KINETIC STUDIES OF THE DISSOLUTION

OF FRESHLY PREPARED FERRIC HYDROXIDE GEL

IN PERCHLORIC ACID MEDIA

A Thesis

submitted to

The Faculty of Graduate Studies and Research

University of Manitoba

In Partial Fulfillment

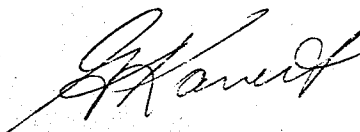of the Requirements for the Degree

MASTER OF SCIENCE

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by

GEORGE ARTHUR KANERT

to my wife

Acknowledgements

I would like to thank Dr. R.H. Betts for
his assistance and guidance during the course
of this research, and the Department of Chemistry
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G. Kanert

ABSTRACT

The exchangeability of oxygen atoms between the dissolving gel and the solvent (0.5 M perchloric acid) was studied with oxygen-18 labelled ferric hydroxide. This study showed that the oxygen atoms were tightly held by these Fe(III) species.

Spectrophotometric studies of the disappearance of color in the dissolved ferric hydroxide samples suggested that it was a pseudo-first-order reaction involving some large soluble Fe(III) species. Anions such as sulfate, fluoride and chloride had an effect on the stability of the color in these solutions.

Spectrophotometric and potentiometric studies on the dissolved ferric hydroxide samples showed that the color in these solutions was due to some large, soluble polymeric Fe(III) species.

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INTRODUCTION 1

1 - 1 FERRIC HYDROXIDE

The red-brown precipitate commonly known as ferric hydroxide and which has been written as $Fe(OH)_3$ has been studied by research workers since the turn of the century. The term "hydroxide" is a misnomer however, and the gelatinous mass should actually be termed hydrous ferric oxide or ferric oxide hydrate, $Fe_2O_3 \cdot nH_2O$, since there is no evidence of any definite hydroxide.

The usual methods of forming this precipitate are:

1. precipitation from a ferric salt solution by the addition of a base

2. slow hydrolysis of a dilute aqueous ferric salt solution.

Workers have gained an understanding of the mechanism of formation of the gel by means of hydrolysis studies of ferric salt solutions. Information has been gained about the constitution and properties of the gel through studies of the gelatinous mass itself.

1 - 2 HYDROLYSIS STUDIES

The hydrolysis of Fe(III) in aqueous solutions has for many years been written as:

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

$$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+$$

$$Fe(OH)_2^+ + H_2O \rightleftharpoons Fe(OH)_3 + H^+$$
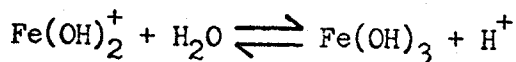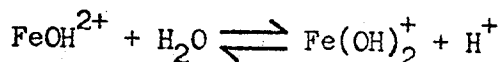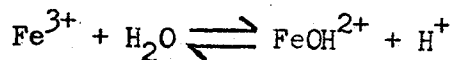
Lamb and Jacques[1] have studied the slow hydrolysis of dilute (0.01 N to 0.005 N) ferric chloride and ferric nitrate solutions by means of conductivity and colorimetric measurements. The progress of the hydrolysis was followed by observing the increase in conductivity with time, with the chloride solutions having a higher conductivity than the nitrate solutions due to the smaller mobility of the nitrate ion. Lamb and Jacques confirmed the marked increase in the speed of the hydrolysis with increasing dilution and temperature in the most concentrated solutions. They found that nitric or hydrochloric, when added either before or after hydrolysis had started in the solutions, decelerated the hydrolysis to the same extent. Sulfuric acid, however, had a duplex effect – the usual decelerating effect of the other acids due to H^+ ion effect and an initial accelerating effect, which was said to be due to the adsorption of sulfate ion by colloidal ferric hydroxide. The progress of the slow hydrolysis was also followed by the measurement of the yellow color which developed in the solutions with time. The results obtained were closely parallel to the conductivity measurements. This, according to Lamb and Jacques, was said to indicate a single colored species – ferric hydroxide – which is formed with the liberated H^+ ion being responsible for the increase in conductivity.

In a spectrophotometric study of ferric perchlorate solutions in the presence of OH^- ions, Rabinowitch and Stockmayer[2] argue that the yellow color of the solutions of hydrolyzing ferric chloride studied by Lamb and Jacques was not due to the formation of ferric

hydroxide, since most ferric salt solutions were yellow even at pH values which preclude the formation of colloidal hydroxide. They found that most complex forms of ferric ion have absorption bands either in the near ultraviolet or the blue violet region of the visible spectrum.

Rabinowitch and Stockmayer were able to separate the absorption curve of the free (hydrated) Fe^{3+} ion from that of $FeOH^{2+}$ in ferric perchlorate – perchloric acid systems. The absorption spectrum of the Fe_{aq}^{3+} ion consisted of a heavy double-peaked absorption band at 200-240 millimicrons and three much weaker absorption bands in the visible region, of which one, at 407 millimicrons was quite sharp and the other two were quite diffuse. $FeOH^{2+}$ made a maximum contribution to the absorption at 325 millimicrons (see Fig. 1-1). The absorption coefficient for Fe^{3+} + $FeOH^{2+}$ at 400 millimicrons was shown to increase with temperature due to increased hydrolysis (see Fig. 1-2).

In the hydrolysis of ferric ion in ferric sulfate solutions, Arden[3] found that the hydrolysis could be explained quantitatively by postulating that the ions Fe^{3+}, $FeOH^{2+}$ and $Fe(OH)_2^+$ were the only ones present in solution. However, the formation of ferric oxypenta-sulfate and ferric pentaoxysulfate which could have been considered as sulfates of Fe_2OH^{5+} and $Fe_2(OH)_5^+$, suggested that perhaps the hydrolysis process occurred through the medium of ions containing two iron atoms. For this assumption to be true, Arden stated that there would have to be an equilibria between Fe^{3+}, Fe_2^{6+}, Fe_2OH^{5+}, $Fe_2(OH)_2^{4+}$, $Fe_2(OH)_4^{2+}$ and $Fe_2(OH)_5^+$. Arden still preferred the monatomic hydrolysis process

- 4 -

FIG. 1-1

Absorption curves of Fe^{3+} (left) and $FeOH^{2+}$ (right).

The scale to the left is for the Fe^{3+} curve and

applies also to the $FeOH^{2+}$ curve if K_H is assumed

to be equal to 1×10^{-3} where K_H is defined as:

$$K_H = \frac{\left[FeOH^{2+}\right]\left[H^+\right]}{\left[Fe^{3+}\right]}$$

The scale to the right is for the product $K_H \epsilon_{FeOH^{2+}}$

where $\epsilon_{FeOH^{2+}}$ is in units of $M^{-1} cm^{-1}$.

The dotted segments of the curve are interpolations.

(Reproduced from Ref.(2))

FIG. 1-1
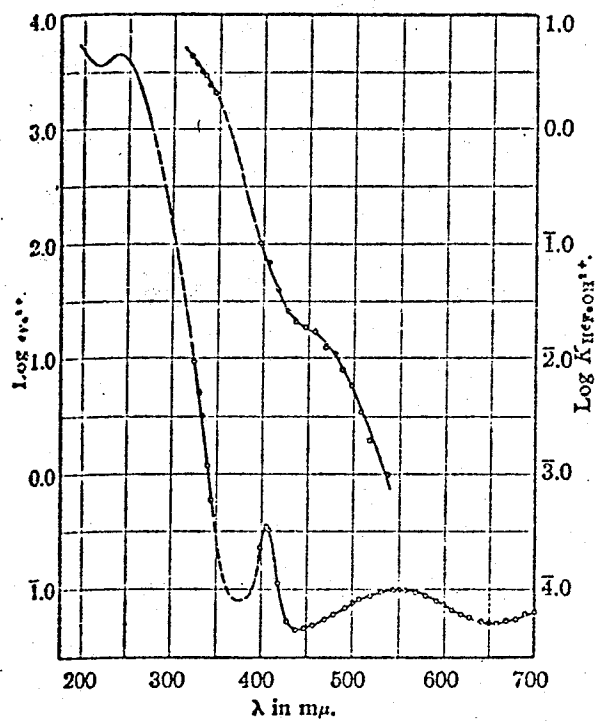
FIG. 1-2

Increase in the absorption coefficient of

Fe^{3+} + $FeOH^{2+}$ at 400 millimicrons with temperature,

due to increased hydrolysis:

$[Fe(ClO_4)_3]$ = 0.10 m./l.; μ = 1.10;

$[HClO_4]$ = 0.5 m./l. $\overline{\epsilon}$ is defined as:

$$\overline{\epsilon} = \frac{1}{d\,[Fe^{3+}]_o}\,log_{10}\frac{I_o}{I}$$

where d is the thickness of the cell and $[Fe^{3+}]_o$

the total concentration of trivalent iron.

(Reproduced from Ref.(2))

FIG. 1-2
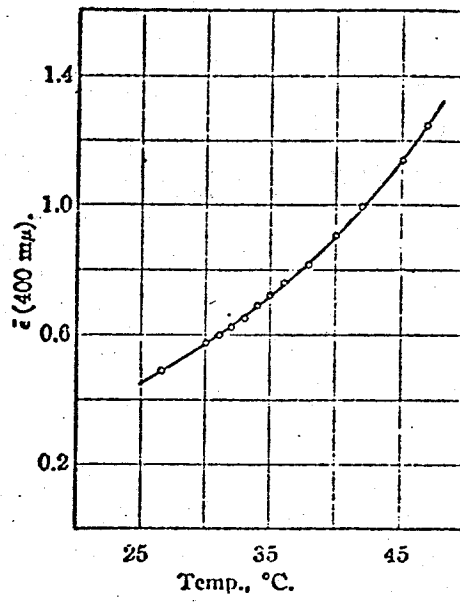
since it gave the simplest mechanism that agreed with the experimental observations.

Hedstrom[4] studied the hydrolysis of ferric perchlorate solutions using glass and redox electrodes, and deduced that the main hydrolysis product in the pH range from zero to 2.5 for his experimental conditions (40 millimolar total iron, 3 M $NaClO_4$ and $25^{o}C$) had the formula $Fe_2(OH)_2^{4+}$ and that mononuclear complexes occurred as by-products, becoming important at low concentrations:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad \ldots (1)$$
$$K_1 = 9.9 \times 10^{-4}$$

$$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+ \qquad \ldots (2)$$
$$K_2 = 5.5 \times 10^{-4}$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \qquad \ldots (3)$$
$$B_{22} = 1.22 \times 10^{-3}$$
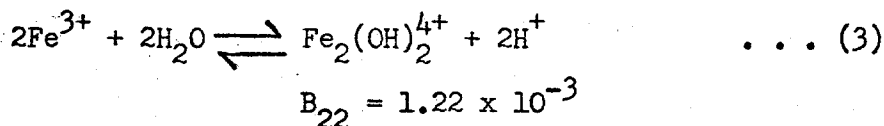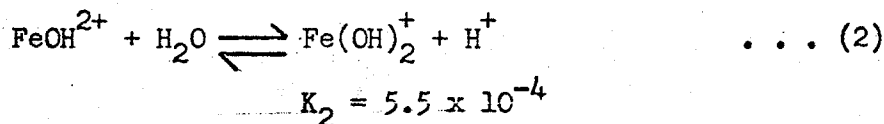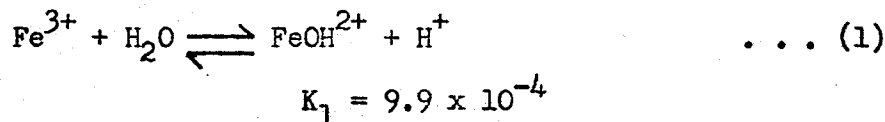
The equilibrium constants were defined as follows:

$$K_1 = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}]}$$

$$K_2 = \frac{[Fe(OH)_2^+][H^+]}{[FeOH^{2+}]}$$

$$B_{22} = \frac{[Fe_2(OH)_2^{4+}][H^+]^2}{[Fe^{3+}]^2}$$

Milburn and Vosburgh[5], in a spectrophotometric study of the hydrolysis of the iron (III) ion, investigated ferric perchlorate solutions at 25° over a wide range of concentrations and ionic strengths.

The optical densities were measured at 340 millimicrons. The results gave evidence to the importance of polynuclear iron (III) species at total iron (III) concentrations of 10^{-3} M or more. Milburn and Vosburgh suggested that the dimeric species was formed by means of the dimerization of the first hydrolysis product:

$$2FeOH^{2+} \rightleftharpoons Fe(OH)_2Fe^{4+}$$
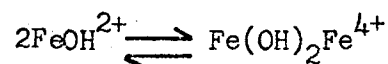
They found k_d (equivalent to $\dfrac{B_{22}}{K_1^2}$ in the constants referred to by Hedstrom[4]), the dimerization constant, to be $16(\pm 5) \times 10^2$ at a temperature of $25°$ and an ionic strength of 3. This agreed well with Hedstrom's value of $15(\pm 2) \times 10^2$ under the same conditions. The dimerization was strongly dependent upon ionic strength, becoming far less important at lower ionic strengths.

Mulay and Selwood[6] studied the hydrolysis of 0.04 M ferric perchlorate solutions containing 3 M $NaClO_4$ under various acidity conditions by means of magnetic susceptibilities and spectrophotometry;

From the measurements of magnetic suceptibility over a range of temperatures the hydrolysis species $Fe_2(OH)_2^{4+}$ was found to be diamagnetic. These workers suggested that the subnormal magnetic moment for iron in hydrous ferric oxide may be due to part of the iron being present in the form of dimers built into the gel structure. The reaction for the formation of the dimer was found to be endothermic with $\Delta H \simeq$ 9.8 kcal per mole.

In their spectrophotometric work, the U.V. absorption of the ferric per-

chlorate solutions was studied at 15° and 51° and also at 25° in

order to compare their results with Hedstrom's[4]. See Fig. 1-3

and Fig. 1-4. For a pH less than zero at 25° only one maximum was

seen: at 240 millimicrons. When the pH was increased to between

1.0 and 1.8 an additional maximum was located at 335 millimicrons

at 15°. The intensity of the peak at 240 millimicrons decreased

when the solutions were heated to 51° while the peak at 335 millimicrons

increased. Solutions with a pH greater than 1.8 produced only a broad

absorption band extending far into the visible region, without any

definite peaks. The solution with a pH of approximately 0.2 shown in

Fig. 1-3 had only one maximum at 240 millimicrons at 15°. When the

solution was heated to 51° an additional maximum at 335 millimicrons

occurred. The peak at 335 millimicrons was established to be almost

entirely due to the dimer and the one at 240 millimicrons due to

contributions from both Fe^{3+} and $FeOH^{2+}$. Mulay and Selwood evaluated

the equilibrium constant for the formation of the dimer (equation (3),

Hedstrom's work) at 15° and 51° and found it to be in agreement with

that calculated from their magnetic data. The value obtained at 25° for B_{22}

from the magnetic data was $(7.3 \pm 0.8) \times 10^{-3}$, as compared to

$(1.22 \pm 0.10) \times 10^{-3}$ obtained by Hedstrom[4] under the same conditions.

The difference was said to be due to the fact that the presence of

the first and second hydrolysis products were ignored in the cal-

culations from the magnetic data and that, since the values of the

molecular concentration of the dimer were based on the difference

between the total iron concentrations and that of the Fe^{3+} ions,

these were somewhat higher than the actual ones. The hydrogen ion

FIG. 1-3

Absorption spectra of 0.04 M ferric perchlorate-
3M sodium perchlorate solutions (light path =
0.005 cm.).

Curve with closed circles is for solution with
pH$<$0 at 25°. Solid and dashed curve with open
circles is for solution with approximate pH of
0.2 at 15 and 51°, respectively.

(Reproduced from Ref.(6))

FIG. 1-3
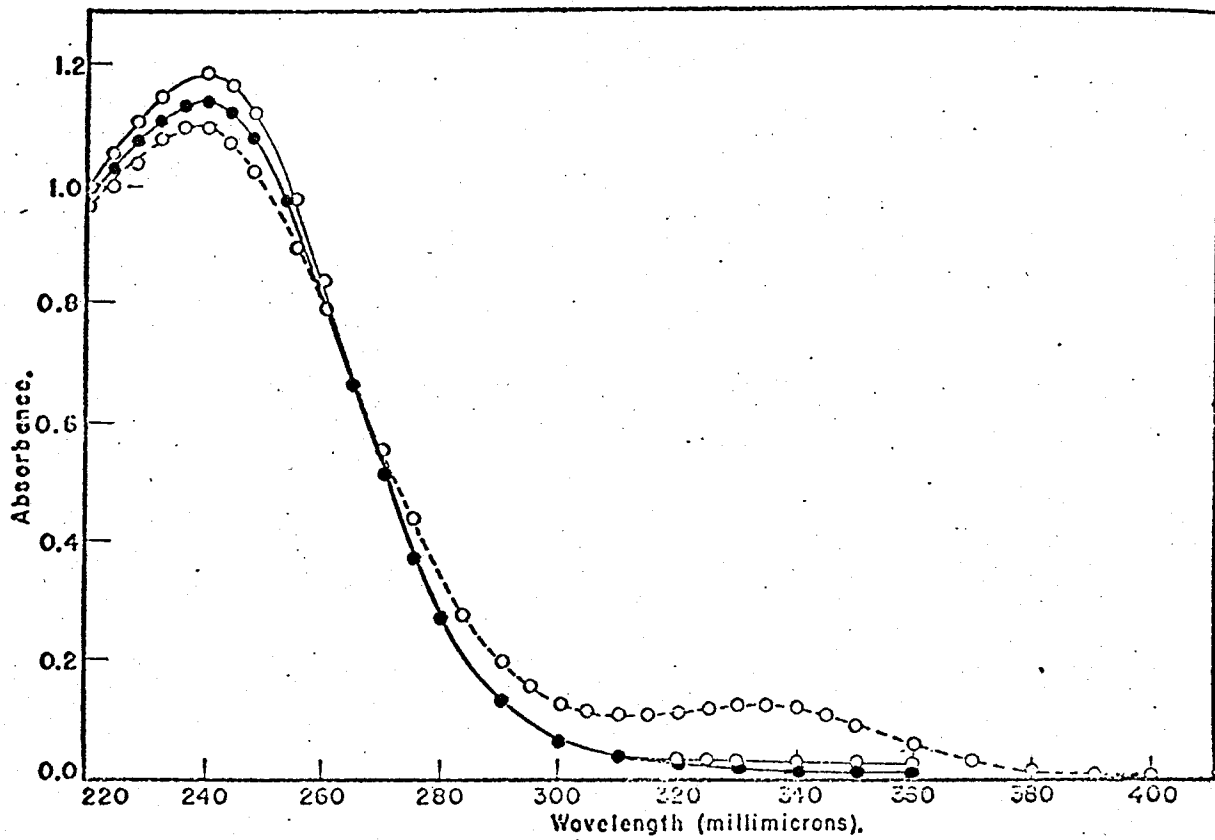
FIG. 1-4

Absorption spectra of 0.04 M ferric perchlorate,

3M sodium perchlorate solutions (light path =

0.005 cm.).

Curves with open, closed and half circles correspond

to solutions with approximate pH of 1.0, 1.7 and 2.0

respectively. Solid and dashed curves correspond

in each case to spectra observed at 15 and 51°,

respectively.

(Reproduced from Ref.(6))

FIG. 1-4
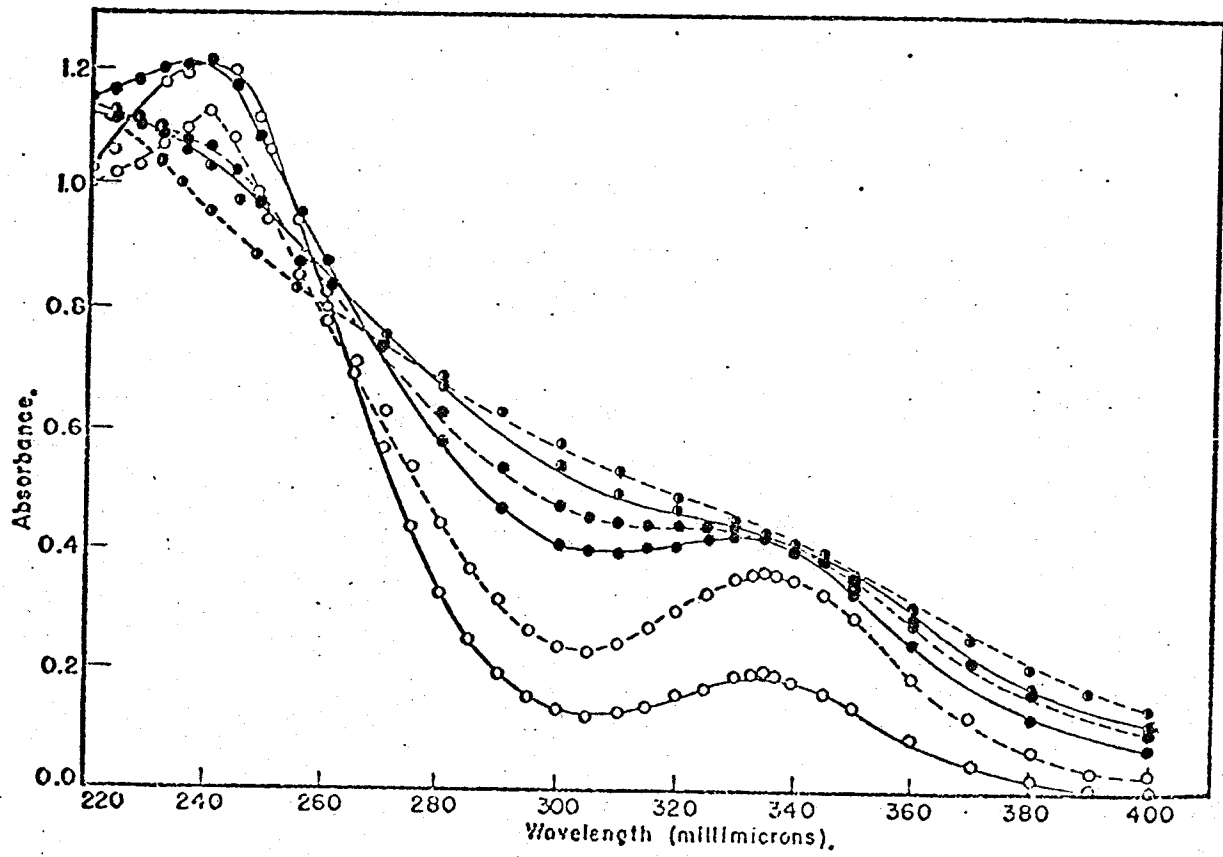
concentrations calculated from the observed pH were also not very precise.

Mulay and Selwood concluded that the dimeric species was probably as suggested by Hedstrom: a binuclear complex with the following possible structure:
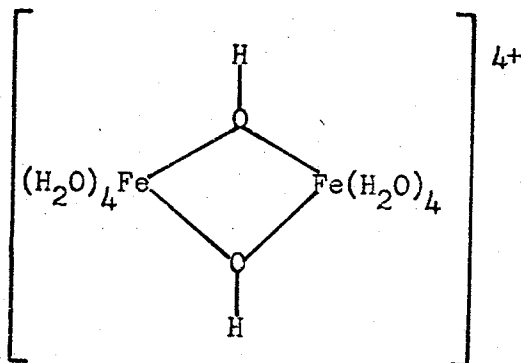
They noted that prior to precipitation of hydrous ferric oxide, almost one-half of the iron in a 0.04 M solution was present as the dimer.

In a review article, Stumm and Lee[7] suggest that the dimer may undergo hydrolytic reactions which could provide additional hydroxides which could then form more bridges, i.e.,

$$\left[Fe_2(H_2O)_8(OH)_2\right]^{4+} + H_2O = \left[Fe_2(H_2O)_7(OH)_3\right]^{3+} + H_3O^+$$

$$\left[Fe_2(H_2O)_7(OH)_3\right]^{3+} + \left[Fe(H_2O)_5(OH)\right]^{2+} = \left[Fe_3(H_2O)_5(OH)_4\right]^{5+} + 7H_2O.$$
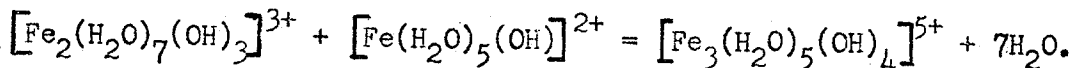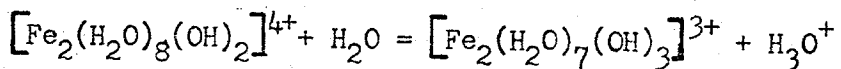
A sequence of such hydrolytic and olation (polymerization) reactions would lead eventually to the formation of metastable colloidal iron hydroxo polymers and ultimately to the formation of insoluble precipitates.

The hydrolysis of 0.3 M ferric nitrate with bicarbonate was studied by Spiro et al[8]. This hydrolysis led to the formation of

a high molecular weight polymer of composition $[Fe(OH)_x(NO_3)_{3-x}]_n$
where x lay between 2.3 and 2.5 and n was in the order of 900. The
polymer formation was monitored by measuring the Schlieren patterns
after ultra-centrifugation. The polymer was isolated and characterized
by means of gel filtration. The polymer size and composition was
found to be nearly independent of the degree of hydrolysis of the
ferric nitrate solutions between 1.0 and 2.0 base equivalents per mole
of Fe. The formation of the polymer was rapid while its dissociation
was very slow. Although the ferric hydroxide precipitated from parti-
ally hydrolyzed ferric nitrate solutions within a few days, solutions
of isolated polymer remained clear indefinitely. This suggested
that the precipitation proceeded not from the polymer, but from low
molecular weight components of the hydrolyzed solutions. Electron
microscopy revealed that the polymer particles were isolated spheres,
most of which were close to $70^{\circ}A$ in diameter. Spiro et al.suggested
that the polycations were chains of ferric ions held together by
double hydroxyl bridges.

Schugar et al[9], in their investigation of the aquo dimer
and polymer produced from the partial neutralization of ferric per-
chlorate solutions with bicarbonate, state that the iron (III) in
these materials is in an intermediate paramagnetic state with
probably two unpaired spins per iron. They show that Mulay and
Selwood's magnetic data[6] is more compatible with a calculated curve
(produced from a plot of the average magnetic moment per Fe (III)
vs. pH) if a paramagnetic dimer is assumed.

Highly colored dimeric species have also been found in vanadium

systems. In experiments done by Newton and Baker[10], vanadium (II) and vanadium (IV) were mixed in perchloric acid. This produced a highly colored substance which was shown to be an intermediate in the reaction

$$V^{2+} + VO^{2+} + 2H^+ \longrightarrow 2V^{3+} + H_2O.$$
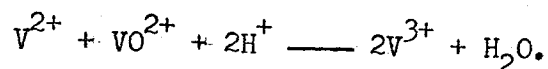
The intermediate was a hydrolytic dimer of V(III) —— VOV^{4+} .

1 - 3 STRUCTURAL STUDIES OF HYDROUS FERRIC OXIDE

Krause and Pilawski[11] called amorphous ferric hydroxide ferric ortho-hydroxide and assigned it this structure:

$$\begin{array}{c} HO \\ \diagdown \\ \diagup \\ HO \end{array} Fe \underline{\quad} O \underline{\quad} \overset{\overset{\displaystyle OH}{|}}{Fe} \underline{\quad} O \underline{\quad} \overset{\overset{\displaystyle OH}{|}}{Fe} \underline{\quad} O \underline{\quad} Fe = O = 2Fe_2O_3 \cdot H_2O.$$
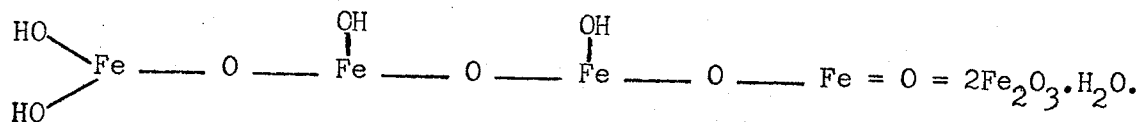
This was one of the first suggestions that ferric hydroxide had a polymeric structure.

Weiser and Milligan[12], in a review article, state that, since the dehydration curves of the brown gel of ferric oxide were smooth curves[13], there could be no hydrates or $Fe(OH)_3$ present. See Fig. 1-5a. Weiser and Milligan had found that a gel, freshly prepared in the cold, was amorphous to X-rays, but after standing at room temperature, in contact with water for several weeks, it had given a band diffraction pattern corresponding to α-Fe_2O_3 or hematite[14]. After several months of aging, the sample had given a sharp hematite pattern. The aging of the brown gel had apparently consisted in the growth of α-Fe_2O_3 crystals too small to give characteristic X-radiograms into crystals large enough to give sharp diffraction lines. This transformation had taken place slowly at room temperature, but more rapidly at higher temperatures.

Weiser and Milligan noted in their review that the only physical

evidence for the formation of a hydrate or hydroxide by the dehydration

of the brown gel had been reported by Thiessen and Köppen[15] in their

experiments on a gel produced from the slow hydrolysis of ferric

ethylate. During the isothermal dehydration of the gel, these

workers had reported breaks or inflection points in the dehydration

curves corresponding to eight and possibly ten different hydrates:

$Fe_2O_3 \cdot nH_2O$ where n = 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.0 and 0.5.

Weiser and Milligan repeated their experiments[14] and failed to find

any breaks in the dehydration curves. See Fig. 1-5b.

Weiser and Milligan concluded that the gelatinous precipitate

of ferric oxide was not made of polymerized bodies or condensation

products resulting from the splitting off of water from the hypothetic-

al ferric hydroxide. The gel was believed to be an agglomerate of

extremely minute crystals of oxide which held large amounts of water

by adsorption and capilllary forces.

An X-ray study of amorphous ferric oxide hydrate gel produced

by precipitation with concentrated ammonia from a ferric nitrate

solution was performed by van der Giessen[16]. The gel was filtered

off by suction and powders for the X-ray analysis were produced by

dehydrating the gel by freezing with liquid nitrogen. The X-ray

analysis showed that the gel consisted of particles about $30A^{\circ}$ large with

a cubic structure. Van der Giessen concluded that iron oxide hydrate

cannot be entirely amorphous and that it is partially crystalline. He

found that the primary particles of the gel had a composition of

approximately $Fe_2O_3 \cdot 1.2H_2O$. He could not however determine whether

FIG. 1-5

1-5a

Dehydration isobars for hydrous ferric oxides.

Curve 1 is for a relatively coarse sample formed

by precipitation of a ferric nitrate solution

with ammonia, and curve 2 is for a finer grained

sample precipitated from a ferric chloride solu-

tion with ammonia.

(Reproduced from Ref.(13))

1-5b

Dehydration isotherms for $Fe_2O_3 \cdot xH_2O$ prepared by

Thiessen's method.

(Reproduced from Ref.(14))

FIG. 1-5
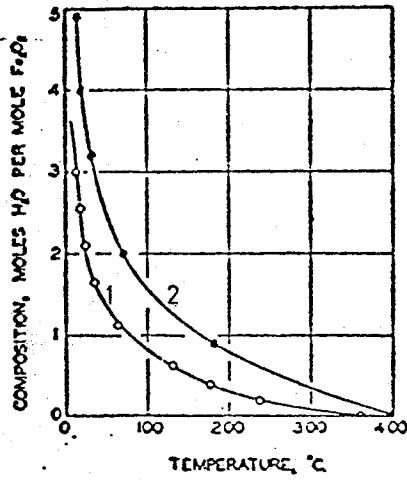
1-5a
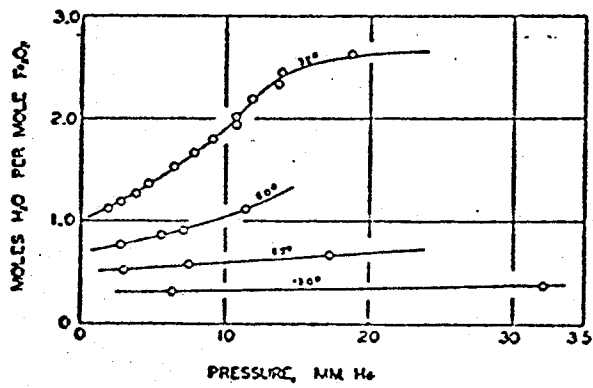
1-5b

the water was present in the lattice or adsorbed on the particle sur-
face.

A ferric colloidal compound produced by hydrolyzing 0.06 M
$Fe(NO_3)_3 \cdot 9H_2O$ at $85^{\circ}C$ was studied by electron optical methods by
Towe and Bradley[17]. The dried colloid was also studied by means of
I.R., X-ray diffraction, differential thermal analysis (D.T.A.) and
chemical analysis. From X-ray and electron diffraction studies the
material was found to have a structure similar to hematite. Towe and
Bradley came to the conclusion that one should not refer to ferric
sols or gels as goethite or as hematite with adsorbed water. From
their I.R. and D.T.A. data they suggested that there was molecular
water present in both the adsorbed and chemically combined state.
The diffraction analysis established that water was an integral part
of the crystal structure but that it could vary in a quantitative
way. This would explain the contradictory presence or absence of
definite hydrates as discussed by Weiser and Milligan[12]. Towe and
Bradley concluded that a variable water content was to be expected
and that the approach to the final hematite end product was closer
in those materials precipitated at elevated temperatures.

Iron (III) hydroxide gels produced from a series of 0.5 molal
ferric nitrate solutions hydrolyzed for varying times and at pH
values up to 1.5 were studied by Atkinson, Posner and Quirk[18].
The types and sizes of crystals produced by aging the gels at $60^{\circ}C$ in
the presence of excess NaOH from 5 minutes to 408 hours were examined
qualitatively by electron microscopy, selected area diffraction and
X-ray diffractometry. Various forms of hematite and goethite crystals

were observed. Iron (III) polymer particles obtained directly by drying the hydrolyzing Fe(III) solutions on specimen grids showed 30-50 A^o diameters as compared with the 70 A^o diameters found by Spiro et al[8]. Samples taken during crystal growth showed gel particles with diameters between 20 and 50 A^o which agreed with those of van der Giessen[16] and Towe and Bradley[17]. Atkinson et al. believed that there was no essential difference between polymer and gel particles except for the properties of the polymer related to its electrical charge.

According to Atkinson et al, only a small proportion of the gel particles formed at precipitation were able to grow into crystals at the expense of the dissolution of other particles during aging. These particles were called crystal nuclei. The identification of very small hematite and goethite crystals as nuclei did not necessarily give any information on the structure of ferric oxide hydrate gels however, since the crystal nuclei were a very small proportion of the gel particles. Atkinson et al. believed there could be several possible reasons for the difference between gel particles which dissolve during crystal growth and crystal nuclei which survive in the gel:

(i) Crystal nuclei could be relatively large particles less likely to commence dissolution than other particles. Atkinson et al. considered this unlikely however, because the gel particles had a relatively narrow size range between 20 and 50 A^o as shown by electron spectroscopy.

(ii) Crystal nuclei could have well-ordered goethite or hematite structures as compared with amorphous particles. This seemed possible

since Spiro et al.[8] had found that their isolated polymer had hydroxyl bridging with little oxo bridging.

(iii) The gel particles could occupy a wide range of states of structural disorder. Only a small proportion of the particles had the goethite or hematite structure sufficiently developed for crystal growth instead of dissolution. The gel particles could have a crystal model similar to that of hematite as suggested by Towe and Bradley[17].

Atkinson et al. believed that the diffraction data obtained by van der Giessen[16] was due to goethite crystals and not due to a new compound $Fe_2O_3.1.2H_2O$ as stated by van der Giessen.

Van der Kraan and Medema[19] prepared iron hydroxide samples with particle sizes between 50 and 220 A^o by hydrolyzing ferric nitrate solutions then aging them in KOH for various lengths of time (2 to 300 minutes), at a temperature of 20 or 100°C. The samples were filtered, air-dried at 50°C, and X-ray diffraction, electronmicroscopy, D.T.A. and surface area measurements were performed. It was found that aging at higher temperatures and for longer periods of time produced larger particles. The products with particle sizes greater than 100 A^o were found to consist of chemically and crystallographically pure α -FeOOH (goethite) with some extra water which was both chemically and physically adsorbed. The products with a particle size below 100 A^o had a relatively labile arrangement of iron, oxygen and water poorly ordered in the form of an iron oxide hydrate. An amorphous sample formed with the least amount of aging produced an X-ray pattern similar to that obtained by van der Giessen[16].

Furuichi, Sato et al. studied the effects of various anions on

the velocity of the dissolution of ferric oxide hydrate in various acids.[20] The gel was prepared from 0.125 M ferric nitrate and 6N NH$_4$OH. The precipitate was washed and filtered off and dried in a partial vacuum for 48 hours, then dried in an oven at 100°C for 6 hours. The material was sieved through a 200-300 mesh, heated to 100°C and then suddenly cooled to room temperature. An X-ray study showed that the sample was amorphous. A 1.2g. sample was dissolved in 120 ml. of acid and samples were removed from the solution at certain intervals and analyzed for Fe^{3+} spectrophotometrically. The oxide hydrate solubility increased according to the order: HCl $>$ H$_2$SO$_4$ $>$ HNO$_3$ $>$ HClO$_4$. It was also found that the velocity of dissolution increased with hydrogen ion concentration. Further experiments were performed with the addition of various anions in various concentrations to the dissolving acid. The effect on the increase in the dissolution rate of the oxide hydrate was in the order: Cl$^-$ $>$ SO$_4^{2-}$ $>$ NO$_3^-$ $>$ ClO$_4^-$. The velocity of the dissolution also increased with increased anion concentration. Furuichi et al. suggest that the hydroxyl group between the ferric oxides in the ferric oxide hydrate structure suggested by Mulay et al.[21]
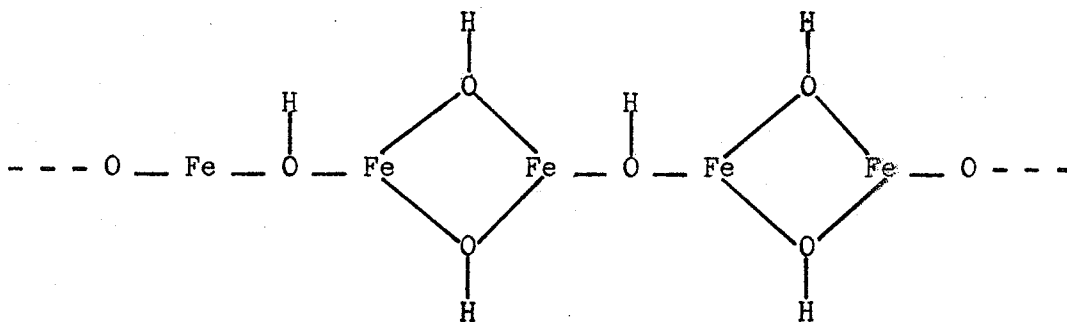
is an active site for the dissolving reaction and that the anion which has a strong tendency to form a complex with Fe(III) promotes the dissolving reaction.

PURPOSE OF THE INVESTIGATION

All previous studies of ferric oxide hydrate have been con-
cerned with its formation during the slow hydrolysis of ferric salt
solutions or with the characterization of the dried and/or aged gel.
It was felt that in order to gain further insight into the character-
istics of ferric oxide hydrate, a study of the dissolution of a
freshly prepared, undried sample in a perchloric acid medium would be
enlightening.

When acid is added to a ferric hydroxide gel, the gel dissolves
slowly forming initially various intermediate Fe(III) products and
eventually Fe^{3+}. By using O^{18}-labelled ferric hydroxide it was felt
that information about the nature of these intermediate species could
be obtained by observing the exchange of oxygen with time between the
dissolving gel and water.

When ferric hydroxide gel is dissolved in acid, a highly colored
solution is produced whose color slowly disappears with time. In a
preliminary study, the disappearance of color with time was observed
spectrophotometrically without too much concern for light scattering
due to particles in the solution. The effect of various inorganic
salts on the stability of the colored solution was also observed. A
later turbidity study showed that the amount of light scattering in
these studies was similar to that for double-distilled water.

In further spectrophotometric studies of the highly colored
solutions prepared in a well-defined way, the effect of various acid con-
tact times with the gel was studied. More detailed studies on the effect of

several inorganic salts on the stability of the colored solution were carried out. The effect of diluting the dissolved ferric hydroxide sample with acid of the same concentration was also observed. Although the final Fe(III) concentrations of the solutions studied were determined colorimetrically with KSCN, potentiometric measurements were employed to determine the change in Fe^{3+} concentratrion in the solutions with time in order to determine how much of the original ferric hydroxide was being converted into Fe^{3+} with time.

Note: The following symbols are used for different iron species:
Fe(III) refers to all iron in the trivalent state.
Fe^{3+} refers specifically to the aqueous ferric ion.

EXPERIMENTAL | 3

3 - 1 MATERIALS

Water enriched to approximately 1.6 atom % oxygen-18 (obtained from YEDA Research and Development Company) was used for the isotope experiments.

Silver cyanide (AgCN, Baker, purified powder) was screened to remove large granules and was then stored under vacuum over phosphorous pentoxide.

A cylinder of ammonia gas (Matheson) was used for preparation of O^{18}-labelled NH_4OH.

The following reagents were used without further treatment:

Ferric chloride ($FeCl_3 \cdot 6H_2O$, U.S.P. grade, Fisher Scientific), perchloric acid ($\sim 12M$, C.P. reagent, C.I.L.), NH_4OH ($\sim 18M$, C.P. reagent, C.I.L.), ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, "Baker Analyzed" Reagent, J.T. Baker Chemical Co.), Na_2SO_4 (anhydrous, reagent, Shawinigan), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, reagent, A.C.S., Allied Chemical), barium hydroxide ($Ba(OH)_2 \cdot 8H_2O$, analytical reagent, Mallinckrodt Chemical Works), KSCN (certified, A.C.S., Fisher), hydrochloric acid ($\sim 12M$, C.P. reagent, C.I.L.), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, reagent, A.C.S., Allied Chemical) and twice-distilled water (obtained from a Corning Model AG-1b still).

3 - 2 APPARATUS

The oxygen-18 study was carried out using a Varian-Mat GD 150 isotope ratio mass spectrometer.

The spectrophotometric studies were conducted with either a

Zeiss PMQ II ultraviolet-visible spectrophotometer or a Perkin-Elmer ultraviolet-visible-near-infrared recording spectrophotometer (Model 450). Unless otherwise stated, the Zeiss spectrophotometer was used in the studies. The turbidity study was carried out on the Zeiss spectrophotometer using Fluorescence Attachment ZFM4 and monochromatic filter M 546 which is transparent to the Hg line at 546 millimicrons.

Potentiometric measurements were performed using an Orion Model 801 digital pH meter (equipped with a Corning platinum inlay electrode (No. 476060) and a Corning calomel reference electrode (No. 476002)).

3 - 3 PREPARATION OF FERRIC HYDROXIDE PRECIPITATE

(A) Oxygen-18 Study

A concentrated oxygen-18 enriched NH_4OH solution was prepared by bubbling ammonia gas through 10 mls. of oxygen-18 enriched water.

A 5 ml. sample of oxygen-18 enriched NH_4OH solution was added to a 1 ml. sample of 2.5 M ferric chloride in a tube with a ground-glass joint. The sample was stirred with a glass rod and the rod rinsed with water. The sample was then centrifuged for approximately 2 minutes in a clinical centrifuge (Model CL, International Equipment Co.) and the supernatant liquid poured off. The sample was washed with 10 mls. of water and centrifuged again. The washing process was repeated for a total of four times in order to remove any Cl^- or excess ammonium hydroxide trapped in the gel. The ferric hydroxide sample was then ready for study.

(B) Spectrophotometric and Potentiometric Studies

A solution containing 0.5 M $FeCl_3 \cdot 6H_2O$ and 0.2 M HCl was prepared. The hydrochloric acid was required to prevent hydrolysis of ferric ion.

A 250 microliter sample of the ferric chloride solution was added with a micro pipette to a 15 ml. centrifuge tube to which approximately 0.5 ml. of water had been added. A 5 ml. sample of 6M NH_4OH was pipetted into the ferric chloride sample and the sample was stirred for 1 minute with a glass stirring rod. The stirring rod was rinsed with water and the centrifuge tube was stoppered with a serum cap. The sample was then centrifuged at 3300 r.p.m. for 2 minutes. After centrifugation, the supernatant liquid was decanted and 5 mls. of water were added to the precipitate. The precipitate and water mixture were stirred with a stirring rod for 1 minute. The stirring rod was then rinsed with water, the centrifuge tube capped, and the tube again centrifuged for 2 minutes. This washing process was repeated for a total of five times.

3 —4 OXYGEN-18 STUDY

The exchangeability of the oxygen atoms in a dissolving ferric hydroxide sample was determined in the following manner:

Approximately 0.1 gms. of AgCN were added to each of five 15 cm. pyrex tubes (1.4 cm. O.D.) which had a slight constriction at the opening. These tubes were attached to the manifold with a torch. A 7 cm. (approx.) narrow constriction was produced about 10 cm. from the end of each tube with the torch. The manifold was then attached to a high vacuum line as. shown in Fig. 3-1.

FIG. 3-1

Manifold and sample tubes for collection of

water vapor samples in O^{18} study.

X denotes position of apparatus for reacting

the perchloric acid with the ferric hydroxide gel.

C denotes the stopcock connecting the manifold

to the vacuum line.

FIG. 3-1
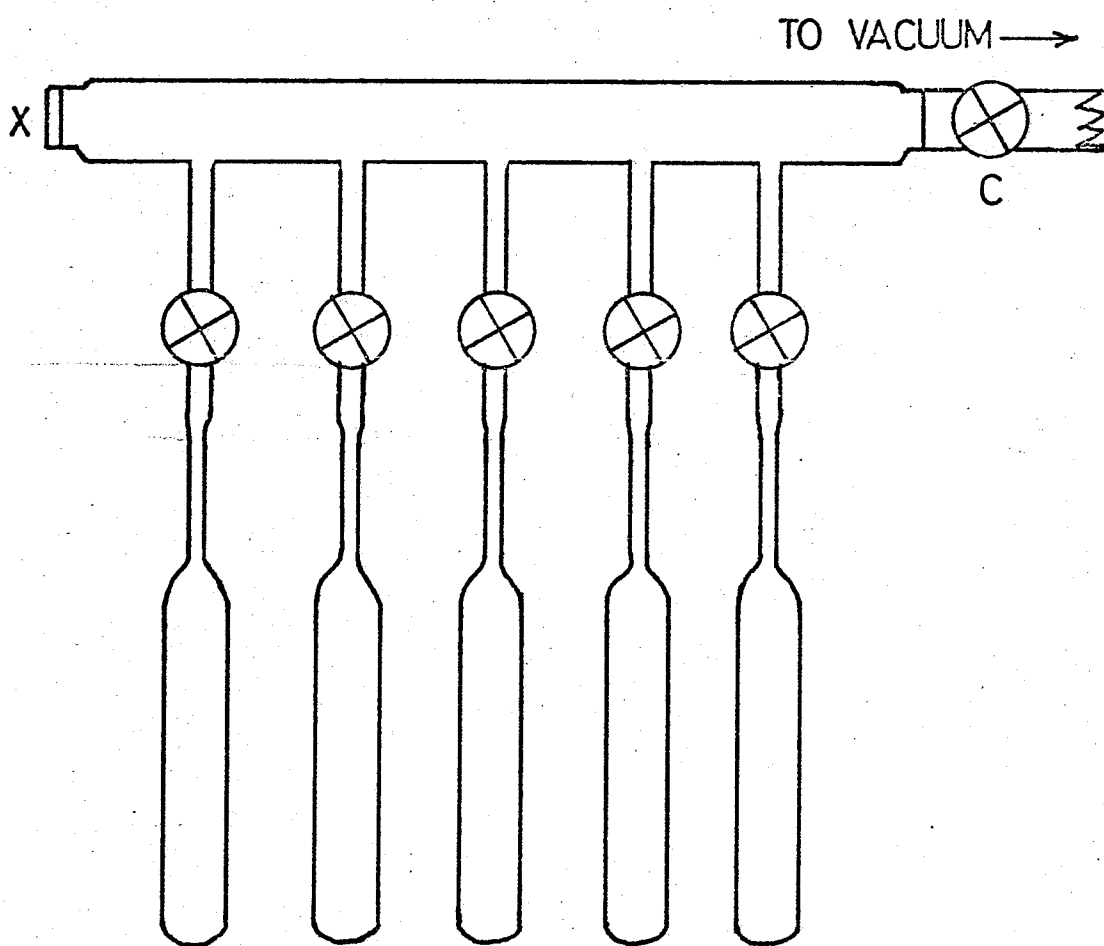
The tube of labelled ferric hydroxide was attached to the apparatus

shown in Fig. 3-2. A 5 ml. sample of 3M $HClO_4$ was added to the bulb.

The apparatus was attached to the manifold at X in Fig. 3-1. Refer to

Figs. 3-1 and 3-2. Stopcocks A and B were closed and stopcock C was

opened. The stopcocks on the sample tubes were opened and the sample

tubes were allowed to pump down. A gentle flame was used to heat the

bottoms of the sample tubes to drive off any water that may have been

trapped in the tubes. After the sample tubes were pumped down, the stop-

cocks on the tubes were closed. A "freeze-dry" technique using a dry ice-

acetone bath was employed to remove any air in both the ferric hydroxide

sample and the perchloric acid. This procedure was repeated three times in

order to ensure that most of the air in acid and sample were removed.

The study was initiated by opening stopcock A and tipping the

acid bulb so that the acid would react with the ferric hydroxide sample.

The stopwatch was started, stopcock A was closed and the sample gently

shaken. Just before 2 minutes had elapsed on the watch, stopcocks B

and C were opened, and the system was swept out, and both stopcocks were

closed. The first sample tube was placed in a liquid nitrogen bath

$(-196^{\circ}C)$. At the 2 minute mark, the stopcock on the first tube was

opened and stopcock B was momentarily opened, causing a water vapour

sample to be condensed in the first sample tube. The stopcock on the first

sample tube was closed, and stopcock C was opened to sweep out the system.

The first sample tube was removed from the manifold by sealing the tube

at the constriction with a torch. The sealed tubes were heated for

approximately 2 hours at 500° C to convert the H_2O to CO_2 by reaction

with AgCN. After the tubes were cooled to room temperature, each was

FIG. 3-2

Apparatus for reacting perchloric acid with

ferric hydroxide gel (stopwatch included for

scale).

FIG. 3-2

placed in the breaker assembly (Fig. 3-3) which was evacuated under high vacuum. After approximately 5 minutes the system was closed from the vacuum pump and the tube was opened by turning the breaker handle. Carbon dioxide was condensed in the previously evacuated bulb with liquid nitrogen, and traces of cyanogen were removed with the trap at $-130^\circ C$ (n-pentane slush located between the breaker and the collection bulb.) After approximately 2 minutes the transfer of CO_2 was complete, and the non-condensible gases, carbon monoxide and nitrogen, were removed by opening the bulb to the vacuum pump momentarily. The isotopic ratio of the carbon dioxide was determined by measuring the ratio of the 46 to the (mass 44 + mass 45) peaks ($C^{12}O^{16}O^{18}$ to ($C^{12}O^{16}O^{16}$ + $C^{13}O^{16}O^{16}$ + $C^{12}O^{17}O^{16}$) ratio) by means of the isotope ratio mass spectrometer. This ratio is referred to as the p-factor and was read directly by means of the double collector procedure.

The results of this oxygen-18 study are shown in Table I on page 52. It can be seen that for about 25 minutes there was little change in the p-factor, due to the slow release of oxygen by the dissolving ferric hydroxide system. The significance of these results will be discussed later.

3 - 5   INITIAL SPECTROPHOTOMETRIC STUDIES

When perchloric acid was added to the freshly prepared ferric hydroxide gel, the gel slowly dissolved, producing a yellow color which eventually disappeared with time. The initial spectrophotometric studies consisted of following this color disappearance with time at

FIG. 3-3

Breaker assembly for CO_2 collection (pencil
used for scale).

FIG. 3-3
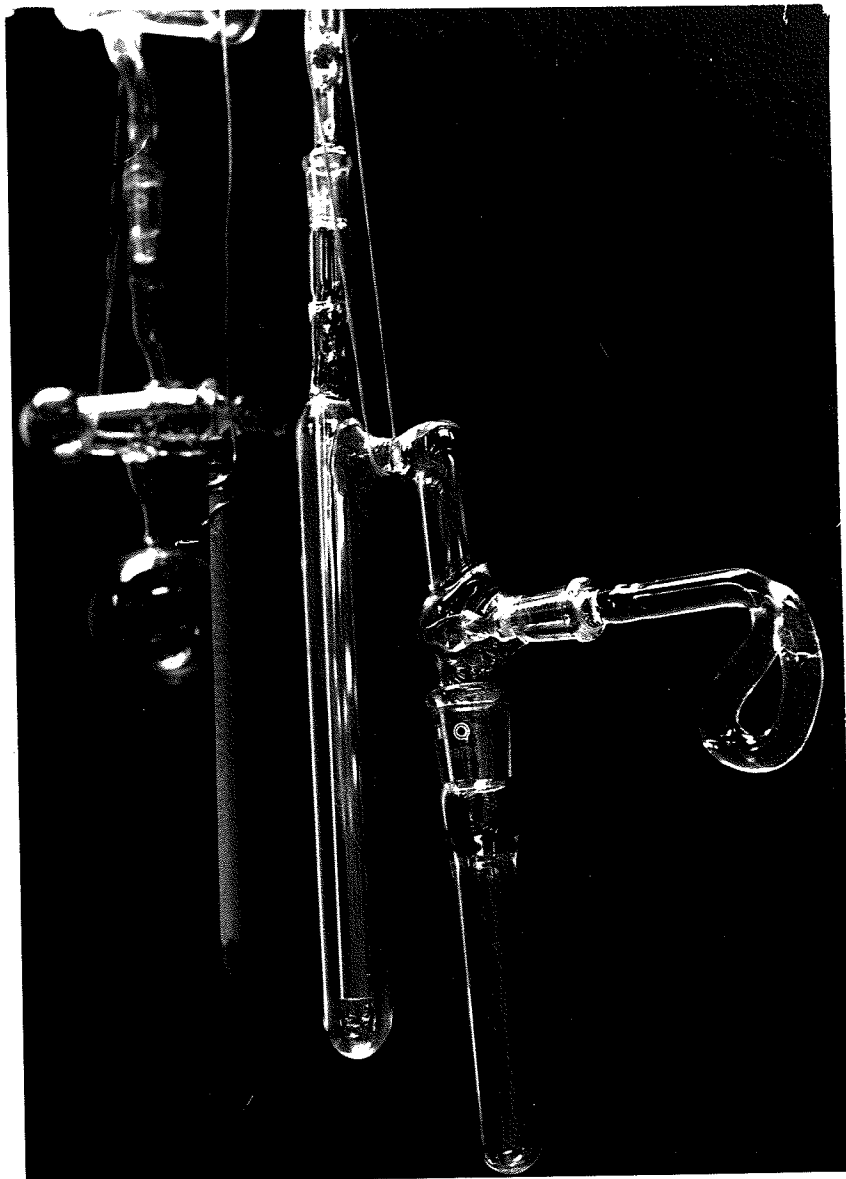
room temperature in the visible wavelength region of the spectrum.

An initial study was undertaken using the Perkin-Elmer recording spectrophotometer to scan the visible spectrum between 350 and 750 millimicrons. The ferric hydroxide sample was prepared as discussed above. Perchloric acid (10 ml., 0.5M) was pipetted into the centrifuge tube containing the gel, and the stopwatch was started. The mixture in the centrifuge tube was stirred with a glass stirring rod and the sample allowed to stand for approximately 20 to 25 minutes until no particles could be seen upon inspection. An aliquot of the sample was then transferred to a 10 mm. glass cell and the cell placed in the spectrophotometer. Twice-distilled water was used as a reference. The visible absorption spectrum was scanned approximately every minute until the spectra remained constant with time. In the spectra obtained the absorption decreased with time and there were no characteristic bands present.

Further studies were carried out at room temperature $(25-26^{\circ}C)$ using the Zeiss spectrophotometer. The wave length of 380 millimicrons was chosen for study primarily for convenience. The spectrophotometric samples were prepared as discussed above. The sample cells were 10 mm. glass cells. The slit width was set at 0.03 mm. and the 380-500 millimicron filter was used. Water was used as a reference. The absorbance readings of the solution at 380 millimicrons were recorded every few minutes until the readings remained constant.

Various volumes of ferrous ammonium sulfate solution were added to the ferric hydroxide-perchloric acid mixture in further studies.

It was hoped that the nature of the dissolving ferric hydroxide gel could be altered by reducing a portion of the gel from a ferric valence state to a ferrous valence state by means of an electron transfer reaction between the added Fe^{2+} ions and the Fe(III) species in the gel.

The same procedure as outlined in the initial studies was followed. Immediately after the acid was added to the gel and the stopwatch started, various volumes of 0.01 M ferrous ammonium sulfate (acidified with concentrated $HClO_4$ to prevent oxidation) were added with a micro pipette to the dissolving sample to give a final ferrous ammonium sulfate concentration of 0.5, 2.5 or 5×10^{-5} molar. (The change in volume of the solutions due to the addition of the ferrous ammonium sulfate solutions was neglected in the calculations.) The sample was stirred and allowed to stand. When no visible particles could be seen in the liquid, an aliquot was transferred to a 10 mm. glass cell and the absorbance readings were recorded as before.

Since the addition of ferrous ammonium sulfate speeded up the disappearance of the yellow color in ferric hydroxide-perchloric acid mixture, additional studies of the effect of ferrous ions were performed using $Fe(ClO_4)_2$.

A 0.1 M $Fe(ClO_4)_2$ solution was made by reacting ferrous sulfate with $Ba(OH)_2$ in a 0.5 M perchloric acid medium to precipitate the sulfate as $BaSO_4$.

Studies using 0.01 M Na_2SO_4 solutions were conducted in order to determine whether or not the sulfate ion had any effect on the stability of the colored solution. Various volumes of Na_2SO_4 were

added in the same manner as in the previous studies to give a
final sulfate concentration of 1, 5 or 10 x 10^{-5} molar.

There was some doubt as to whether or not sufficient time
was allowed for the acid to react with the ferric hydroxide before
a sample of the liquid was studied spectrophotometrically. When
no particles could be seen in the solutions when held to the
light, spectrophotometric studies were begun. There may have
been particles in the solution sufficiently large to cause
light scattering in the spectrophotometric studies. In order to
verify whether sufficient time was allowed, a turbidity study was
carried out. The apparatus was set up as shown in Fig. 3-4. The
light from the Hg lamp source would be scattered by any particles
present and this scattering was monitored at an angle of 90° to
the incident light through the bottom of the sample cell (10 mm.
quartz). A glass turbidity standard which came with the instru-
ment was used and set at an arbitrary value of 100 on the trans-
mittance scale.

A freshly prepared ferric hydroxide sample was reacted
with 10 ml. of 0.5 M $HClO_4$ and the stopwatch started. The sample
was stirred and then allowed to stand for a period of 20-25 minutes
until no particles could be seen upon inspection of the solution
by holding it up to the light. An aliquot of the solution was
poured into a 10 mm. quartz cell equipped with an optically polished
bottom. The decrease in turbidity of the sample with time was
recorded by means of the decrease with time in the transmittance

FIG. 3-4

Apparatus for turbidity study.

(Courtesy Carl Zeiss Instruments)

1. Mercury Lamp

2. Condenser

3. Monochromatic filter

4. Cell

5. Lens

6. Plane mirror

7. Lens

8. Lens

9. Photoelectric receiver of PMQ II

- 42 -

FIG. 3-4
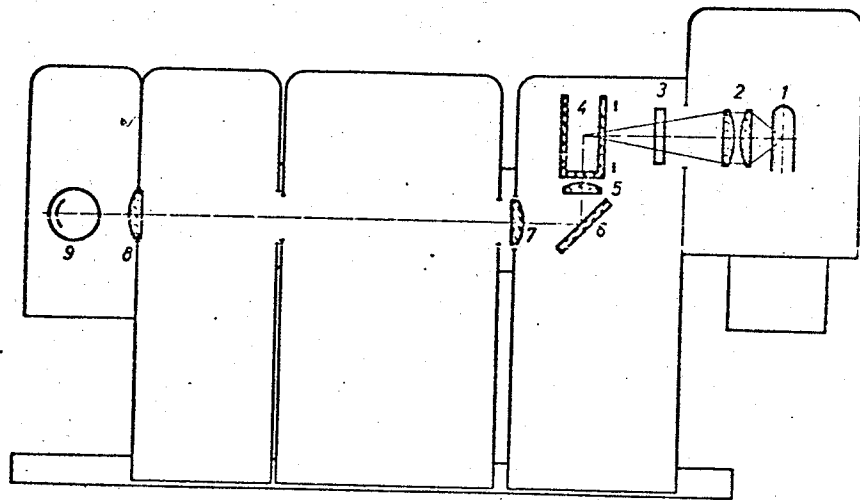
readings of the light scattered at 90° through the bottom of the cell at 546 millimicrons. The readings were continued until they remained constant.

3 - 6 DETERMINATION OF Fe(III) CONCENTRATION

In the following spectrophotometric work, it was felt that a knowledge of the final Fe(III) concentrations in the solutions would help to inter-relate the data from various spectrophotometric studies. It was also required for the potentiometric studies.

A standard Fe(III) solution containing 0.02590 M ferric ammonium sulfate solution made up in 0.5 M $HClO_4$ was prepared. Aliquots of 2, 4, 6 and 8 mls. of the stock solution were added to four 10 ml. volumetric flasks and the flasks diluted to the mark with 0.5 M $HClO_4$. A 100 microliter sample was taken from one of the volumetric flasks and was added to a 25 ml. volumetric flask containing approximately 15 mls. of 0.5 M $HClO_4$. A 500 microliter aliquot of 1 M KSCN was added and the solution was diluted to the mark with 0.5 M $HClO_4$. The solution was shaken and then placed in a thermostat at $25^{\circ}C$ for 10 minutes. An aliquot was poured into a 10 mm. glass cell and the absorbance at 460 millimicrons was recorded using 0.5 M $HClO_4$ as a reference. The cell holders in the spectrophotometer were also thermostated at $25^{\circ}C$. The other solutions were run in the same manner. The relation between absorbance and concentration of Fe(III) followed Beer's law as shown in Fig. 3-5.

FIG. 3-5

Beer's law relation for stock Fe(III) solution

using KSCN to form colorimetric complex.

Absorbance measured at 460 millimicrons using

1 cm. cells.   Temp. 25.0°C.
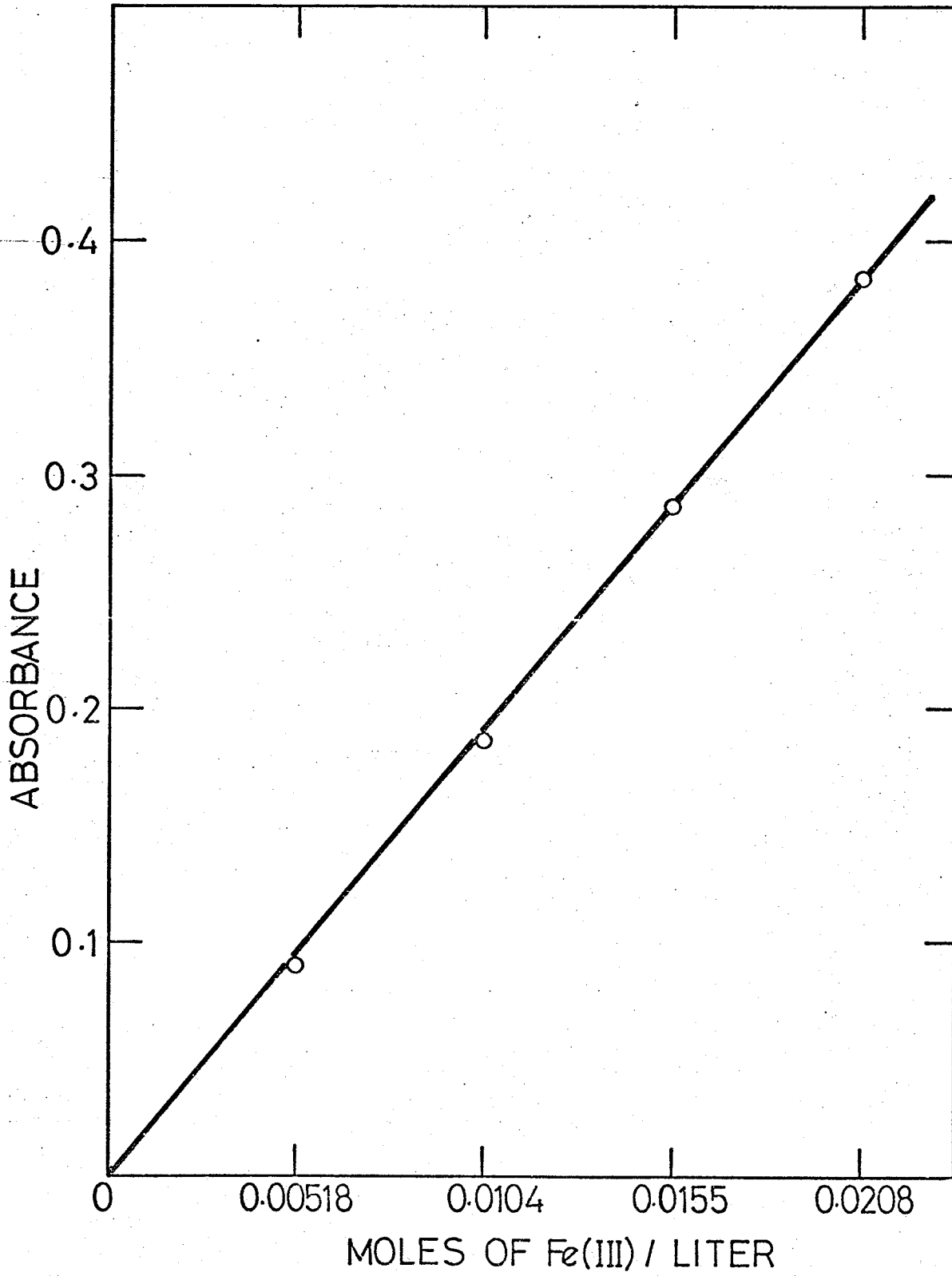
The final Fe(III) concentrations of the dissolved ferric hydroxide samples used in the following spectrophotometric studies were determined using the thiocyanate method as described above. The Fe(III) concentration of the ferric chloride sample used to prepare the ferric hydroxide sample was also determined in a similar way.

3 - 7 MORE DETAILED SPECTROPHOTOMETRIC STUDIES

The time in which the ferric hydroxide gel remained in contact with the acid was varied in order to determine whether or not the properties of the Fe(III) species formed from the gel varied with time.

The procedure followed was:

Ten milliliters of 0.5 M $HClO_4$ were added to the ferric hydroxide sample in the usual manner and the stopwatch was started. The sample was stirred for 1 minute and then, after a certain length of time, the sample was centrifuged for 2 minutes at 3300 r.p.m. An aliquot of the centrifuged solution was decanted into a 10 mm. glass cell and the change in absorbance with time at 380 millimicrons was observed using 0.5 M $HClO_4$ as a reference. The Fe(III) concentration in the cell at the termination of the experiment was determined in the manner previously described. Other samples with various acid contact times were studied in the same manner.

It was known that various anions such as the Cl^- ion formed

complexes with Fe(III) species in solution.[22] Studies were conducted
on the effect various anions, in the form of ferrous ammonium sulfate,
ammonium sulfate, sodium chloride and sodium fluoride, had on the
stability of the color in the centrifuged solution of the dissolving
ferric hydroxide samples.

The ferric hydroxide sample prepared in the usual manner was
allowed to remain in contact with the acid for 18 minutes in a thermo-
stat at $25^{\circ}C$. The sample was then centrifuged for 2 minutes and a 3.5
ml. aliquot was pipetted into a 10 mm. glass cell placed in the
thermostated cell holder in the spectrophotometer. An equal volume
of 0.5 M $HClO_4$ was used as a reference. The change in absorbance with
time was recorded for several readings until 34 minutes had elapsed
from the time $t = 0$ (time of addition of acid). At this moment,
various volumes of 0.010 M ferrous ammonium sulfate, 0.010 M ammonium
sulfate, 0.013 M sodium chloride or 0.50 M sodium fluoride to give
concentrations up to $2.8 \times 10^{-4}M$ in SO_4^{2-}, $1.9 \times 10^{-4}M$ in Cl^- or
$7.0 \times 10^{-3}M$ in F^- were added with a micro pipette to both the sample
and the $HClO_4$ reference. The solutions in the cells were stirred and
the absorbance readings continued until they remained constant. The
final Fe(III) concentration of the sample was determined in the usual
manner.

Further experiments dealing with the effect of various anions
on the stability of the color of the centrifuged solution were con-
ducted using the Perkin-Elmer recording spectrophotometer in order to
scan the visible spectrum between 350 and 750 millimicrons. The
samples were prepared as described above with a SO_4^{2-} concentration in the

cell of 5.8 x 10^{-5}M in the form of $(NH_4)_2SO_4$. The F^- concentration used was 2.8 x 10^{-3}M in the form of NaF.

A study was conducted to determine whether or not the time of addition of the anions had any effect on the stability of the colored solution. The procedure described above using the Zeiss spectrophotometer was followed, with the exception that the gel was in contact with the acid for only 13 minutes before centrifuging, and that two samples of centrifuged solution and two references were used in the spectrophotometer. After 28 minutes had elapsed from time t = 0, 50 microliters of 0.010 M $(NH_4)_2SO_4$ were added to one centrifuged solution and to one reference, and the solutions were stirred. The absorbance readings were continued for both solutions. After 34 minutes from time t = 0, a 50 microliter sample of 0.010 M $(NH_4)_2SO_4$ was added to the second centrifuged solution and reference. The readings were again continued until the absorbance readings became constant for each solution.

A study was carried out observing the absorbance of a ferric hydroxide sample prepared in the usual manner (18 minute acid contact time etc.) at 335 millimicrons using 10 mm. quartz cells and 0.5 M $HClO_4$ as a reference. This study was carried out in order to determine if some evidence of the presence of the dimeric species $Fe_2(OH)_2^{4+}$ could be observed. Evidence for this species had been observed at 335 millicrons by Mulay and Selwood[6] in the hydrolysis of ferric perchlorate solutions.

Studies in which the concentration of the centrifuged solution

was varied were performed in order to determine whether or not the observed change in absorbance with time was a first-order reaction.

The absorbance studies were carried out at 335 millimicrons as described above, until 40 minutes had elapsed since the acid had been added to the ferric hydroxide sample. At this point, a sample of the solution in the cell was removed and diluted with 0.5 M $HClO_4$ in a volumetric flask. A portion of the original solution was set aside to determine the final Fe(III) content at the end of the experiment. An aliquot of the diluted sample was poured into the same 10 mm. cell used previously and the absorbance readings were continued until they remained constant.

3 - 8 POTENTIOMETRIC STUDY

A potentiometric study of a centrifuged solution of a ferric hydroxide sample prepared in the usual manner was considered necessary, in order to determine the Fe^{3+} concentration at any time t.

The potential of the cell (E),

$$Pt \mid Hg \mid Hg_2^{2+} \parallel Fe^{3+}, Fe^{2+} \mid Pt$$

0.1 M KCl saturated with   0.5 M $HClO_4$
Hg_2Cl_2
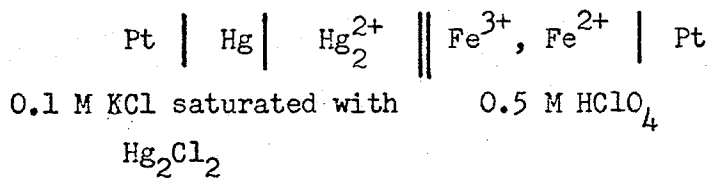
is given by:

$$E = E^o - 0.059 \log \frac{[Fe^{2+}] [Hg_2^{2+}]^{\frac{1}{2}}}{[Fe^{3+}]}$$

at 25^oC where E^o is the standard E.M.F.

If $[Fe^{2+}]$ and $[Hg_2^{2+}]$ are maintained constant, then change in potential with time, ΔE, as the dissolved ferric hydroxide dissociates into smaller structures and gradually forms more and more Fe^{3+} is given by:

$$\Delta E = 0.059 \log \frac{\left[Fe^{3+}\right]_\infty}{\left[Fe^{3+}\right]_t}$$

where $\left[Fe^{3+}\right]_\infty$ is the ferric ion concentration at the termination

of the study and $\left[Fe^{3+}\right]_t$ is the ferric ion concentration at any other

time t. Furthermore, if one knows $\left[Fe^{3+}\right]_\infty$, clearly a measure-

ment of the change in potential with time, ΔE, would give the ferric

ion concentration $\left[Fe^{3+}\right]_t$ at any particular time t.

The potentiometric study was carried out as follows:

Potentiometric measurements on a standard Fe^{3+}-Fe^{2+} solution

were performed in order to determine the mean deviation of the potential

measurements. A 20 ml. sample of 0.1 M $Fe(ClO_4)_2$ plus a 10 ml. sample

of 0.01 M ferric nitrate were added to a 50 ml. beaker. A stirring

bar was placed in the solution and the electrodes were placed in the

solution. The stirrer was started and after allowing the solution

to equilibriate for approximately 5 minutes, millivolt readings were

taken for 30 minutes at 1 minute intervals.

A freshly prepared ferric hydroxide sample was reacted with 10

mls. of 0.5 M $HClO_4$ in the usual manner and the stopwatch started.

The sample was stirred for 1 minute and was then placed in a 25° thermo-

stat for 18 minutes. The sample was then centrifuged for 2 minutes.

The centrifuged solution was poured into a 50 ml. beaker containing

20 mls. of 0.1 M ferrous perchlorate. Millivolt readings were carried

out in a fashion similar to the standard Fe^{3+}-Fe^{2+} system. The readings

were recorded for about 55 minutes after the acid was added to the

ferric hydroxide sample.

In our study, the value employed for $\left[\text{Fe}^{3+}\right]_\infty$ was the final Fe(III) concentration of a dissolved ferric hydroxide sample used for a spectrophotometric study whose acid contact time was 18 minutes. This Fe(III) concentration would be approximately the same as the ferric ion concentration at the termination of the study, since after this length of time most of the Fe(III) would be in the form of the ferric ion, Fe^{3+}.

3 - 9 TREATMENT OF DATA

In the initial studies, using the Zeiss spectrophotmeter, the final absorbance reading (i.e. the constant value obtained) was subtracted from all previous absorbance measurements. The corrected absorbance readings, termed the net absorbance, were plotted against time on a semi-log scale to determine whether or not there was evidence of a first-order reaction.

In the more detailed spectrophotometric studies after the net absorbance was calculated, the absorbance per mole of Fe(III) per liter was calculated using the final Fe(III) concentration determined colorimetrically. The absorbance per mole of Fe(III) per liter was plotted against time on a semi-log scale. In the experiments for which the recording spectrophotometer was used, the absorbance values were obtained from the recorded spectra at wavelengths of 360, 380, 400 and 425 millimicrons. After the net absorbance had been calculated, the absorbance per mole of Fe(III) per liter was plotted against time in the usual manner.

4 - 1 OXYGEN-18 STUDY

Table I
Change in O-18 Content of Solvent
(where p_o, the p-factor before exchange for the acid was 0.00368)

Time (min.)	p-factor
2	0.00381
6	0.00382
13	0.00386
25	0.00389
55	0.00414

4 - 2 INITIAL SPECTROPHOTOMETRIC STUDIES

A typical semi-log plot of the net absorbance versus time at 380 millimicrons employing the Zeiss spectrophotometer is shown in Fig. 4-1. The half-life, $t_{\frac{1}{2}}$, for the color disappearance in the dissolved ferric hydroxide was calculated and the values for the half-lives for repeated experiments on identical samples are shown in Table II. The treatment of the experimental results obtained from run #1 is presented in the Appendix and is representative of the manner in which the other data were treated.

FIG. 4-1

Rate of color disappearance for dissolved ferric

hydroxide sample at 380 millimicrons using

1 cm. cells. Temp. $26.5^{\circ}C$

FIG. 4-1
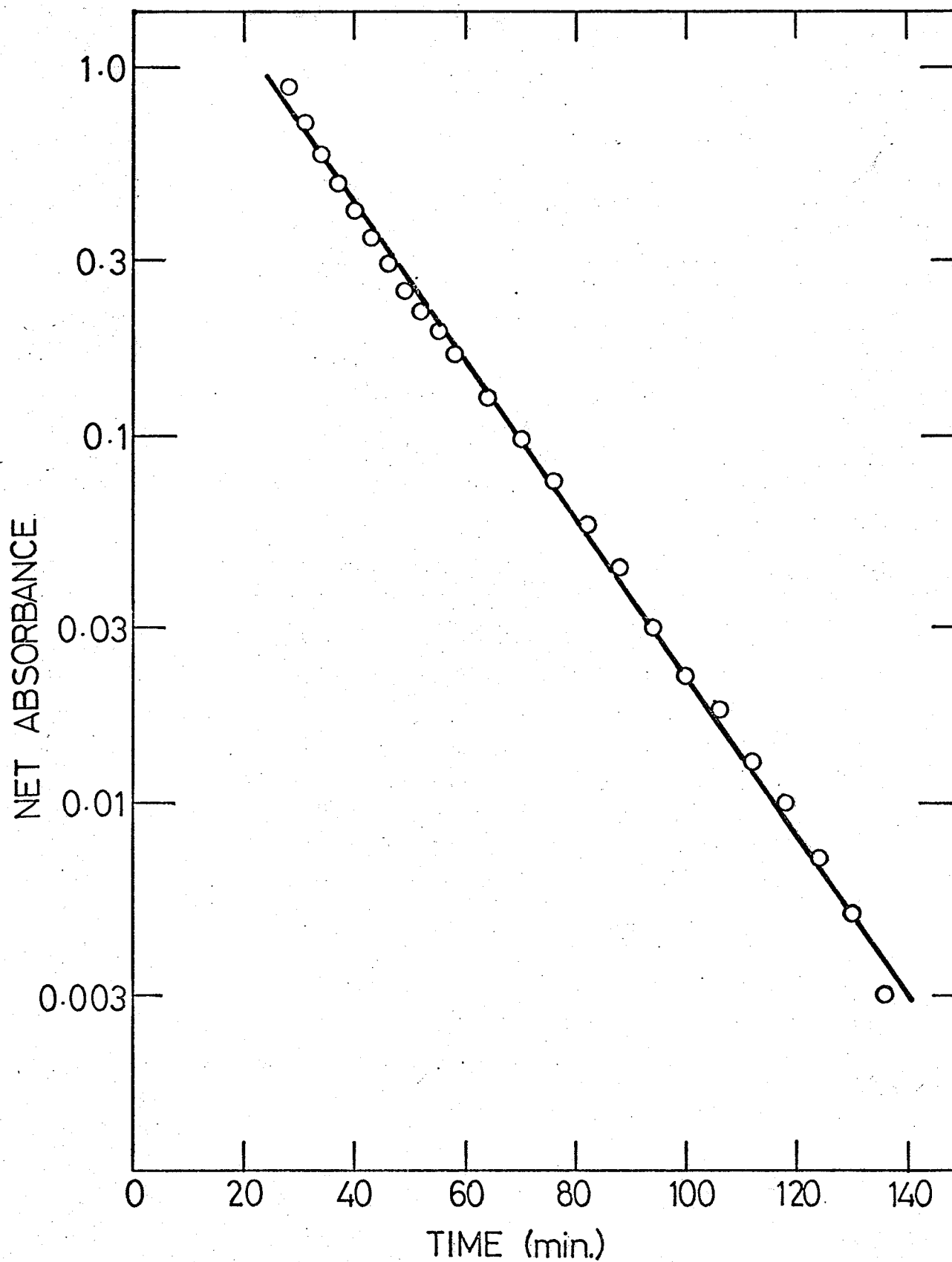
Table II

Reproducibility of Rate of Color Disappearance in

Dissolved Ferric Hydroxide Solutions

Run	Temp. $^{\circ}$C	$t_{\frac{1}{2}}$(min.)
1	26.5	13.0
2	27.0	13.0
3	25.7	14.0

The effect of various concentrations of ferrous ammonium sulfate on the rate of color disappearance in the dissolved ferric hydroxide solution is shown in Fig. 4-2. Similar results were obtained using various concentrations of sodium sulfate. The results are shown in Table III showing the sulfate ion concentrations and the half-lives for the color disappearance.

Ferrous perchlorate in concentrations up to 10^{-3}M produced no marked effect on the rate of color disappearance in the solution.

FIG. 4-2

Effect of various concentrations of ferrous

ammonium sulfate on rate of color disappearance

in dissolved ferric hydroxide solutions at 380

millimicrons using 1 cm. cells. Temp. 25.0^{o}C.

⬤ - 0.5 x 10^{-5}M ferrous ammonium sulfate

◯ - 2.5 x 10^{-5}M ferrous ammonium sulfate

◐ - 5.0 x 10^{-5}M ferrous ammonium sulfate

- 58 -
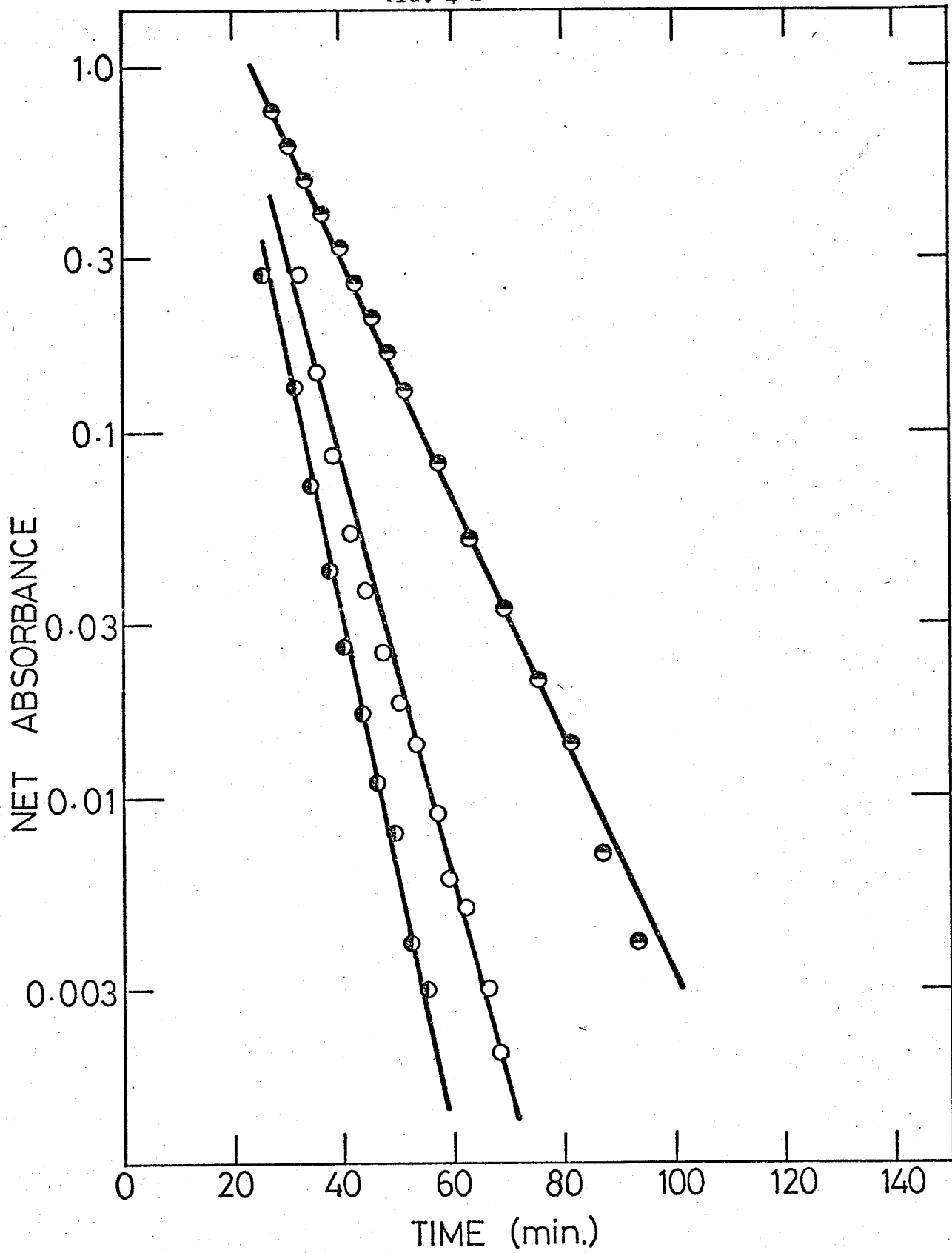
Table III

Effect of Various Sulfate Concentrations on the Rate of Color

Disappearance in Dissolved Ferric Hydroxide Solutions

Inorganic Salt	$[SO_4^{2-}]$ (M)	$t_{\frac{1}{2}}$ (min.)
none	none	13.0
Ferrous ammonium sulfate	1×10^{-5}	9.0
	5×10^{-5}	5.5
	10×10^{-5}	4.5
Sodium sulfate	1×10^{-5}	8.0
	5×10^{-5}	6.0
	10×10^{-5}	5.0

The results of the turbidity study is shown in Fig. 4-3 where

the change in transmittance of the light scattered at 90° through the

bottom of the cell is plotted against time. The transmittance decreases

with time as the particles in the solution become smaller. As a com-

parison, the transmittance for twice-distilled water is about 15.5%

for the same procedure.

4 - 3 MORE DETAILED SPECTROPHOTOMETRIC STUDIES

The results obtained from varying the acid contact time are

shown in Table IV where the initial Fe(III) concentration is the con-

centration of the Fe(III) in the ferric chloride solution used to pro-

duce the gel. The amount of Fe(III) dissolved with various acid contact

times is shown in Fig. 4-4.

FIG. 4-3

Turbidity study showing decrease with time of

light scattered at 90° from angle of incidence

through bottom of cell at $26.0^{\circ}C$.

FIG. 4-3
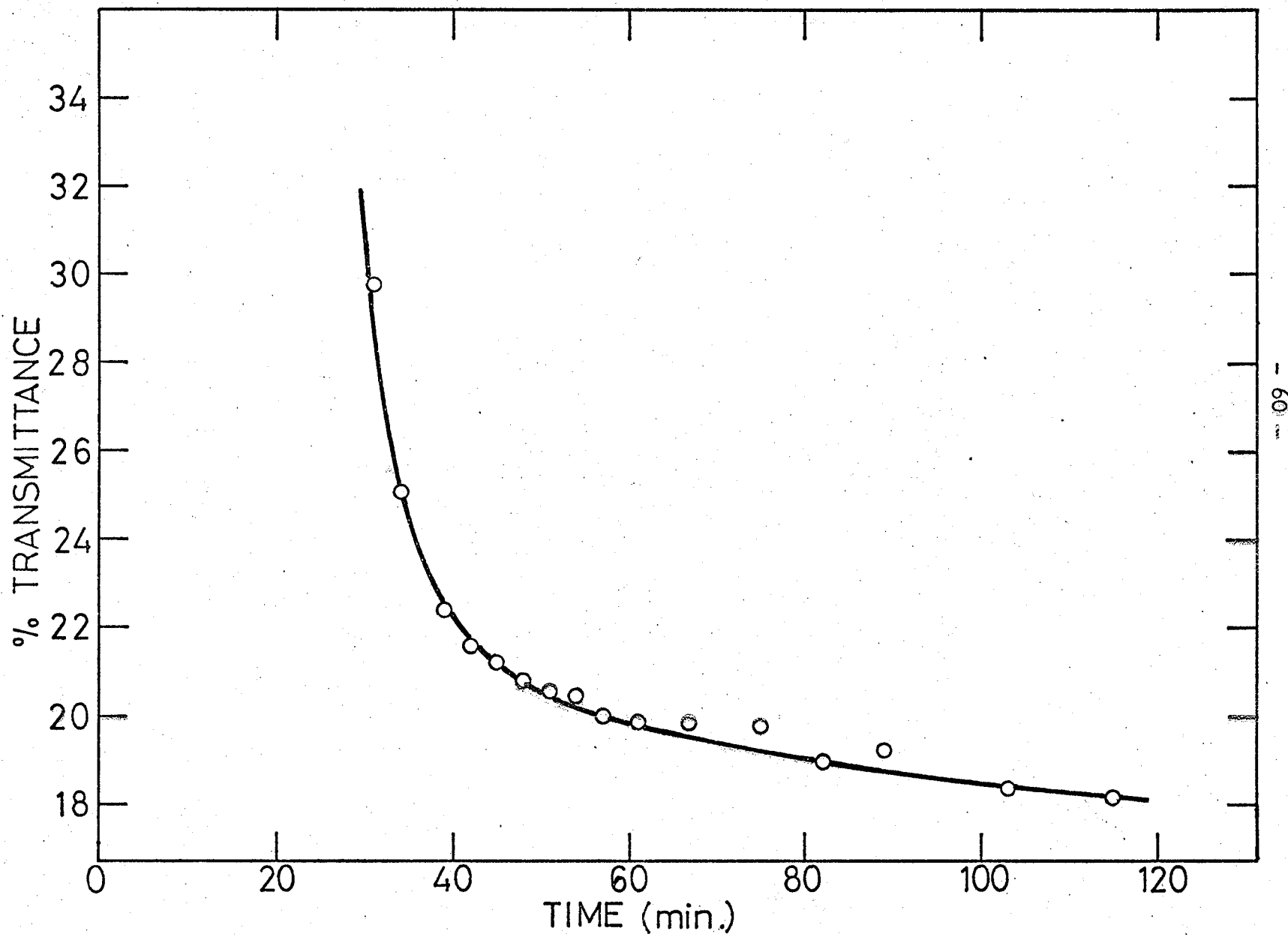
FIG. 4-4

Variation of amount of Fe(III) dissolved from

gel with acid contact time at $25.0^{\circ}C$.

FIG. 4-4
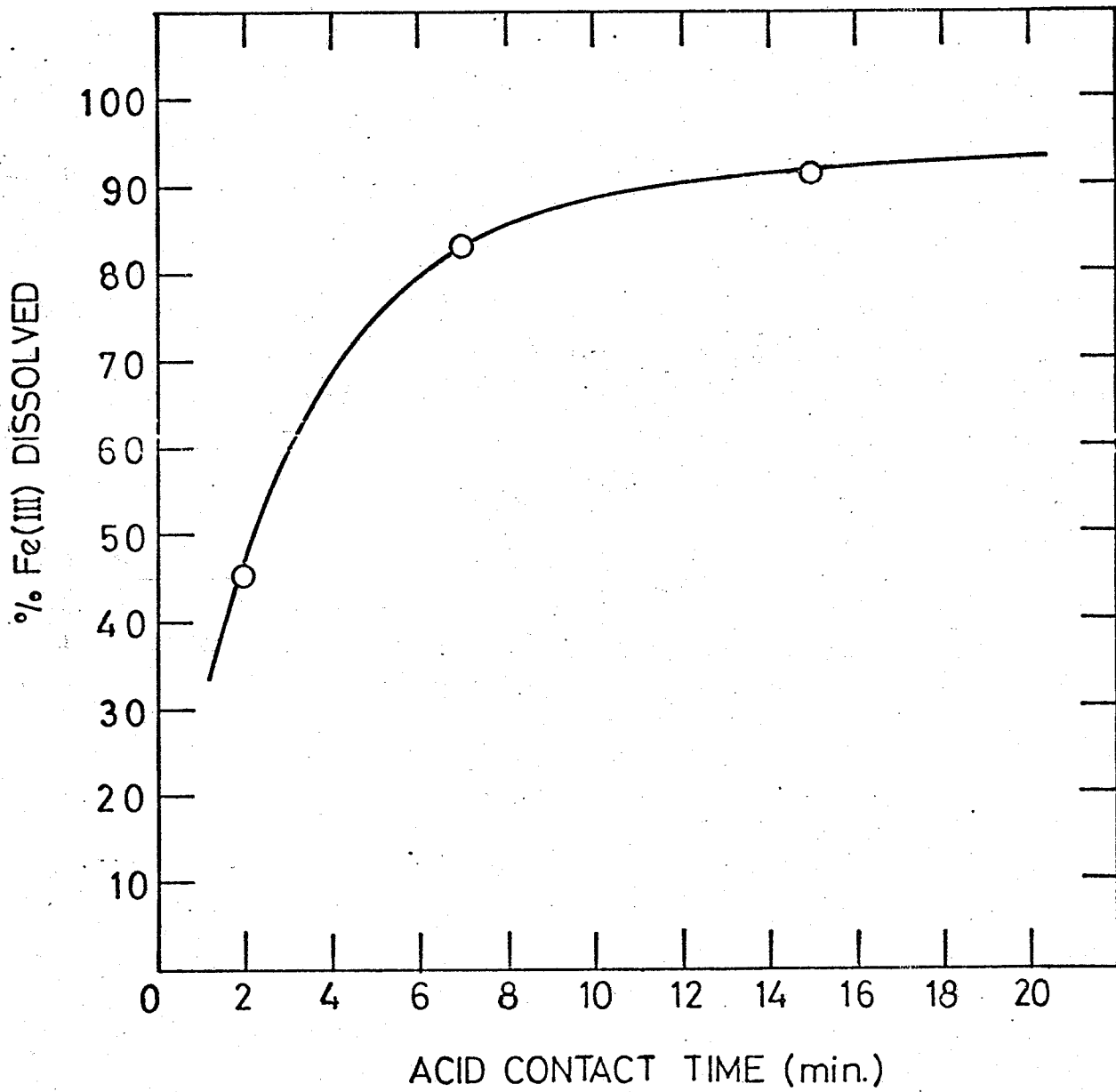
Table IV

Effect of Acid Contact Time on Stability of

Color of Centrifuged Solution

Acid contact time (min.)	$t_{\frac{1}{2}}$ (min.)	Final $\left[Fe(III)\right]$ .moles/l.	Initial $\left[Fe(III)\right]$ moles/l	% dissolved
2.0	3.5	6.61×10^{-3}	14.5×10^{-3}	45.5
7.0	6.5	12.0×10^{-3}	14.5×10^{-3}	83.1
15.0	8.5	13.2×10^{-3}	14.5×10^{-3}	91.0

The effect of adding 1.4×10^{-3} M fluoride ion in the form of NaF on the stability of the color of the centrifuged solution is shown in Fig. 4-5. The effects of various concentrations of F^-, SO_4^{2-} and Cl^- on the half-life of the disappearance of the color of the centrifuged solution are shown in Table V. In this table $t_{\frac{1}{2}}^{I}$ represents the half-life of the reaction before the addition of the various anions and $t_{\frac{1}{2}}^{II}$ represents the half-life after the addition.

FIG. 4-5

Effect of 1.4×10^{-3} M F$^-$ ion on the stability

of the color at 25.0°C of the centrifuged

solution at 380 millimicrons using 1 cm. cells.

Fluoride ion (as NaF) added at 34 minutes.

FIG. 4-5
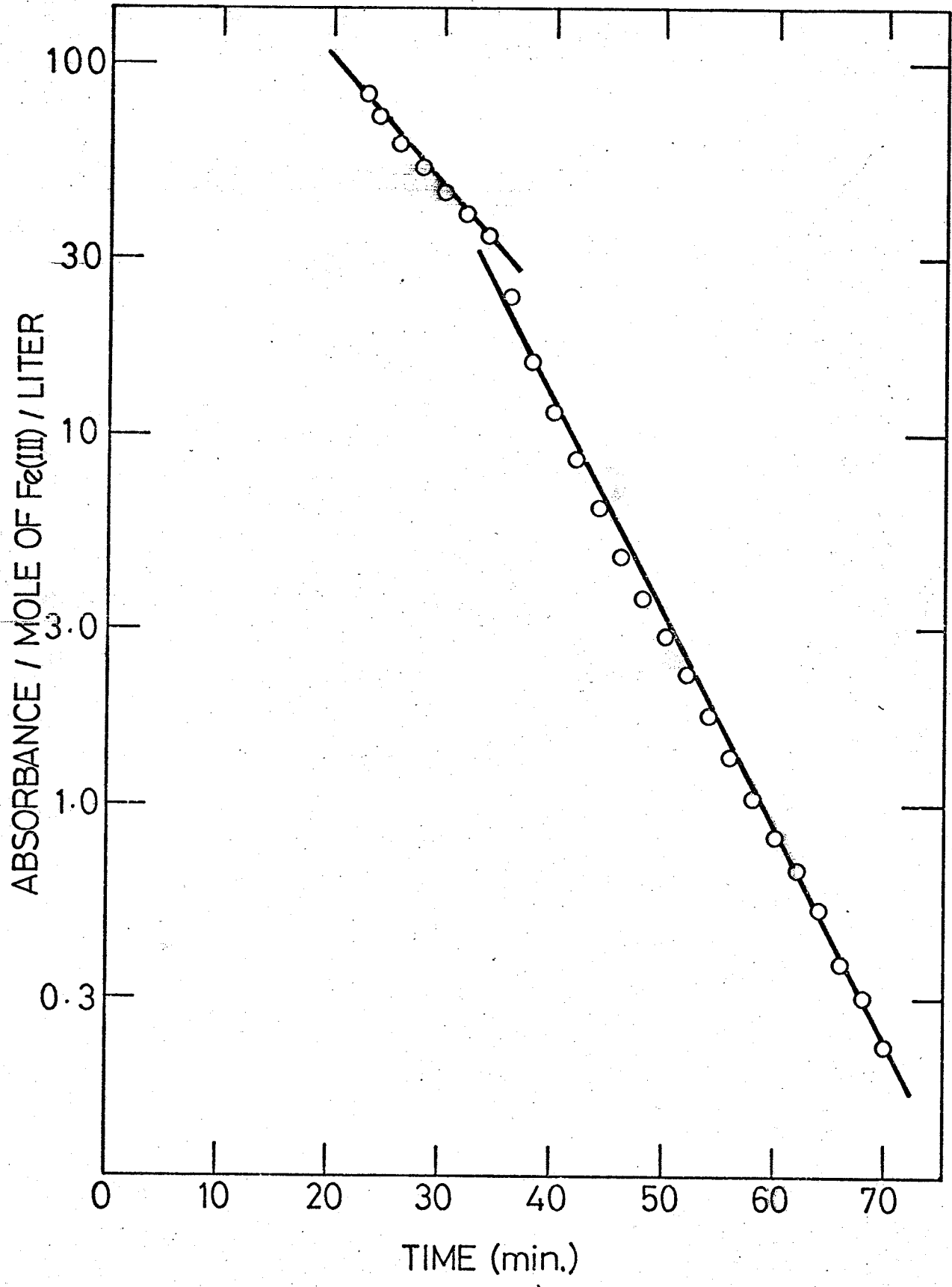
Table V

Effect of Various Anions on Stability of Color
of Centrifuged Solution

Final $[Fe(III)]$ moles/l.	$[F^-]$ moles/l.	$[SO_4^{2-}]$ moles/l.	$[Cl^-]$ moles/l.	I $t_{\frac{1}{2}}$ (min.)	II $t_{\frac{1}{2}}$ (min.)
		Sodium Fluoride			
0.0133	1.4×10^{-3}	–	–	9.3	5.3
0.0131	2.8×10^{-3}	–	–	9.8	3.9
0.0133	7.0×10^{-3}	–	–	9.5	1.9
		Ferrous Ammonium Sulfate			
0.0134	–	5.7×10^{-5}	–	9.1	4.3
0.0134	–	11×10^{-5}	–	9.4	3.7
0.0134	–	28×10^{-5}	–	9.2	2.6
		Ammonium Sulfate			
0.0134	–	2.9×10^{-5}	–	9.2	7.0
0.0136	–	5.8×10^{-5}	–	9.0	3.8
0.0136	–	15×10^{-5}	–	9.3	3.2
		Sodium Chloride			
0.0138	–	–	3.7×10^{-5}	8.8	10.7
0.0136	–	–	19×10^{-5}	8.9	11.2

The results obtained with the recording spectrophotometer on a sample containing 2.8×10^{-3} M NaF is shown in Fig. 4-6. Note that the slopes of the lines are nearly parallel before the addition of the F^- and that the lines are not parallel after the addition of the anion. Similar effects were noted for a sample containing 5.8×10^{-5} M SO_4^{2-} in the form of ammonium sulfate.

FIG. 4-6

Effect of 2.8×10^{-3}M F$^-$ ion on stability of

color at 25.5°C of centrifuged solution at various

wavelengths using 1 cm. cells.

⬤ - 360 millimicrons

△ - 380 millimicrons

◯ - 400 millimicrons

◓ - 425 millimicrons

Fluoride ion (as NaF) added at 34 minutes.

FIG. 4-6
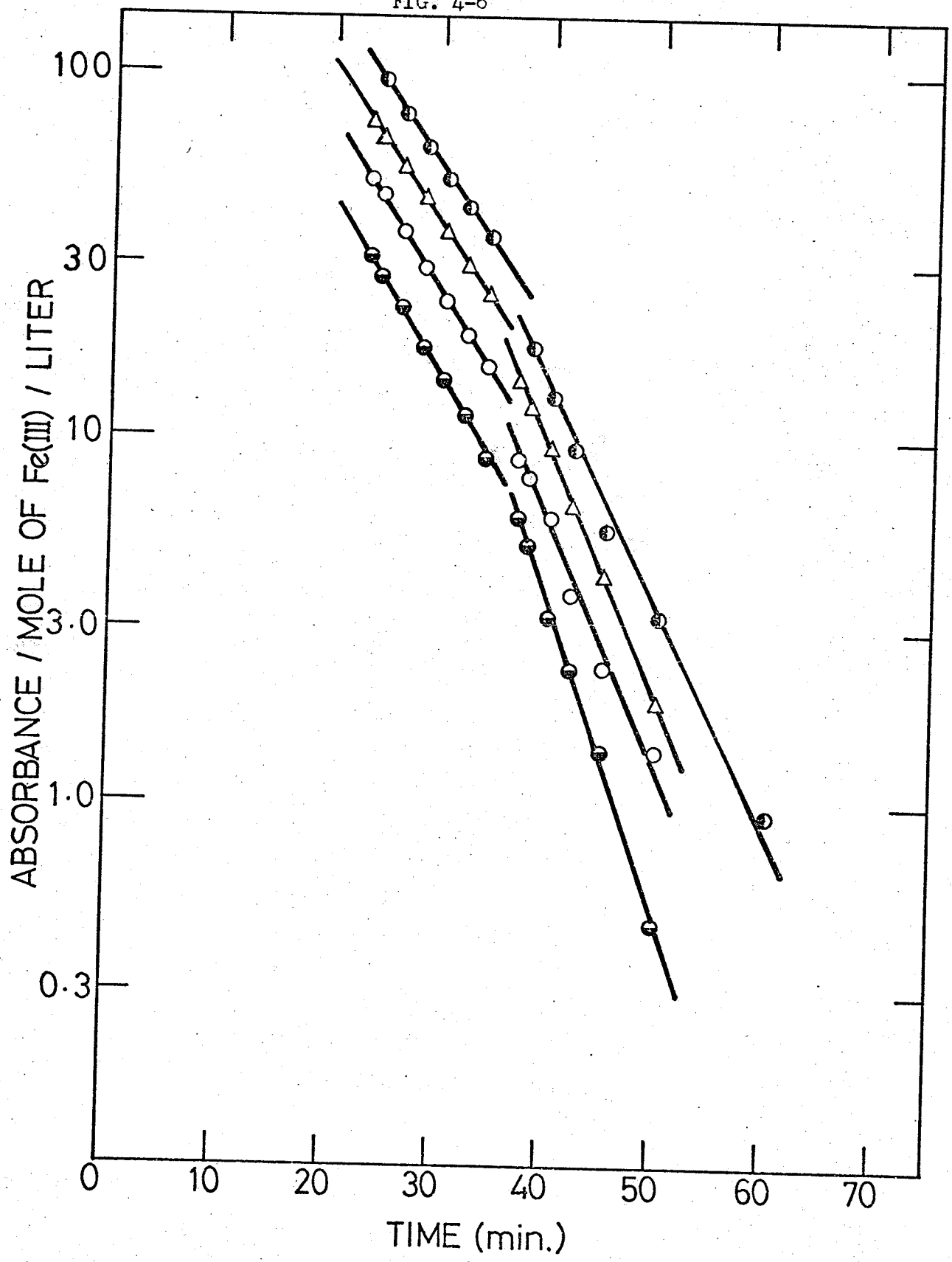
The effect of the time of addition of 50 microliters of 0.01 M $(NH_4)_2SO_4$ (to give a final sulfate concentration of $15 \times 10^{-5}M$) on the stability of the color of the centrifuged solution is shown in Fig. 4-7.

The change in the absorbance spectrum with time measured at 335 millimicrons was not markedly different from that obtained at 380 millimicrons. No evidence for the appearance of the species $Fe_2(OH)_2^{4+}$ could be found from the absorption spectrum.

The effect of varying the concentration of the centrifuged solution on the half-life of the color disappearance in the solution is shown in Table VI where $t_{\frac{1}{2}}^{I}$ represents the half-life before dilution of the centrifuged solution and $t_{\frac{1}{2}}^{II}$ represents the half-life after dilution. A representative graph for a 1 ml. solution diluted to 2.5 mls. at 335 millimicrons is shown in Fig. 4-8. The treatment of the experimental results obtained from sample #3 is presented in the Appendix and is representative of the manner in which the other data were treated.

Table VI

Effect of Dilution with 0.5 M $HClO_4$ on Stability
of Color of Centrifuged Solution

Sample	Volume to Which 1 ml. of Solution Diluted (mls.)	$t_{\frac{1}{2}}^{I}$ (min.)	$t_{\frac{1}{2}}^{II}$ (min.)
1	10.	10.5	4.3
2	5.	10.0	5.0
3	2.5	9.3	6.0

FIG. 4-7

Effect of time of addition of 50 microliters of

0.01 M $(NH_4)_2SO_4$ on stability of color at $25.0^{\circ}C$

of centrifuged solution at 380 millimicrons using

1 cm. cells.

    O - $(NH_4)_2SO_4$ added after t = 28 min.

    △ - $(NH_4)_2SO_4$ added after t = 34 min.
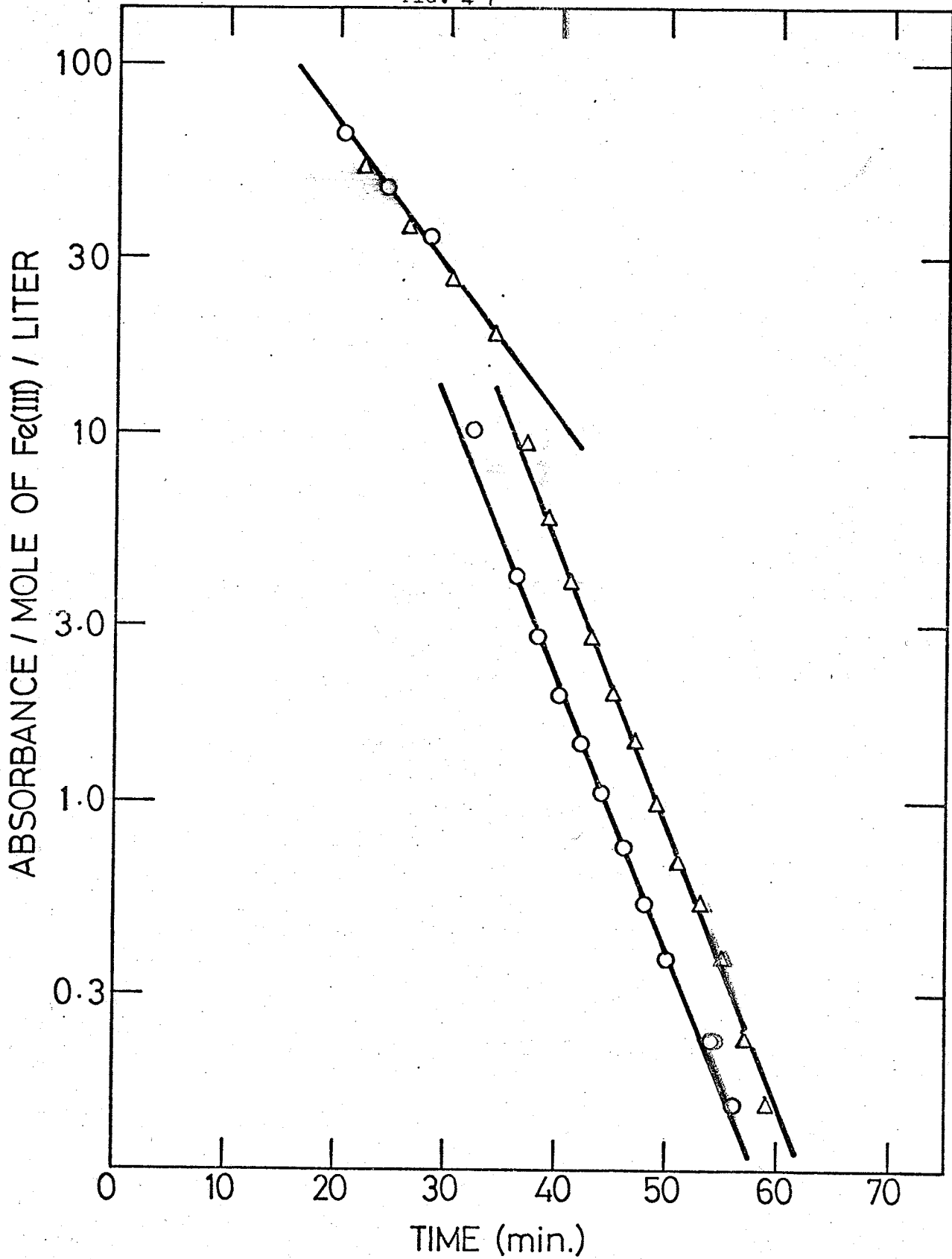
FIG. 4-8

Effect on stability of color at 25.0°C in centri-

fuged solution by diluting 1 ml. of solution

to 2.5 mls. with 0.5 M HClO$_4$.

Wavelength: 335 millimicrons

Cells: 1 cm. quartz

Sample diluted at t = 40 min.

FIG. 4-8
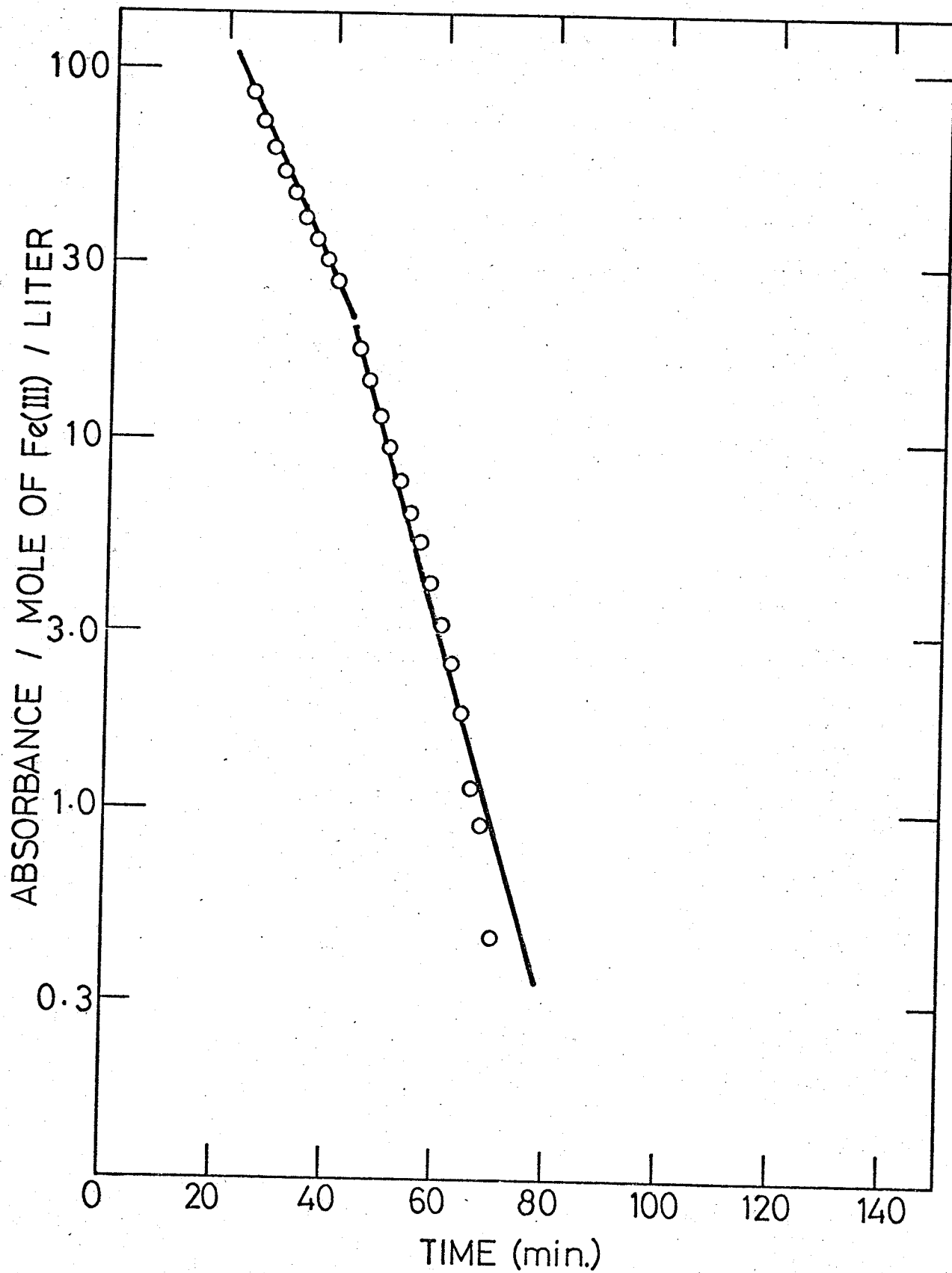
4 - 4 POTENTIOMETRIC STUDIES

For a standard Fe^{3+}-Fe^{2+} system a mean deviation of ± 0.6 millivolts was obtained in the millivolt readings over a period of 30 minutes. This deviation is represented by the vertical bars in Fig. 4-9.

The change in potential with time for a ferric hydroxide sample is shown in Fig. 4-9 with the deviation in millivolt readings taken into account. Using the values of the potential at t = 55 min. (E_{55}) and at any time t, (E_t) from the curve, the values for the change in potential with time ΔE were calculated. The tabulation of the results and the ferric ion concentration at any time t, $[Fe^{3+}]_t$, are shown in Table VII.

Table VII

Potentiometric Determination of Change in

$[Fe^{3+}]$ with Time

t (min.)	E_t millivolts	ΔE Volts	$\dfrac{\Delta E}{0.059}$	$\dfrac{[Fe^{3+}]_\infty}{[Fe^{3+}]_t}$	$[Fe^{3+}]_t$ moles/l. x 10^3
22	436.2	3.9×10^{-3}	0.0661	1.17	9.58
30	437.7	2.4×10^{-3}	0.0407	1.10	10.2
35	438.2	1.9×10^{-3}	0.0322	1.08	10.4
40	438.8	1.3×10^{-3}	0.0220	1.05	10.7
45	439.4	0.7×10^{-3}	0.0119	1.03	10.9
50	439.9	0.2×10^{-3}	0.00339	1.01	11.1
55	440.1	0.0	0.0	1.0	11.2

FIG. 4-9

Potentiometric study, with respect to time, of

centrifuged dissolved ferric hydroxide solution

at approximately $25^{\circ}C$.

FIG. 4-9
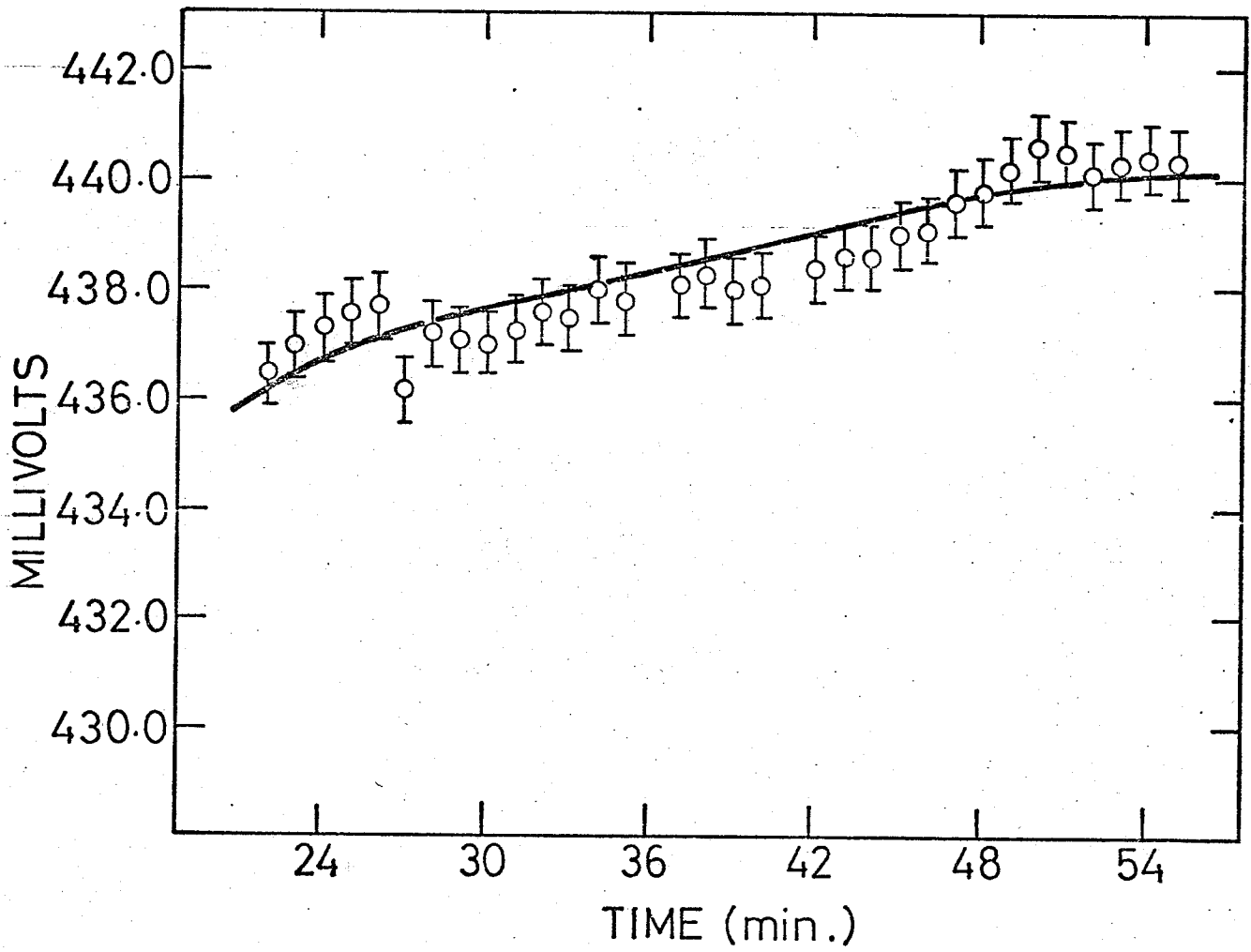
5 - 1 OXYGEN-18 STUDY

Table I shows that there was very little increase in the O^{18} content of the solvent for the first 25 minutes of the reaction. During the first 10-15 minutes of the reaction there was still some undissolved ferric hydroxide gel in the acid solution. This would account for the small change in O^{18} content of the solvent initially. However, even after 25 minutes, when the solution appeared homogeneous, there was still a slow increase in the O^{18} content of the solvent and it was not until 55 minutes had elapsed that there was a marked increase in the p-factor. This suggested that the oxygen atoms in the dissolved Fe(III) species are tightly held and do not exchange easily. Hunt and Taube[23], in an oxygen-18 study on the exchange of water between hydrated ferric ion and solvent at low acid concentrations, found that there was a slight initial hold-back of oxygen by the ferric ion. They attributed this effect to the presence of hydrolyzed species in the system. They argued that oxygen, incorporated in the condensed forms as bridges between iron atoms, could be expected to exchange slowly and could account for the exchange effects. The ferric solutions used by Hunt and Taube had been aged for a sufficient length of time to permit the formation of condensed structures before the enriched water was added. Thus the slow change in p-factor with time in our study could possibly be due to the bridge structures between the ferric ions in the suggested polymeric structure of the Fe(III) species. Our results also suggest that these bridge-structured species have a relatively long life-time in the acid solution before they are dissociated into species which show rapid exchange of oxygen with the solvent (eg. $FeOH^{2+}$, $Fe_2(OH)_4^{2+}$ and Fe_{aq}^{3+}).

5 - 2 SPECTROPHOTOMETRIC AND POTENTIOMETRIC STUDIES

The approximately straight line plot (with a slight "sag" around
t = 60 min.) of the absorbance against time on a semi-log scale obtained in
the initial studies and shown in Fig. 4-1 suggests that there was a pseudo-
first-order reaction for the color disappearance in the dissolved ferric
hydroxide solutions. The reproducibility of the half-lives obtained for
identically prepared samples suggests that the ferric hydroxide gel pro-
duced is not of variable constitution.

The turbidity study (Fig. 4-3) showed that approximately 40 minutes
after the addition of acid, the solution was free of particles which would
have caused serious light scattering. This study confirmed that the
waiting interval before spectrophotometric studies were started was suf-
ficient to ensure that the absorption readings were not erroneous due to
light scattering.

The approximately straight line plots of absorbance versus time on
a semi-log scale obtained in the spectrophotometric studies can be explained
in the following manner:

The disappearance of the color in the solutions of dissolved ferric
hydroxide gels is due to the conversion of large soluble Fe(III)-containing
structures into smaller fragments and eventually into Fe^{3+}_{aq}, which is es-
sentially colorless (it actually has a pale violet color at pH of 1). The
large soluble structures are assumed to have, per iron atom, the largest
extinction coefficients, and as the structures are broken down into smaller
and smaller units, the extinction coefficients per atom of iron are assumed
to decrease.

It is assumed that the rate law for the disappearance of the primary

large solute structure is pseudo-first-order, i.e.,

$$\frac{d}{dt} \left[Fe_x \right] = -k \left[Fe_x \right]$$

where $\left[Fe_x \right]$ represents the concentration of the primary large structure, and k is presumably hydrogen ion dependent, etc.

If we assume that the slowest step in the process of color disappearance involves the attack on Fe_x species, all species with smaller structures like Fe_{x-a} (where a is an integral number) react much more quickly and hence, kinetically, we have a situation in which the first process is rate controlling and the processes can be written as:

$$Fe_x \xrightarrow{k} Fe_{(x-a)} + Fe_a$$
$$\downarrow k_{(x-a)} \qquad \downarrow k_a$$
$$\text{etc.} \qquad \text{etc.}$$
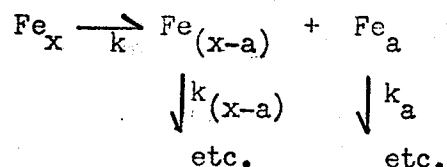
This argument is strictly analogous to the first order decay of a series of radioactive nuclides, for which the <u>first</u> member in the chain has the longest life.

$$A \xrightarrow{\Lambda_A} B \xrightarrow{\Lambda_B} C \xrightarrow{\Lambda_C} D \xrightarrow{\Lambda_D} F \text{ (stable)}$$
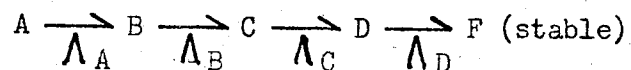
where Λ_A, Λ_B, etc. are the decay constants for the respective species.

At t = 0, only A (whose concentration is A_o) is present. At any time t, the concentration of species A is given by:

$$A_t = A_o e^{-\Lambda_A t} \qquad \qquad \cdots (1)$$

$$\text{and } \frac{dB}{dt} = \Lambda_A A_t - \Lambda_B B_t$$

$$= \Lambda_A A_o e^{-\Lambda_A t} - \Lambda_B B_t \qquad \cdots (2)$$

where A_t and B_t represent the concentration of A and B at time t.

Equation (2) has a general solution of the form:

$$B_t = \frac{\Lambda_A A_o}{\Lambda_B - \Lambda_A} (e^{-\Lambda_A t} - e^{-\Lambda_B t}) \qquad \ldots (3)$$

After a sufficiently long time, $e^{-\Lambda_B t} \ll e^{-\Lambda_A t}$ and thus equation (3) becomes:

$$B_t = \frac{\Lambda_A A_o}{\Lambda_B - \Lambda_A} e^{-\Lambda_A t} \qquad \ldots (4)$$

Effectively all of A disappears and is converted to B, which after reaching a maximum concentration (dependent upon the relative values of Λ_A and Λ_B), disappears at the same rate as A as is shown in sketch A.
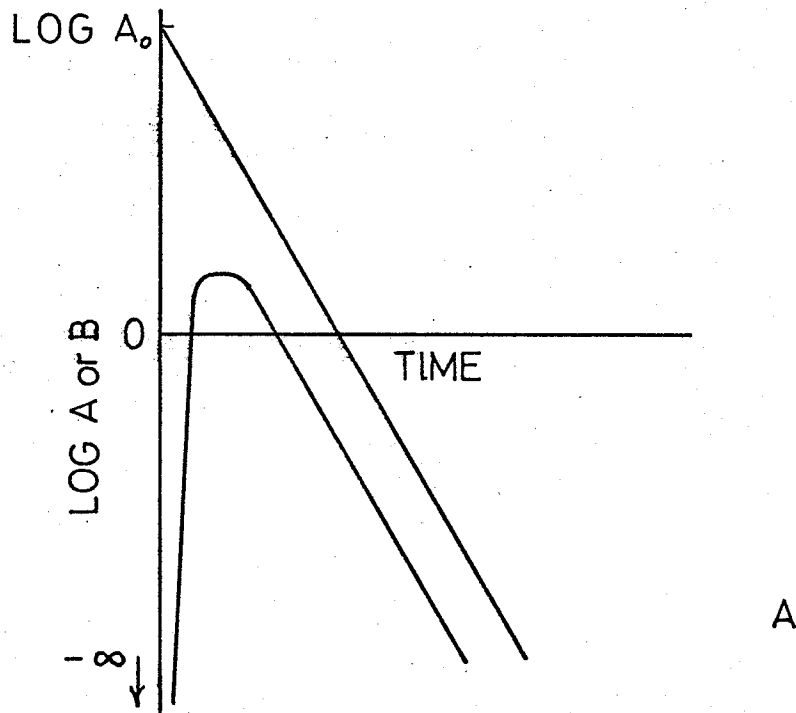
The sum of log (A + B) versus time would give a plot such as that shown in sketch B.
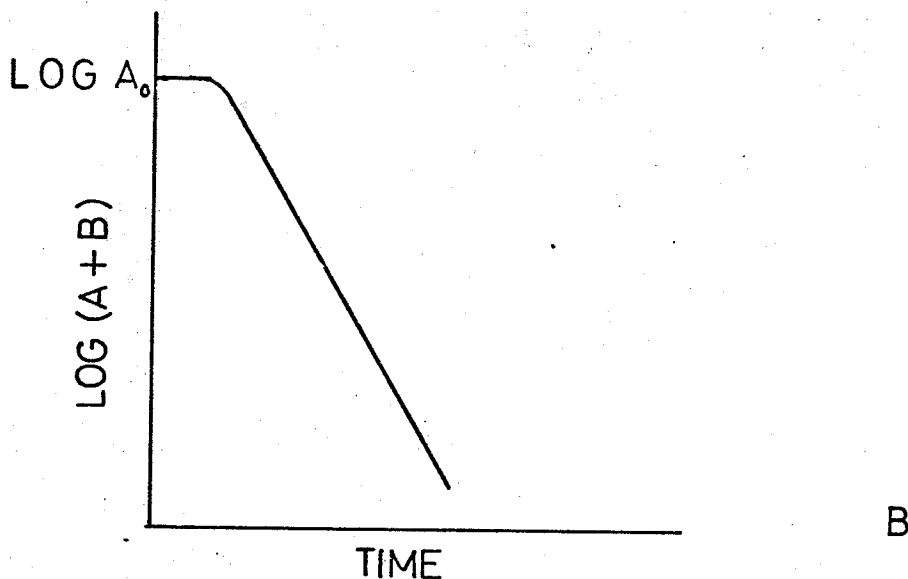
In the early stages of A ——⟶ B, the sum of A + B is nearly constant.
After a short time, the change in concentration with time follows the rate
of decay of either A or B with time.

The graph as shown in sketch B was not what was observed in our
spectrophotometric studies. In order to account for our results, we have
to observe some property that weighs A relative to B (i.e. light absorption)
and we have to assume that B was longer-lived than A. Thus if we assume
a 10-fold difference in extinction coefficients (i.e. $\epsilon_A = 10\,\epsilon_B$) the
following type of graph is obtained:
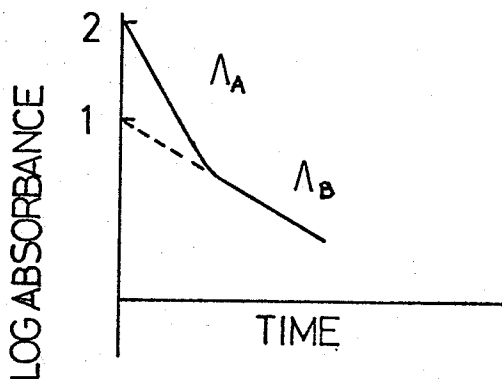
This is in qualitative accord with our spectrophotometric results which show some slight evidence for the long-lived tail, and suggest that the first-order rate constant for the attack on the large soluble Fe(III) species in our solutions is larger than for the remainder and that the extinction coefficients of the secondary species are not as large as compared to the original large Fe(III) species.

The studies on the effect of the variation of acid contact time (Table IV) showed that the half-life for the rate of disappearance of color in the centrifuged solution increased with the contact time of the acid with the gel. This suggests that, as the ferric hydroxide gel is broken down into simpler Fe(III) species on contact with the acid, the simpler soluble species are dissolved preferentially over the more complicated species. The samples with a longer acid contact time would have a larger amount of the more complex soluble species and hence would have a larger half-life as compared to the samples which have predominately less complex species.

The fact that Fe^{2+} ions in concentrations of up to 10^{-3} M in the form of $Fe(ClO_4)_2$ had no marked effect on the rate of disappearance of color in the dissolved ferric hydroxide samples suggests that there was no electron transfer reaction between the Fe^{2+} ion and the Fe(III) species in dissolved ferric hydroxide solutions. Appreciable electron transfer would confer Fe(II)-like properties on the large species, and make it readily soluble in acid. According to the Franck-Condon principle, electrons move much faster than nuclei, so that electronic transitions are complete before any significant nuclear changes take place. One of the factors opposing the ready transfer of electrons is the difference in environment of the oxidized and reduced forms of the species[24]. This was probably

the case in our studies where the ferrous ion was in the simple hydrated form while the Fe(III) species may have been in a more complex form, thus minimizing the possibility of an electron transfer reaction.

From the results in Table III, it appears that the decrease in the half-life of the process of color disappearance in the dissolved ferric hydroxide solutions was due to the SO_4^{2-} ion and not due to the Fe^{2+} ion. The results for the same concentrations of SO_4^{2-} in the form of ferrous ammonium sulfate or sodium sulfate were similar and the variations between the half-life values were probably due to experimental error in drawing the straight line through the points in the graphs.

In the more detailed studies on the effect of various anions on the rate of color disappearance in the centrifuged solution (shown in Table V), it was found that the Cl^- ion had a decelerating effect on the rate. This was probably due to the formation of chloro complexes by the aqueous ferric ions in the solution formed during the dissociation of the large polymeric Fe(III) species. These chloro complexes are yellow in color as are the hydroxy Fe(III) species. Thus the rate of color disappearance would be slower due to the formation of these chloro complexes along with the disappearance of the hydroxy species. From the results in Table V, it can be seen that both the SO_4^{2-} ion and the F^- ion have an accelerating effect on the rate of color disappearance, with the SO_4^{2-} ion having the greater effect. By forming a complex with some Fe(III) species in the dissolving ferric hydroxide, the SO_4^{2-} and F^- ions may have been able to accelerate the dissociation of the larger Fe(III) species into simpler Fe(III) species. With the pH and anion concentrations used in our studies, the F^- and SO_4^{2-} ions in the solutions were in the form

HF and HSO_4^- respectively, due to weakness of these acids. Both HSO_4^- and HF are known to form complexes with Fe(III) species[25, 26]. The greater accelerating effect on the rate of color disappearance by the HSO_4^- ion may have been due to the fact that its negative charge allowed it to penetrate more easily into the charged polymeric hydroxy structure and form a complex. In those studies employing the recording spectrophotometer, the plots of the change in absorbance with time at various wave-lengths were parallel before the addition of the solution containing the complexing anion (see Fig. 4-6). After the addition of the anionic species, the plots were no longer parallel, suggesting that some larger Fe(III) species in the solution were dissociated into smaller Fe(III) species more quickly than others.

The effect of the time of addition of 50 microliter samples of 0.01 M $(NH_4)_2SO_4$ on the rate of color disappearance in the centrifuged solution, as shown in Fig. 4-7, suggested that it did not matter when the $(NH_4)_2SO_4$ solution was added. The plots after the addition of the solutions were essentially parallel. This suggested that the rate of color disappearance in the centrifuged solution was a pseudo-first-order reaction dependent on some particular Fe(III) species and that the SO_4^{2-} ion increased the rate of the reaction by increasing the speed at which this Fe(III) species dissociated into smaller Fe(III) species. If the reaction was not pseudo-first-order, there should have been a difference in the half-lives for the addition of SO_4^{2-} ions at two different times since there would be a change in concentration of the various Fe(III) species present in the solution.

Studies on the effect of diluting the centrifuged solution showed that, as the solution was diluted, the half-life of the reaction decreased

approximately with the cube root of the volume change factor of the solution as can be seen in Table VIII. $t_{\frac{1}{2}}^{II}$ refers to the half-life of the color disappearance in the diluted solution and $t_{\frac{1}{2}}^{I}$ refers to the same quantity in the undiluted solution, for which the volume change factor is unity.

Table VIII
Variation of Half-Life of Color Disappearance with
Cube Root of Volume Change Factor

Volume Change Factor	Cube Root of Volume Change Factor	Change in Half-Life $(t_{\frac{1}{2}}^{I} / t_{\frac{1}{2}}^{II})$
10	2.2	2.4
5	1.7	2.0
2.5	1.4	1.6

A possible explanation for this behaviour is the following:

As the acid attacks the large soluble polynuclear iron species, smaller Fe(III) species are broken off from the large species. Since these polyions (both the large species and the smaller species) have a net charge distributed over them, there is a possibility that within these polyions there are localized dipoles of some sort. When the smaller Fe(III) species are broken off from the larger species, these smaller species are still physically held close to the larger species in an agglomerate by means of some sort of dipole-dipole interaction. The retention of these smaller species by the large species would inhibit the further attack of the larger species by H^{+} ions, e.g. by physical masking of one particle by another. However, when the solution is diluted, the distance between the large species and the smaller species is increased and there is less interaction between them. The smaller species would tend to be less firmly associated with the larger species

and this would account for the decreasing stability of the color in the solution.

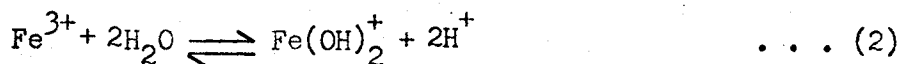A spectrophotometric study, not detailed in the Experimental Section, showed, as expected, that there was a H^+ ion dependence on the rate of color disappearance in the centrifuged solution. The color was found to disappear more slowly with more dilute acid in accord with the results of Furuichi, et al.[20] who found a H^+ ion dependence on the rate of dissolution of ferric hydroxide precipitate.

From our potentiometric studies the concentration of hydrated ferric ion, Fe_{aq}^{3+}, could be determined at any time during the reaction. Using data from Mulay and Selwood's work[6] along with information obtained from our spectrophotometric and potentiometric studies, the species responsible for the color in the centrifuged liquid can be shown to be some polynuclear species of Fe(III). The argument is outlined as follows:

The hydrolysis of Fe^{3+} was described by the following equations using equilibrium constants derived by Hedstrom[4].

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad \ldots (1)$$
$$k_{11} = 9.0 \times 10^{-4}$$

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+ \qquad \ldots (2)$$
$$k_{12} = 4.9 \times 10^{-7}$$
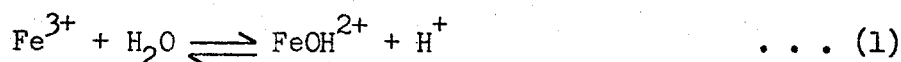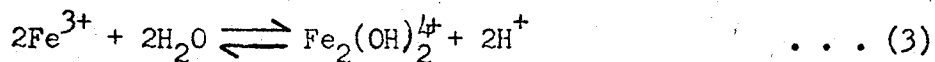
$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \qquad \ldots (3)$$
$$k_{22} = 1.22 \times 10^{-3}$$

In the above expressions the concentrations were taken as moles per liter of solution and the temperature was $25^\circ C$. The equilibrium constants were defined as follows:

$$k_{11} = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}]}$$

$$k_{12} = \frac{[Fe(OH)_2^+][H^+]^2}{[Fe^{3+}]}$$

$$k_{22} = \frac{[Fe_2(OH)_2^{4+}][H^+]^2}{[Fe^{3+}]^2}$$

The total iron concentration involved in the hydrolysis (neglecting $[Fe(OH)_2^+]$ as being unimportant) can be written as:

$$[Fe_T] = [Fe^{3+}] + [FeOH^{2+}] + 2[Fe_2(OH)_2^{4+}]$$

$$= [Fe^{3+}]\left\{1 + \frac{k_{11}}{[H^+]} + \frac{2k_{22}[Fe^{3+}]}{[H^+]^2}\right\} \quad \dots (4)$$

Now, if $[H^+] = 10^{-1}$,

$$\frac{k_{11}}{[H^+]} = 9 \times 10^{-3}$$

and $\dfrac{k_{22}}{[H^+]^2} = 0.122$

equation (4) becomes:

$$[Fe_T] = [Fe^{3+}]\left\{1.009 + 0.244[Fe^{3+}]\right\}$$

$$= 1.009[Fe^{3+}] + 0.244[Fe^{3+}]^2 \quad \dots (5)$$

The total iron concentration $[Fe_T]$ used by Mulay and Selwood was 0.04M. This value was used to solve equation (5) to give $[Fe^{3+}]$. The ferric ion concentration calculated was 0.0393 M.

Now, $\left[FeOH^{2+}\right] = k_{11} \dfrac{\left[Fe^{3+}\right]}{\left[H^+\right]}$ . . . . (6)

$$= 9 \times 10^{-3} \times 0.0393$$

$$= 3.53 \times 10^{-4} \text{ M}$$

and $\left[Fe_2(OH)_2^{4+}\right] = k_{22} \dfrac{\left[Fe^{3+}\right]^2}{\left[H^+\right]^2}$

$$= 1.88 \times 10^{-4} \text{ M} .$$

Using these calculated concentrations for Fe^{3+}, $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$, the molar extinction coefficient, $\epsilon_{Fe_2(OH)_2^{4+}}$, for $Fe_2(OH)_2^{4+}$ at 380 millimicrons can be calculated as follows:

The absorbance of 0.04 M Fe(III) solution at pH 1.0 at 380 milli-microns for a temperature of 15° using a 1 cm. cell was approximately 10.0 as obtained from Fig. 1-4.

$$\therefore 10.0 = \left[Fe^{3+}\right] \epsilon_{Fe^{3+}} + \left[FeOH^{2+}\right] \epsilon_{FeOH^{2+}}$$

$$+ \left[Fe_2(OH)_2^{4+}\right] \epsilon_{Fe_2(OH)_2^{4+}}$$

$$= (3.93 \times 10^{-2} \times 0.1) + (3.53 \times 10^{-4} \times 2 \times 10^2)$$

$$+ 1.88 \times 10^{-4} \epsilon_{Fe(OH)_2^{4+}}$$

(The values for the extinction coefficients, $\epsilon_{Fe^{3+}}$ and $\epsilon_{FeOH^{2+}}$, were obtained from Rabinowitch[22].)

$$= 7.46 \times 10^{-2} + 1.88 \times 10^{-4} \epsilon_{Fe(OH)_2^{4+}}$$

$$\therefore \epsilon_{Fe_2(OH)_2^{4+}} = 5.28 \times 10^4$$

In one of our spectrophotometric studies on a usually prepared ferric hydroxide sample (18 min. acid contact time etc.) the absorbance at 380 millimicrons at time t = 30 minutes was 0.383. The Fe(III) content of the centrifuged solution was 0.0112 M. The Fe^{3+} content of a similar centrifuged solution at t = 30 minutes determined potentiometrically was 0.0102 M (see Table VII). Therefore the contribution to the absorbance for a 1 cm. cell by the Fe^{3+} ion in our studies is:

$$A_{Fe^{3+}} = \epsilon_{Fe^{3+}} b \left[Fe^{3+}\right]$$
$$= 0.1 \times 1 \times 0.0102$$
$$= 1.02 \times 10^{-3}$$

where $\epsilon_{Fe^{3+}}$ is the extinction coefficient for Fe^{3+} and b is the optical path length in centimeters.

From equation (6), the $FeOH^{2+}$ concentration can be calculated as:

$$\left[FeOH^{2+}\right] = \frac{9 \times 10^{-4} \times 1.02 \times 10^{-2}}{0.5}$$
$$= 1.84 \times 10^{-5} M$$

The contribution to the absorbance in our studies by $FeOH^{2+}$ is:

$$A_{FeOH^{2+}} = \epsilon_{FeOH^{2+}} b \left[FeOH^{2+}\right]$$
$$= 2 \times 10^{2} \times 1 \times 1.84 \times 10^{-5}$$
$$= 3.68 \times 10^{-3}$$

where $\epsilon_{FeOH^{2+}}$ is the extinction coefficient for $FeOH^{2+}$.

It can be seen that the contribution of either Fe^{3+} or $FeOH^{2+}$ to the absorbance at 380 millicrons is negligible. The potentio-metric study described earlier show that 91% of the Fe(III) species present in solution after 30 minutes is in the form of the aqueous ferric ion Fe^{3+}_{aq}

(Table VII). The remaining 9% must account for virtually all of the color in the solution. If we assume that the colored species is the dimer studied by Mulay and Selwood, then its absorbance at 380 millimicrons for a 1 cm. cell would be

$$A = \epsilon_{Fe_2(OH)_2^{4+}} b \left[Fe_2(OH)_2^{4+} \right]$$

$$= 5.28 \times 10^4 \times 1 \times 5 \times 10^{-4}$$

$$= 26.5$$

where $\epsilon_{Fe_2(OH)_2^{4+}}$ is extinction coefficient calculated above and $\left[Fe_2(OH)^{4+} \right]$ is one-half the concentration of the iron present in forms other than Fe_{aq}^{3+} (0.001M).

The calculated absorbance is much larger than the value observed (0.383). Therefore it appears that the observed absorbance is not due to a dimeric species of Fe(III). This appears reasonable since Conocchioli, et al.[27] showed that the dissociation of the dimer $Fe_2(OH)_2^{4+}$ was rapid and was given by the equation:

$$k_d = k_1 + k_2 \left[H^+ \right]$$

where $k_1 = 0.35$ sec^{-1} and $k_2 = 3.5$M^{-1} sec^{-1} at 25°C. Thus, even if the dimer were responsible for the color in the solution, its short life-time would cause the color to disappear rapidly. The rapid dissociation of the dimer also explains why no evidence for its presence was found at 335 millimicrons in the spectrophotometric study mentioned earlier.

If one assumes that the molar extinction coefficient for a polymeric species is approximately 5×10^5 (approximately the largest extinction coefficient obtainable), then the concentration of the polymeric Fe(III) species to give an absorbance reading of 0.383 for a 1 cm. cell is:

$$c = \frac{A}{\epsilon\, b}$$

$$= \frac{0.383}{5 \times 10^5 \times 1}$$

$$= 7.66 \times 10^{-7} M$$

where c = concentration in moles/l.

ϵ = molar extinction coefficient for polymer

b = path length in centimeters

A = absorbance

$\therefore$ the number of iron atoms per molecule of polymer is

$$\frac{1 \times 10^{-3}}{7.66 \times 10^{-7}} = 1.31 \times 10^3$$

This value is in accord with the value obtained by Spiro et al.[8] for an isolated soluble polymer with the formula $\left[Fe(OH)_x(NO_3)_{3-x} \right]_n$ where n was in the order of 900. Thus it appears that the rate of color disappearance in the centrifuged solution is due to the disappearance of some polymeric Fe(III) species. From the results of the O-18 study, it would appear that this Fe(III) polymer dissociates very slowly.

Suggestions For Further Studies

In order to gain further understanding of the intermediate species formed during the dissolution of ferric hydroxide gels in acids, techniques have to be developed to study these species. Ultracentrifuge techniques could possibly be used to follow the dissociation of the large soluble Fe(III) species into smaller species by means of changes in the Schlieren patterns. Another possibility for study is the use of membrane diffusion to determine the change in size of the soluble polymeric Fe(III) species with time - as the sizes of the polymeric species decrease, there should be an accompanying change in the rate of diffusion.

Sample Initial Spectrophotometric Run

Data for run number 1 from Section 4 - 2 dealing with the initial spectrophotometric studies at 26.5°C using the Zeiss spectrophotometer at 380 millimicrons with 1 cm. glass cells are shown below in Table IX.

Table IX

Spectrophotometric Study of the Color Disappearance in
Dissolved Ferric Hydroxide Solution at 380 Millimicrons

Time (min.)	Absorbance	Net Absorbance
28	0.930	0.894
31	0.751	0.715
34	0.619	0.583
37	0.520	0.484
40	0.442	0.406
43	0.380	0.344
46	0.329	0.293
49	0.285	0.249
52	0.255	0.219
55	0.227	0.191
58	0.202	0.166
64	0.163	0.127
70	0.133	0.097
76	0.111	0.075
82	0.093	0.057
88	0.080	0.044
94	0.066	0.030
100	0.060	0.024
106	0.054	0.018
112	0.049	0.013
118	0.046	0.010
124	0.043	0.007
130	0.041	0.005

Table IX (Continued) Spectrophotometric Study of the Color Disappearance in Dissolved Ferric Hydroxide Solution at 380 Millimicrons

Time (min.)	Absorbance	Net Absorbance
136	0.039	0.003
142	0.038	0.002
148	0.036	0.0
154	0.036	0.0

The net absorbance values obtained were plotted against time on a semi-log scale.

Sample of Treatment of Data Obtained in

Dilution Studies on the Centrifuged Solution

Data from sample number 3 from section 4 - 3 dealing with the spectrophotometric study of a centrifuged solution of dissolved ferric hydroxide at $25.0^{\circ}C$ which had been diluted 2.5 times with 0.5 M $HClO_4$ are shown below in Table X. The wavelength studied was 335 millimicrons and 1 cm. quartz cells were used.

For up to t = 40 minutes the net absorbance was calculated from the absorbance at the end of a spectrophotometric study at the same wavelength for an undiluted centrifuged sample. This absorbance value was 0.162. After t = 40 (when the solution was diluted), the absorbance value used to calculate the net absorbance was 0.076 (the absorbance at the termination of the spectrophotometric study on the diluted solution). The final Fe(III) concentration employed to calculate the absorbance per mole of Fe(III) per liter up to t = 40 minutes was 0.0110 M while after t = 40 minutes the value 0.0044 M was employed to account for the dilution.

The absorbance per mole of Fe(III) per liter was plotted against time on a semi-log plot.

Table X

Spectrophotometric Study of Stability of Color in
Centrifuged Solution Diluted 2.5 Times with 0.5 M HClO$_4$

Time (min.)	Absorbance	Net Absorbance	Absorbance Per Mole of Fe(III) Per Liter
22	1.29	1.13	103
24	1.11	0.948	86.2
26	0.960	0.798	72.5
28	0.841	0.679	61.7
30	0.750	0.588	53.5
32	0.669	0.507	46.1
34	0.600	0.438	39.8
36	0.545	0.383	34.8
38	0.498	0.336	30.5
40	0.456	0.294	26.7
44	0.153	0.077	17.5
46	0.139	0.063	14.3
48	0.127	0.051	11.6
50	0.118	0.042	9.55
52	0.110	0.034	7.73
54	0.104	0.028	6.36
56	0.099	0.023	5.23
58	0.094	0.018	4.09
60	0.090	0.014	3.18
62	0.087	0.011	2.50
64	0.084	0.008	1.82
66	0.081	0.005	1.14
68	0.080	0.004	0.909
70	0.078	0.002	0.455
72	0.076	0.0	0.0
74	0.076	0.0	0.0

REFERENCES

1. Lamb, A.B., and Jacques, A.G.
   J. Am. Chem. Soc.
   60, 967 (1938)

2. Rabinowitch, E. and Stockmayer, W.H.
   ibid, 64, 335 (1942)

3. Arden, T.V.
   J. Chem. Soc.
   350 (1951)

4. Hedstrom, B.O.A.
   Ark. Kemi.
   6, 1 (1953)

5. Milburn, R.M., and Vosburgh, W.C.
   J. Am. Chem. Soc.
   77, 1352 (1955)

6. Mulay, L.N., Selwood, P.W.
   ibid, 77, 2693 (1955)

7. Stumm, W., and Lee, G.F.
   Schweiz. Z. Hydrol.
   22, 295 (1960)

8. Spiro, T.G., Allerton, S.E. et al.
   J. Am. Chem. Soc.
   88, 2721 (1966)

9. Schugar, H., Walling, C. et al.
   ibid, 89, 3712 (1967)

10. Newton, T.W., and Baker, F.B.
    Inorg. Chem.
    3, 569 (1964)

11. Krause, A., and Pilawski, K.
    Z. anorg. allgem. Chem.
    197, 301 (1931)

12. Weiser, H.B., and Milligan, W.O.
    Chem. Rev.
    25, 1 (1939)

13. Simon, A., and Schmidt, T.
    Kolloid - Z., Zsigmondy Festschrift
    36, 65 (1925)

14. Weiser, H.B. and Milligan, W.O.
    J. Phys. Chem.
    39, 25 (1935)

15. Thiessen, P.A., and Köppen, R.
    Z. anorg. Chem.
    189, 113 (1930)

16. van der Giessen, A.A.
    J. Inorg. Nucl. Chem.
    28, 2155 (1966)

17. Towe, K.M., and Bradley, W.F.
    J. Colloid Interface Sci.
    24, 384 (1967)

18. Atkinson, R.J., Posner, A.M., and Quirk, J.P.
    J. Inorg. Nucl. Chem.
    30, 2371 (1968)

19. van der Kraan, A.M., and Medema, J.
    ibid, 31, 2039 (1969)

20. Furuichi, R., Sato, N. et al.
    J. Kogyo Kagaku.
    72 (7), 1455 (1969)

21. Mulay, L.N., and Copenaylor, M.
    "Advances in the Chemistry of Coordination
    Compounds" (1961) Macmillan

22. Rabinowitch, E.
    Reviews of Modern Physics
    14, 112 (1942)

23. Hunt, J.T., and Taube, H.
    J. Chem. Phys.
    19, 602 (1951)

24. Sykes, A.G.
    "Kinetics of Inorganic Reactions"
    p. 153
    Pergamon Press (1966)

25. Willix, R.L.S.
    Trans. Faraday Soc.
    59, 1315 (1963)

26. Connick, R.E. et al.
    J. Am. Chem. Soc.
    $\underline{78}$, 1827 (1956)

27. Conocchioli, J.T., Hamilton, Jr., E.J., and Sutin, N.
    J. Am. Chem. Soc.
    $\underline{87}$, 926 (1965)