^0$ (equation 20) = −52.6 (± 3.7) e.u.

## Table I

Variation of E (equation 16) with pH for the Tris(pyridine 2-aldoxime)-iron(III)/iron(II) System

T = 25.0 ± 0.1°C, I = 0.047 M,

PAL/Fe = 36, $K_3 = 9.55 \times 10^{-8}$ (ref.2 & eq. 10')

| pH | Ecal(mv) | Correction term (mv)* | E (mv) | $0.059\frac{K_3 + h}{K_3}$mv | $E_T$(mv) |
|---|---|---|---|---|---|
| 7.45** | 74.7 ± .6 | 19.3 | 338.4 | 8.0 ± .4 | 330.4 ± 1.0 |
| 7.30 | 78.5 ± .5 | 19.3 | 342.2 | 10.8 ± .4 | 331.4 ± 0.9 |
| 7.20 | 80.7 ± .2 | 19.3 | 344.4 | 12.8 ± .4 | 331.6 ± 0.6 |
| 6.97*** | 105.5 ± .4 | 1.3 | 349.9 | 19.3 ± .6 | 331.9 ± 1.0 |
| 6.96 | 87.0 ± .2 | 19.3 | 350.7 | 19.6 ± .6 | 331.1 ± 0.8 |
| 6.87 | 91.0 ± .3 | 19.3 | 354.7 | 22.7 ± .7 | 332.0 ± 1.0 |
| 6.79 | 94.4 ± .4 | 19.3 | 358.0 | 25.5 ± .7 | 332.6 ± 1.1 |
| 6.71 | 97.6 ± .6 | 19.3 | 361.3 | 28.6 ± .8 | 332.7 ± 1.4 |
| 6.50 | 106.5 ± .5 | 19.3 | 370.2 | 37.5 ± .9 | 332.7 ± 1.4 |
| 6.45*** | 125.9 ± .5 | 1.3 | 371.6 | 39.8 ± .9 | 331.8 ± 1.4 |
| 6.25 | 119.0 ± 1.0 | 19.3 | 382.7 | 49.6 ± 1.0 | 331.1 ± 2.0 |
| 6.05 | 127.7 ± .6 | 19.3 | 391.4 | 60.0 ± 1.0 | 331.4 ± 1.6 |
|  |  |  |  | Mean $E_T$ = | 331.9 ± 1.2 |

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* See p. 17.

** I = 0.055 M, $K_3 = 9.77 \times 10^{-8}$.

*** PAL/Fe = 100.

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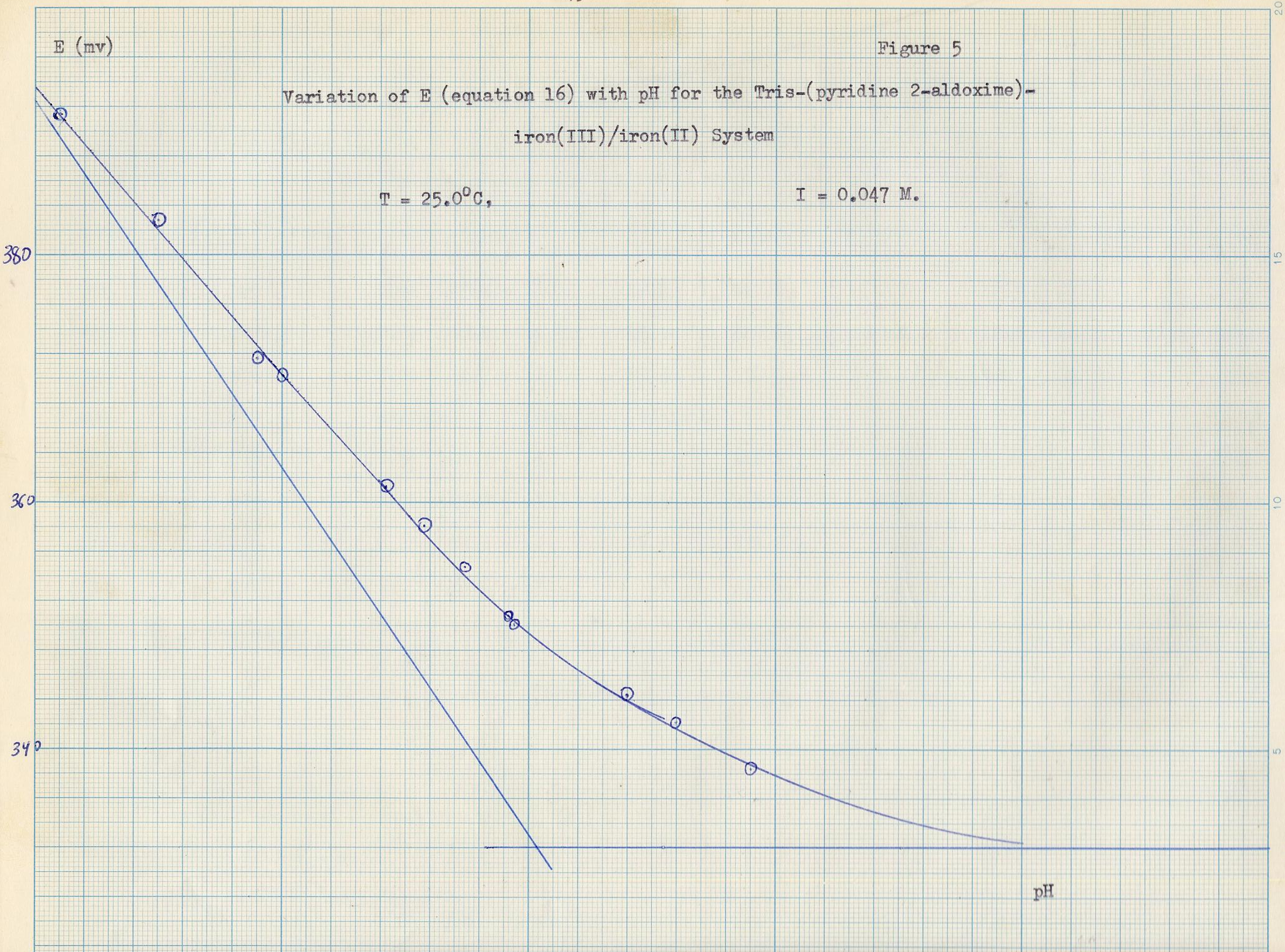
Figure 5

Variation of E (equation 16) with pH for the Tris-(pyridine 2-aldoxime)-iron(III)/iron(II) System

T = 25.0°C, I = 0.047 M.



## Table 2

Variation of $E_T$ with I for the Tris-(pyridine 2-aldoxime)-iron(III)/iron(II) System

$T = 25.0 \pm 0.1^{\circ}C$, PAL/Fe = 36.

| I (M) | $(I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})) - .3I$ | pH | $E_{cal}$ (mv) | Correction term (mv)* | E (mv) | $K_3 \times 10^8$ ** | $.059 \log \frac{K_3 + h}{K_3}$ | $E_T$ (mv |
|---|---|---|---|---|---|---|---|---|
| .079 | 0.195 | 7.22 | 77.5 ± .5 | 19.3 | 341.2 | 10.7 | 11.5 ± .4 | 329.7 ± |
| .059 | 0.179 | 7.20 | 80.8 ± .4 | 19.3 | 344.5 | 10.0 | 12.8 ± .4 | 331.7 ± |
| .055 | $0.73_5$ | 7.45 | 74.7 ± .6 | 19.3 | 338.4 | 9.77 | 8.0 ± .4 | 330.4 ± |
| .047 | 0.164 | average | from | table 1 | | | | 331.9 ± |
| .040 | 0.155 | 6.58 | 102.7 ± .4 | 19.3 | 366.4 | 9.33 | 34.4 ± .8 | 332.0 ± |
| .025 | $0.129_5$ | 6.91 | 89.4 ± .3 | 19.3 | 353.1 | 8.91 | 22.3 ± .8 | 330.8 ± |
| .020 | 0.118 | 6.88 | 94.5 ± .4 | 19.3 | 358.2 | 8.71 | 23.7 ± .7 | 334.5 ± |
| .0095 | 0.087 | 6.62 | 124.4 ± .4 | 1.3*** | 370.1 | 8.51 | 34.4 ± .8 | 335.7 ± |
| .004 | $0.058_5$ | 6.18 | 131.2 ± .2 | 19.3 | 394.9 | 8.32 | 56.3 ± 1 | 338.6 ± |
| .004 | $0.058_5$ | 6.33 | 121.9 ± .3 | 19.3 | 385.6 | 8.32 | 48.6 ± 1 | 337.0 ± |

* See p. 17.

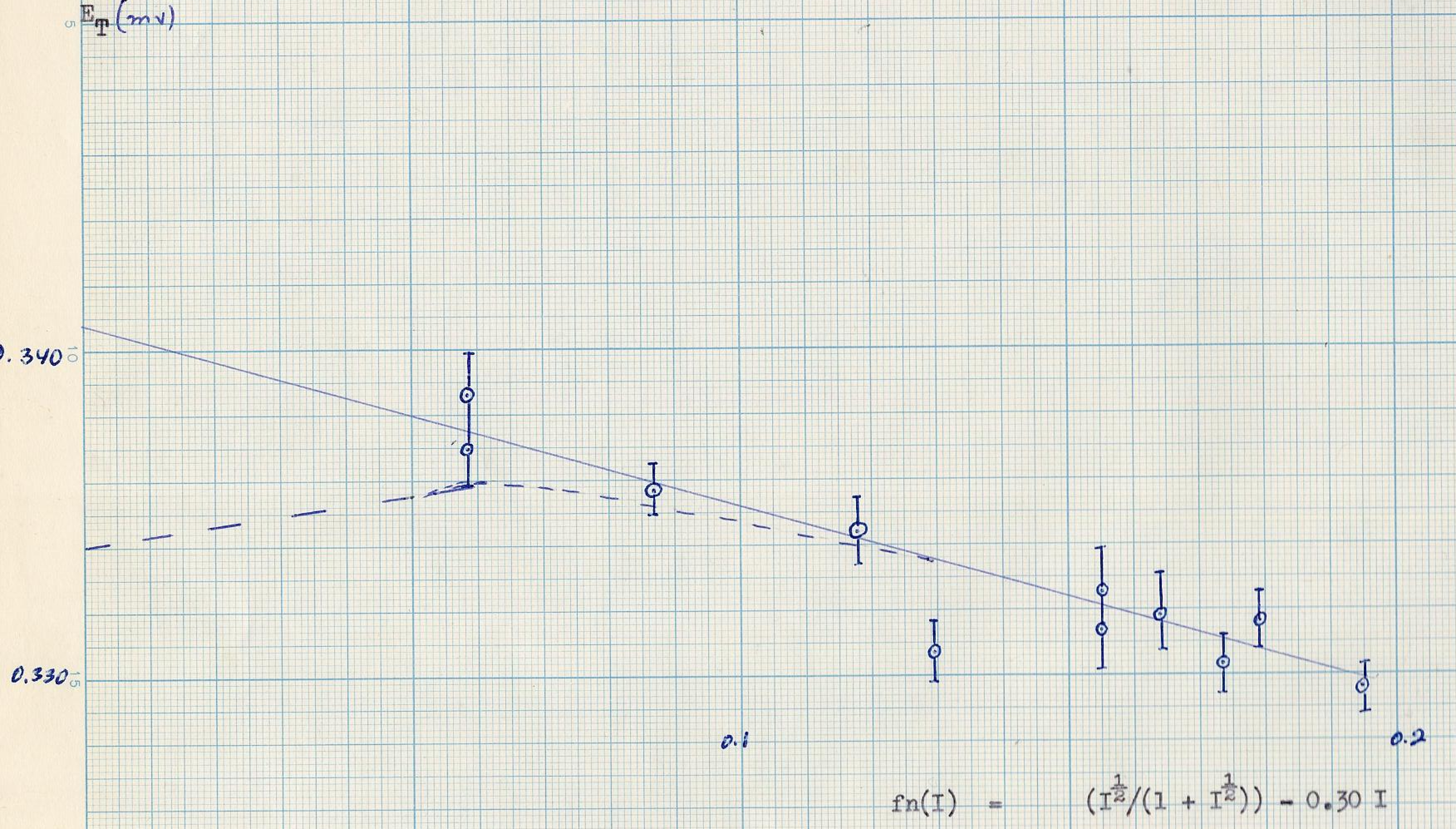
** Reference (2) and equation (10').

*** PAL/Fe = 100.

Figure 6

Variation of $E_T$ with I for the Tris-(pyridine 2-aldoxime)iron(III)/iron(II) System

T = 25°C.



## Table 3

Variation of $E_T$ with T for the Tris-(pyridine 2-aldoxime)-iron(III)/iron(II) System

I = 0.047 M, $K_3 = 9.55 \times 10^{-8}$ [*], PAL/Fe = 36.

| T(°C) | pH | $E_{cal}$(mv) | Correction term (mv) [**] | E (mv) | .059 log ($K_3$ + h/$K_3$)(mv) | $E_T$ (mv) |
|---|---|---|---|---|---|---|
| 15.0 | 6.83 | 109.2 ± .4 | 19.3 | 379.3 | 23.9 ± .7 | 355.4 ± 1.1 |
| 20.0 | 6.81 | 101.8 ± .5 | 19.3 | 368.7 | 24.7 ± .7 | 344.0 ± 1.2 |
| 25.0 | 6.79 | 94.4 ± .4 | 19.3 | 358.1 | 25.5 ± .7 | 332.6 ± 1.1 |
| 30.0 | 6.78 | 86.1 ± .5 | 19.3 | 347.1 | 25.9 ± .8 | 321.2 ± 1.3 |

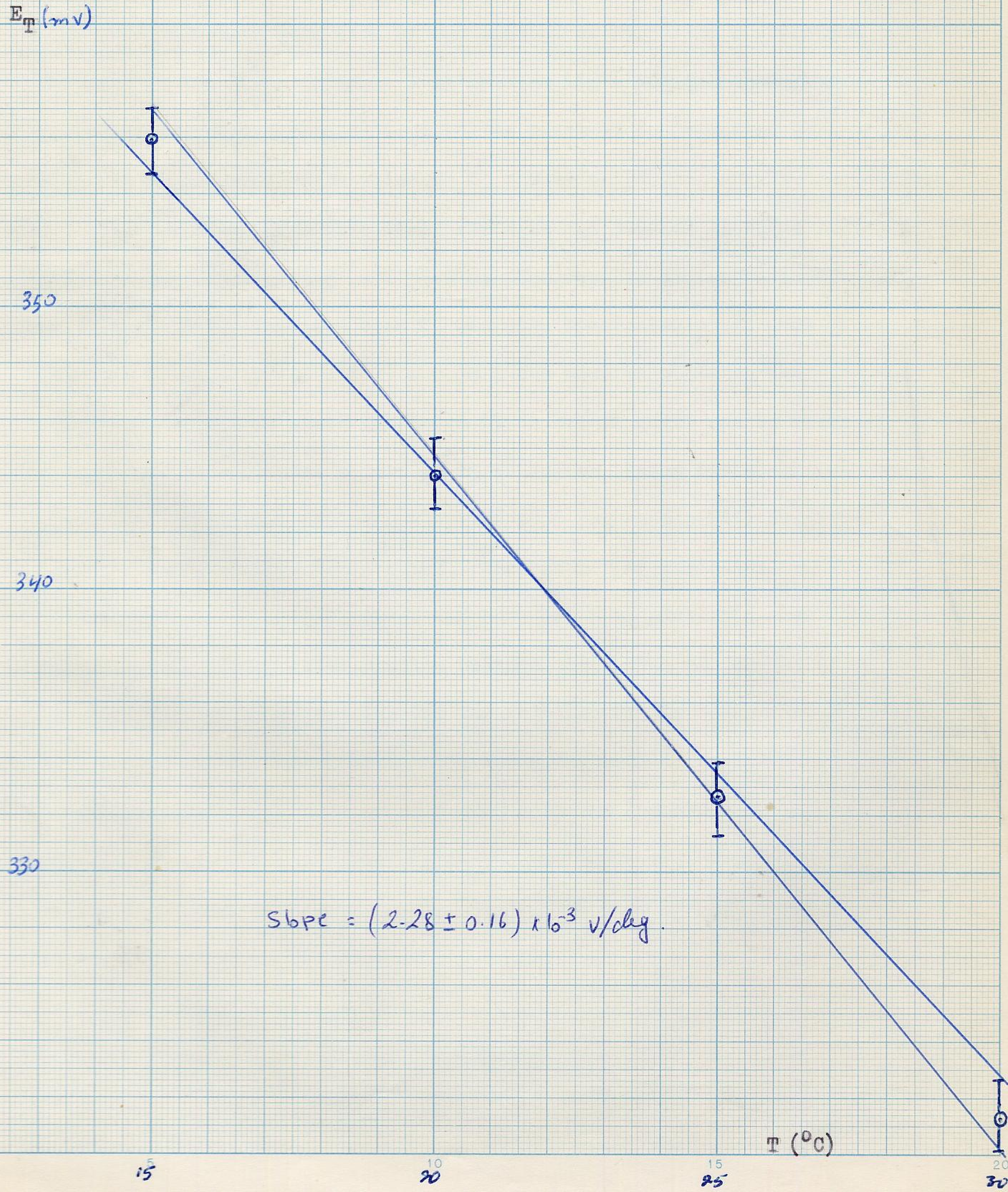
[*] Reference (2) and equation (10').

[**] See p. 17.

Figure 7

Variation of $E_T$ with T for the Tris-(pyridine 2-aldoxime)-iron(III)/iron(II) System

I = .047 M.



Slope = $(2.28 \pm 0.16) \times 10^{-3}$ v/deg.

## RESULTS - EQUILIBRIUM CONSTANT

The procedure described above for the meaurement of the equilibrium constant K (equation 23') was followed over a range of pH, ionic strength, and temperature.

The variation of K with pH was studied at 25.4° and I = 0.058 M. The results are given in table 4 which also lists the corresponding values of the pH independent equilibrium constant $K_T$ (equation 25), yielding a (constant) mean value of $K_T = 1.49 \pm .12$.

The variation of K with ionic strength was studied at three temperatures: 15.0°, 25.4° and 35.0°C. The results are summarized in tables 5 & 6. In every case $K_T$ has also been calculated. The function $fn(I) = (I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})) - 0.30\ I$ was used in plotting the values of log $K_T$, as shown in figure 8. A smooth curve can be drawn through the experimental points at 25.4° and on linear extrapolation along the theoretical limiting slope of +3.0 (equation 26'') it gives $\log K_T^o = \bar{1}.680$ or $K_T^o = 0.48_0 \pm .03$. The results at the other temperatures cover a small range and have not been similarly extrapolated. Using interpolation between the curves at the three temperatures, an average value for the enthalpy of the reaction can be obtained in the region of I 0.06 where the mean $d(\log K_T/dT = -0.0092(\pm 0.0015)\ deg^{-1}$ and consequently mean $\Delta H$ (equation 29) = $-3.74(\pm .61)$ kcal/mole. This may be assumed to be approximately equal to the value $\Delta H^o$ at I = 0. Again interpolating to get the results at 25.0° we have:

$$K_T^o = 0.483\ (\pm .03).$$

$$\Delta G^o = 0.432\ (\pm .027)\ \text{kcal/mole}.$$

$\Delta H^0 = -3.74\ (\pm .61)$ kcal/mole.

$\Delta S^0 = -14.0\ (\pm 2.0)$ e.u.

The above results may now be used to get the value of the redox potential $E^0_T$ for the tris-(pyridine 2-aldoxime)-iron(III)/iron(II) complex. Using the data for the hexacyanoferrate(III)/(II) system[7], for which $E^0$ ($25^0$ and I = 0) = $0.362(\pm .0015)$ volt, $\Delta H^0_1 = -27.0(\pm .3)$ kcal/mole, and $\Delta S^0_1 = -62.6(\pm 1.1)$ e.u., we get

$\Delta G^0_1$ (equation 31) = $-8.35(\pm .03)$ kcal/mole.

$\Delta G^0_2$ (equation 32) = $\Delta G^0_1 - \Delta G^0 = -nFE^0_T$

$= -8.78(\pm .05)$ kcal/mole

$E^0_T$ (equation 36) = $0.381(\pm .002)$ volt.

$\Delta H^0_2 = \Delta H^0_1 - \Delta H^0$

$= -23.3(\pm 1.1)$ kcal/mole

$\Delta S^0_2 = -48.6(\pm 3.1)$ e.u.

These results correspond to the values which were determined potentiometrically, and the two sets of results are given below for the reaction: $P(III)^0 + \frac{1}{2}H_2 = P(II)^- + H^+$

| | Potentiometry | Equilibrium |
|---|---|---|
| $E^0_T$ (volt) | $0.341(\pm .002)$ | $0.381\ (\pm .002)$ |
| $\Delta H^0 = \Delta H^0_1$ (kcal/mole) | $-23.5\ (\pm 1.1)$ | $-23.3\ (\pm 1.1)$ |
| $\Delta S^0 = \Delta S^0_1$ (e.u.) | $-52.6\ (\pm 3.7)$ | $-48.6\ (\pm 3.1)$ |

## Table 4

Variation of K (equation 23') with pH

$T = 25.4 \pm 0.1^{\circ}C$, $I = 0.058$ M,

PAL/Fe = 10, $K_3 = 9.77 \times 10^{-8}$ *

| pH | K | $K_T$ (equation 25) |
|---|---|---|
| 6.13 | 0.165 ± .007 | 1.42 ± .06 |
| 6.49 | 0.320 ± .012 | 1.39 ± .05 |
| 6.76 | 0.544 ± .029 | 1.47 ± .08 |
| 6.93 | 0.737 ± .032 | 1.62 ± .07 |
| 7.07 ** | 0.825 ± .010 | 1.54 ± .02 |
| | Mean K = | 1.49 ± .12 |

* Reference (2) and equation (10').

** PAL/Fe = 100.

## Table 5

Variation of K (equation 23') with I

$T = 25.4 \pm .1^{\circ}C$, PAL/Fe = 10.

| I (N) | pH | K | $(I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})) - .3\ I$ | $10^8 K_3$ ** | $K_T$ | $\log K_T$ |
|---|---|---|---|---|---|---|
| .006* | 6.92 | .316 ± .018 | 0.070 | 7.95 | $0.79_5$ ± .05 | $\bar{1}.900$ ± .027 |
| $.009_5$* | 7.00 | .409 ± .001 | 0.086 | 8.13 | 0.91 ± .002 | $\bar{1}.959$ ± .010 |
| .017* | 7.01 | .458 ± .015 | 0.109 | 8.51 | $0.98_5$ ± .03 | $\bar{1}.993$ ± .013 |
| .025 | 6.83 | .420 ± .012 | 0.129 | 8.66 | 1.26 ± $.03_5$ | 0.100 ± .014 |
| .0316* | 6.96 | .653 ± .038 | $0.141_5$ | 8.80 | 1.47 ± $.08_5$ | 0.167 ± .024 |
| .058 | (average | from table 4) | 0.177 | 9.77 | 1.49 ± .12 | 0.173 ± .035 |
| .062* | 6.84 | .594 ± .027 | 0.182 | 10.0 | 1.40 ± .064 | 0.146 ± .018 |
| .075 | 6.76 | .611 ± .015 | $0.192_5$ | 10.23 | 1.65 ± .04 | 0.217 ± .010 |
| .112 | 6.70 | .719 ± .020 | 0.217 | 11.2 | 2.00 ± $.05_5$ | 0.301 ± .012 |

* PAL/Fe = 110

** Reference (2) and equation (10').

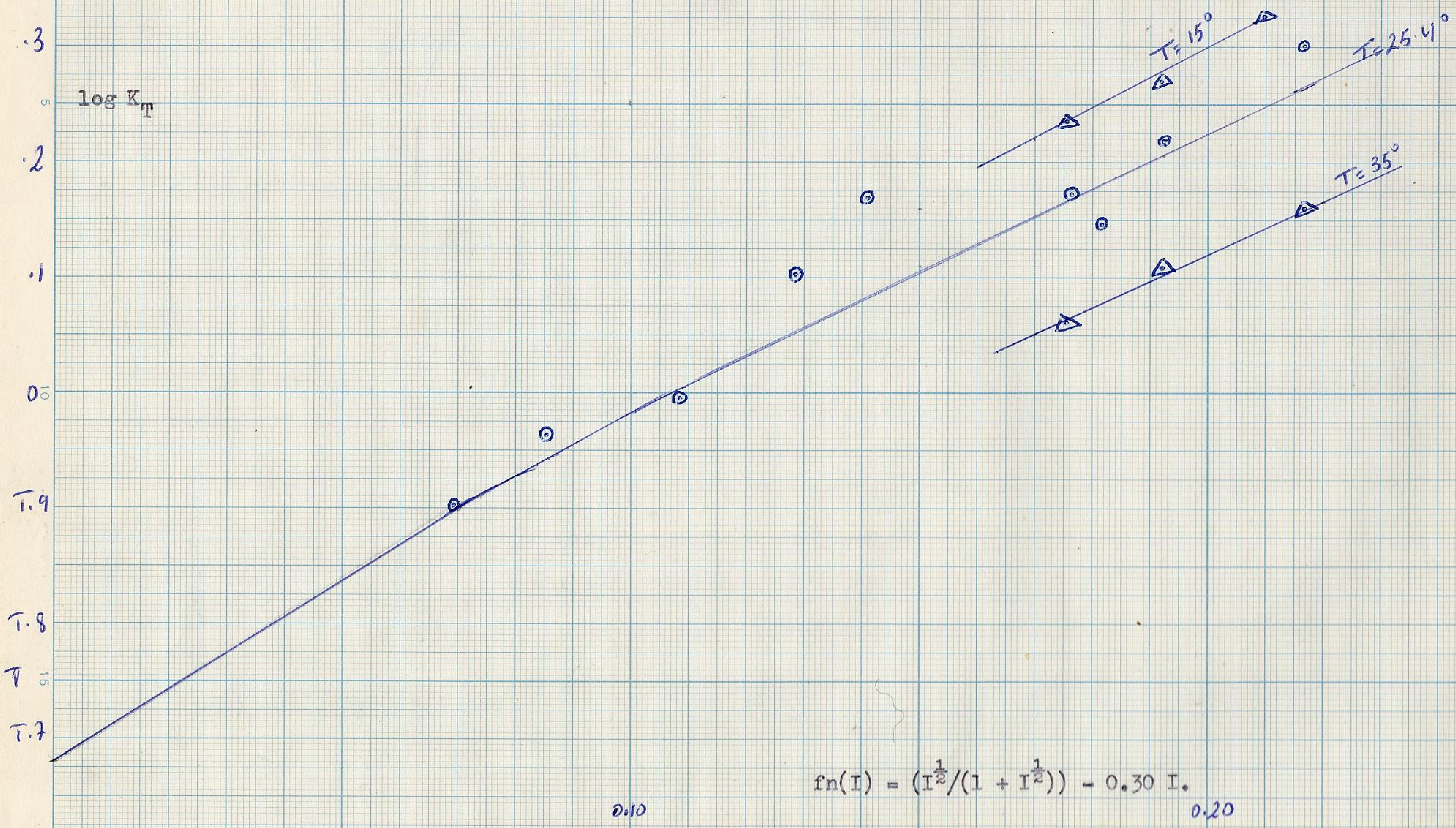
## Table 6

Variation of K (equation 23') with I

| $T(^{o}C)$ | I(M) | pH | K | $(I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})) - .3\ I$ | $K_T$ | $\log K_T$ |
|---|---|---|---|---|---|---|
| 35.0 | .112 | 6.77 | .59 ± .02 | .217 | 1.45 ± .05 | .162 ± .016 |
| 35.0 | .075 | 6.76 | .49 ± .01 | $.192_5$ | 1.29 ± .03 | .110 ± .011 |
| 35.0 | .057 | 6.75 | .42 ± .03 | .176 | 1.15 ± .07 | .060 ± .025 |
| 15.0 | .100 | 6.83 | .89 ± .06 | .210 | 2.12 ± .15 | .326 ± .030 |
| 15.0 | .075 | 6.81 | .73 ± .03 | $.192_5$ | 1.87 ± .06 | .272 ± .015 |
| 15.0 | .057 | 6.80 | .64 ± .02 | .176 | 1.71 ± .06 | .234 ± .016 |

Figure 8

Variation of K with I at 35.0, 25.4, and 15°C.



## DISCUSSION

The work described in this thesis has shown that the cell reaction of equation (6):

$$P(III)^0 + \frac{1}{2}H_2 = P(II)^- + H^+$$

is characterized by a redox potential which is of the same order of magnitude as that of the hexacyanoferrate (III)/(II) system, and by a favorable (large negative) enthalpy change but an unfavorable (large negative) entropy change. Table 7[7] summarizes available thermodynamic data on complex ions and includes the above results. Inspection of the table shows that the enthalpy and entropy changes are characteristic, but that the other complexes with nitrogen heterocyclic ligands have a much higher redox potential. It is interesting to consider the significance for this.

The stabilization of oxidation states of transition metal ions through complex formation is well known. Reference to table 7 shows that the redox potential of the $Fe(III)^{3+}/Fe(II)^{2+}$ system, which is 0.771 volt, may be either increased or decreased upon formation of complex ions. In general anionic ligand like $CN^-$, $F^-$ and $PO_4^{3-}$ reduces the value of E; that is, they stabilize iron in its higher oxidation state and make the Fe(III) complex a weaker oxidizing agent than $Fe^{3+}$ aquo ions. On the other hand, the nitrogen heterocyclic ligands like phenanthroline and 2,2'-dipyridyl increase redox potential to about 1 volt; that is, they stabilize iron in its lower oxidation state and make the Fe(III) complex a stronger oxidizing agent than $Fe^{3+}$ aquo ions.

On the above basis, one can easily account for the fact that

## Table 7

Comparative Thermodynamic Data (at 25$^0$ and zero ionic strength) on some Redox Equilibria

for some Complex Ions

| | | $E^0$ (volt) | $\Delta H^0$ kcal/mole | $\Delta S^0$ e.u. | $S^0(II) - S^0(III)$ e.u. |
|---|---|---|---|---|---|
| (a) | $Fe^{3+}$ aq. + $\frac{1}{2}H_2$ = $Fe^{2+}$ aq. + $H^+$ | 0.771 | -9.95 | 26.4 | 42.0 |
| (b) | $Fe(CN)_6^{3-} + \frac{1}{2}H_2 = Fe(CN)_6^{4-} + H^+$ | 0.362 | -27.0 | -62.6 | -47.0 |
| (c) | $Fe(CN)_4dipy^{\ 1-} + \frac{1}{2}H_2 = Fe(CN)_4\ dipy^{\ 2-} + H^+$ | 0.542 | -27.4 | -50.0 | -34.4 |
| (d) | $Fe(dipy)_3^{\ 3+} + \frac{1}{2}H_2 = Fe(dipy)_3^{\ 2+} + H^+$ | 1.120 | -32.7 | -23.2 | - 7.6 |
| (e) | $Fe(dipy(CH_3)_2^{\ 3+} + \frac{1}{2}H_2 = Fe\ dipy(CH_3)_2^{\ 2+}$ | 0.941 | -26.8 | -17.1 | - 1.5 |
| (f) | $Fe(phen)_3^{\ 3+} + \frac{1}{2}H_2 = Fe(phen)_3^{\ 2+} + H^+$ | 1.147 | -32.7 | -20.8 | - 5.2 |
| (g) | $Fe(PAO)_3^{\ 0} + \frac{1}{2}H_2 = Fe(PAO)_3^{\ -1} + H^+$ | 0.341 | -23.5 | -52.6 | -37.0 |
| (h) | $Ru(dipy)_3^{\ 3+} + \frac{1}{2}H_2 = Ru(dipy)_3^{\ 2+} + H^+$ | 1.374 | -36.3 | -15.8 | - 0.2 |

the redox potential is low for the PAL complex. For, if the ligand is regarded as a simple anion $(PAO)^-$, its effect would be like that of the above anions, hence the lower redox potential. However, if we consider the ligand to be of the dipyridyl type, we must take the ionization of the oxime groups into account. It can be shown that the redox potential for the system involving unionized PAL, $Fe(PAOH)_3^{3+}/Fe(PAOH)_3^{2+}$, is related to the redox potential of the triply ionized system by the equation

$$E_0^0 = E_T^0 + (RT/F)\ln(1 + h/K_3 + h^2/K_3K_2 + h^3/K_3K_2K_1)$$

where $K_1$, $K_2$, $K_3$ are the successive ionization constants in the complex (equations 2, 3, 4). Taking $K_3 \sim 10^{-7}$, $K_2 \sim 3 \times 10^{-4}$ and assuming $K_1 \sim 10^{-1}$, we get the hypothetical redox potential for the system $Fe(PAOH)_3^{3+}/Fe(PAOH)_3^{2+}$ at $h = 1$, $E_0^0 \sim 1.0$ volt, which is of the order of magnitude expected for neutral ligands of this type.

Viewed thermodynamically, redox potentials are free energies and are therefore determined by the two factors: enthalpy and entropy. Martell and Calvin (1952)[12] give a general interpretation of the stabilization of oxidation states for complex ions along the following lines. In anionic complexes, the entropy factor is unfavorable because the reduced complex ion carries a higher (negative) charge and therefore restricts the degrees of freedom of solvent molecules in the vicinity of the ion to a greater extent than the oxidized form. This effect tends to decrease redox potentials. On the other hand, the electron-pairing factor is favorable ($\Delta H$ negative for strong bonding), and this tends to increase redox potentials. Martell and Calvin assume that in anionic complexes the entropy factor predominates, and so they conclude that the net result is a decrease in redox potential.

This interpretation may be applied to the case of the PAL complexes. Thus, from table 7 we can see that $\Delta S^0$ for the cell reaction involving the PAL complexes is about 78 e.u. lower than that for the $Fe^{3+}/Fe^{2+}$ system, whereas $\Delta H^0$ is lower by 14 kcal/mole. Since 78 e.u. correspond to about 26 kcal/mole, it is clear that the entropy factor predominates. This interpretation also applies to the hexacyanoferrate(III)/(II) system.

In the case of the o-phenanthroline and similar complexes, Martell and Calvin state that only the electron pairing effect is important[12]. However, the data in table 7 shows that both factors are important but that the energy factor predominates thereby increasing the redox potential over that of $Fe^{3+}/Fe^{2+}$.

Emeleus and Anderson (1960)[13] give their interpretation in terms of heats of hydration and bond formation and assume that the various free energy changes are likely to be dominated by the heat terms $\Delta H$. That is, stabilization is said to be determined by the difference in the equilibrium constants for the substitution of $H_2O$ by ligand molecules in the complexes of the two oxidation states. Furthermore, of the various terms, the most important factor is likely to come from differences in binding energy of the ligand derived from the two oxidation states. In general, ligands with strong $\sigma$-bond donor properties favor the stability of the higher oxidation state, and ligands with $\pi$-bond acceptor properties but weaker $\sigma$-bond donor properties favor the stability of the lower oxidation state (at least with elements having 3 or more electrons in the $d_\varepsilon$ triplet of orbitals, as in the case with iron).

The detailed interpretation of stability of oxidation states in solution is of course more complicated as it should take into account the ligand-field strength and splitting energies of the d orbitals in the metal as well as entropy considerations.

The importance of entropy considerations can be seen in another way. Thus the last column in table 7 gives the difference between the partial molal entropies of the complex ion in its two oxidation states. This difference is related to the entropy change for the cell reaction by the equation:

$$\begin{aligned}\Delta S^{o} &= \bar{S}^{o}(II) - \bar{S}^{o}(III) + \bar{S}^{o}(H^{+}) - \tfrac{1}{2}\bar{S}^{o}(H_2)\\ &= \bar{S}^{o}(II) - \bar{S}^{o}(III) - 15.6 \quad \text{e.u.}\end{aligned}$$

It can be seen that there is no simple relation between the charges on the complex ions and the partial molal entropy differences. Clearly, the chemical nature of the ligand, as well as its charge and size determine the partial molal entropy of an ion. Entropy effects cannot therefore be ignored in the discussion of the thermodynamics of complex ions.

Another interesting respect of the results is the apparent discrepancy between the value of the redox potential as determined potentiometrically ($E^{o} = 0.341$ v.) and that from equilibrium constant meaurements ($E^{o} = 0.381$ v.). Considering that the chemistry of the reaction has been well established[2], reproducibility and internal consistency all carefully checked, and precision being better than ± 2 mv. on each result, it may seem odd that the results should vary by so much. There are three possible lines of explanation for this discrepancy:

(1) The Rhodium Electrode: In the preliminary experiments, rhodium

was found to give quicker response and more stable potentials, but it gave values which were 30-40 mv. lower than the bright platinum electrode (see page 21). It was decided to use rhodium in the meaurements, since both Pt and Rh are well known inert electrodes and Rh has already been used successfully for complex ions[8]. It is interesting that this difference of 30-40 mv. is about the same as the discrepancy in the results. This is clearly a matter which should be further checked, especially in view of the fact that the experimental E values did not show the expected limiting Debye-Huckel dependence on ionic strength (see figure 6).

(2) The Hexacyanoferrate System: In the equilibrium experiments the concentrations of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ were about $10^{-4}$ M each. It is known that the ions undergo aquatisation, that $Fe(CN)_6^{4-}$ is photosensitive to U.V. light, and that autoxidation of $Fe(CN)_6^{4-}$ in very dilute solutions is appreciable. These difficulties might be thought to have affected the equilibrium results. However, internal consistency and reproducibility were good and so it is not likely that this factor was significant under the conditions of these experiments.

(3) Ion Association: It is now generally recognized that ion association occurs in solutions of electrolytes, and that the simple Debye-Huckel treatment of activity coefficients does not apply to the case of large (complex) ions or to multivalent ions even in dilute solutions. Bjerrum (1926 was the first to propose ion-pair formation as one cause for deviation from Debye-Huckel behavior. Davies, in his recent book[10], has reviewed the evidence and the ideas on this subject. Davies's empirical equation for activity coefficients:

$$-\log f_{\pm} = 0.50\ Z_1Z_2(I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.30\ I)$$

is said to fit experimental data with a precision of 1.6% up to I = 0.1 M. This form was used in plotting the above results as a function of ionic strength, and it was found to give better linear plots than the function $0.5\ Z_1Z_2(I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}))$.

Davies [10] also gives pK values (-log dissociation constants) for a large number of ion-pairs. For instance, he gives pK = 2.3 for $K^+.Fe(CN)_6^{4-}$ which corresponds to less than 10% association in solutions more dilute than $10^{-3}$M, using an activity coefficient value of 0.5. No data on $HPO_4^{2-}$ or $NH_4^+$ ion-pairs are given; if these associate, they probably do so to a small extent. There is also the uncoordinated Fe(III) ion which in some experiments was up to 25% of the total concentrations of $5 \times 10^{-4}$M. Considering these factors, it seems reasonable to put an upper limit of about 20% for the formation of ion-pairs.

What would be the effect of such ion-pairing? Clearly, there will be a decrease in the concentration of ions and consequently, in the ionic strength. A change in charge would also be expected to affect the limiting slope in an ionic strength plot; but with 20% ion association and small charges on the species (see equation 6), this effect cannot be significant. Similarly, there cannot be much change in redox potential an a result of ion association in such dilute solutions.

It is of course possible, and in some cases necessary, to investigate further some of these problems. For instance, redox potential measurements could be repeated in the absence of oxygen, in the absence of $NH_4^+$, and with gold or platinum electrodes in place of rhodium. Equilibrium measurements could be repeated at higher concentrations of reactants in order to reduce the possibility of side reactions. Phosphate buffers could be replaced by another buffer system as a check on specific salt effects.

It would be particularly interesting to make a comparative thermodynamic study of the tris-(pyridine 2-aldoxime) and the bis-(pyridine 2,6-dialdoxime) complexes with iron. These systems possess similar structures but they differ in charge by 1 unit. The study of these systems could therefore give a measure of the influence of an additional unit (negative) charge on redox potential, entropy etc. Conversely, the effect of the metal on the acid ionization of the oxime groups in the two cases may also be compared.

In conclusion it may be said that although work of this kind presents many difficulties in experiment and in interpretation, it is nevertheless of significance at least in so far as it helps in the elucidation of some aspects of the physical chemistry of complex ions in aqueous solution.

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