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POTENTIOMETRIC AND EQUILIBRIUM STUDIES ON THE IRON COMPLEXES

OF

PYRIDINE-2,6-DIALDOXIME

BY

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ABSTRACT

This work is concerned with oxidation-reduction potentials and related thermodynamics of complex ions in aqueous solutions. The systems studied are the iron(II) and iron(III) complexes of Pyridine-2,6-dialdoxime, an N,N,N-tridentate ligand with two ionizable oxime groups.

This study was undertaken with special reference to the mutual thermodynamic influence of the metal-ion and the ligand, namely:

1. The variation of redox potential with pH and ionic strength as a result of ionization of the side groups.
2. The change in the thermodynamic parameters for the ionizations of the side groups as a result of chelation of the ligand to the metal ion.

The stoichiometry of both complexes was investigated spectrophotometrically and found to be 1 mole metal to 2 moles ligand in both cases, within the experimental range, pH 3 to 6. Determinations of equilibrium constants indicated that both complexes are stable under the experimental conditions employed.

On the basis, potentiometric work was carried out and the redox potential E was measured over a wide range of pH (3 to 6), ionic strength (0.006 to 0.06M) and temperature (15, 20, 25, 27.5 and 30°C). Analysis of the pH variation of E with reference to the various ionization equilibria

involved, yielded the value for the pH-independent redox potential E_i for the half cell: $\text{Fe(III)P}_2^{-1} + e^{-1} = \text{Fe(II)P}_2^{-2}$. The variation of E_i with ionic strength and temperature led to the evaluation of the standard redox potential $E_i^0 = 0.204$ volt, and its corresponding enthalpy and entropy changes for the cell reaction, $\Delta H_i^0 = -27$ kcal/mole, $\Delta S_i^0 = -66.9$ e.u.

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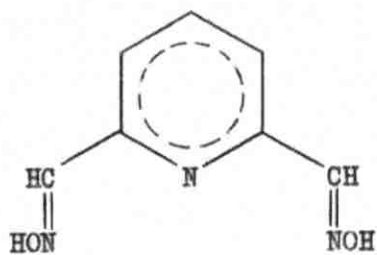
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LIST OF SYMBOLS

DIPAL	: Pyridine-2,6-dialdoxime
PH ₂	: Pyridine-2,6-dialdoxime (diprotic acid species)
P ⁻²	: Pyridine-2,6-dialdoxime di-anion (conjugate base)
PAL	: Pyridine-2-aldoxime anion
Complex(II)	: bis-(Pyridine-2,6-dialdoxime)-iron(II) complex
Complex(III)	: bis-(Pyridine-2,6-dialdoxime)-iron(III) complex
K ₀₁ , K ₀₂	: successive ionization constants for the two oxime groups in DIPAL
K ₁ , K ₂ , K ₃ , K ₄	: successive ionization constants for the four oxime groups complex(II)
K ₁ ['] , K ₂ ['] , K ₃ ['] , K ₄ [']	: successive ionization constants for the four oxime groups complex(III)
K _{obs}	: Formation constant for complex(II) at given pH, I and T.
K _{obs} [']	: Formation constant for complex(III) at given pH, I and T
K _i	: pH-independent formation constant for complex(II) at given I and T
K _i [']	: pH-independent formation constant for complex(III) at given I and T
K _i ⁰	: pH-independent formation constant for complex(II) at given T and I = 0
E _{cal}	: cell EMF with respect to saturated calomel electrode

- E : Redox potential for equimolar total concentrations of complex(III) and complex(II) at given pH, I and T
- E_i : pH-independent redox potential for equimolar concentrations of complex(III) and complex(II) at given I and T
- E^0 : Standard redox potential at given pH, T and I = 0
- E_i^0 : pH-independent standard redox potential at given T and I = 0
- h : a_{H^+} obtained from pH measurements assuming pH = $-\log a_{H^+}$
- I : Ionic strength
- a : activity
- f : activity coefficient
- A : Absorbance at given wavelength
- A_{100} : Absorbance for the completely formed complex at given pH, I and T



Pyridine-2,6-dialdoxime

INTRODUCTION

The present work is a thermodynamic study of the oxidation-reduction equilibrium of bis-(pyridine-2,6-dialdoxime)-iron(III)/iron(II) complex ion system in dilute aqueous solution. It forms part of a series of investigations on complex ions with particular reference to redox potentials and ionization constants.

In recent years, rapid expansion has taken place in the field of coordination chemistry, especially in the physico-chemical measurement of stability constants for metal-ion complexes with inorganic as well as organic ligands. An authoritative compilation is available covering all data up to the end of 1960, and including some more recent ones as well.¹ However, data on redox potentials of complex ions are not extensive, and in most cases temperature variation has not been investigated. Thus, very few enthalpy and entropy values are available for redox cell reactions involving complex ions.

Moreover, 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 solutions. George, Hanania and Irvine² 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 most aquo ions form protonated complexes, their equilibria may also involve unusual entropy changes which need further examination. Similarly, many types of reactions involve protonated transition states, thus the interpretation of kinetic data also requires a more thorough understanding of entropies and their changes in reactions involving ions.

From another point of view, the results of kinetic and thermodynamic studies of complex ions have biological implications. It is known that hemoproteins are iron complexes, Vitamin B₁₂ and its derivatives are cobalt complexes, and many enzymes are metalloproteins. It has also recently been established that carcinogenic processes are related to chelation.³ Thus, the study of the biochemical role of these substances involves coordination chemistry. Since so many biological systems are coordination compounds, selected complex ions may be used as models for their analogous macromolecules. The reason for this is the following: generally, the factors affecting stability and reactivity of coordination compounds in aqueous solution are charge, conjugation, steric hindrance, H-bonding and hydrophobic forces. These effects cannot be investigated individually in macromolecules. However, by use of "simple" complex ions as models studies can be carried out on systems where only one or two factors operate.

The above idea has been applied by Hanania and Irvine^{4,5} in their studies of the effect of coordination to iron(II) on the thermodynamics of ionization of acidic groups in selected organic ligands. Their study of the 2,2'-Pyridylimidazoline-iron(II) system⁴ showed that the

acid strength of the imidazolium group increases from pK^0 8.9 in the free ligand to pK^0 6.1 in the complex, the change appearing mainly as enthalpy rather than an entropy effect. This increase in acid strength was attributed to the increased positive charge in the complex relative to the free ligand; thus the effect being electrostatic in nature. In their study of the Pyridine-2-aldoxime-iron(II) system⁵, they also showed that the acid strength of oxime side groups in the ligand increased from pK 10.2 in the free ligand to pK 7.1 the third ionization in the complex, the change again appearing mainly as enthalpy rather than an entropy effect. The charge types being the same (0 to -1) in both cases, the effect was attributed to extra stabilization of the conjugate base of the complex through resonance, the effect being mainly electronic. If however, one compares the second ionization on this complex (charge types +1 to 0) with the ionization on the free ligand (charge types 0 to -1), Hanania and Irvine's results showed that the acid strength of the oxime group is increased from pK 10.2 in the free ligand to pK 3.3 in the complex. This much larger effect is attributed to both electrostatic as well as conjugation factors.

Thus, the determination 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. The data from complex ions can be used in placing limits on the influence of the metal on the thermodynamics of ionization for metal-linked groups in macromolecules.

The study of complex ions involving ligands with acidic side groups can be used to investigate the converse effect, namely the effect

of acid-base equilibria in the ligand on the redox potential of the metal. This problem, which is thermodynamically equivalent to the above one, has received very little attention. Its study requires measurements of E^0 for a variety of complex ion systems with differing number of ionizable side groups on the ligands.

In the present work, the Pyridine-2,6-dialdoxime molecule is used as a tridentate N-ligand with two ionizable oxime side groups. Its iron(II) and iron(III) complexes may be regarded as model compounds and the thermodynamic values obtained from this study can be compared with other systems such as the iron(III)/iron(II)-Pyridine-2-aldoxime system.⁶ These two systems have similar structures but different overall charges; consequently one gets a measure of the influence of the metal ligand field on linked ionizations, as well as the influence of ionizations on redox potentials of complex ions.

An attempt has therefore been made to study potentiometrically the oxidation-reduction equilibrium involving the iron(II) and iron(III) complexes of Pyridine-2,6-dialdoxime covering as wide a range of experimental conditions as possible. The composition and stability of both complexes were first determined and shown to be adequate for precise thermodynamic work, and on this basis the redox potential measurements were conducted as described in the following chapters.

THEORY

Pyridine-2,6-dialdoxime reacts rapidly with ferrous ions in dilute acidic aqueous solutions to form a well defined red iron(II) complex ion, and rather slowly with ferric ions to form the corresponding well defined red iron(III) complex ion. The 1 to 2 stoichiometry of both reactions is based on the following evidence:

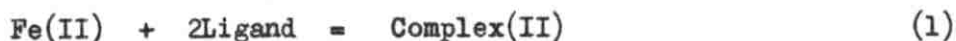
1. Pyridine-2,6-dialdoxime has an N,N,N-tridentate structure with spatial configuration and bond lengths suitable for octahedral chelation of iron, as can be shown with Courtauld atomic models.

2. The composition of both complexes has been determined over the pH range 3 to 7 by Job method of continuous variation and shown to be 1 mole iron to 2 moles ligand in both cases.

3. The calculations of the formation constants have all been based on a 1 to 2 stoichiometry; the constancy of K with varying reactant concentrations over a wide range confirms the above assumption.

I. Formation of Fe(II) complex

The reaction between Pyridine-2,6-dialdoxime and iron(II) may be represented by the equilibrium:



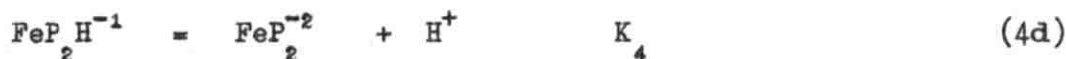
In this equation, Fe(II) represents ferrous ions which are assumed to have negligible or constant degree of association with counter ions

over the range of experimental conditions (pH 3 to 6). "Ligand" is a molecule of Pyridine-2,6-dialdoxime, PH_2 , having two weakly acidic oxime groups the ionizations of which may be represented as follows:



where $\text{p}K_{01} \sim 10.1$ and $\text{p}K_{02} \sim 10.9$ at 25°C .⁷

Complex(II) is a molecule of bis-(Pyridine-2,6-dialdoxime)-iron(II), $\text{Fe}(\text{PH}_2)_2^{+2}$, which undergoes four successive ionizations:



where at 25°C $\text{p}K_4 \sim 7.2$ ⁷, and from the present work $\text{p}K_3 \sim 4.9$ and $\text{p}K_2 \sim 4.5$.

The ionization in equation (4a), with $\text{p}K_1$, is immeasurably strong.

Comparison with the corresponding reaction of ferrous ions with α, α' -dipyridyl⁸ would suggest that the reaction represented by equation (1) occurs in two stages. The overall equilibrium constant, K_{obs} , at finite ionic strength, pH and temperature is defined in terms of molar concentrations at equilibrium:

$$K_{\text{obs}} = \frac{\sum (\text{Complex(II)})}{(\text{Fe}^{+2}) \left\{ \sum (\text{Ligand}) \right\}^2} \quad (5)$$

where, at a given pH,

$$\sum (\text{Complex(II)}) = (\text{FeP}_2\text{H}_4^{+2}) + (\text{FeP}_2\text{H}_3^{+1}) + (\text{FeP}_2\text{H}_2^0) + (\text{FeP}_2\text{H}^{-1}) + (\text{FeP}_2^{-2}) \quad (6)$$

and

$$\sum (\text{Ligand}) = (\text{PH}_2^0) + (\text{PH}^{-1}) + (\text{P}^{-2}) \quad (7)$$

From equations (4a), (4b), (4c) and (4d), it can be shown that

$$(\text{FeP}_2\text{H}_3^{+1}) = K_1 (\text{FeP}_2\text{H}_4^{+2}) / h \quad (8a)$$

$$(\text{FeP}_2\text{H}_2^0) = K_2 (\text{FeP}_2\text{H}_3^{+1}) / h = K_1 K_2 (\text{FeP}_2\text{H}_4^{+2}) / h^2 \quad (8b)$$

$$(\text{FeP}_2\text{H}^{-1}) = K_3 (\text{FeP}_2\text{H}_2^0) / h = K_1 K_2 K_3 (\text{FeP}_2\text{H}_4^{+2}) / h^3 \quad (8c)$$

$$(\text{FeP}_2^{-2}) = K_4 (\text{FeP}_2\text{H}^{-1}) / h = K_1 K_2 K_3 K_4 (\text{FeP}_2\text{H}_4^{+2}) / h^4 \quad (8d)$$

Thus,

$$\sum (\text{Complex(II)}) = (\text{FeP}_2\text{H}_4^{+2}) \left\{ 1 + \frac{K_1}{h} + \frac{K_1 K_2}{h^2} + \frac{K_1 K_2 K_3}{h^3} + \frac{K_1 K_2 K_3 K_4}{h^4} \right\} \quad (9)$$

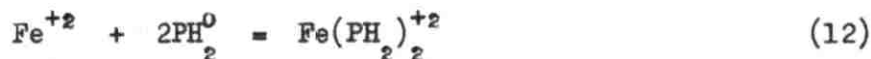
In the same way, from equations (2) and (3), it can be shown that

$$\sum (\text{Ligand}) = (\text{PH}_2^0) \left\{ 1 + \frac{K_{01}}{h} + \frac{K_{01} K_{02}}{h^2} \right\} \quad (10)$$

Substituting from equations (9) and (10) into equation (5),

$$K_{\text{obs}} = \frac{(\text{FeP}_2\text{H}_4^{+2})}{(\text{Fe}^{+2})(\text{PH}_2^0)^2} \frac{\left\{ 1 + \frac{K_1}{h} + \frac{K_1 K_2}{h^2} + \frac{K_1 K_2 K_3}{h^3} + \frac{K_1 K_2 K_3 K_4}{h^4} \right\}}{\left\{ 1 + \frac{K_{01}}{h} + \frac{K_{01} K_{02}}{h^2} \right\}^2} \quad (11)$$

Equation (11) expresses the observed equilibrium constant in terms of pH, the various ionization constants and the concentrations of reactants and products in the hypothetical pH-independent equilibrium



for which the pH-independent equilibrium constant at given ionic strength and temperature is expressed in terms of molar concentrations of the species, namely,

$$K_1 = (\text{FeP}_2\text{H}_4^{+2}) / (\text{Fe}^{+2})(\text{PH}_2^0)^2 \quad (13)$$

Hence K_{obs} and K_i are related as follows:

$$K_i = K_{obs} \frac{\left\{ 1 + \frac{K_{O1}}{h} + \frac{K_{O1}K_{O2}}{h^2} \right\}^2}{\left\{ 1 + \frac{K_1}{h} + \frac{K_1K_2}{h^2} + \frac{K_1K_2K_3}{h^3} + \frac{K_1K_2K_3K_4}{h^4} \right\}} \quad (14)$$

Thus from measurements of the equilibrium constant K_{obs} at given pH, ionic strength and temperature, and using the known values of K_4 , K_3 , K_2 , K_{O1} , K_{O2} (and estimated value for K_1), it is possible to calculate the corresponding value for the pH-independent constant K_i .

Since experimental results are confined to the range of pH 3 to 5, equation (14) may be simplified by neglecting the contribution from K_4 , K_{O1} and K_{O2} , yielding

$$K_i = K_{obs} / \left\{ 1 + \frac{K_1}{h} + \frac{K_1K_2}{h^2} + \frac{K_1K_2K_3}{h^3} \right\} \quad (15)$$

a relation which is used in subsequent calculations.

The above pH-independent formation constant K_i is obtained at a given ionic strength and temperature. To get the thermodynamic value, K_i^0 , at zero ionic strength, it is necessary to get a relation for the ionic strength dependence of K_i .

Since equation (12) involves no charge change (+2 to +2), it follows that at ionic strength low enough for the Debye Hückel limiting equation to hold, K_i is independent of ionic strength and hence equal to K_i^0 .

The standard enthalpy change for the reaction represented by equation (12) could be obtained from measurements of K_i at several

temperatures assuming constant heat capacities and using the thermodynamic relation

$$\Delta H_i^0 = -R \left\{ \frac{d \ln K_i^0}{d \left(\frac{1}{T} \right)} \right\} \quad (16)$$

and hence the standard entropy change at given temperature is also obtained using the relation

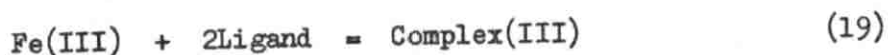
$$\Delta S_i^0 = (\Delta H_i^0 - \Delta G_i^0) / T \quad (17)$$

where

$$\Delta G_i^0 = -RT \ln K_i^0 \quad (18)$$

II. Formation of Fe(III) complex

The reaction between Pyridine-2,6-dialdoxime and iron(III) may be represented in a manner similar to that used for the iron(II) complex above, namely:



The ferric ions are assumed to have a negligible or constant degree of association with counter ions. "Ligand" represents a molecule of Pyridine-2,6-dialdoxime, PH_2 , with two weakly acidic oxime groups (equations 2 and 3). Complex(III) is a molecule of bis-(Pyridine-2,6-dialdoxime)-iron(III), $\text{Fe}(\text{PH}_2)_2^3$, which also undergoes four successive ionizations:





where, from the present work, $\text{p}K'_4 \sim 6$; the first three ionizations are immeasurably strong.

Like the ferrous reaction represented by equation (1), the ferric reaction represented by equation (19) is expected to occur in two stages with an overall equilibrium constant K'_{obs} , at finite ionic strength, pH and temperature, which is defined in terms of molar concentrations:

$$K'_{\text{obs}} = \frac{\sum(\text{Complex(III)})}{(\text{Fe}^{+3}) \{ \sum(\text{Ligand}) \}^2} \quad (21)$$

where

$$\sum(\text{Complex(III)}) = (\text{FeP}_2\text{H}_4^{+3}) + (\text{FeP}_2\text{H}_3^{+2}) + (\text{FeP}_2\text{H}_2^{+1}) + (\text{FeP}_2\text{H}^0) + (\text{FeP}_2^{-1}) \quad (22)$$

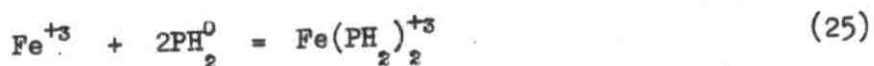
Following the same steps as with the ferrous complex, it can be shown that K'_{obs} varies with pH and the various ionizations constants in accordance with a relation parallel to that of equation (11), namely,

$$K'_{\text{obs}} = \frac{(\text{FeP}_2\text{H}_4^{+3})}{(\text{Fe}^{+3})(\text{PH}_2^0)^2} \frac{\left\{ 1 + \frac{K'_1}{h} + \frac{K'_1 K'_2}{h^2} + \frac{K'_1 K'_2 K'_3}{h^3} + \frac{K'_1 K'_2 K'_3 K'_4}{h^4} \right\}}{\left\{ 1 + \frac{K_{01}}{h} + \frac{K_{01} K_{02}}{h^2} \right\}^2} \quad (23)$$

and consequently,

$$K'_i = K'_{\text{obs}} \frac{\left\{ 1 + \frac{K_{01}}{h} + \frac{K_{01} K_{02}}{h^2} \right\}^2}{\left\{ 1 + \frac{K'_1}{h} + \frac{K'_1 K'_2}{h^2} + \frac{K'_1 K'_2 K'_3}{h^3} + \frac{K'_1 K'_2 K'_3 K'_4}{h^4} \right\}} \quad (24)$$

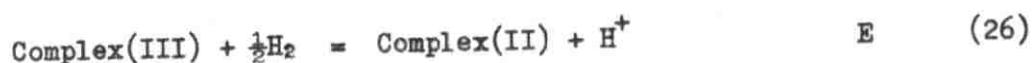
where K_1' is the pH-independent equilibrium constant at given ionic strength and temperature pertaining to the hypothetical equilibrium



which is equivalent to equation (12). Here again equations (16), (17) and (18) lead to the evaluation of the standard enthalpy and entropy changes.

III. Redox Cell Reaction

The redox cell reaction for the system bis-(Pyridine-2,6-dialdoxime)-iron(III) / bis-(Pyridine-2,6-dialdoxime)-iron(II) can be represented in general terms as follows:



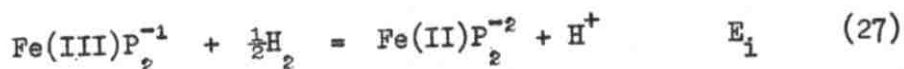
where the redox potential, E , is the potential of a half-cell comprising equimolar total concentrations of oxidant and reductant at given pH, ionic strength and temperature, measured against standard hydrogen electrode (S.H.E.). Complex(III) and Complex(II) are bis-(Pyridine-2,6-dialdoxime)-iron(III) and bis-(Pyridine-2,6-dialdoxime)-iron(II), both of which undergo four successive ionizations as previously indicated.

Since the contributions to the total molar concentrations of oxidant and reductant of the different species involved depend on pH, it follows that at a given temperature and ionic strength the redox potential will depend on pH.

Dependence of redox potential on pH

A relation for the variation of the measured redox potential, E ,

with pH can be obtained with reference to the hypothetical cell reaction involving the fully ionized species.



where E_i is the pH-independent redox potential for equimolar concentrations of Fe(III)P_2^{-1} and Fe(II)P_2^{-2} , relative to S.H.E.

Thus at a given pH, ionic strength and temperature, E depends on the concentrations of the fully ionized oxidant and reductant species as follows:

$$E = E_i + \frac{RT}{nF} \ln \frac{(\text{Fe(III)P}_2^{-1})}{(\text{Fe(II)P}_2^{-2})} \quad (28)$$

whereby for equimolar total concentrations of oxidant and reductant and pH high enough for both oxidized and reduced species to be completely ionized, at constant temperature and ionic strength, the measured redox potential E is equal to E_i .

The relation between the total concentration of complex and the various ionized species is shown in equations (6) and (22). Following the same steps as before, it can be shown that at a given pH,

$$\sum (\text{Complex(II)}) = (\text{Fe(II)P}_2^{-2}) \left\{ 1 + \frac{h}{K_4} + \frac{h^2}{K_4 K_3} + \frac{h^3}{K_4 K_3 K_2} + \frac{h^4}{K_4 K_3 K_2 K_1} \right\} \quad (29)$$

and similarly for Complex(III),

$$\sum (\text{Complex(III)}) = (\text{Fe(III)P}_2^{-1}) \left\{ 1 + \frac{h}{K_4} + \frac{h^2}{K_4 K_3} + \frac{h^3}{K_4 K_3 K_2} + \frac{h^4}{K_4 K_3 K_2 K_1} \right\} \quad (30)$$

By rearranging equations (29) and (30), we get

$$(\text{Fe(II)}\text{P}_2^{-2}) = \sum(\text{Complex(II)}) / \left\{ 1 + \frac{h}{K_4} + \frac{h^2}{K_4 K_3} + \frac{h^3}{K_4 K_3 K_2} + \frac{h^4}{K_4 K_3 K_2 K_1} \right\} \quad (31)$$

and

$$(\text{Fe(III)}\text{P}_2^{-1}) = \sum(\text{Complex(III)}) / \left\{ 1 + \frac{h}{K'_4} + \frac{h^2}{K'_4 K'_3} + \frac{h^3}{K'_4 K'_3 K'_2} + \frac{h^4}{K'_4 K'_3 K'_2 K'_1} \right\} \quad (32)$$

Substituting from equations (31) and (32) into equation (28),

$$E = E_i + \frac{RT}{nF} \ln \frac{\sum(\text{Complex(III)})}{\sum(\text{Complex(II)})} \frac{\left\{ 1 + \frac{h}{K_4} + \frac{h^2}{K_4 K_3} + \frac{h^3}{K_4 K_3 K_2} + \frac{h^4}{K_4 K_3 K_2 K_1} \right\}}{\left\{ 1 + \frac{h}{K'_4} + \frac{h^2}{K'_4 K'_3} + \frac{h^3}{K'_4 K'_3 K'_2} + \frac{h^4}{K'_4 K'_3 K'_2 K'_1} \right\}} \quad (33)$$

Since experimental results are confined to total equimolar concentrations of oxidant and reductant in the pH range 3 to 6.5, equation (33) may be simplified by neglecting the contribution from K_1 , K'_1 , K'_2 and K'_3 , yielding

$$E = E_i + \frac{RT}{nF} \ln \left\{ 1 + \frac{h}{K_4} + \frac{h^2}{K_4 K_3} + \frac{h^3}{K_4 K_3 K_2} \right\} / \left\{ 1 + \frac{h}{K'_4} \right\} \quad (34)$$

which gives the relation between the measured redox potential, E, for equimolar concentrations of oxidant and reductant, and the pH-independent redox potential E_i , in terms of pH and the various ionizations constants.

This value of E_i for the hypothetical cell reaction given by equation (27) is obtained at a given ionic strength and temperature. To get the thermodynamic pH-independent standard redox potential E_i^0 , it is also necessary to investigate the effect of ionic strength on E_i .

Dependence of redox potential on ionic strength

At a given pH and temperature, the measured redox potential E is given by:

$$E = E^0 + \frac{RT}{nF} \ln \frac{\sum a_o}{\sum a_R} \quad (35)$$

where E^0 is the standard redox potential and $\sum a_o$ and $\sum a_R$ are the total molar activities of oxidant and reductant respectively. For the pH-independent equilibrium (equation 27), where the total molar concentrations are equal to the actual concentrations of the species, equation (35) yields

$$E_i = E_i^0 + \frac{RT}{nF} \ln \frac{f_o}{f_R} \quad (36)$$

where f_o and f_R are the activity coefficients for the fully ionized oxidant and reductant species, $Fe(III)P_2^{-1}$ and $Fe(II)P_2^{-2}$ respectively. In sufficiently dilute solutions, one may use a Debye-Hückel type of equation for activity coefficients⁹

$$-\log f_i = Az_i^2 I^{\frac{1}{2}} / (1 + 2I^{\frac{1}{2}}) \quad (37)$$

where the constant $A = 0.509$ at $25^{\circ}C$, z_i is the charge on the ion i and I is the total molar ionic strength of the solution.

Substituting into equation (36) leads to

$$E_i = E_i^0 + 2.303 \frac{RT}{nF} A (z_R^2 - z_o^2) I^{\frac{1}{2}} / (1 + 2I^{\frac{1}{2}}) \quad (38)$$

where z_R = charge on reductant and z_o = charge on oxidant.

For the cell reaction in equation (27), equation (38) reduces to

$$E_i = E_i^0 + 0.089 I^{\frac{1}{2}} / (1 + 2I^{\frac{1}{2}}) \quad (39)$$

which gives the relation of the pH-independent redox potential at finite low ionic strength to the thermodynamic pH-independent redox potential

at $I = 0$.

Dependence of redox potential on temperature

The variation of redox potential 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 to 30°C, the activities of the ions are independent of temperature, one can write

$$dE_i/dT = dE_i^0/dT \quad (40)$$

where dE_i/dT is the change of the pH-independent redox potential with temperature at finite low ionic strength, and dE_i^0/dT is the change of the thermodynamic pH-independent standard redox potential with temperature.

Using the thermodynamic relations,

$$\Delta H_i^0 = nF(TdE_i^0/dT - E_i^0) \quad (41)$$

and

$$\Delta S_i^0 = nFdE_i^0/dT \quad (42)$$

ΔH_i^0 and ΔS_i^0 can be evaluated; referring to the cell reaction in equation (27).

EXPERIMENTAL

I. - Materials and Methods

Ferrous Ammonium Sulfate

Anal. R $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was used. Complex(II) was prepared from the same sample of this salt throughout. The purity of this salt had previously been investigated⁶ and found to be 99.9%; consequently a 0.1% increase in the weight of the samples was applied.

Ferric Ammonium Sulfate

Anal. R $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was used. Complex(III) was prepared from the same sample of this salt throughout. The purity of this salt had also previously been investigated⁶ and found to be 98.6%; thus, a 1.4% increase in the weight of the samples was applied.

Pyridine-2,6-dialdoxime

A sample of Pyridine-2,6-dialdoxime was purchased from Aldrich Chemical Co. Inc., U.S.A. It was recrystallized from water and the melting point determined and found to be 215-216°C (literature value¹⁰ 215-216°).

Perchloric Acid

70% HClO_4 (Merck, pro analysi grade) was used from which a standard solution (about 1N) was prepared and used throughout the redox potential measurements.

Sodium Hydroxide

Merck, pro analysi grade NaOH was used, dissolved in redistilled

deionized water and standardized against AnalaR potassium hydrogen phthalate.

Potassium Chloride

AnalaR KCl was used for the preparation of salt bridges for the redox potential and pH measurements.

Sodium Chloride

Merck, pro analysi grade NaCl was used for adjusting solutions to the required ionic strength.

Potassium Hydrogen Phthalate

AnalaR salt was used for the preparation of buffers used in the equilibrium measurements.

Water

Redistilled deionized water was used for making up all solutions.

All spectrophotometric measurements were made on a Unicam S.P. 500 UV-VIS spectrophotometer using glass cells. Temperature was controlled to $\pm 0.1^{\circ}$ or better by circulating water from a thermostated water bath (WACO Lo-Temp Bath, Chicago, U.S.A.).

All redox potential and pH measurements were taken on a pH meter (Radiometer, type PHM4) which read to 0.1 mv and 0.002 pH units. Temperature was also controlled to within $\pm 0.1^{\circ}$ by circulating water from a thermostated water bath as above.

II.- Solutions

Ferrous Ammonium Sulfate

Solutions were prepared by weighing 100.1% of the required amount

of salt. For equilibrium measurements, stock solutions were made usually $2.0 \times 10^{-3} \text{M}$. For redox potential measurements, HClO_4 (2 moles acid/1 mole Fe(II)) was added before making up stock solutions, usually $1.0 \times 10^{-2} \text{M}$.

Ferric Ammonium Sulfate

Solutions were prepared by weighing 101.4% of the required amount of the salt. HClO_4 (2 moles acid / 1 mole Fe(III)) was added before making up to total volume with water and filtering from the tiny insoluble residue, yielding stock solutions of $1.0 \times 10^{-2} \text{M}$ for redox potential measurements and $2.5 \times 10^{-3} \text{M}$ for equilibrium measurements.

Pyridine-2,6-dialdoxime

Solutions were prepared by weighing the required amount, dissolving it in hot water, cooling, and making up to total volume with water. $1.0 \times 10^{-2} \text{M}$ and $5.0 \times 10^{-3} \text{M}$ solutions were usually prepared. Solutions involving concentrations higher than $1.0 \times 10^{-2} \text{M}$ could not be prepared as this is about the limit of solubility of DIPAL in water at room temperature.

Buffers

A series of phthalate buffers (pH 3.0 to 5.0) were prepared by adding HCl or NaOH to potassium hydrogen phthalate solutions in the appropriate ratios and making up to the total volume with water. A few phosphate buffers (pH 6.0 and 7.0) were also prepared by adding NaOH to $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ in the appropriate ratios and making up to the total volume with water. In some cases NaCl was added to adjust the ionic strength. These buffers were used for the spectrophotometric measurements.

Standard phthalate and phosphate buffers were also prepared for calibrating the pH meter before taking pH measurements. The pH values of these buffers, as given by the National Bureau of Standards¹¹, are given

below. 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 units

<u>Standard buffer</u>	<u>pH_s (NBS standards)</u>				
	<u>15.0°C</u>	<u>20.0°C</u>	<u>25.0°C</u>	<u>27.5°C</u>	<u>30.0°C.</u>
0.05M KHP	4.00	4.01	4.01	4.01	4.01
0.025M KH ₂ PO ₄)	6.90	6.88	6.86	6.85	6.85
0.025M Na ₂ HPO ₄)					

III.- Determination of Composition of Complexes

The composition of both complexes (equations 1 and 19) was determined spectrophotometrically by the Job method of continuous variation. Absorbances were read at wavelengths between 460 and 560 m μ , as both complexes absorb strongly in this region while the absorbance due to ferrous and ferric ions and DIPAL is negligible.⁷ Details of the method were as follows:

A. Complex(II)

Freshly prepared ferrous solutions were mixed with freshly prepared DIPAL solutions in various molar ratios and let stand for a few minutes to ensure attainment of equilibrium. Buffer was then added to adjust pH and the absorbances of the solutions measured in some cases at 500 m μ and in other cases at 560 m μ . The absorbance values were then plotted vs mole fraction of ferrous ion, the maximum absorbance corresponding to the stoichiometric composition of the complex.

Measurements were made at room temperature and $I \sim 0.025M$ in the range of pH 3.0 to 7.0. The data are given in Table (Ia) and the results

at pH 3.0 and 6.0 are shown in Fig. (1a). It is seen that, under the experimental conditions, complex(II) involves a 1 to 2 stoichiometry, i.e. 1 mole Fe(II) to 2 moles DIPAL.

B. Complex(III)

Mixtures of ferric ion and DIPAL solutions containing various ratios of Fe(III) to DIPAL were prepared in a manner similar to that described for complex(II), and the absorbance measured in some cases at 460 m μ and in other cases at 500 m μ .

Measurements were also made at room temperature and $I \sim 0.025M$ in the range of pH 3.0 to 7.0. The data are given in Table (Ib) and the results at pH 3.0 and 6.0 are shown in Fig. (1b). Here again, it is seen that, under the experimental conditions, complex(III) involves a 1 to 2 stoichiometry, i.e. 1 mole Fe(III) to 2 moles DIPAL.

TABLE (1a)

Determination of composition of complex(II) by the Job method of continuous variation at room temperature and $I \sim 0.025M$

* $[Fe(II)] = 2.5 \times 10^{-3}M$; $[DIPAL] = 2.5 \times 10^{-3}M$; Absorbance measured at $\lambda = 500$ m μ . against buffer as blank.

** $[Fe(II)] = 1.0 \times 10^{-3}M$; $[DIPAL] = 1.0 \times 10^{-3}M$; Absorbance measured at $\lambda = 560$ m μ . against buffer as blank.

8.0 ml buffer added in each case.

<u>ml Fe(II)</u>	<u>ml DIPAL</u>	<u>Mole fraction of Fe(II)</u>	<u>pH</u>				
			<u>*</u>	<u>*</u>	<u>*</u>	<u>**</u>	<u>**</u>
			<u>3.07</u>	<u>4.08</u>	<u>5.10</u>	<u>5.98</u>	<u>7.07</u>
1.6	0.4	0.8	0.014	0.086	0.232	0.083	0.114
1.4	0.6	0.7	0.026	0.151	0.350	0.130	0.170
1.2	0.8	0.6	0.040	0.206	0.474	0.180	0.234
1.0	1.0	0.5	0.048	0.269	0.581	0.220	0.294
0.8	1.2	0.4	0.056	0.316	0.679	0.267	0.353
0.6	1.4	0.3	0.0585	0.339	0.704	0.252	0.311
0.4	1.6	0.2	0.0515	0.289	0.540	0.174	0.214
0.3	1.7	0.15	0.0420	0.240	0.408	-	-
0.2	1.8	0.1	0.033	0.190	0.280	0.091	0.115

TABLE (1b)

Determination of composition of complex(III) by the Job method of continuous variation at room temperature and $I \sim 0.025M$

* $[Fe(III)] = 5.0 \times 10^{-3}M$; $[DIPAL] = 5.0 \times 10^{-3}M$; Absorbance measured at $\lambda = 500 \text{ m}\mu$. against buffer as blank.

** $[Fe(III)] = 1.0 \times 10^{-3}M$; $[DIPAL] = 1.0 \times 10^{-3}M$; Absorbance measured at $\lambda = 460 \text{ m}\mu$. against buffer as blank.

8 ml buffer added in each case.

<u>ml Fe(III)</u>	<u>ml DIPAL</u>	<u>Mole fraction of Fe(III)</u>	<u>pH</u>				
			*	*	*	**	**
			<u>3.07</u>	<u>4.07</u>	<u>5.09</u>	<u>6.00</u>	<u>7.06</u>
1.6	0.4	0.8	-	-	-	0.040	0.082
1.4	0.6	0.7	0.180	0.265	0.373	0.085	0.111
1.3	0.7	0.65	0.217	0.318	0.455	-	-
1.2	0.8	0.6	0.252	0.373	0.537	0.127	0.141
1.0	1.0	0.5	0.300	0.460	0.708	0.168	0.172
0.8	1.2	0.4	0.332	0.500	0.860	0.197	0.184
0.6	1.4	0.3	0.340	0.520	0.943	0.209	0.200
0.5	1.5	0.25	-	-	-	0.207	0.208
0.4	1.6	0.2	0.320	0.456	0.704	0.193	0.193
0.3	1.7	0.15	0.248	0.363	0.577	-	-
0.2	1.8	0.1	0.168	0.260	0.447	0.115	0.115

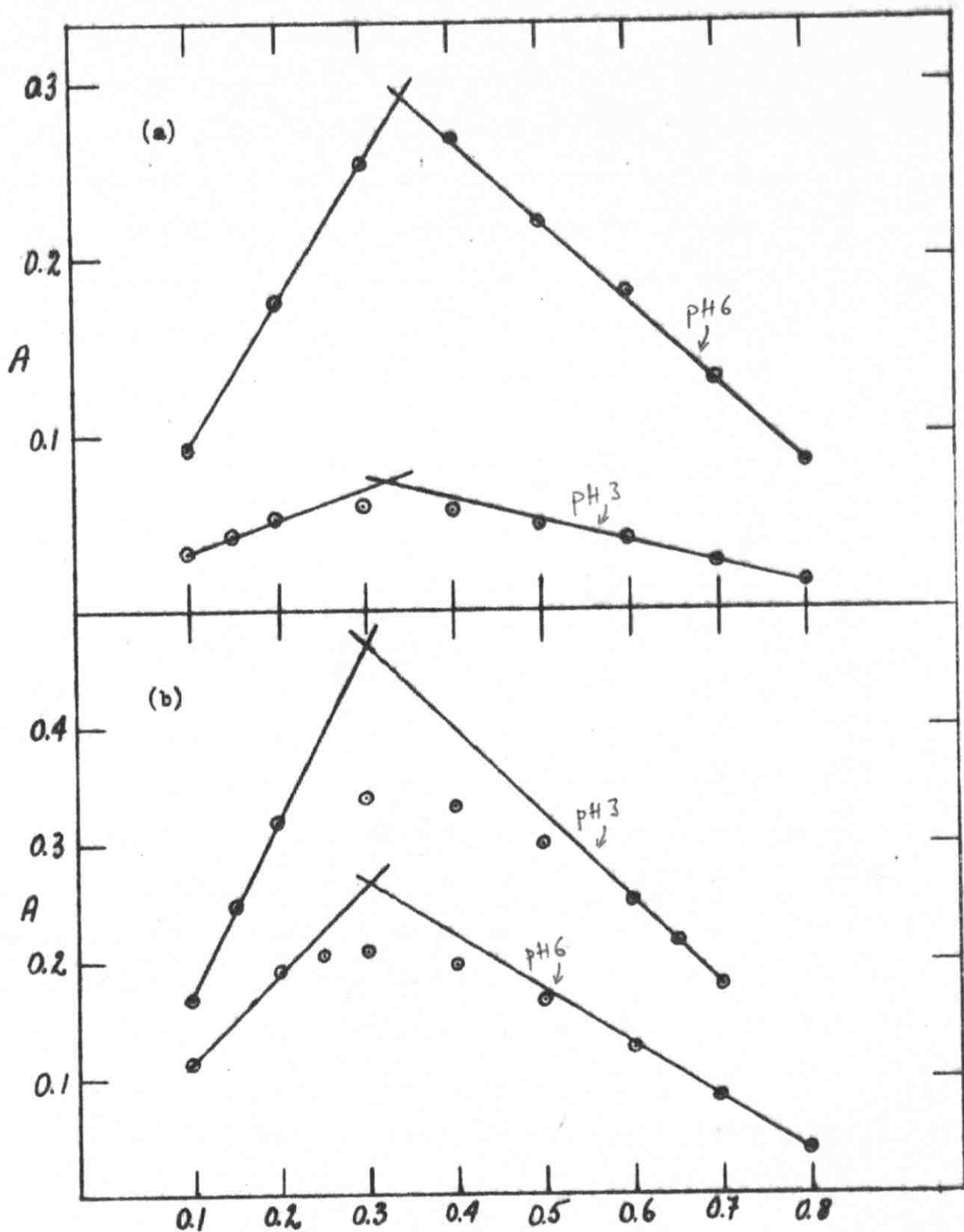


Fig. 1 Determination of composition of complex by method of continuous variation: (a) complex(II); (b) complex(III). Data from Table 1 (a,b).

IV.- Measurement of Formation Constant

Formation constants were measured spectrophotometrically for both complex(II) and complex(III). In the case of complex(II), absorbance measurements were made at 500 m μ , as, at this wavelength, the absorbance of the complex is almost independent of pH (see spectral data in Table 2). In the case of complex(III), absorbance measurements were made at 460 m μ .

A. Method

The method used in the determination of the formation constant of complex(II) was the following:

1.0 ml of freshly prepared $2.0 \times 10^{-3} M$ Fe(II) was pipetted into a tube to which 10.0 ml of buffer solution were then added. The mixture was placed in a water bath to attain the required temperature. 3.0 ml of this mixture were then pipetted into a clean dry spectrophotometric glass cell and the absorbance read, using buffer solution as a reference. DIPAL solution of known concentration (1.0×10^{-2} or $5.0 \times 10^{-3} M$) was then added in 0.01 or 0.02 ml aliquots from a microburette into the cell containing the Fe(II)-buffer mixture. After mixing, the absorbance was measured. The addition of DIPAL was continued until about 0.20 ml were added the absorbance being measured after every addition. The pH of the solution was then measured on a pH meter previously calibrated with standard phthalate buffer, using a glass electrode and a saturated calomel electrode in a thermostated unit with a saturated KCl salt bridge.

In order to get the absorbance reading corresponding to 100% complex, solid DIPAL was added to the original solution containing Fe(II) and buffer, the solution filtered, and the absorbance measured as above.

Since, at $\lambda = 500 m\mu$, the only species that absorbs is complex(II),

TABLE 2

Absorption spectra (400-580 m μ) of complex(II) at pH 3, 4 and 5 and of complex(III) at pH 4; using 8 mm spacers in 10 mm cells.

[Fe(II)] = [Fe(III)] = $2.5 \times 10^{-4} M$ with excess DIPAL and buffer

Data given as absorbance/2 mm path in cell.

λ (m μ)	<u>Complex(II)</u>			<u>Complex(III)</u>
	<u>pH 3</u>	<u>pH 4</u>	<u>pH 5</u>	<u>pH 4</u>
400	0.260	0.258	0.241	0.200
405	0.288	0.280	0.257	0.207
410	0.316	0.304	0.278	0.214
415	0.347	0.337	0.307	0.225
420	0.380	0.372	0.339	0.240
425	0.417	0.415	0.379	0.257
430	0.441	0.452	0.423	0.269
435	0.443	0.473	0.472	0.273
440	0.419	0.475	0.516	0.270
445	-	0.460	0.540	-
450	0.346	0.429	0.529	0.243
460	0.298	0.351	0.437	0.204
470	0.284	0.314	0.360	0.183
480	0.293	0.310	0.332	0.173
490	0.312	0.323	0.333	0.171
500	0.338	0.340	0.341	0.173
510	0.354	0.354	0.350	0.175
520	0.351	0.363	0.367	0.175
530	0.332	0.363	0.384	0.173
540	0.294	0.347	0.390	0.163
550	0.239	0.301	0.378	0.142
560	0.172	0.233	0.303	0.114
580	0.078	0.117	0.176	0.061

a formation constant can be calculated for every absorbance reading, so long as a correction factor is made on the absorbance values for the dilution from the addition of DIPAL solution. The method used for the calculation of the formation constant, K_{obs} , is shown in (C). The above method was also followed in the determination of the formation constant for the corresponding complex(III).

B. Estimation of Ionic Strength

As stated above, the equilibrium mixture contained 1.0 ml Fe(II) ($2.0 \times 10^{-3} M$) + 10.0 ml buffer (I = 0.030M) + 0.20 ml or less DIPAL. The total molar ionic strength of the mixture neglecting the dilution effect due to the addition of DIPAL, is as follows:

Buffer:	$I = 0.030 \times 10.0/11.0$	= 0.027 M
Fe(II) salt:	Under conditions of experiment, assume 25% complex formed.	
	$\underline{Fe^{+2}}$: $I = 2.0 \times 10^{-3} \times (1.0/11.0) \times 0.75 \times 4/2$	= 0.00027
	$\underline{NH_4^+}$: $I = 2 \times 2.0 \times 10^{-3} \times (1.0/11.0) \times 1/2$	= 0.00018
	$\underline{SO_4^{-2}}$: $I = 2 \times 2.0 \times 10^{-3} \times (1.0/11.0) \times 4/2$	= 0.00072
Complex(II):	Contribution of complex(II) to I may be assumed negligible being $< 10^{-4} M$.	_____
	Total I =	0.028 M

Since DIPAL solution is added to 3.0 ml making final volume about 3.2 ml,

$$\text{mean } I = \frac{3.0}{3.1} \times 0.028 = 0.027 \pm 0.001 M$$

C. Calculation of Formation Constant, K_{obs}

After every addition, of DIPAL during the experiment, the measured absorbance, A' , is corrected for dilution (A). The ratio A/A_{100} , where A_{100} is the absorbance of the completely formed complex(II), gives the percentage complex formation. This allows calculation of the concentration of complex formed and free iron(II) at equilibrium. After every addition, the total concentration of DIPAL is also obtained by allowing for dilution. The concentration of free DIPAL is then obtained from the following relationship: $\text{free [DIPAL]} = \text{total [DIPAL]} - 2 [\text{Complex(II)}]$.

Thus knowing the concentrations of complex(II), free Fe(II) and DIPAL at equilibrium, K_{obs} can be calculated using equation (5).

D. Sample Run

The following details are taken from an actual experiment performed:

Date: November 29, 1964

T = $25.0 \pm 0.1^{\circ}\text{C}$. pH = 4.10 I = 0.027 M

Concentration of Fe(II) stock = $2.0 \times 10^{-3}\text{M}$

Concentration of DIPAL stock = $1.0 \times 10^{-2}\text{M}$

1.0 ml Fe(II) stock + 10.0 ml buffer / 11.0 ml mixture

3.0 ml mixture + DIPAL ($1.0 \times 10^{-2}\text{M}$) added from microburette.

The data are given in Table (3).

Result: mean $K_{obs} = (1.38 \pm 0.02) \times 10^7$.

TABLE 3

Data for sample run described in text

m1 DIPAL	A'	A	% rxn	[Complex(II)]	[Free Fe(II)]	[Total DIPAL]	[Free DIPAL]	10 ⁷ K _{obs}
0.00	0.000							
0.02	0.037	0.0372	3.72	6.73x10 ⁻⁶	1.75x10 ⁻⁴	6.63x10 ⁻⁵	5.28x10 ⁻⁵	1.38
0.03	0.070	0.0706	7.06	1.28x10 ⁻⁵	1.69x10 ⁻⁴	9.91x10 ⁻⁵	7.65x10 ⁻⁵	1.30
0.04	0.106	0.1074	10.74	1.96x10 ⁻⁵	1.62x10 ⁻⁴	1.32x10 ⁻⁴	9.24x10 ⁻⁵	1.41
0.05	0.144	0.1463	14.63	2.66x10 ⁻⁵	1.55x10 ⁻⁴	1.64x10 ⁻⁴	1.11x10 ⁻⁴	1.40
0.06	0.183	0.1867	18.67	3.40x10 ⁻⁵	1.48x10 ⁻⁴	1.96x10 ⁻⁴	1.28x10 ⁻⁴	1.40
0.07	0.222	0.2270	22.70	4.13x10 ⁻⁵	1.41x10 ⁻⁴	2.28x10 ⁻⁴	1.45x10 ⁻⁴	1.39
0.08	0.259	0.2660	26.60	4.84x10 ⁻⁵	1.33x10 ⁻⁴	2.60x10 ⁻⁴	1.63x10 ⁻⁴	1.36
0.09	0.298	0.3070	30.70	5.59x10 ⁻⁵	1.26x10 ⁻⁴	2.91x10 ⁻⁴	1.79x10 ⁻⁴	1.38
0.10	0.335	0.3460	34.60	6.30x10 ⁻⁵	1.19x10 ⁻⁴	3.23x10 ⁻⁴	1.97x10 ⁻⁴	1.37
0.11	0.368	0.3820	38.20	6.95x10 ⁻⁵	1.12x10 ⁻⁴	3.54x10 ⁻⁴	2.15x10 ⁻⁴	1.39
0.12	0.405	0.4210	42.10	7.65x10 ⁻⁵	1.05x10 ⁻⁴	3.85x10 ⁻⁴	2.32x10 ⁻⁴	1.35
0.13	0.438	0.4565	45.65	8.30x10 ⁻⁵	9.90x10 ⁻⁵	4.15x10 ⁻⁴	2.49x10 ⁻⁴	1.36
excess	1.000	1.0000						

mean K_{obs} = (1.38±0.02)x10⁷

V.- Measurement of Redox Potential

A. Apparatus

A thermostated cell was set up, its two half cells consisting of two small glass cylinders 8 cm long and 1.5 cm diameter across which the agar-KCl bridge could sit. The bridge was made by dissolving 4 gms agar-agar powder and 35 gms KCl in 100 ml water, boiling for a few minutes, and sucking the liquid into teflon tubing previously bent into an appropriate U shape. The liquid in the bridge was allowed to cool and solidify into a gel. The bridges were always kept in saturated KCl solution and a fresh bridge was used for every experiment.

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

The other half cell contained an equimolar mixture of complex(II) and complex(III) at given pH, I and T. A rhodium electrode dipped into the mixture when potentiometric measurements were being taken. When measuring pH, a glass electrode was dipped into the half cell in its original position. All through potentiometric and pH measurements the solution was mixed with a magnetic stirrer.

B. Method

All redox potential measurements were made on equimolar mixtures of complex(II) and complex(III). The pH of the solution was adjusted with NaOH, not with buffer. The reason for this was the following: the limit of DIPAL solubility (about 0.01M in water) limited the maximum DIPAL/Fe ratio that could be attained. This in turn limited the concentration of Fe(II). Thus dilution with buffer gave $[\text{Complex}] \sim 1.5 \times 10^{-4} \text{M}$ or less, a concentration which is too low for stable potentials.

The solutions of complex(II) and complex(III) were prepared as follows: About 2 ml of DIPAL (0.010M) were added to 0.25 ml Fe(II) stock (0.010M) in a tube and 0.25 ml Fe(III) stock (0.010M) in another tube, and the mixtures let stand for about 15 min. to ensure complete complex formation. About 0.2 ml NaOH (0.05M) was then added to make total volume 2.5 ml in each case. The amounts of DIPAL and NaOH were calculate to yield the required pH.

While the solutions were standing to ensure complete complex formation, the pH-meter was calibrated. The solutions of complex(II) and complex(III) were then mixed and immediately placed in the half cell with the rhodium electrode. The potential was followed with time and usually it either rose or dropped until about 10 to 15 min., after which it remained constant. The rhodium electrode was then removed, a glass electrode dipped into the solution and the pH measured. Finally, the pH-meter was rechecked with standard buffer and in almost all cases the pH value obtained agreed with the actual value of the buffer to within ± 0.01 .

The ratio of concentrations, DIPAL / Fe , in every case was about 8:1 which, from the high value of the formation constants obtained, it was assumed that in most cases, the complexes were completely formed (see discussion). A few measurements were made using DIPAL/Fe ratios of 12:1 and 16:1 and the redox potential values obtained were the same as those with DIPAL/Fe ratio of 8:1 under the same conditions of pH, I and T.

The redox potential values obtained were vs. saturated calomel electrode and can be represented as $E_{cal.}$. To get the E values corresponding to equation (26), the value of the saturated calomel electrode at that particular temperature¹² was added to the measured $E_{cal.}$.

The ionic strength of the solutions was kept constant over the entire pH range by calculating for every pH the contribution of each individual species in a manner similar to that used for the formation constants measurements, and adding NaCl to make up to the total required value of I.

C. Sample Run

Date: July 28, 1964

T = 25.0°C pH = 4.47 I = 0.020M

Solution (1): 0.25 ml Fe(II) (0.010M) + 2.06 ml DIPAL (0.010M)
 + 0.19 ml NaOH (0.05M)

Solution (2): 0.25 ml Fe(III) (0.010M) + 2.06 ml DIPAL (0.010M)
 + 0.19 ml NaOH (0.05M)

Solutions (1) and (2) were mixed and cell EMF measured with rhodium vs. saturated calomel electrode.

Variation of $E_{cal.}$ with time:

t(min.)	5	7	10	15	20	25
$E_{cal.}$ (mv)	100.5	99.0	98.2	97.2	97.0	97.0

Fig. (2)

Effect of time on redox cell EMF (data from Sample Run)

$$E_{cal.} = 0.0970 \text{ volts}; E = 0.0970 + 0.2444 = 0.3414 \text{ volts.}$$

RESULTS

I.- Formation Constants

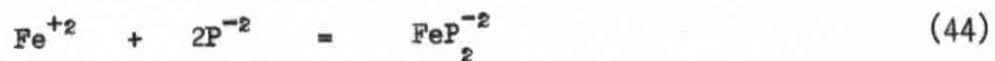
The procedure described above for measuring K_{obs} , the formation constant of the ferrous complex, was followed in extending the measurements over the pH range 3.3 to 5.1, at 25.0°C and $I = 0.027M$. The results are given in Table (4) which also lists the corresponding values of the pH-independent formation constant, K_1 , for the equilibrium in equation (12). K_1 values were calculated using equation (15), for which the values of K_3 and K_2 are taken from the redox results (see Table 12 below) and K_1 is obtained by successive approximations. The mean value of K_1 was found to be $(2.5 \pm 0.1)10^5 M^{-2}$.

The corresponding formation constant for the ferric complex, K'_{obs} , was determined at three pH values at 30.3°C and $I = 0.044M$, the results of which are given in Table (5). In this case it is not possible to obtain a K'_1 value for the equilibrium in equation (25) because three of the four ionization constants of complex(III) involved in equation (24) cannot be determined with any degree of certainty from the redox or equilibrium data (see Table 12).

It is possible, however, to calculate pH-independent values for the fully ionized species corresponding to the hypothetical reaction



and the corresponding ferrous reaction



Such calculations were not attempted, since the primary aim of the above measurements was to establish the order of magnitude of the formation constants for both complexes. The results indicate that the complexes are stable in the range of experimental conditions.

TABLE 4

Variation of K_{obs} (equation 1) with pH at $T = 25.0^{\circ}\text{C}$ and $I = 0.027\text{M}$. The corresponding pH-independent formation constant, K_i , for the reaction in equation (12) is calculated using equation (15), and the constants $K_1 = 3.0 \times 10^{-3}$, $K_2 = 3.16 \times 10^{-5}$, $K_3 = 1.26 \times 10^{-5}$. Estimated mean uncertainty in K_i is $\pm 4\%$.

<u>pH</u>	<u>K_{obs}</u>	<u>$10^5 K_i \text{ (M}^{-2}\text{)}$</u>
3.30	$(1.80 \pm 0.03) \times 10^6$	2.44
3.50	$(2.85 \pm 0.03) \times 10^6$	2.48
3.72	$(4.80 \pm 0.03) \times 10^6$	2.45
4.10	$(1.38 \pm 0.02) \times 10^7$	2.55
4.28	$(2.48 \pm 0.03) \times 10^7$	2.46
4.48	$(5.25 \pm 0.04) \times 10^7$	2.49
4.67	$(1.35 \pm 0.03) \times 10^8$	2.46
4.90	$(3.50 \pm 0.02) \times 10^8$	2.42
5.08	$(9.90 \pm 0.04) \times 10^8$	2.60
	Mean K_i	= $(2.5 \pm 0.1) \times 10^5$

TABLE 5

Variation of K'_{obs} (equation 19) with pH at $T = 30.3^{\circ}\text{C}$ and $I = 0.044\text{M}$

<u>pH</u>	<u>K'_{obs}</u>
4.24	$(2.8 \pm 0.7) \times 10^7$
5.03	$(5.4 \pm 0.6) \times 10^7$
5.94	$(1.5 \pm 0.4) \times 10^8$

II.- Redox Potentials

Following the procedure previously described, the redox potential, E , for the bis-(Pyridine-2,6-dialdoxime)-iron(III)/iron(II) system was measured over the entire pH range of stability of the complexes, at several temperatures and ionic strengths.

The pH variation of E was investigated at 20.0, 25.0, and 30.0°C, all at $I = 0.020M$, covering the pH range 3 to 6.5. A few measurements were also made at 15.0 and 27.5°C and $I = 0.02M$ within the pH range 6.0 to 6.5.

The results at 25.0°C are illustrated in Fig. (3) where E values are plotted against pH. The shape of the curve and preliminary analysis showed that in the pH range 3 to 6.5, two ionizations are involved with the ferrous complex and one ionization with the ferric complex. Stable measurements could not be made beyond pH 6.5 probably due to decomposition of the complexes. Consequently, it was not possible directly to reach the pH-independent region which corresponds to the cell reaction involving the fully ionized species (equation 27).

The analysis was carried out as follows:

From previous work⁷, the fourth ionization on the ferrous complex is known to have $pK_4 = 7.22$ at $T = 25.0^\circ C$ and $I = 0.020M$. At $pH > 6.0$, the contributions of K_3 and K_2 in equation (34) are assumed negligible and thus E_i values are calculated using successive approximations to get the value of K_4' . The E_i values obtained using equation (34) and neglecting the contributions of K_3 and K_2 are represented in Table (6) as E_i'' . At $pH < 6$, the contribution of K_3 in equation (34) cannot be neglected; consequently, at $pH > 5.4$, assuming the contribution of K_2 in equation (34) as negligible, E_i values are recalculated using successive approximations

to get the value of K_3 . The E_i values obtained by neglecting the contribution of K_2 in equation (34) are represented in Table (6) as E_i' . Finally, knowing the values of K_4 , K_3 and K_4' and using successive approximations to get the value of K_2 , E_i values are calculated over the entire pH range as shown in Table (6).

The mean value of the pH-independent redox potential, E_i , at 25.0°C and $I = 0.020M$, was found to be 0.213 ± 0.002 volts.

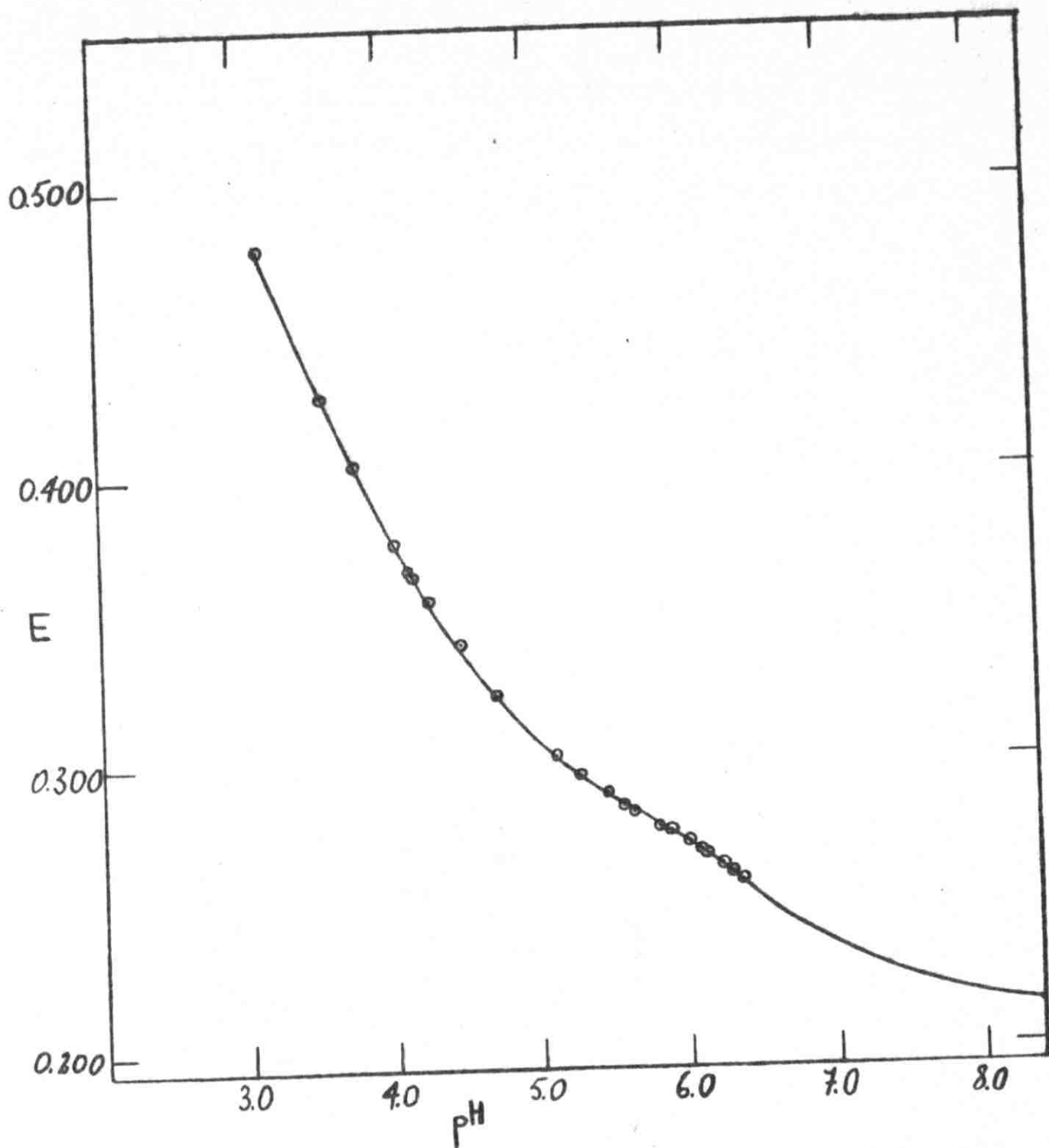


Fig. 3 Variation of E_{oxal} with pH for the bis-(Pyridine-2,6-dialdoxime)-iron(III)/iron(II) system at 25.0°C and $I = 0.020M$. Experimental points (Table 6); theoretical curve (equation 34).

TABLE 6

Variation of the redox potential, E , (equation 26) with pH, at $T = 25.0^{\circ}\text{C}$ and $I = 0.020\text{M}$. E_{cal} is the measured redox potential (vs. satd. calomel electrode). E_i'' and E_i' are as defined in the text; E_i is the pH-independent redox potential (equation 27).

$$K_4 = 6.02 \times 10^{-8}, K_3 = 1.26 \times 10^{-5}, K_2 = 3.16 \times 10^{-5}, K_4^1 = 1.20 \times 10^{-6}.$$

<u>pH</u>	<u>E_{cal}</u>	<u>E</u>	<u>E_i''</u>	<u>E_i'</u>	<u>E_i</u>
6.38	0.0140	0.2584	0.2129	0.2125	0.2125
6.31	0.0170	0.2614	0.2132	0.2126	0.2126
6.24	0.0200	0.2644	0.2139	0.2129	0.2129
6.11	0.0240	0.2684	0.2135	0.2121	0.2121
6.10	0.0250	0.2694	0.2143	0.2128	0.2128
6.01	0.0280	0.2724	0.2145	0.2128	0.2128
5.90	0.0320	0.2764	0.2155	0.2132	0.2131
5.82	0.0330	0.2774		0.2117	0.2115
5.64	0.0380	0.2824		0.2114	0.2112
5.58	0.0400	0.2844		0.2118	0.2115
5.46	0.0450	0.2894			0.2129
5.28	0.0510	0.2954			0.2134
5.12	0.0580	0.3024			0.2138
4.71	0.0790	0.3234			0.2138
4.47	0.0970	0.3414			0.2136
4.25	0.1120	0.3564			0.2138
4.16	0.1200	0.3644			0.2127
4.13	0.1220	0.3664			0.2122
4.03	0.1320	0.3764			0.2124
3.75	0.1590	0.4034			0.2110
3.55	0.1830	0.4274			0.2115
3.13	0.2340	0.4784			0.2144

$$\text{Mean } E_i = \underline{\underline{0.213 \pm 0.002 \text{ volt}}}$$

The variation of the redox potential, E , with ionic strength was studied over the range 0.006M to 0.06M at 25.0°C and pH 6.3, and the results are shown in Table (7).

The values of the pH-independent redox potential, E_i , at each ionic strength can be obtained from equation (34) so long as the corresponding values of the ionization constants involved are known at each ionic strength. The theoretical ionic strength variation of each of these ionization constants may be assumed to follow the Debye Hückel equation (37), so that

$$pK = pK^0 + A(z_R^2 - z_P^2) I^{\frac{1}{2}} / (1 + 2I^{\frac{1}{2}}) \quad (45)$$

where z_R = charge on complex; z_P = charge on its conjugate base.

The results as well as the corresponding values of E_i are also given in Table (7).

The plot of E_i vs. $I^{\frac{1}{2}} / (1 + 2I^{\frac{1}{2}})$ is shown in Fig. (4). Linear extrapolation along the theoretical slope of 0.089 (equation 39) to zero ionic strength, yields $E_i^0 = 0.204 \pm 0.002$. This extrapolated value is the thermodynamic pH-independent redox potential at 25.0°C for the cell reaction given by equation (27).

TABLE 7

Variation of redox potential, E, (equation 26) with ionic strength, at 25.0°C and pH 6.30. The pH-independent value E_i is calculated using equation (34) and the corresponding ionization constants as described in the text.

<u>I(M)</u>	<u>$I^{\frac{1}{2}}/(1+2I^{\frac{1}{2}})$</u>	<u>E</u>	<u>pK₄</u>	<u>pK₃</u>	<u>pK₂</u>	<u>pK₄'</u>	<u>E_i (+0.002)volt</u>
0.0064	0.069	0.261	7.28	4.92	4.48	5.94	0.210
0.010	0.083	0.261	7.26	4.91	4.49	5.93	0.211
0.020	0.110	0.261	7.22	4.90	4.50	5.92	0.213
0.040	0.143	0.261	7.17	4.88	4.52	5.90	0.215
0.060	0.165	0.261	7.14	4.87	4.53	5.89	0.217

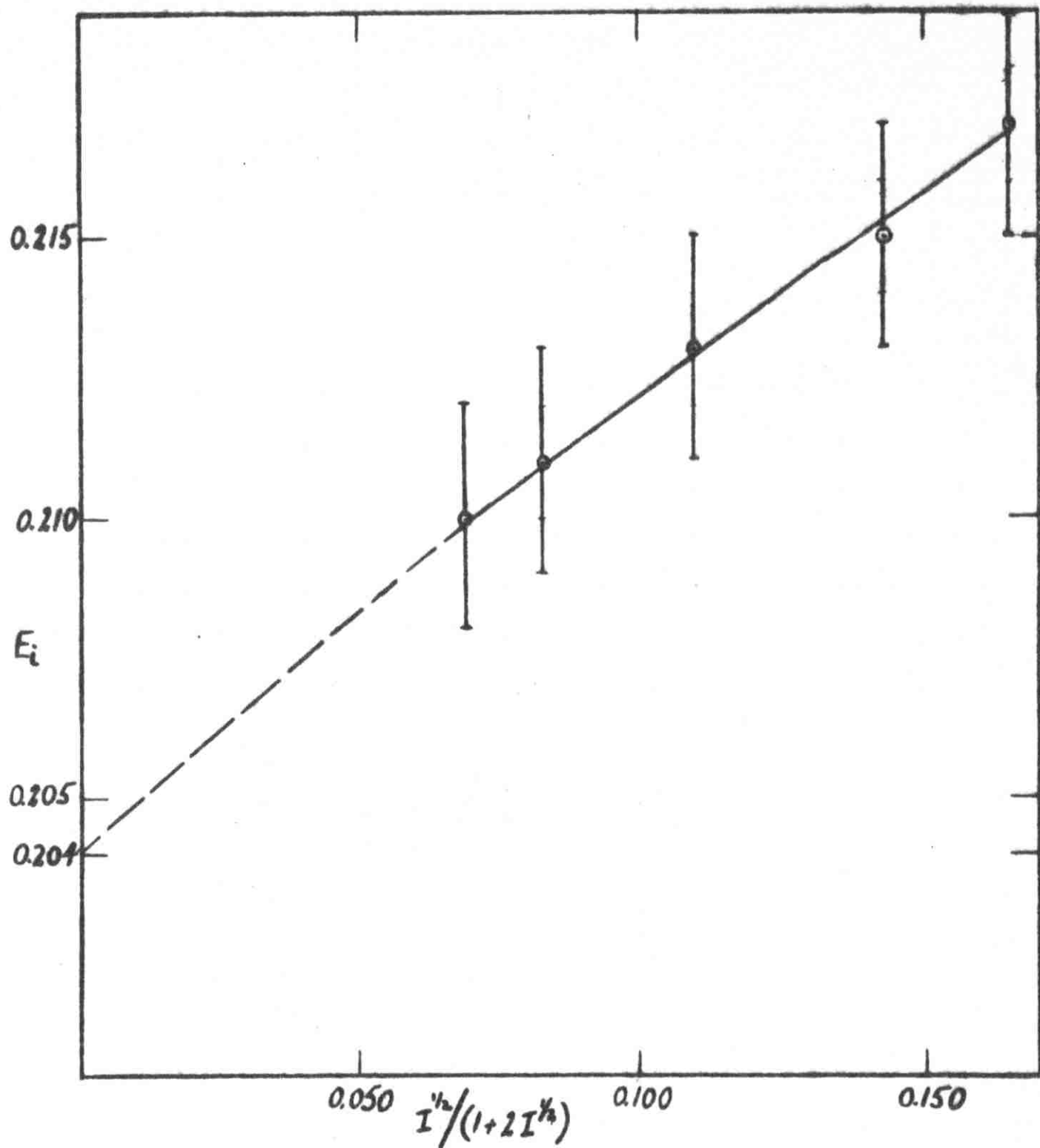


Fig. 4 Variation of E_i (eq. 27) with ionic strength at 25.0°C.
Extrapolation along theoretical slope yields $E_i = 0.204$ volts.

The variation of the redox potential, E, with pH was repeated at 15.0, 20.0, 27.5, and 30.0°C at I = 0.020M, and the results are given in Tables (8), (9), (10) and (11) which also list the corresponding E_i values calculated in a manner similar to that used for the 25.0°C results. The various ionization constants were again obtained by successive approximations and Table (12) lists the values at several temperatures and I = 0.020M.

In Fig. (5) the various E_i values obtained at 15.0, 20.0, 25.0, 27.5, and 30.0°C are plotted against temperature. The linear slope gives $dE_i/dT = -0.0029 \pm 0.0002$ volt/degree. Using equation (40) and (41) and the value of E_i^0 at 25.0°C (0.204 ± 0.002 volt), at 25.0°C, ΔH_i^0 is found to be -27.0 ± 1.4 kcal/mole, and using equation (42), ΔS_i^0 is found to be -66.9 ± 4.6 e.u.

Thus, the thermodynamic quantities at 25.0°C and I = 0 for the cell reaction represented by equation (27) may now be summarized as follows:

$$\begin{aligned} E_i^0 &= 0.204 (\pm 0.002) \text{ volt.} \\ \Delta H_i^0 &= -27.0 (\pm 1.4) \text{ kcal/mole.} \\ \Delta S_i^0 &= -66.9 (\pm 4.6) \text{ e.u.} \end{aligned}$$

TABLE 8

Variation of the redox potential, E, with pH at T = 15.0°C and I = 0.020M.

$E_{\text{cal.}}$ is the measured redox potential (vs. satd. calomel electrode). E_i is the pH-independent redox potential (equation 27). $K_4 = 6.02 \times 10^{-6}$, $K_3 = 1.26 \times 10^{-5}$, $K_4' = 1.00 \times 10^{-6}$.

<u>pH</u>	<u>$E_{\text{cal.}}$</u>	<u>E</u>	<u>E_i</u>
6.55	0.0290	0.2798	0.2424
6.35	0.0350	0.2858	0.2413
6.30	0.0380	0.2888	0.2426
6.20	0.0415	0.2923	0.2427
6.10	0.0445	0.2953	0.2425
6.02	0.0500	0.3008	<u>0.2421</u>

Mean $E_i = 0.242 \pm 0.002$ volt.

TABLE 9

Variation of the redox potential, E , with pH at $T = 20.0^{\circ}\text{C}$ and $I = 0.020M$.

E_{cal} is the measured redox potential (vs. satd. calomel electrode). E_i

is the pH-independent redox potential (equation 27). $K_4 = 6.02 \times 10^{-8}$,

$K_3 = 1.23 \times 10^{-5}$, $K_2 = 3.55 \times 10^{-5}$, $K_4' = 1.10 \times 10^{-6}$.

<u>pH</u>	<u>E_{cal}</u>	<u>E</u>	<u>E_i</u>
6.57	0.0190	0.2666	0.2287
6.42	0.0255	0.2731	0.2298
6.38	0.0265	0.2741	0.2292
6.22	0.0320	0.2796	0.2290
6.14	0.0335	0.2811	0.2277
6.04	0.0365	0.2841	0.2275
5.94	0.0410	0.2886	0.2290
5.90	0.0415	0.2891	0.2282
5.80	0.0435	0.2911	0.2270
5.64	0.0500	0.2976	0.2286
5.58	0.0500	0.2976	0.2270
5.38	0.0570	0.3046	0.2280
5.32	0.0600	0.3076	0.2291
5.08	0.0680	0.3156	0.2290
4.78	0.0825	0.3301	0.2296
4.58	0.0955	0.3431	0.2298
4.18	0.1260	0.3736	0.2289
3.93	0.1465	0.3941	0.2282
3.79	0.1610	0.4086	0.2288
3.66	0.1760	0.4236	0.2290
3.61	0.1820	0.4296	0.2298
3.47	0.1970	0.4446	<u>0.2290</u>

Mean $E_i = 0.229 \pm 0.002$ volt.

TABLE 10

Variation of the redox potential, E , with pH at $T = 27.5^{\circ}\text{C}$ and $I = 0.020\text{M}$.

E_{cal} is the measured redox potential (vs. satd. calomel electrode). E_i is the pH-independent redox potential (equation 27). $K_4 = 6.02 \times 10^{-8}$, $K_3 = 1.26 \times 10^{-5}$, $K_4^i = 1.26 \times 10^{-6}$.

<u>pH</u>	<u>E_{cal}</u>	<u>E</u>	<u>E_i</u>
6.30	0.0140	0.2565	0.2063
6.18	0.0180	0.2605	0.2058
6.10	0.0210	0.2635	0.2059
6.04	0.0225	0.2650	0.2053
5.93	0.0270	0.2695	0.2060
5.60	0.0380	0.2805	<u>0.2069</u>

Mean $E_i = 0.206 \pm 0.002$ volt.

TABLE 11

Variation of the redox potential, E , with pH at $T = 30.0^{\circ}\text{C}$ and $I = 0.020\text{M}$.

E_{cal} is the measured redox potential (vs. satd. calomel electrode). E_i is the pH-independent redox potential (equation 27). $K_4 = 6.02 \times 10^{-8}$, $K_3 = 1.26 \times 10^{-5}$, $K_2 = 2.82 \times 10^{-5}$, $K_4' = 1.38 \times 10^{-6}$.

<u>pH</u>	<u>E_{cal}</u>	<u>E</u>	<u>E_i</u>
6.46	0.0040	0.2450	0.2003
6.30	0.0105	0.2515	0.2003
6.18	0.0160	0.2570	0.2010
6.09	0.0190	0.2600	0.2006
6.02	0.0200	0.2610	0.1993
5.94	0.0235	0.2645	0.1997
5.88	0.0260	0.2670	0.2000
5.78	0.0280	0.2690	0.1986
5.64	0.0320	0.2730	0.1980
5.50	0.0380	0.2790	0.1996
5.46	0.0380	0.2790	0.1984
5.26	0.0470	0.2880	0.2008
5.20	0.0495	0.2905	0.2010
4.96	0.0595	0.3005	0.2007
4.80	0.0680	0.3090	0.2009
4.59	0.0810	0.3220	0.2000
4.38	0.0960	0.3370	0.1981
4.01	0.1320	0.3730	0.1980
3.66	0.1700	0.4110	0.1976
3.16	0.2280	0.4690	<u>0.1976</u>

Mean $E_i = 0.199 \pm 0.002$ volt.

TABLE 12

Variation of ionization constants with temperature, involving complex(II) (equation 4a, 4b, 4c, 4d), and complex(III) (equations 20a, 20b, 20c, 20d) at I = 0.020M. pK_4 (ref. 7); pK_3 , pK_2 and pK_4^{\dagger} (analysis of redox data in text); pK_1 (analysis of equilibrium data in text).

<u>Temp. (°C)</u>	<u>Complex(II)</u>				<u>Complex(III)</u>			
	<u>pK_4</u>	<u>pK_3</u>	<u>pK_2</u>	<u>pK_1</u>	<u>pK_4^{\dagger}</u>	<u>pK_3^{\dagger}</u>	<u>pK_2^{\dagger}</u>	<u>pK_1^{\dagger}</u>
15.0	7.22	-	-	-	6.00	-	-	-
20.0	7.22	4.91	4.45	-	5.96	-	-	-
25.0	7.22	4.90	4.50	2.52	5.92	-	-	-
27.5	7.22	-	-	-	5.90	-	-	-
30.0	7.22	4.90	4.55	-	5.86	-	-	-

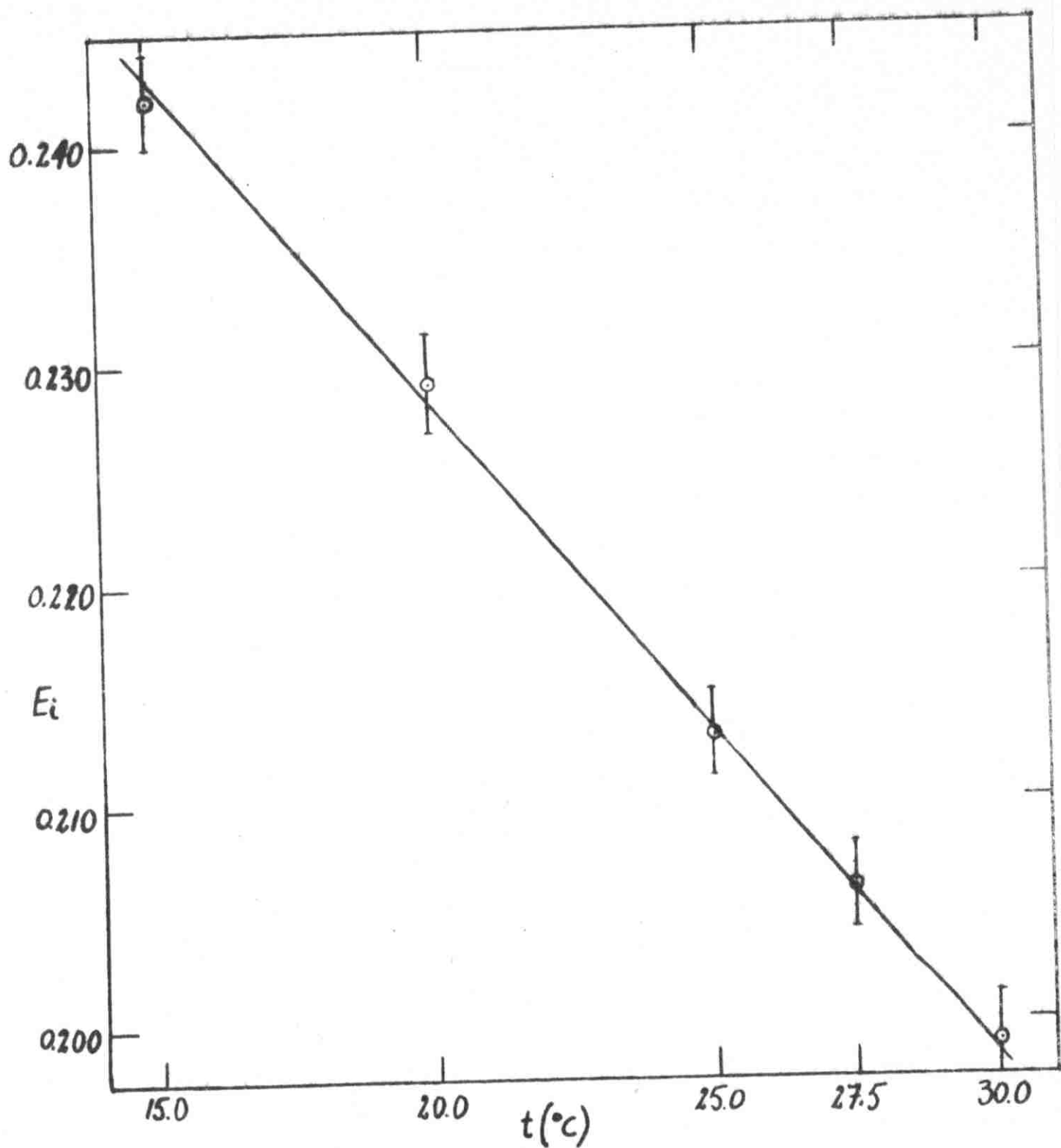


Fig. 5 Variation of E_i (eq. 27) with temperature at $I = 0.020M$

DISCUSSION

Although the primary aim of the above work was the determination of thermodynamic quantities for the Pyridine-2,6-dialdoxime iron(III)/iron(II) redox couple (equation 27), it was necessary to establish first the limits of stability for both complex(II) and complex(III). Measurements of their formation constants were therefore made; and the results (Tables 4 and 5) show that both complexes are stable within the range pH 3 to 6, with favorable free energies of formation, K_{obs} being of the order 10^6 or greater.

The uncertainty in K_{obs} is seen in Table (4) to be about $\pm 1\%$; the calculations yielding K_i values to $\pm 4\%$. This precision indicates that a more extensive study on formation constants can be undertaken; thus it is possible to obtain thermodynamic parameters for the formation equilibria represented by equations (12) and (25).

In the measurement of the redox potential, E , at given pH, I and T, the uncertainty involved in most cases was ± 0.5 mv. Gold, platinum and rhodium electrodes were used in preliminary experiments and it was found that only the rhodium electrode gave concordant results. The electrode was also checked by measuring the redox potential of the Hexacyanoferrate system at given T and I, and the results obtained agreed with the values given by Hanania et al.¹³

All redox potential measurements were made using equimolar mixtures

of complex(II) and complex(III). In the preparation of both complexes the ratio of total molar concentrations DIPAL/Fe was 8:1, the final total $[Fe] = 5.0 \times 10^{-4}M$. In the range $4 > pH > 3$, $K_{obs} \gg 10^6$ in both cases (see Tables 4 and 5) giving complex formation $\gg 90\%$. Since the formation constants are about equal for the two complexes, it may be assumed that approximately equal amounts of complex(III) and complex(II) are formed, and therefore the effect of incomplete complex formation on E is minimal. For $pH \gg 4$, $K_{obs} \gg 10^7$ (see Tables 4 and 5) giving complex formation $\gg 99\%$ in both cases. Measurements could not be extended to the range of $pH > 6.5$ as the potentials varied with time without eventually coming to a constant value. This is probably due to hydrolysis, especially of complex(III).

Further evidence of the internal consistency of the results comes from the ionic strength variation of E at pH 6.3 and 25.0°C. The plot of E_i vs. $I^{\frac{1}{2}} / (1 + 2I^{\frac{1}{2}})$, shown in Fig. 4, has a linear limiting slope which fits reasonably well the theoretical slope 0.089 given by equation (39). This "agreement" indicates that ion association, a phenomenon often observed in solutions of electrolytes, is negligible under the conditions of these experiments.

The pH-independent redox potential, E_i (equation 27), was calculated according to equation (34) which involves four ionization constants, only one of which (K_4) is known from previous work.⁷ As mentioned above (results), the values of K_3 , K_2 and K_4^1 were obtained from analysis of the data by a method of successive approximations. The values of E_i obtained in this manner are precise to within 2 mv, and the derived thermodynamic quantities have an uncertainty of about 5%.

It is interesting to consider the results obtained in the present work from two viewpoints:

- a) Influence of the ionizations of oxime side groups on redox potential of the metal.
- b) Influence of the metal-ion on the ionizations of acidic side groups.

Influence of the ionization of oxime side groups on redox potential.

The thermodynamic parameters of the redox cell reaction (equation 27) may be compared with available thermodynamic data reported for other systems given in Table (13) which also includes the present results.

Inspection of the table shows that complexes with N-ligands can be divided into three categories according to their charge types:

- 1) Iron(III)/iron(II) phenanthroline and dipyridyl systems:
charge $+3 \rightarrow +2$; $E^0 > 1$ volt; $\Delta H^0 \sim -33$ kcal/mole; $\Delta S^0 \sim -22$ e.u.
- 2) Iron(III)/iron(II) pyridine-2-aldoxime system: charge $0 \rightarrow -1$;
 $E^0 = 0.35$ volt; $\Delta H^0 = -20$ kcal/mole; $\Delta S^0 = -40$ e.u.
- 3) Iron(III)/iron(II) pyridine-2,6-dialdoxime system: charge
 $-1 \rightarrow -2$; $E^0 = 0.20$ volt; $\Delta H^0 = -27$ kcal/mole; $\Delta S^0 = -67$ e.u.

These results indicate that as the charge on the complex ion gets more negative, its redox potential decreases and the differences in molar entropy between reductant and oxidant, $S^0(\text{III}) - S^0(\text{II})$, become more negative, whereas no regular trend in enthalpy is observed.

The stabilization of oxidation states of transition metal ions through complex formation is well known. Table (13) shows that the redox potential of the $\text{Fe}^{+3} \text{ aq.} / \text{Fe}^{+2} \text{ aq.}$ system, which is 0.771 volt,

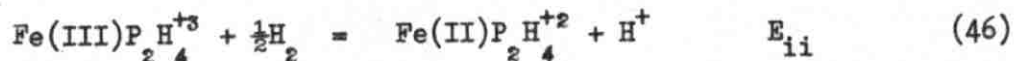
TABLE 13

Thermodynamic data on Redox Equilibria for some complex ions at 25.0°C and I = 0

	F^0	ΔF^0 (kcal/mole)	ΔS^0 (e.u.)	Ref.
$Fe^{+3} aq. + \frac{1}{2}H_2 = Fe^{+2} aq. + H^+$	0.771	-9.95	26.4	14
$Fe(CN)_6^{-3} + \frac{1}{2}H_2 = Fe(CN)_6^{-4} + H^+$	0.362	-27.0	-62.6	13
$Fe(CN)_4dipy^{-1} + \frac{1}{2}H_2 = Fe(CN)_4dipy^{-2} + H^+$	0.542	-27.4	-50.0	15
$Fe(dipy)_5^{+3} + \frac{1}{2}H_2 = Fe(dipy)_5^{+2} + H^+$	1.120	-32.7	-23.2	15
$Fe(dipy(CH_3)_2)_5^{+3} + \frac{1}{2}H_2 = Fe(dipy(CH_3)_2)_5^{+2} + H^+$	0.941	-26.8	-17.1	16
$Fe(phen)_5^{+3} + \frac{1}{2}H_2 = Fe(phen)_5^{+2} + H^+$	1.147	-32.7	-20.8	15
$Fe(PAL)_5^0 + \frac{1}{2}H_2 = Fe(PAL)_5^{-1} + H^+$	0.346	-20.0	-40.3	6
$FeP_2^{-1} + \frac{1}{2}H_2 = FeP_2^{-2} + H^+$	0.204	-27.0	-66.9	(This work)
$Ru(dipy)_3^{+3} + \frac{1}{2}H_2 = Ru(dipy)_3^{+2} + H^+$	1.374	-36.3	-15.8	15
$Os(dipy)_3^{+3} + \frac{1}{2}H_2 = Os(dipy)_3^{+2} + H^+$	0.878	-24.7	-14.8	17
$IrCl_6^{-2} + \frac{1}{2}H_2 = IrCl_6^{-3} + H^+$	0.867	-29.4	-31.5	18

may be either increased or decreased upon formation of complex ions. In general, ligands like CN^- , F^- and PO_4^{3-} reduce the value of E thus stabilizing iron in its higher oxidation state. On the other hand, nitrogen heterocyclic ligands like phenanthroline and 2,2'-dipyridyl increase the redox potential to about 1.0 volt, stabilizing iron in its lower oxidation state.

On the above basis, the low redox potential for the iron(III)/iron(II) pyridine-2-aldoxime and pyridine-2,6-dialdoxime systems gives the impression that these systems are similar to the iron(III)/iron(II) systems with CN^- or F^- as ligands. However, both pyridine-2-aldoxime and pyridine-2,6-dialdoxime are N-ligands similar to phenanthroline and dipyridyl in structure and probably also in bond type, the only difference being the ionizable oxime side groups. Strictly, therefore, to compare these systems with the phenanthroline and dipyridyl systems one should consider their hypothetical equilibria involving fully unionized species. For the pyridine-2,6-dialdoxime system, this would be:



The redox potential for this cell reaction can be calculated if all the ionization constants on both complex(III) and complex(II) were known. For complex(II), it was possible to obtain all four ionization constants; however, only the fourth ionization constant could be deduced for complex(III), and it is therefore not possible to obtain the value of E_{ii} with any degree of certainty. A consideration of the differences in free energies of the ionizations of the side groups in complex(III) and complex(II), the former being a stronger acid than the latter, shows that

the sum of the free energy differences for the ionizations in complex(III) is less than in the case of complex(II). Consequently, the free energy difference for the equilibrium involving the fully unionized species is expected to be more negative than for the one involving the fully ionized species, and thus $E_{ii} > E_i$.

In contrast, it was possible to carry out the above type of calculation in the case of the analogous but simpler pyridine-2-aldoxime system.⁶ The pH-independent redox potential for this system (corresponding to equation 46) was shown to be about 1 volt. This suggests that if such a calculation were also possible for the pyridine-2,6-dialdoxime system, the value of E_{ii} would also be of the order of 1 volt, like that of the phenanthroline and dipyridyl systems.

A similar consideration of enthalpies and entropies for the cell reaction would lead one to expect that the ΔH^0 and ΔS^0 values for the hypothetical equilibrium involving the fully unionized species (equation 46) should approach the corresponding value in the phenanthroline and dipyridyl systems. The presence of unionized but highly polar oxime groups in the pyridine-2,6-dialdoxime molecule may however produce a small entropy effect due to differences in freezing of librations of water molecules around the oxidant as compared to the reductant.

Influence of the metal on the ionization of the oxime groups

Hanania and Irvine^{4,5} have shown that the acid strength of a group in a compound increases upon coordination with a metal ion (see Introduction). Furthermore this effect is composite in that electrostatic factors as well as conjugation could contribute to the net effect of coordination

on ionization.

The effect of coordination on the ionization of oxime groups can be demonstrated by the values obtained for the ionization constants of the oxime groups in both complexes as compared with the ionization constants reported for the free ligand, pyridine-2,6-dialdoxime.⁷

If we compare the second ionization of the oxime group in the free ligand (equation 3) with the fourth ionization in complex(II) (equation 4d) it is seen that the charge types in both cases are -1 to -2. However in the ligand, $pK_{02}^0 = 10.9$ ⁷ while the corresponding ionization in the complex has $pK_4^0 = 7.2$.⁷ This increase in acid strength was accounted for by the fact that the conjugate base of the complex is stabilized through resonance to a greater extent than the conjugate base of the free ligand.

It is also interesting to observe that the fourth ionization in complex(II) (equation 4d) is weaker than the fourth ionization in complex (III) (equation 20d), $pK_4 = 7.22$ as compared with $pK_4^1 \sim 6.0$. In both cases the conjugate base is the same the only difference being the charge types, -1 to -2 as compared with 0 to -1. The differences in acidities can thus be attributed to electrostatic factors.

In a recent paper, Freiser et al¹⁹ report ionization constants for the oxime groups in pyridine-2,6-dialdoxime complexes of Ni(II), Mn(II) and Zn(II). These complexes are shown to involve a 1:2 stoichiometry, but because these metal ions do not form octahedral low spin complexes, it is assumed that one of the two oxime groups in each ligand is not involved in the bidentate bonding of tetrahedral or planar chelation. Their work is mainly concerned with stability, constants; nevertheless, inspection of their results shows that the acid strength of the non-

bonded oxime groups has increased upon coordination with these metal ions. The increase in acidity is slight compared with the increase observed for the iron complexes in the present work. The difference is probably due to the fact that in the former case the oxime group is free while in the latter the N of the oxime group is directly bonded to the metal ion. The order of increasing acidity is reported by Freiser et al to be as expected $Ni > Zn > Mn$, also parallel to the chelate stability.

The above discussion shows that information on such systems is very limited, and that there is need for more extensive thermodynamic studies of complex ions in aqueous solutions. In particular, it is important to examine those complexes which possess special structural features, such as acidic side groups involving H-bonding. Systems involving different charge types or different degrees of conjugation need to be investigated. Finally, the effect of different metal ions on the thermodynamics of ionization of acidic side groups requires a comparative study.

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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