UCRL-17564

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NUCLEAR MAGNETIC RESONANCE RELAXATION
OF OXYGEN-17 IN AQUEOUS SOLUTIONS OF FERRIC ION

Malcolm Robert Judkins
(Ph. D. Thesis)

May 1967

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UCRL-17561

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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NUCLEAR MAGNETIC RESONANCE RELAXATION OF OXYGEN-17 IN AQUEOUS SOLUTIONS OF FERRIC ION

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May 1967

ABSTRACT

The O^{17} NMR signal in aqueous solutions of ferric ion was studied as a function of temperature, frequency, and solution composition in order to separate the various effects arising from ferric ion and its hydrolyzed species. The principal species affecting the O^{17} NMR width by water exchange were found to be Fe^{3+}, $FeOH^{2+}$, and $Fe_3(OH)_4^{5+}$.

The ferric ion produces line broadening arising from exchange out of both a first and an outer coordination sphere. The first coordination sphere waters exchange slowly enough to be in the exchange controlled region. The outer coordination sphere exchange is rapid and the O^{17} nuclear spin is probably relaxed by a combination of scalar coupling and $\Delta\omega$ mechanisms. The first and outer coordination sphere effects cannot be separated unequivocally and consequently only a range of values is reported for the exchange rates.

It appears that $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$ are in the relaxation controlled region for the water exchange. Only a lower limit for the exchange rate from the first coordination sphere is given. The relaxation seems to be a consequence of both scalar coupling and $\Delta\omega$ mechanisms. The species $Fe_2(OH)_2^{4+}$ does not contribute measurably to the line broadening, presumably because of a low magnetic moment.

I. INTRODUCTION

A. Background

In the last two decades many new techniques have been developed for the study of extremely rapid chemical reactions.[1] In some cases it is now possible to measure reaction rates in solution which approach the highest values conceivable based on current theory. One of these newer techniques uses the broadening of the nuclear magnetic resonance line as a measure of exchange rates between two or more sites. The oxygen-17 NMR in water is ideally suited for ligand exchange studies on solvated metal ions where one of the exchanging ligands is a water molecule. A major criterion for this technique is that the magnetic environment of the water molecule be greatly different in the vicinity of the metal ion from that in the bulk of solution. Generally this means the metal ion must be paramagnetic. Proton NMR can also be used in this manner, but usually chemical exchange of the whole water molecule is not the dominant influence in the line broadening.

One further criterion is that the exchange proceed at a sufficiently rapid rate for the broadening to be observable. This means ligand lifetimes should be less than ca 0.01 sec. The shortest observable lifetime is governed by the slowness of the diffusion in the ligand exchange.

Connick and coworkers have studied the water exchange from the first coordination sphere of many paramagnetic metal ions by observing the broadening of the solvent water signal.[2] In principle one could also study the broadening of the ligand water signal. However, the signal is much weaker because of the difference in population of the two sites

and is much broader than the solvent signal because of the close proximity of the paramagnetic metal ion.

One ion which has been studied extensively is ferric ion.[3-5] The most recent determination of the aquo ligand lifetime is some hundred fold longer than the first reported experimental value. It was this disagreement and also the possibility of obtaining the rates of water exchange on the various hydrolyzed ferric species which led to this study of the aqueous ferric system.

It is useful to consider, qualitatively, the range of exchange rates which might be encountered in a system of this sort and their effect on the oxygen-17 signal. There is the trivial case of extremely slow or nonexistant exchange where the solvent water signal is virtually unchanged. Also any diamagnetic metal complexes which undergo ligand water exchange will produce little effect on the solvent signal. Exchange from a first coordination sphere is usually considered to be the dominant effect because of the rapid decrease in influence of the paramagnetic ion with distance. However, exchange from an outer coordination sphere may provide some line broadening, depending on the lifetime of the outer coordination sphere and other factors. This effect would be most evident when exchange from the first coordination sphere is too slow to change the bulk water signal.

As the exchange rate from the first coordination sphere is increased by some means, such as raising the temperature, the broadening of the bulk water signal becomes directly related to the chemical exchange rate and thus increases also. When the ligand water experiences the full effect of the metal ion environment before it returns to the solvent waters, the broadening is dependent on the exchange rate and shows an Arrhenius

temperature dependence.

If the exchange rate is enhanced sufficiently, the broadening will no longer depend upon the exchange step. It rather depends upon the rate at which the oxygen-17 nucleus of the ligand water molecule responds to the presence of the metal ion. This rate is inversely proportional to the so-called relaxation time for the specific interaction of the oxygen-17 with its new environment. Here the broadening is only a measure of a lower limit to the chemical exchange rate, although in a few instances where the chemical exchange rate influences the relaxation time, the actual rate may be obtained from the data. An application of the theory for the relaxation processes will delineate these instances.

B. Ferric Ion

Ferric ion, iron (III), is a d^5 ⟨Ar⟩ system where ⟨Ar⟩ is the closed shell configuration of argon. In aqueous solutions ferric ion forms a high spin (5/2) aquo complex which is presumed to be 6-fold coordinated and to have octahedral symmetry. Under weakly acidic conditions, the iron hydrolyzes to form inner-sphere complexes of the sort: $FeOH^{2+}$, $Fe(OH)_2^{+}$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$; where the ligand waters have been omitted for simplicity. Under more nearly neutral conditions, the iron forms high molecular weight polymers which are only slowly destroyed in strongly acidic media.[6] The rate of formation of $Fe_2(OH)_2^{4+}$ has been studied[7] and is slow compared to the water chemical exchange rate.

Numerous attempts have been made to obtain stability constants for the hydrolysis products.[8-11] The most reliable works seem to be those of Hedstrom[10] and Biedermann.[11] They used the EMF method in 3 M (Na^+) ClO_4^- solutions at 25°C.

Heats for formation of the hydroxy species have been reported by several workers.[8,12,13] Since it appears from this NMR study that $Fe_3(OH)_4^{5+}$ is an important species in the exchange, Schlyter's corrected values[11] have been used in conjunction with Biedermann's equilibrium quotients[12] in the analysis of the NMR data. No other workers seem to have encountered conditions where $Fe_3(OH)_4^{5+}$ was important.

The values that were reported are:

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad k_{11} = (9.0 \pm 1.0) \cdot 10^{-4}\ M$$
$$\Delta H = 14.7 \pm 1.8\ Kcal$$

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^{+} + 2H^+ \qquad k_{21} = (4.9 \pm 1.0) \cdot 10^{-7}\ M^2$$
$$\Delta H \text{ not reported}$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \qquad k_{22} = (1.10 \pm 0.02) \cdot 10^{-3}\ M$$
$$\Delta H = 8.4 \pm 0.7\ Kcal$$

$$3Fe^{3+} + 4H_2O \rightleftharpoons Fe_3(OH)_4^{5+} + 4H^+ \qquad k_{43} = (1.7 \pm 0.2) \cdot 10^{-6}\ M^2$$
$$\Delta H = 17.6 \pm 1.9\ Kcal$$

The stability constants will vary with ionic composition of the solution. It was necessary to estimate corrections for such effects. The two most plausible procedures seemed to be to assume constancy of the stability constants for a given ionic strength or constancy for a given total perchlorate concentration. The latter procedure was chosen for the following reasons. First of all, the NMR solutions are far outside the region of the Debye-Hückel limiting law. Secondly, Olson and Simonson[14] found that their stability constant for $FeOH^{2+}$ correlated better with total perchlorate concentration rather than with ionic

strength for solutions containing 0.02 M and 0.04 M perchlorate ion as they changed the inert salt cation from sodium to barium to lanthanum. This behavior is rationalized on the basis that ions of opposite charge determine primarily activity coefficients and only positively charged ions were involved, as is the case in the above equilibria. Actually, it was found that the use of ionic strength dependence for the stability constants does not alter the trends in the data or the general conclusions.

The perchlorate ion dependence of the stability constants k_{11} and k_{22} was assumed to be identical to Milburn and Vosburgh's[9] data for $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$, but with a match to Biedermann's data at 3 M perchlorate. The concentration quotient for $Fe_3(OH)_4^{5+}$ was recast in the form

$$\frac{3}{2}\ Fe_2(OH)_2^{4+} + H_2O \rightleftharpoons Fe_3(OH)_4^{5+} + H^+$$

$$k = 0.0466$$

$$\Delta H = 5.0 \text{ Kcal}$$

Based on a Debye-Hückel type argument, this equation would have only a small ionic strength dependence and in the absence of any experimental information it was assumed that k is independent of ionic strength or perchlorate concentration.

II. THEORY

A. General Comments

Bloch's equations and subsequent theories of the NMR phenomena have been discussed extensively by many workers. The reader may wish to read references 15-21 for a fuller explanation of the theory, and in particular, Marianelli's thesis.[20] For the conditions of magnetic field modulation with sideband detection of the NMR signal as employed in this laboratory, the observed first sideband signal has the form[22]

$$S = \frac{\pm \frac{2}{\beta} [J_1(\beta)]^2 \gamma H_1 T_2 M_0}{1 + (\Delta\omega_\pm T_2)^2 + (\gamma H_1)^2 T_1 T_2 [J_1(\beta)]^2} \qquad (1)$$

$$\beta = \frac{\gamma H_m}{\omega_m} \qquad \omega_\pm = \omega_0 - \omega \pm \omega_m$$

where S is the observed signal

J_1 is the Bessel function of the first kind

γ is the magnetogyric ratio

T_1 and T_2 are the nuclear longitudinal and transverse relaxation times, respectively

H_1 is one-half the amplitude of the radio frequency field

ω is the frequency of the rf field

ω_0 is the precessional frequency of the nuclei

M_0 is the equilibrium value of the magnetization of the sample

H_m is the amplitude of the modulation field, and

ω_m is the frequency of the modulation field.

This equation is normally used under conditions of negligible saturation,

i.e., $\left\{(\gamma H_1)^2 T_1 T_2 [J_1(\beta)]^2\right\} \ll 1$, and is restricted to slow passage conditions, and to the condition that $\omega_m > 1/T_2$.

The line broadening is related to the transverse relaxation time by

$$\frac{\delta\omega}{2} = \frac{1}{T_2} \tag{2}$$

where $\delta\omega$ is the total width at half maximum of the signal. The signals are calibrated by realizing that the separation of the first sidebands is $2\omega_m$.

B. Theoretical Equations for T_1 and T_2

1. T_2 in the Presence of Exchange

When the atoms containing the nuclei under investigation take part in exchange between two or more magnetically distinct environments, the expression for $1/T_2$ is considerably more complicated. It is still measured by the width of the peak, but it reflects the influence of the other environments. McConnell[23] has treated this situation and Swift and Connick[2] have extended the treatment to the case of a dilute solution of a paramagnetic ion. For the steady state condition without saturation, they found

$$\frac{1}{T_2} = \frac{1}{T_{2_{H_2O}}} + \frac{1}{\tau_{H_2O}} \left[\frac{\frac{1}{T_{2m}\tau_m} + \frac{1}{T_{2m}^2} + \Delta\omega_m^2}{\left(\frac{1}{T_{2m}} + \frac{1}{\tau_m}\right)^2 + \Delta\omega_m^2} \right] \tag{3}$$

where

τ_a is the lifetime of the molecule in environment a

T_{2a} is the transverse relaxation time in environment a in the absence of exchange

$\Delta\omega_m = \left(\omega_{H_2O} - \omega_m\right)$ is the difference in precessional frequencies in the two environments

The increased width arising from the presence of the paramagnetic ion is defined as

$$\frac{1}{T_{2p}} = \frac{1}{T_2} - \frac{1}{T_{2H_2O}} \tag{4}$$

and under conditions of equilibrium

$$\frac{1}{\tau_m} n\left[M^{+p}\right] = \frac{1}{\tau_{H_2O}} \left[H_2O\right]_{bulk} \tag{5}$$

or

$$\frac{1}{\tau_{H_2O}} = \frac{p_m}{\tau_m} \qquad \text{defining} \qquad p_m = \frac{n\left[M^{+p}\right]}{\left[H_2O\right]_b}$$

where $\left[H_2O\right]_{bulk}$ and $n\left[M^{+p}\right]$ are the concentrations of water molecules in the two water environments, n being the number of coordinated waters.

There are two limiting regions for $1/T_{2p}$. If the water lifetime is long compared to T_{2m} or $\Delta\omega_m$ $\left(1/\tau_m \ll 1/T_{2m} + |\Delta\omega_m|\right)$, then

$$\frac{1}{T_{2p}} = \frac{1}{\tau_{H_2O}} = \frac{p_m}{\tau_m} \ . \tag{6}$$

If the exchange is rapid and to the point where $1/\tau_m \gg 1/T_{2m} + |\Delta\omega_m|$, then

$$\frac{1}{T_{2p}} = \frac{p_m}{T_{2m}} + p_m \tau_m \Delta\omega_m^2 \ . \tag{7}$$

The first limit is commonly known as chemical exchange control and the second as relaxation control. The mechanisms responsible for relaxation of aqueous oxygen-17 will be discussed in the next section.

2. T_2 Relaxation Phenomena

The principal mechanisms of relaxation of the oxygen-17 nucleus when it is part of a ligand bound to a paramagnetic metal ion are a) $\Delta\omega$ mechanism, b) dipole-dipole, c) scalar coupling, d) quadrupole, and e) anisotropic chemical shift. Only the analytic expressions will be presented since excellent discussions have been referred to previously.

a. $\Delta\omega$ Mechanism. For this case the relaxation controlled expression for $1/T_{2p}$ is dominated by the $P_m(\Delta\omega_m)^2\tau_m$ term. The $\Delta\omega_m$ is given by the equation of Bloembergen[24]

$$\frac{\Delta\omega_m}{\omega_o} = \frac{S(S+1)\,A(\gamma_s/\gamma_N)}{3KT} \qquad (8)$$

where S is the spin angular momentum of the paramagnetic ion

A is the scalar coupling constant

γ_s is the magnetogyric ratio for the electron

γ_N is the magnetogyric ratio for the nucleus

ω_o is the precessional frequency of the nucleus

k is Boltzmann's constant

T is absolute temperature

The interruption mechanism for this effect is the exchange of the bound ligand with the bulk solution.

All the following mechanisms appear in the region where the relaxation is controlled by the term:

$$\frac{1}{T_{2p}} = \frac{P_m}{T_{2m}} \quad .$$

b. Dipole-Dipole Mechanism.

$$\frac{1}{T_{2p}} = \frac{S(S+1)\,\gamma_I^2\,\gamma_S^2\,\hbar^2}{15\,r^6}\,P_m\left\{4\tau_{1b} + \frac{\tau_{2b}}{1+\left(\omega_I-\omega_S\right)^2\tau_{2b}^2} + \frac{3\tau_{1b}}{1+\omega_I^2\,\tau_{1b}^2} + \frac{6\tau_{2b}}{1+\omega_S^2\,\tau_{2b}^2} + \frac{6\tau_{2b}}{1+\left(\omega_I+\omega_S\right)^2\tau_{2b}^2}\right\} \quad (9)$$

where r is the dipole-dipole distance. The following symbols are defined as:

$$\frac{1}{\tau_{1b}} = \frac{1}{\tau_m} + \frac{1}{\tau_r} + \frac{1}{T_{1e}}$$

$$\frac{1}{\tau_{2b}} = \frac{1}{\tau_m} + \frac{1}{\tau_r} + \frac{1}{T_{2e}}$$

The quantity τ_r is the tumbling time and is given approximately by Stoke's formula according to the equation

$$\tau_r = \frac{4\pi\eta a^3}{3kT}$$

where a is the radius of the tumbling sphere

η is the bulk viscosity

T_{1e}, T_{2e} are longitudinal and transverse electron relaxation times. Other terms have been defined previously.

Since $\omega_S \gg \omega_I$ and $\omega_I\tau_{1b} \ll 1$ for the oxygen-17 - ferric system, the expression reduces to

$$\frac{1}{T_{2p}} = \frac{S(S+1)\,\gamma_I^2\,\gamma_S^2\,\hbar^2}{15\,r^6}\,P_m\left\{7\tau_{1b} + \frac{13\tau_{2b}}{1+\omega_S^2\,\tau_{2b}^2}\right\} \quad (10)$$

c. Scalar Coupling

$$\frac{1}{T_{2p}} = \frac{S(S+1)}{3}\left(\frac{A}{\hbar}\right)^2 P_m\left[\tau_{c1} + \frac{\tau_{c2}}{1+(\omega_s)^2\,\tau_{c2}^{\,2}}\right] \qquad (11)$$

where

$$\frac{1}{\tau_{c1}} = \frac{1}{\tau_m} + \frac{1}{T_{1e}}$$

$$\frac{1}{\tau_{c2}} = \frac{1}{\tau_m} + \frac{1}{T_{2e}}$$

Here A is the scalar coupling constant and $\omega_I \tau_{c2} \ll 1$ has been used.

d. Quadrupole Coupling

$$\frac{1}{T_{2p}} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\left(1+\frac{n^2}{3}\right)\left(\frac{eq\,Q}{\hbar}\right)^2 P_m\,\tau_d \qquad (12)$$

where it has been assumed that $\omega_o \tau_d \ll 1$

I is the nuclear spin quantum number

n is a measure of the axial asymmetry of the electric field gradient

Q is the quadrupole moment of the nucleus

eq is the largest principle component of the electric field gradient

$1/\tau_d = 1/\tau_m + 1/\tau_r$

e. Anisotropic Chemical Shift

$$\frac{1}{T_{2p}} = \frac{14}{40}\,\omega_o^{\,2}\,\delta_{zz}^{\,3}\left(1+\frac{n^2}{3}\right) P_m\,\tau_d \qquad (13)$$

assuming $\omega_o^2 \tau_d^2 \ll 1$

where δ_{zz} is the component along the z axis of the diagonalized chemical shift tensor $\underset{\sim}{\beta}$ belonging to the Hamiltonian $\left(-\gamma_o \vec{H} \cdot \underset{\sim}{\beta} \cdot \bar{I}\right)$

n is given by $\left(\delta_{xx} - \delta_{yy}\right)/\delta_{zz}$

It can be clearly seen from the above equations that, under certain circunstances, the water exchange rate on the metal ion can be obtained from a knowledge of the relaxation mechanism being observed.

III. EXPERIMENTAL

NMR measurements of the T_2 of oxygen-17 were made on a Varian Associates Model V4311 high resolution spectrometer at 8.134 MHz or a Varian Model V4200 wide line spectrometer at a frequency of 2.0 MHz. The signals were detected using the sideband technique. The modulation and detection were performed by a PAR Model JB-8 lock-in amplifier. A Bogen audio amplifier Model CHA-10 amplified the modulation signal which was then applied to the sweep coils of the Varian probe. Most data were taken using a modulation frequency of 500 cps and under conditions where the first sideband was optimized ($\gamma H_m/\omega_m = 0.68$ where γ is the magnetogyric ratio; H_m, the amplitude of the modulation magnetic field; ω_m, the modulation frequency). At modulation frequencies of ca 1000 Hz, H_m could not be made sufficiently large to optimize the first sideband which resulted in a slight decrease in signal to noise.

All measurements were made under conditions of slow passage and negligible saturation. The gross magnetic field was swept at speeds from ca 300 milligauss/min to 1000 milligauss/min. The detected signal was filtered with time constants from 0.1 to 0.6 sec.

The samples were contained in 10 mm O.D. pyrex glass tubes having a (18/9) ball joint. The cap had a thermocouple well which extended down to the solution. Changes in pH were achieved by adding 11.85 M perchloric acid with lambda pipettes.

Temperature change was obtained by passing heated or cooled dry nitrogen in the annular space between the sample and the dewared insert in the probe.[20] A Varian EPR temperature control unit operating from a regulated voltage source was used to heat above ambient temperature. A

split gas flow system was used below room temperature with acetone-dry ice as the cold bath. Two copper-constantan thermocouples were used to measure the temperature, one inside and one below the sample. The difference did not exceed 1°C and an average was chosen as the actual temperature of the sample. Temperature control was within 0.5°C.

Sample Preparation

The perchlorate salt was chosen for the sample preparation since perchlorate is believed to form only weak complexes with metal ions. Sutton[25] and others have reported evidence for a ferric-perchlorate complex, but Coll *et al.*[26] attribute the observed shift in the optical spectrum to partial dehydration of the ferric ion.

The stock ferric perchlorate solution was made by dissolving iron sponge in 4 M nitric acid and then fuming with 70% perchloric acid. The crystals of ferric perchlorate were washed with 70% perchloric acid and then sucked partially dry in a fitted glass funnel. The iron sponge (99.999%) was purchased from United Mineral and Chemical Corp., New York, agents for Johnson, Matthey and Co., Ltd., London, Grade I, Lot No. S1994. The sponge has a typical analysis of 2 ppm manganese. Ten ppm is at most a 6 sec^{-1} contribution to the linewidth of a 0.2 M ferric solution, which is within experimental error. Reagent grade ferric nitrate contains ca 100 ppm manganese.

The solution was tested for nitrate ion with the brucene sulfate spot test.[27] The α-nitroso-β-naphthol spot test was used for cobaltous ion.[28] The manganese was analyzed by oxidizing with potassium persulfate, complexing the iron with phosphoric acid, and observing the solution spectrophotometrically at 5250 Å with a limit of detectibility ~ 5 ppm. All the tests were negative.

The total iron was analyzed by titration with ethylenediaminetetracetic acid using Variamine B blue as the indicator.[29] The total hydrogen ion was determined by complexing the iron with oxalate and titrating the acid with 0.1000 N NaOH back to the pH of the oxalate solution.[39] Sodium gravimetric analysis was performed by the analytical laboratory by precipitation with zinc uranyl acetate. Sodium bicarbonate was used to destroy some of the excess perchloric acid.

All NMR measurements using the high purity iron were made with hydrogen normalized 10% O^{17} water obtained from the Oak Ridge National Laboratory. The water was weighed and a known volume of the stock ferric solution was added. Dissolved oxygen was not removed as this does not affect the width of the H_2O^{17} NMR signal appreciably.

All viscosity measurements were made with an Oswalt capillary viscometer in a constant temperature bath regulated to 0.1°C.

Spectrophotometric measurements were made in thermostatted cells on either a Cary 14 or a Beckmann DU.

Marianelli's[20] reported values of T_2 of oxygen-17 in water were used as the water blank, with correction for the change in viscosity of the various NMR solutions, assuming the width of the blank to be proportional to the viscosity.

IV. RESULTS AND DISCUSSION

A. Ferric Ion

All of the previous efforts at studying oxygen-17 NMR in aqueous ferric solutions have been directed toward obtaining the rate of water exchange from the first coordination sphere of the hexaquoiron (III) species. The recent availability of 10% enriched oxygen-17 water now makes a more accurate measurement possible. In Fig. 1 the temperature dependence of $1/T_{2p}$ is shown for a 0.375 M ferric solution with 1.7 M perchloric acid. Approximately 0.08 percent of the total iron is present as hydrolyzed species and this contributes ca six percent of the observed $1/T_{2p}$ at room temperature and is smaller at higher temperatures. From the shape of the curve it is apparent that it is a composite of several effects operating over the observed temperature range. In the high temperature region, the dominant effect is the exchange of water molecules from the first coordination sphere. In this region the relaxation is much more rapid than the chemical exchange, and the $1/T_{2p}$ expression reduces to:

$$\frac{1}{T_{2p}} \doteq \frac{p_m}{\tau_m}$$

as proposed by Genser.[5]

1. Outer Sphere Effects

In the region near room temperature or below (Fig. 1) other effects become comparable with the exchange from the first coordination sphere. The first coordination sphere is in the chemical exchange controlled region and can only give a decreasing contribution to $1/T_{2p}$ with decreasing

temperature. The change in water blank arising from an increase in the viscosity for the solution has been taken into account. Furthermore, the linewidth per mole per liter of ferric ion is nearly independent of the concentration of ferric ion, indicating that the effect at low temperatures arises primarily as a result of the presence of the ferric ion in solution. Therefore, this effect must originate in an outer coordination sphere of the ferric ion.

The unhappy task of resolving the data into the component contributions must now be faced. From the temperature dependence at low temperature, it is obvious that the observed effect is due to some relaxation controlled phenomenon. If this were the only information available, the experimental curve could be resolved into any one of a family of lines. Additional information is available, but, even still, the interpretation is subject to a very great deal of uncertainty.

The nature of the outer coordination sphere must be decided upon in order to estimate the magnitudes of the possible relaxation effects. It will be assumed that the effect arises only from a second coordination sphere composed of eight water molecules, each resting on one of the faces of the octahedron. Based upon the ionic radii for iron (III) (0.64Å) and oxygen (1.40Å), the internuclear distance from the iron to the second coordination sphere oxygen is 3.43Å if the oxygen just touches the first coordination sphere waters. Calculation of the relaxation effects due to dipole-dipole and to quadrupole interactions of the oxygen nucleus with the iron can now be performed.

2. Dipole-Dipole and Quadrupole Relaxation Mechanisms

The expression for the dipole-dipole relaxation has been given previously in the theory section, Equation 10. The ferric ion T_{1e} has not

been measured, so it has been assumed to be identical to T_{2e} which is 5.8×10^{-11} sec at 25°C for this solution. The rotational correlation time τ_r can be calculated from Stokes' formula

$$\tau_r = \frac{4\pi\eta a^3}{3kT}$$

Assuming a radius of 4.83Å and a viscosity of 1.18 centipoise, τ_r is calculated to be 1.35×10^{-10} at 25°C if the whole second coordination sphere rotates as a group. The exchange time, τ_m, will be assumed long compared to the other times. This calculation gives a contribution to the observed $1/T_{2p}$ of 22 sec^{-1} at 25°C. The competition between T_{1e} and τ_r is such as to give this contribution a maximum slightly above 25°C and a moderate dropping off at higher and low temperatures.

The quadrupole calculation is relatively straightforward. The eqQ/h for oxygen-17 in the water molecule has been measured in the vapor phase by microwave by Townes and Stevenson[31] and is -8.13 Mc with $\eta = 0.7$. If it is assumed that these values are unchanged for the ferric system, then $1/T_{2p} = 700$ sec^{-1} at 25°C with $[Fe^{+3}] = 0.375$ M. The interruption by τ_r was treated as in the dipole-dipole case and chemical exchange was assumed to be slow.

Clearly this is a much bigger effect than is observed. It must be conjectured that the water molecule in the second coordination sphere is still capable of sufficiently random motion to provide no appreciable broadening. It should be noted this is not in conflict with the use of the τ_r for the dipole-dipole calculation. A rotation of the water molecule attached to one face of the octahedron has no effect on the dipole-dipole relaxation; the whole complex must rotate so as to change the

direction of the vector between the dipoles with respect to the laboratory coordinate system in order for relaxation to take place in dipole-dipole coupling.

3. Scalar Coupling and $\Delta\omega$ Mechanism

Other possible mechanisms of relaxation must now be considered. The scalar coupling and the $\Delta\omega$ mechanism contain the scalar coupling constant which must either be estimated or measured. There is a significant chemical shift of the bulk waters from the signal of pure water as is shown in Fig. 3. The 1/T temperature dependence is an indication of complete averaging of the shift through rapid chemical exchange. This can be seen from the equation for the shift of the bulk water resonance arising from the presence of a paramagnetic specie[2]

$$\Delta\omega_{H_2O} = \frac{p_m \Delta\omega_m}{\tau_m^2 \left\{ \left[\frac{1}{T_{2m}} + \frac{1}{\tau_m} \right]^2 + \Delta\omega_m^2 \right\}} \tag{14}$$

where the symbols have been defined as in Eqn. 3. In the limit of fast exchange,

$$\text{i.e.} \quad \frac{1}{\tau_m} \gg \frac{1}{T_{2m}} + |\Delta\omega_m| ,$$

$$\Delta\omega_{H_2O} = p_m \Delta\omega_m$$

and $\Delta\omega_{H_2O}$ then has the 1/T dependence of $\Delta\omega_m$ (Eqn. 8).

Since the second coordination sphere is in the fast exchange limit, i.e. relaxation control, at these temperatures, but not the first coordination sphere, the shift must arise from the second coordination sphere.

Upon substitution from Eqn. 8, the equation relating the observed shift to the scalar coupling constant for oxygen-17 in the second coordination sphere is obtained.

$$\Delta\omega_{H_2O} = \frac{S(S+1)\,A\left(\gamma_s/\gamma_N\right)}{3kT}\; p_m\,\omega_o$$

This gives

$$\frac{A}{\hbar} = 3.07\times10^{6}\ \text{rad sec}^{-1}$$

for the second coordination sphere waters.

For comparison a scalar coupling constant for the second coordination sphere waters of chromium (III) can be calculated from the data of Alei[32] and is

$$\frac{A}{\hbar} = 2.16\times10^{6}\ \text{rad sec}^{-1}$$

The waters on chromium (III) in the first coordination sphere exchange with a half life of ~ 40 hours,[33] so the observed shift must come from outside the first coordination sphere. The similarity of the two constants lends support to the idea of the outer sphere effect with ferric ion.

The calculation of the contribution to the linewidth from scalar coupling is now straightforward, assuming that the interruption is T_{1e} and not τ_m, as assumed previously.

$$\frac{1}{T_{2p}} = 95.5\ \text{sec}^{-1} \quad \text{at } 25^\circ\text{C} \quad [Fe^{+3}] = 0.375\ \text{M}$$

The term $\tau_{c2}/\left(1+\omega_s^{2}\tau_{c2}^{2}\right)$ of Eq. (11) was neglected since $\omega_s^{2}\tau_{c2}^{2} \geq 207$ at

14 kilogauss and $T_{1e} \geq T_{2e}$ for all cases.

A word of comment is now necessary. The sum of the contribution to $1/T_{2p}$ from dipole-dipole and from scalar coupling has exceeded the measured $1/T_{2p}$ at 25°C. This could be due to two problems with the calculations. Stokes' formula is only a rough estimate of the actual rotational rate in the solution. Secondly, the number of second coordinate waters may be different from the value which was assumed, for example because of replacement by perchlorate ions. A third possibility, that of very rapid chemical exchange, will be considered later.

In attempting to resolve the experimental curve in Fig. 1 into its component parts, the dipole-dipole contribution was neglected and the scalar coupling was assumed to be interrupted by T_{1e} and have the temperature dependence of the T_{1e}. Neglecting the dipole-dipole part is certainly not a good assumption, but it is also embarrassing to be able to account for more linewidth than is observed. Further, the dipole-dipole calculations are not exact enough to permit the correction to be made precisely.

4. Values of T_{2e} and T_{1e}

The T_{1e} is not known, so the measured T_{2e} and its temperature dependence in a solution of natural water made up to be identical to the NMR solution was used. It is necessary to measure the T_{2e} in a solution which is the same as the NMR solution. At these iron concentrations, it is believed that the electronic dipolar interaction becomes important as a relaxation mechanism for T_{1e} and T_{2e} and could affect both of them equally. Also increasing the solution viscosity at constant temperature would shorten both T_{1e} and T_{2e} for the case of $\omega_s \tau_c \ll 1$.

Another approximation was made in order to interpret the data. The T_{2e} measured at fields of ca 3.5 kilogauss was used to calculate the scalar coupling relaxation at fields of ca 14 kilogauss. It is quite possible that the T_{2e} has a frequency dependence, and not necessarily the same as the T_{1e} frequency dependence. However, there seems to be no method for measuring T_{2e} or T_{1e} at 14 kilogauss at the present time.

5. Resolution of the Experimental Curve

a. First Coordination Sphere. With all these variables and uncertainties, and having no good handle on any one of them, the interpretation of the NMR data at low temperatures must be viewed with considerable reservation. However, persevering with the approximations which have been made, the NMR curve can be resolved into three straight lines as is shown in Fig. 1.

The chemical exchange line for the first coordination sphere corresponds to an enthalpy of activation of 18.4 kcal and an entropy of activation of 12.8 e.u. Intuitively, this entropy value is a bit too large. Also, the previous water exchange studies with the transition metal ions found entropies whose absolute values were less than ca 6 e.u. The lifetime for a water molecule in the first coordination sphere is calculated to be 6.7×10^{-3} sec at 25°C.

Since the entropy of activation is so large, repositioning the scalar coupling line to produce an entropy nearer zero might be of interest. There is no other rationale for making the change. However, since the value of T_{1e} at 14 kilogauss is unknown, such a changed line is perhaps as satisfactory as the line drawn in Fig. 1. One of the many possible changes has been made for Fig. 2, where the $\Delta H^{\ddagger}$ is now 14.1 kcal, $S^{\ddagger}$ is now +1 e.u., and the water lifetime in the first coordination

sphere is 2.4×10^{-3} sec. This resolution does not account for the observed frequency dependence at $10^3/T = 3.40$, however.

The three previously reported values for the lifetime of a water in the first coordination sphere of ferric ion are all shorter than 9×10^{-3} sec. The values from Connick and Poulson[3] and from Connick and Stover[4] are 9×10^{-7} sec and 4.16×10^{-5} sec respectively. A small part of the discrepancy could be due to poorer signal to noise ratio in these earlier experiments since they were run with natural abundance and 0.7% enriched oxygen-17 water respectively. However, the principal difficulty probably arose from a significant Mn^{+2} impurity in their ferric salts such as was found in the early series of experiments for the thesis. Since Mn^{+2} contributes such a large linewidth per mole per liter, ca five mole percent impurity would account for Connick and Poulson's observation. Genser[5] found linewidths nearly comparable to those reported here. He did not perform experiments below room temperature and therefore did not recognize the presence of second coordination sphere contributions at room temperature. His lifetime, 3.3×10^{-4} sec, is shorter by the amount of the second coordination sphere contribution.

b. <u>Second Coordination Sphere.</u> From the large temperature dependence of the low temperature line, $\Delta\omega$ relaxation would appear to dominate in that region. Furthermore, the low temperature points have a strong frequency dependence. Of course, this could also come from scalar coupling interrupted by a frequency dependent T_{1e}. However, the large temperature dependence would argue against the latter interpretation, subject of course to the uncertainty of the previous placement of the frequency independent scalar coupling line.

If the former interpretation is correct, then the lifetime of a

water molecule in the second coordination sphere is approximately 4.2×10^{-8} sec with $\Delta H^{\ddagger}$ = 9.9 kcal and $\Delta S^{\ddagger}$ = 8.4 e.u. for Fig. 1. For Fig. 2, the lifetime is 6.9×10^{-8} sec with $\Delta H^{\ddagger}$ = 7.5 kcal and $\Delta S^{\ddagger}$ = -5.0 e.u. These lifetimes are longer than T_{1e} as was assumed previously. Presuming that the lifetime is roughly dependent on the strength of the electrostatic attraction between the metal ion and the water molecule (ze^2/r), it is interesting to compare this lifetime with the lifetime in the first coordination sphere of manganese (II) which is isoelectronic with iron (III). Taking the rate from the iron data and correcting for the different oxygen-metal distances and the change in charge, a value of 9×10^{-8} sec is predicted for Mn^{+2} vs a measured value of 3.22×10^{-8} sec. In view of the crudeness of the approximation, the agreement is striking.

The frequency dependence of the T_{1e} deserves some comment. The relaxation mechanisms for T_{1e} and T_{2e} are not understood at the present time, however, the relaxation might be of the form proposed by McGarvey[34]

$$\frac{1}{T_{1e}} = \left(\frac{16\pi^2}{25}\right)\frac{D^2}{h^2}\left\{\frac{67\,\tau_c}{1+\omega_s^2\tau_c^2} + \frac{52\,\tau_c}{1+4\omega_s^2\tau_c^2}\right\} \qquad (15)$$

We will not consider T_{2e} since at all experimental fields and temperatures (except near 0°C) the T_{2e} term is small in the scalar coupling expression (Eqn. 11). In the limit of $\omega_s^2\tau_c^2 \ll 1$, T_{1e} reduces to

$$T_{1e} = \frac{25h^2}{1904\pi^2D^2\,\tau_c}$$

In the limit of large ω_s, i.e. $\omega_s^2\tau_c^2 \gg 1$, T_{1e} has the form

$$T_{1e} = \frac{5h^2\,\omega_s^2\tau_c}{256\pi^2D^2}$$

As the temperature of the solution is lowered, τ_c becomes longer and T_{1e} should start to change to the high frequency limit. This could give a frequency dependence to the scalar coupling at low temperatures, but the activation energy from Fig. 1 or Fig. 2 seems to be larger than one would expect from τ_c.

6. Rapid Chemical Exchange

Another possibility for the relaxation mechanisms is that they are interrupted principally by chemical exchange. This idea has the advantage that it overcomes the problem of calculating larger linewidths than are observed. However, it does not allow for the observed frequency dependence at low temperature and therefore seems unlikely to be the explanation.

It might be thought that a way to circumvent the lack of low temperature frequency dependence and still retain chemical exchange as the interruption mechanism is to assume that scalar coupling is interrupted principally by chemical exchange at room temperature and is interrupted at lower temperatures by T_{1e} in the $\omega^2\tau_c$ region. The two correlation or interruption times would be combined at all temperatures according to $1/\tau_{c1} = 1/\tau_m + 1/T_{1e}$. When the contributions from the two effects are added, the resulting curve has just the opposite curvature to the experimental curve irrespective of the relative values of the enthalpies of the two processes. This explanation must, therefore, be discarded.

It seems reasonable, then, that the NMR experimental curve can be resolved into the three regions: slow chemical exchange from the first coordination sphere of the ferric ion, scalar coupling relaxation for the second coordination sphere interrupted by T_{1e}, and $\Delta\omega$ relaxation for the second coordination sphere. The absolute values for these interactions cannot be determined exactly since none of the lines can be accurately fixed.

7. Relaxation Control for the First Coordination Sphere

The waters exchanging from the first coordination sphere of ferric ion are in the exchange controlled region, but the question arises of how rapid the exchange could become before relaxation control becomes noticeable. A lower limit to the temperature can be calculated by assuming that the $\Delta\omega$ mechanism would be dominant in the relaxation controlled region. If some other mechanism is more effective than $\Delta\omega$, then the exchange controlled region would be extended to a higher temperature.

At the point of equal contributions to $1/T_{2p}$ from chemical exchange and from $\Delta\omega$ relaxation, the following relation is true:

$$\frac{p_m}{\tau_m} = p_m \Delta\omega^2 \tau_m$$

and upon cancellation of terms, $\tau_m = \left|\frac{1}{\Delta\omega}\right|$.

Calculation of $\Delta\omega$ is not straightforward. The scalar coupling constant could be obtained from a chemical shift measurement of the bulk waters. However, when the NMR broadening is strongly in the exchange controlled region, the chemical shift of the bulk waters is extremely small and would be hidden in the large shift due to the second coordination sphere waters. Therefore, the coupling constant must be estimated. It seems likely that it should be at least as large as the value for Mn^{+2} ($A/h = 9.2\times10^6$ cps).[2]

Thus τ_m is calculated to be ca 9×10^{-7} sec. This value of τ_m should be reached near 140°C if the $\Delta H^{\ddagger}$ value of 18.4 Kcal is assumed. Since the calculation depends upon the choice of the activation enthalpy for the exchange and upon the estimation of the scalar coupling constant, a smaller enthalpy or a larger coupling constant would move the temperature higher. Also some other more effective relaxation mechanism would have the same effect.

8. Summary

The broadening of the oxygen-17 NMR from water exchange on unhydrolyzed ferric ion arises from two separable exchange sites. The first coordination sphere waters exchange sufficiently slowly to be in the exchange controlled region. Depending upon the linewidth attributed to exchange from the second coordination sphere, differing values of ligand water lifetimes in the first coordination sphere can be obtained and correspondingly differing values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. For the resolution made in Fig. 1, the lifetime is 6.7×10^{-3} sec, $\Delta H^{\ddagger}$ = 18.4 kcal, and $\Delta S^{\ddagger}$ = 12.8 e.u. A lower limit to these values can be obtained by drawing a line tangent to the high temperature part of the experimental curve. This gives values of ca $\Delta H^{\ddagger}$ = 12.8 kcal, $\Delta S^{\ddagger}$ = -3 e.u. and a lifetime of 1.62×10^{-3} sec.

A comparison with other values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ which have been reported is interesting. Genser[5] reports $\Delta H^{\ddagger}$ = 8.9 ± 1.0 kcal and $\Delta S^{\ddagger}$ = -13 ± 4 e.u. for the water exchange on ferric ion. His $\Delta H^{\ddagger}$ would be somewhat larger if he had used a viscosity corrected water blank and correspondingly a more positive value of $\Delta S^{\ddagger}$ would have been found. It is possible that his values were in error because of contributions to the width from the second coordination sphere. He worked with nitrate rather than perchlorate solutions and this may account for some of the differences.

Swift and Connick[2] measured $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for a number of the doubly charged transition metal ions.

Ion	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, e.u.
Mn^{+2}	8.1	2.9
Fe^{+2}	7.7	-3.0
Co^{+2}	8.0	-4.1
Ni^{+2}	11.6	0.6

It can be seen that all of the activation entropies are small. The enthalpies all have similar values except for Ni^{+2} which has an unusually high energy for the reaction intermediate. The enthalpy of activation for water exchange on ferric ion is larger as would be expected if the rate is influenced by an electrostatic effect.

It has been noted previously that rates of water exchange are quite similar to rates of water replacement by sulfate ion on metal cations. The latter rate for ferric ion has been measured by Wendt and Strehlow[35] by pressure jump. The experimentally derived quantity is the product of the equilibrium quotient for sulfate moving from the bulk solution into the outer coordination sphere and of the rate at which the sulfate in the outer coordination sphere moves into the first coordination sphere to replace a water molecule. If the former equilibrium quotient is assumed to be identical to the value for Al^{+3}, $19 \pm 3\ M^{-1}$,[36] then the rate constant for movement of the sulfate from the second to the first coordination sphere is ca 50 sec^{-1} for ferric ion at 25°, a value not greatly different from the water exchange rate of 150 sec^{-1}.

Marianelli[20] has reported the only other water exchange rate for a plus three ion and gives a lifetime of 1.1×10^{-9} sec for a water in the first coordination sphere of gadolinium. He also reports $\Delta H^{\ddagger} = 3.1$ kcal and $\Delta S^{\ddagger} = -7$ e.u. The high rate reflects the relatively large radius.

Outer coordination sphere effects have been attributed to a second coordination sphere composed of eight equivalent waters located on the octahedral faces of the first coordination sphere. The observed temperature dependence indicates the exchange is in the relaxation controlled region. From the observed chemical shift, the scalar coupling constant has a value of 3.06×10^{6} rad sec^{-1} for the second coordination sphere

waters. At room temperature, the relaxation appears to be predominantly controlled by scalar coupling interrupted by T_{1e}. At lower temperatures the relaxation has a frequency dependence which could arise from either a frequency dependence in T_{1e} or a contribution from the $\Delta\omega$ mechanism. Assuming the latter effect because of the large temperature dependence for the line, a lifetime of a water molecule in the second coordination sphere can be calculated as $4\text{-}7\times10^{-8}$ sec. Before this value can be accepted the interpretation proposed needs further verification.

B. Hydrolyzed Species

Genser[5] has noted previously that the rate of water exchange on ferric ion appears to be enhanced by the insertion of a hydroxide ion in the first coordination sphere. Blatt[18] noted that chloride ion produced a similar effect. Qualitatively these effects can be explained by realizing that the kinetics of the exchange are related to the electrostatic force between the ferric ion and the water molecule, and the presence of a chloride or an hydroxide ion in the first coordination sphere reduces the effective charge on the ferric ion.

Obtaining the water exchange rate for the various ferric hydroxy species requires a detailed knowledge of their equilibria in solution. The hydroxy species are equilibrated too rapidly in solution to be separated on an ion exchange column and studied individually, as is possible with the analogous chromium (III) species. The $FeOH^{2+}$ is presumed to be formed rapidly by proton transfer with a first order rate constant of ca 3×10^{7} sec^{-1}.[37] The dimerization of $FeOH^{2+}$ to form $Fe_2(OH)_2^{4+}$ has a rate constant of 450 ± 50 M^{-1} sec^{-1} at 25°C and the dimer dissociation has a rate constant of 1 ± 0.5 sec^{-1}.[7] No work has been reported on the kinetics of formation of $Fe(OH)_2^{+}$ or $Fe_3(OH)_4^{5+}$, but the NMR solutions seemed to equilibrate within ca 15 minutes following addition of acid. Linewidth measurements made at various temperatures displayed no slow changes or hysteresis effects lasting longer than ca 15 minutes.

1. Determination of the Major Contributors to the NMR Width

Because of the great preponderance of equilibrium data on $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$, the initial resolution of the NMR data was attempted with only these two species and free ferric ion. The data cannot be fitted

by either hydrolyzed species individually, or by a combination. The linewidth from the two species can be written in the form:

$$\frac{1}{T_{2ph}} = a\left[FeOH^{2+}\right] + b\left[Fe_2(OH)_2^{4+}\right] \tag{16}$$

where

$$\frac{1}{T_{2ph}} = \frac{1}{T_{2p}} - \frac{1}{T_{2_{Fe^{+3}}}}$$

and

$\frac{1}{T_{2_{Fe^{+3}}}}$ is the linewidth from free ferric ion

a is the increase in the water O^{17} linewidth per mole per liter of $FeOH^{2+}$

b is the increase in the water O^{17} linewidth per mole per liter of $Fe_2(OH)_2^{4+}$

A plot of $1/\left(T_{2ph}[FeOH^{2+}]\right)$ vs $\left[Fe_2(OH)_2^{4+}\right]/\left[FeOH^{2+}\right]$ should give a straight line of slope b and an intercept a. The line should be independent of total iron concentration if the data can be explained with only these two species and assuming a and b to be independent of iron concentration. A typical plot is shown in Fig. 4. The equilibrium quotients reported by Biedermann were used for calculating the concentrations of species from the known stoichiometric iron and hydrogen ion concentration. Clearly the discrepancy is outside the experimental error. Also, the range of total perchlorate concentration is sufficiently small that it is very unlikely that this effect could be attributed to changes in the equilibrium quotients with solution composition.

This discrepancy could not be resolved by the use of other stability constants from the literature. Biedermann has reported the presence of an additional hydrolyzed species, $Fe_3(OH)_4^{5+}$.[11] A check of the calculated concentrations of the hydroxy species in the solutions of Fig. 4 reveals that the upper curve, corresponding to 0.1 M $Fe(ClO_4)_3$, contains appreciably more $Fe_3(OH)_4^{5+}$ than the lower curve for equal concentrations of $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$ (see Fig. 5). Assuming the simplest case of linewidth contributions from $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$, $1/T_{2ph}$ can similarly be resolved by

$$\frac{1}{T_{2ph}[FeOH^{2+}]} = a + c\,\frac{\left[Fe_3(OH)_4^{5+}\right]}{\left[FeOH^{2+}\right]} \qquad (17)$$

where c is the increase in the water O^{17} linewidth per mole per liter of $Fe_3(OH)_4^{5+}$.

A typical plot is shown in Fig. 6. Biedermann's equilibrium quotients were used. The agreement between the points for the two iron concentrations is satisfactory. The sets of points do not match perfectly, however, and the individual sets seem to have a slight curvature. Similar plots were obtained at other temperatures using the enthalpies for the equilibria reported by Sillen[12] from the work of Schlyter (Fig. 7,8). It is most likely that the discrepancies are due to uncertainties in the perchlorate ion dependence of the stability constants, to uncertainties in the enthalpies of formation at other than 25°C, or, to a lesser extent, to uncertainties in the stoichiometric hydrogen ion concentration.

2. <u>Lower Limits to τ_m</u>

At 25° the intercept gives a molar contribution from $FeOH^{2+}$ of 5.95×10^4 rad sec^{-1} M^{-1} and the slope gives a molar contribution from $Fe_3(OH)_4^{5+}$

of 3.14×10^5 rad sec^{-1} M^{-1}. In the temperature interval from 18° to 44°C both $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$ maintain their respective contribution per mole to within ca ± 20% with no significant trends as the temperature changes (Table 5).

In order to establish a lower limit for the lifetime of an oxygen-17 on either species, some assumption must be made about the mechanism. It seems highly likely that the waters of $FeOH^{2+}$ are considerably more labile than the hydroxide group. While the five waters cannot be exactly equivalent in their exchange behavior, in the absence of information on their differences it will be assumed that all five behave kinetically the same. Then the rate at which a particular water molecule leaves the first coordination sphere must be equal to or greater than $1/\left(P_m T_{2p}\right) = 6.6 \times 10^5$ sec^{-1} at 25°, as is seen from Eq. (3). Correspondingly the lifetime of a water molecule is equal to or less than 1.5×10^{-6} sec.

Since the proton transfer on and off $FeOH^{2+}$ may be more rapid than the whole water exchange, it is possible that all first coordination sphere oxygens associated with $FeOH^{2+}$ become equivalent more rapidly than they undergo chemical exchange. Then the exchange lifetime of a particular one of the six first coordination sphere oxygens is 1.8×10^{-6} sec as an upper limit. The lifetime of a proton on $Fe(H_2O)_6^{3+}$ is ca 4×10^{-7} sec at 25°C;[37] therefore the lifetime of a $FeOH^{2+}$ before it adds a proton would range from 10^{-8} to 10^{-10} sec for the acidities used here.

The structure of $Fe_3(OH)_4^{5+}$ is unknown. In fact Biedermann is the only person who has noted its existence. The structure will be assumed to be linear and double hydroxy bridged between the iron atoms. From the slow decomposition rate for $Fe_2(OH)_2^{4+}$, it seems reasonable to assume

that the hydroxy bridge oxygens exchange too slowly to be observed in the NMR broadening. This leaves a first coordination sphere hydration number of ten for $Fe_3(OH)_4^{5+}$ or a lifetime of a bound water of 5.8×10^{-7} sec as an upper limit, assuming the waters can be treated as equivalent kinetically.

The slope obtained for each species is directly dependent upon the choice of value for the enthalpy of formation of the species. Schlyter's corrected value for $FeOH^{2+}$, $\Delta H = 14.7 \pm 1.8$ kcal, seems to give a somewhat large value for the entropy change, i.e. $\Delta S = 35$ e.u. If, instead, Milburn's data were to be used with their more reasonable entropy change, i.e. $\Delta H = 10.2 \pm 0.3$ kcal, $\Delta S = 21 \pm 1$ e.u., then the broadening caused by $FeOH^{2+}$ would have an activation enthalpy of ca +4 kcal.

Milburn did not encounter conditions where the concentration of $Fe_3(OH)_4^{5+}$ was comparable to the concentrations of the other hydrolyzed species, and assuming its molar extinction coefficient might be the same order of magnitude it should have been unimportant in his work. Therefore there is no stability constant for $Fe_3(OH)_4^{5+}$ which was measured on a basis consistent with Milburn's work.

3. <u>The Dimer and Other Species</u>

The lack of coincidence of the curves for different total iron concentration cannot be attributed to a contribution from the dimer $Fe_2(OH)_2^{4+}$. For the same value of $[Fe_3(OH)_4^{5+}]/[FeOH^{2+}]$ the lower curve of Fig. 6 has a higher concentration of the dimer as shown in Fig. 5. Since the concentration of the dimer is comparable to the $FeOH^{2+}$ concentration, the dimer must either exhibit a much slower exchange rate or have a much less efficient relaxation mechanism, as might occur through a much reduced

paramagnetism due to spin pairing. Since the exchange is rapid on both $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$, a slow water exchange rate on $Fe_2(OH)_2^{4+}$ seems unlikely. Also, Mulay and Selwood[38] have concluded that the dimer is diamagnetic, although the interpretation of their data leaves some uncertainty in this result.

The discrepancy between the curves could possibly be explained by some higher molecular weight species than the dimer or trimer, but the uncertainties in the corrections to the data which have been made so far make such an interpretation ambiguous. The $Fe(OH)_2^{2+}$ does not appear to contribute to the broadening, as would be expected from its low concentration.

A majority of the NMR solutions were measured only over a limited temperature range. In order to check the fit to the experimental data above 44°C with the previously obtained values of a and c, the predicted linewidths for the 0.214 M $Fe(ClO_4)_3$ solution with 0.037 M $HClO_4$ were calculated from the concentrations of Fe^{+3}, $FeOH^{2+}$, and $Fe_3(OH)_4^{5+}$. At temperatures above ca 50°C the predicted linewidth from the various ferric species is smaller than the observed linewidth, $1/T_{2p}$. At 52°C the predicted $1/T_{2p}$ is ca 90% of the observed $1/T_{2p}$, and at 70°C the predicted value is ca 75% of the observed $1/T_{2p}$. This could be due to uncertainties in the enthalpies of the equilibria, to the formation of a new species, or to a change in the relaxation mechanism.

4. Frequency Dependence

In an attempt to study the frequency dependence of the relaxation mechanisms for $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$, a new solution was prepared which was 0.189 M $Fe(ClO_4)_3$ and 0.0327 M $HClO_4$. This solution gave a value of

$1/T_{2p}$ which was ca 20% greater than would have been predicted from the calculated concentrations and the values of a and c at room temperature. The reason for this discrepancy is not known.

The linewidth of this solution was measured at 8.134 MHz and 2.00 MHz at 21, 32, and 40°C. The linewidth decreased at the lower frequency (Solution 14). This decrease means that the exchange on one or both species is in the relaxation controlled region since the exchange controlled region is frequency independent.

The relaxation mechanisms which give rise to this type of frequency dependence are $\Delta\omega$ mechanism and scalar coupling mechanism interrupted by the T_{1e} when the latter is frequency dependent.

The linewidth contribution from $Fe_3(OH)_4^{5+}$ at 8.134 MHz is slightly smaller than the observed decrease in linewidth between the two frequencies in the experimental temperature range. Therefore the exchange on this species could be relaxed by a totally frequency dependent mechanism and the whole effect attributed to $Fe_3(OH)_4^{5+}$. On the other hand, the $FeOH^{2+}$ linewidth contribution at 8.134 MHz is greater than the observed decrease. If the frequency dependence is attributed to $FeOH^{2+}$, then the relaxation must be made up of a frequency dependent part and a frequency independent part such as a mixture of $\Delta\omega$ and frequency independent scalar coupling. Also a scalar coupling composed of frequency dependent and frequency independent parts could produce the observed effects. The observed frequency dependence could also arise from a contribution from both species.

From the negligible temperature dependence of the linewidth per mole per liter for both species at 8 MHz, scalar coupling would seem to be the dominant mechanism. However, the changeover from one mechanism to the other could also appear to produce a temperature independent

relaxation. A full range of change in iron and hydrogen ion concentration at different NMR frequencies could perhaps differentiate between the contributions from the two species. Yet the lack of information about T_{1e} and T_{2e} of $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$ would be a severe handicap to any interpretation.

If $FeOH^{2+}$ is assumed to have the same scalar coupling constant as Mn^{+2}, then a chemical shift of the bulk waters can be calculated for Solution 14

$$\frac{\Delta\omega_{meas}}{2\pi} = 62 \text{ cps} \qquad \text{at } 8.13 \text{ MHz and } 25^\circ\text{C.}$$

This is large enough to be measured, except for the masking effect of the large shift due to the second coordination sphere of the Fe^{+3} ion (see Part A). A lower limit to the observed shift for this solution can be calculated by assuming that the shift is due solely to free ferric ion. Using the observed shift at 8.134 MHz of 540 cps in the 0.375 M $Fe(ClO_4)_3$ solution at 25°C, a shift of 245 cps is calculated for the 0.189 M $Fe(ClO_4)_3$ solution from the unhydrolyzed ferric ion. The measured shift is 210 cps at 25°C. The reason for this discrepancy is not known.

As can be seen from the interpretation of the NMR data, a more exacting study of the equilibrium constants in the ferric perchlorate system is necessary for a complete interpretation.

5. Summary

From the results of this work it is concluded that $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$ are the principal hydroxy species whose water exchange contributes to the broadening of the NMR signal. The water exchange from the dimer, $Fe_2(OH)_2^{4+}$, does not appear to contribute to the linewidth,

probably because of a reduced magnetism, but a small contribution to the linewidth cannot be ruled out. The concentration of $Fe(OH)_2^+$ is too low to have any influence on the NMR linewidth.

Both $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$ exhibit an unchanged linewidth per mole per liter as the temperature is changed from ca 18°C to 44°C. This suggests that they both are in the relaxation controlled region of the chemical exchange. Of course, a change in the chosen value of the enthalpy of formation for either species would change the derived linewidth temperature dependence by approximately the same number of kcal so the temperature effect is not definitive proof of relaxation control.

The other argument for relaxation control is related to the large linewidth per mole per liter of both species. Adopting the same scalar coupling constant for $FeOH^{2+}$ as has been observed for Mn^{+2}, it is possible to calculate the correlation time for scalar coupling relaxation. Scalar coupling or the $\Delta\omega$ mechanism are the only relaxation mechanisms which are strong enough to produce the observed linewidths. The correlation time is calculated to be ca 5×10^{-11} sec which is very close to the observed T_{2e} for ferric ion. Alternatively if the relaxation is assumed to arise entirely from the $\Delta\omega$ mechanism, the lifetime of the water molecule in the first coordination sphere of $FeOH^{2+}$ is calculated to be ca 5×10^{-7} sec. The upper limit for the lifetime of one of six equivalent waters calculated directly from the linewidth is ca 1.8×10^{-6} sec. These calculations are all consistent with relaxation control.

Since the linewidth per mole per liter for $Fe_3(OH)_4^{5+}$ is approximately the same per iron atom as for $FeOH^{2+}$, $Fe_3(OH)_4^{5+}$ is probably also in the relaxation controlled region. This might be expected since the average

charge per iron atom is just slightly less for $Fe_3(OH)_4^{5+}$ than for $FeOH^{2+}$ and thus the exchange rate would be expected to be higher for $Fe_3(OH)_4^{5+}$. An upper limit for the lifetime of a water molecule on $Fe_3(OH)_4^{5+}$ is 5.8×10^{-7} sec assuming ten labile water molecules.

Since both $FeOH^{2+}$ and $Fe_3(OH)_4^{5+}$ are believed to be in the relaxation controlled region, one would expect to be able to measure a chemical shift of the bulk waters arising from the rapid exchange. In fact the observed shift in Solution 14 is smaller than the calculated shift arising from the free ferric ion alone. The reason for this serious discrepancy is not known. It would be explained if $FeOH^{2+}$ produced a diamagnetic shift, but it is not easy to see how such an effect would arise.

Eigen[39] reports the rate of water replacement by sulfate on $FeOH^{2+}$ in the form of a bimolecular rate constant for the overall exchange. The value is $\sim 3\times10^5$ M^{-1} sec^{-1} as compared to a value for unhydrolyzed ferric ion of $\sim 3\times10^3$ M^{-1} sec^{-1}, i.e., a 10^2-fold increase for the hydrolyzed species. The water exchange rate for $FeOH^{2+}$ appears to be ca 3×10^3-fold greater than for Fe^{3+}.

C. The T_2 of Oxygen-17 in Water

Meiboom[40] has suggested that the T_2 of oxygen-17 in water is governed by quadrupole relaxation interrupted by tumbling. There is some newer evidence to substantiate this claim. Marianelli[20] has shown that T_1 equals T_2 and that the linewidth is directly dependent on the ratio of the viscosity to the absolute temperature. However, these effects are characteristic of both dipolar relaxation and quadrupole relaxation in the narrow limit ($\omega_I\tau_c \ll 1$).

In the course of the experimental work for this thesis, it was

noticed that samples of enriched water gave differing linewidths. In particular, a sample of 1.2% O^{17} and ca 50% deuterium enrichment gave a linewidth ($1/\pi T_2$) of 54 cps at 25°C. Another sample containing 10% O^{17} and normal abundance deuterium gave a linewidth of 49 cps. The viscosity of the highly enriched deuterium is ca 10% greater than that of normal water. Clearly the linewidth depends again on the viscosity. However, if oxygen-17 were relaxed by the dipolar mechanism, the deuterium enriched sample would be expected to give a smaller linewidth since the magnetogyric ratio is smaller for deuterium than for hydrogen (see Equation 10).

ACKNOWLEDGMENTS

I would like to thank Professor Robert E. Connick for his patient counsel during the course of this work. I wish to also thank Jim Chang for a great deal of assistance with the ESR work and Professor Rollie J. Myers for discussions about ESR. In particular, many thanks go to Dr. Alex von Zelewsky, the chemist's chemist, for his kind help with a struggling graduate student. I am grateful for the secretarial assistance of Miss Sharon Sparks and the electronic assistance of Mr. Phil Eggers and Mr. Frank Papen.

I am indebted to my parents for their constant encouragement in the pursuit of my education.

This work was done under the auspices of the United States Atomic Energy Commission through the Lawrence Radiation Laboratory.

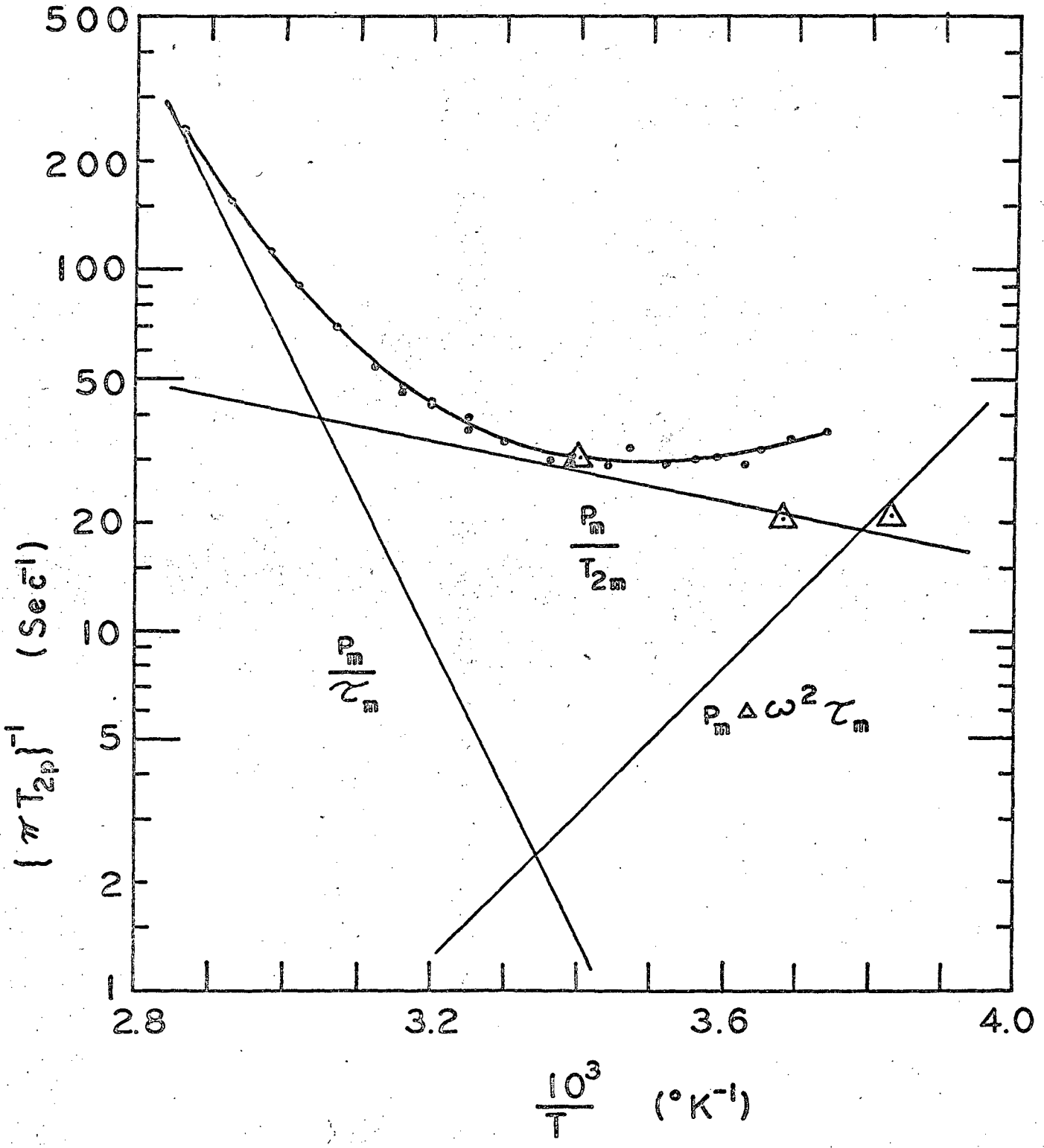

Fig. 1. The temperature dependence of log T_{2p}^{-1} as a function of frequency for Solution 13. ⊙ - 8.134 MHz data; Δ - 2.00 MHz data.

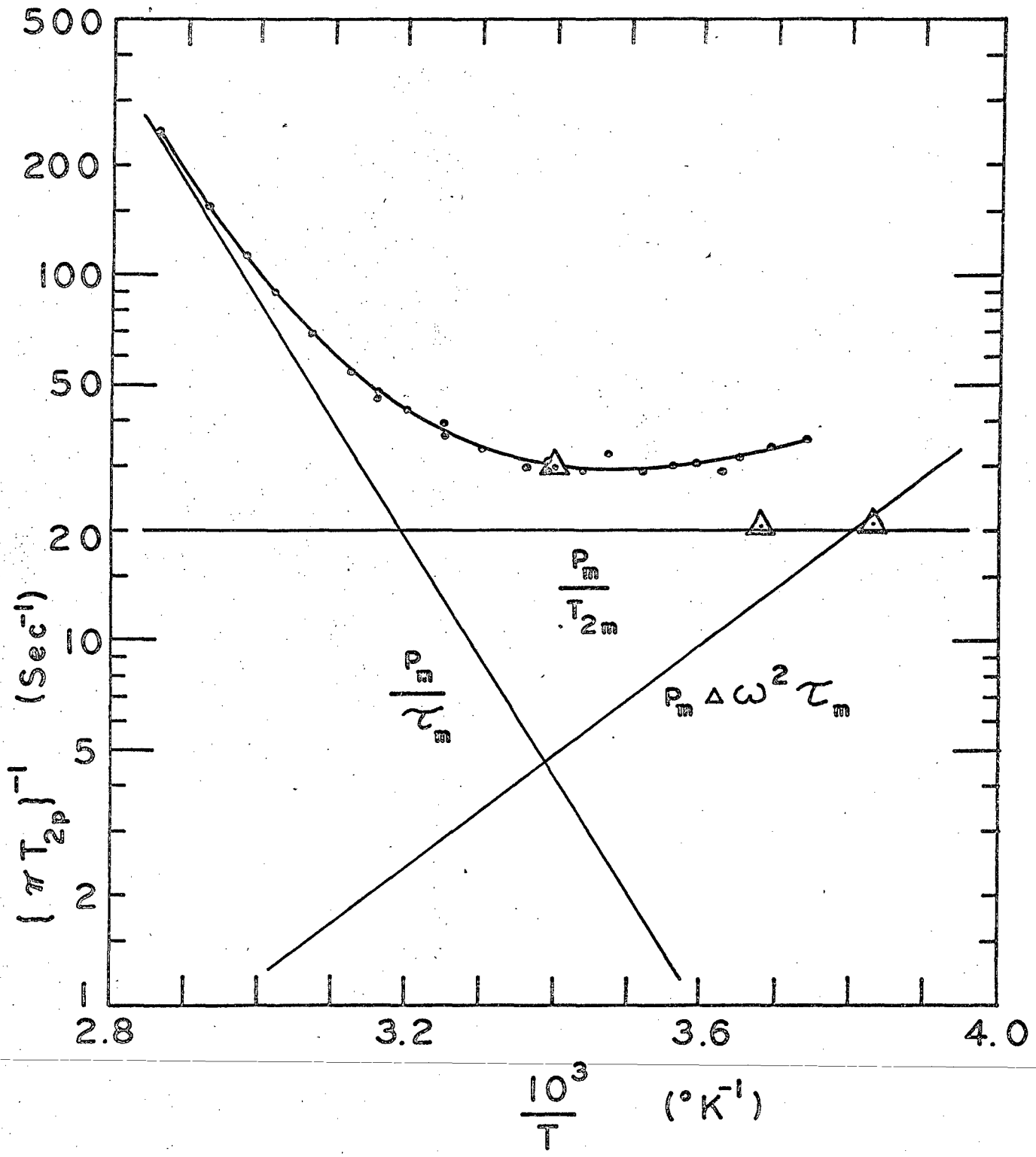

Fig. 2. The temperature dependence of log T_{2p}^{-1} as a function of frequency for Solution 13. ● - 8.134 MHz data; Δ - 2.00 MHz data.

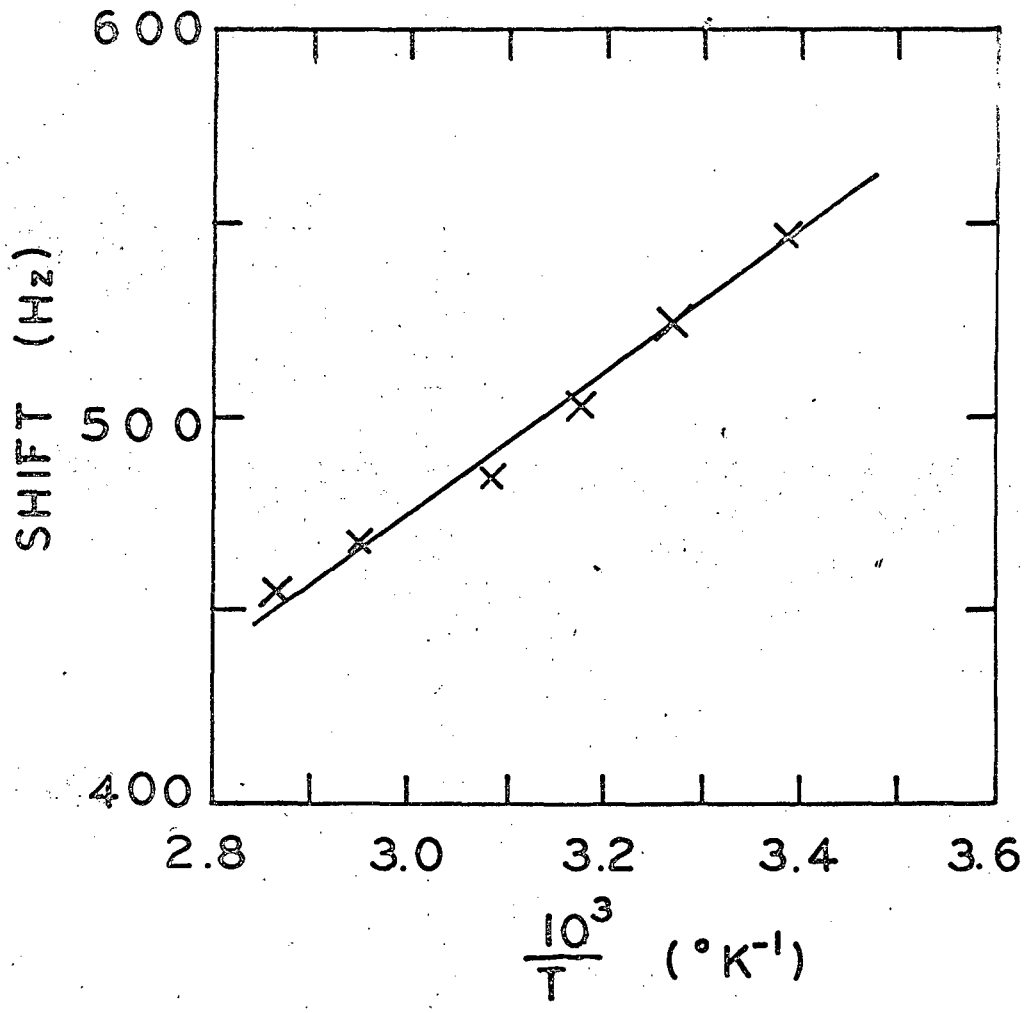

Fig. 3. Paramagnetic shift of O^{17} resonance of bulk water at 8.134 MHz for Solution 13.

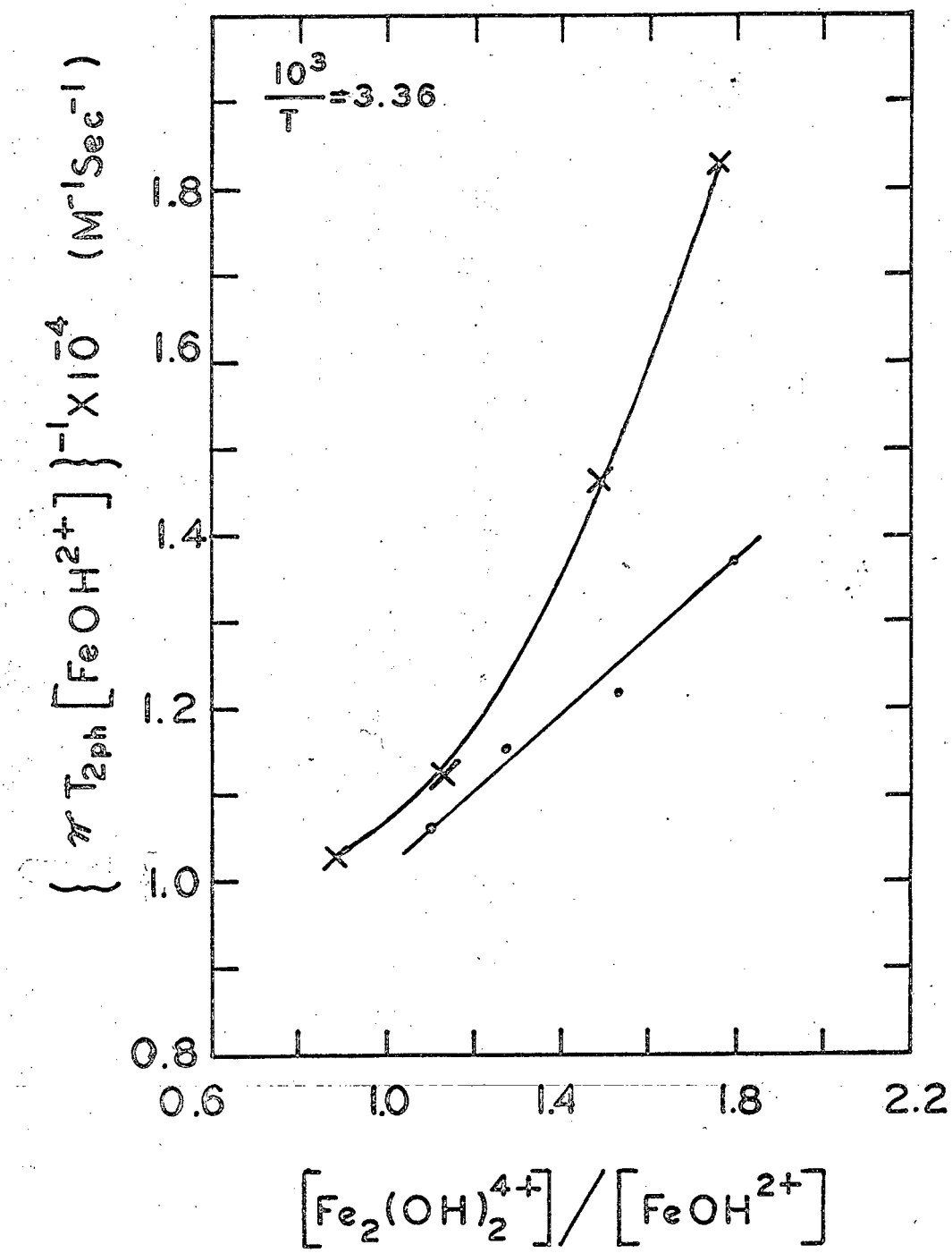

Fig. 4. Dependence of $\{T_{2ph}[FeOH^{2+}]\}^{-1}$ on $[Fe_2(OH)_2^{4+}]/[FeOH^{2+}]$ at 25°C.
⊙ - Solutions 1-4 containing ca 0.2 M Fe(III);
X - Solutions 8-11 containing ca 0.1 M Fe(III).

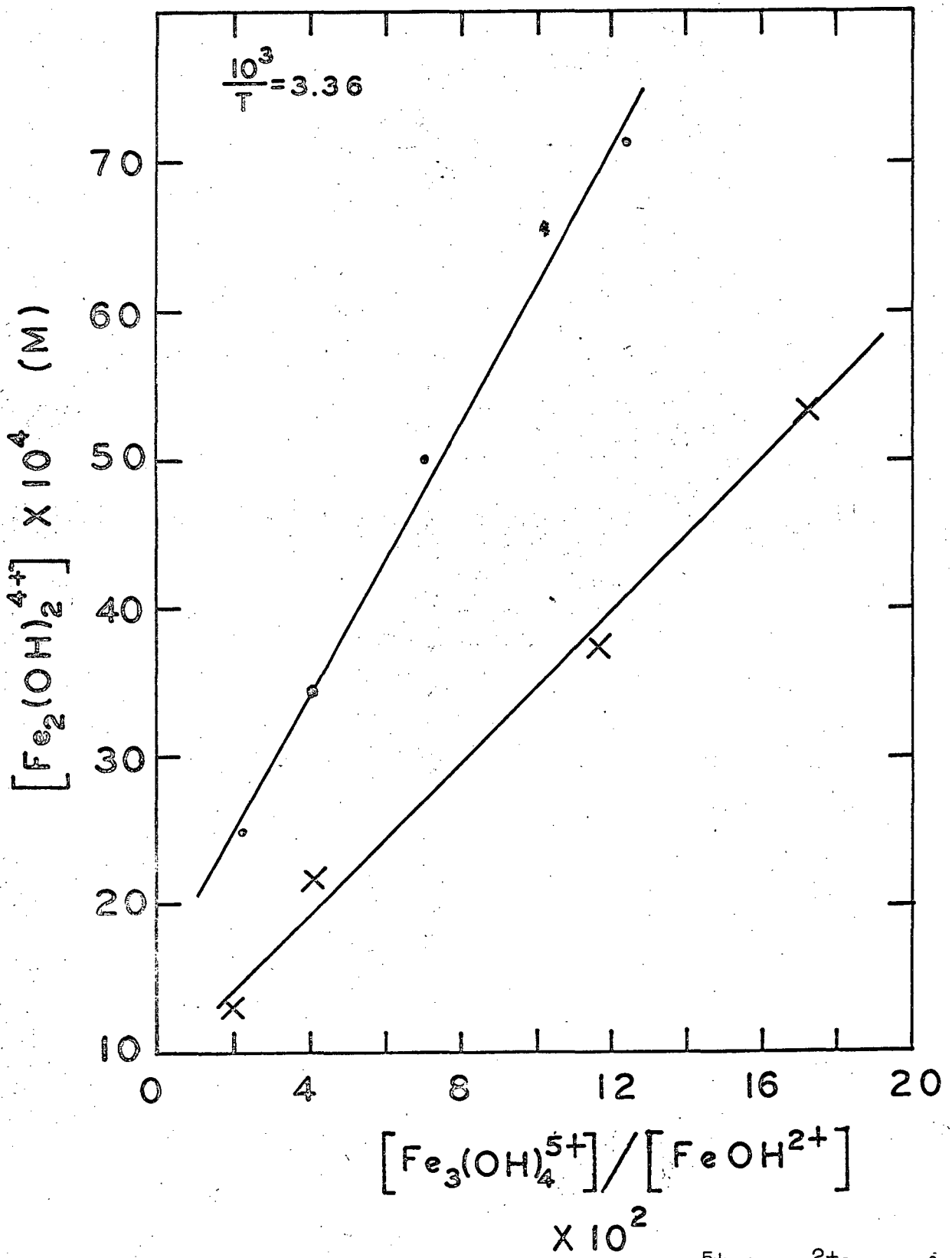

Fig. 5. Dimer concentration as a function of $[Fe_3(OH)_4^{5+}]/[FeOH^{2+}]$ at 25°C. ⊙ - Solutions 1-4 containing ca 0.2 M Fe(III); X - Solutions 8-11 containing ca 0.1 M Fe(III).

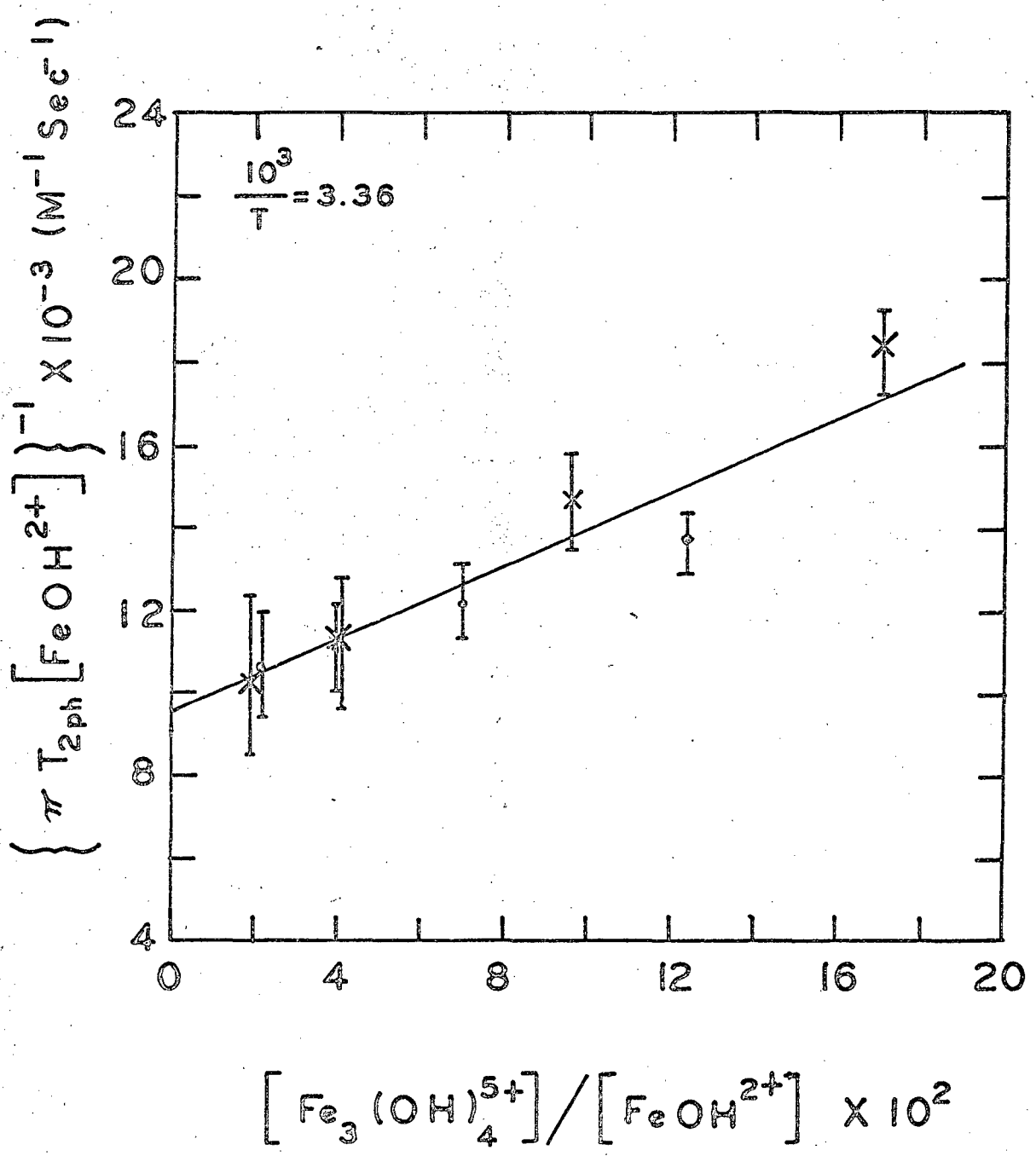

Fig. 6. Dependence of $\left\{T_{2ph}[FeOH^{2+}]\right\}^{-1}$ on $[Fe_3(OH)_4{}^{5+}]/[FeOH^{2+}]$ at 25°C.

⊙ - Solutions 1-4 containing ca 0.2 M Fe(III);

X - Solutions 8-11 containing ca 0.1 M Fe(III).

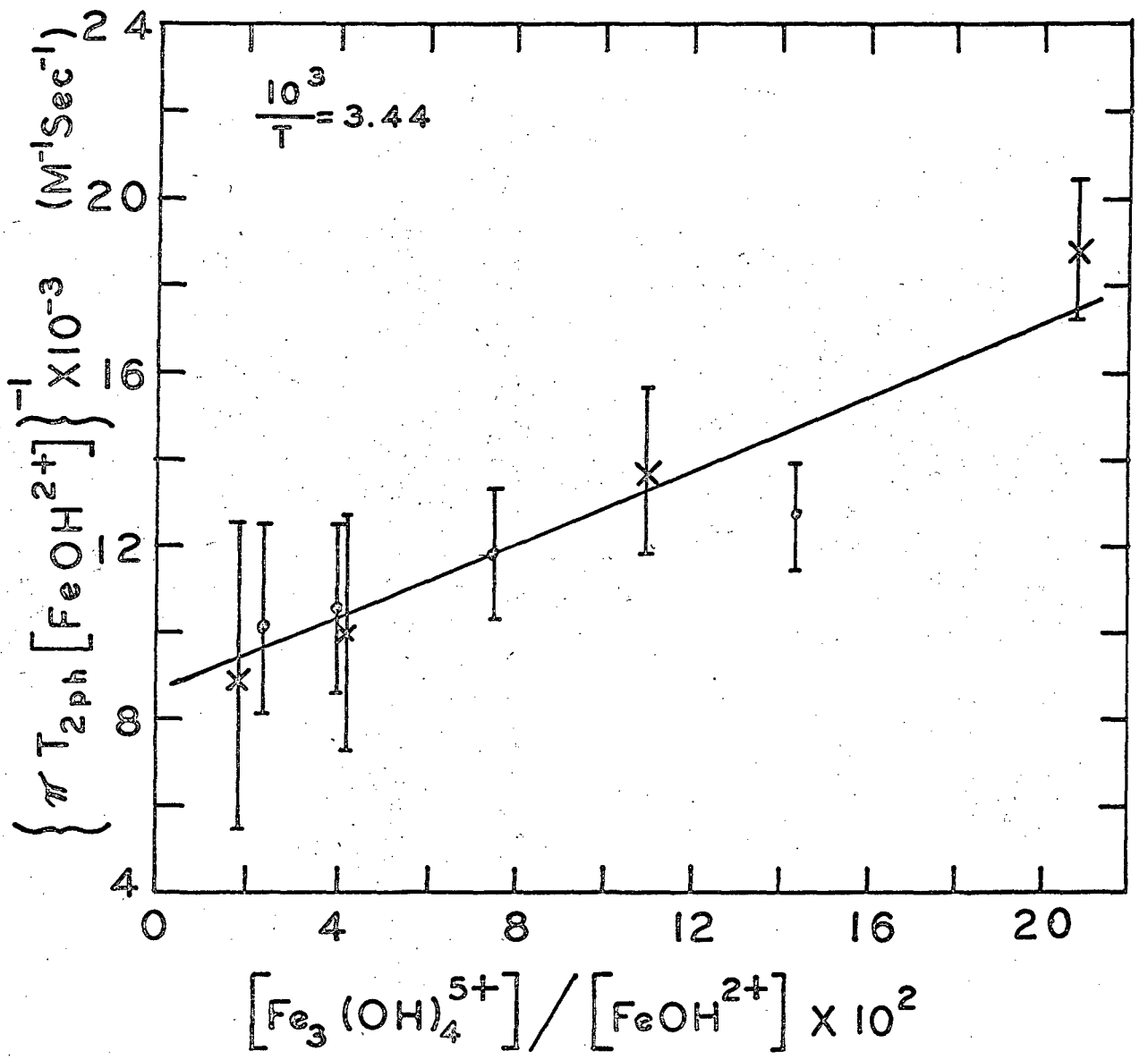

Fig. 7. Dependence of $\{T_{2ph}[FeOH^{2+}]\}^{-1}$ on $[Fe_3(OH)_4^{5+}]/[FeOH^{2+}]$ at 17°C.

o - Solutions 1-4 containing ca 0.2 M Fe(III);

X - Solutions 8-11 containing ca 0.1 M Fe(III).

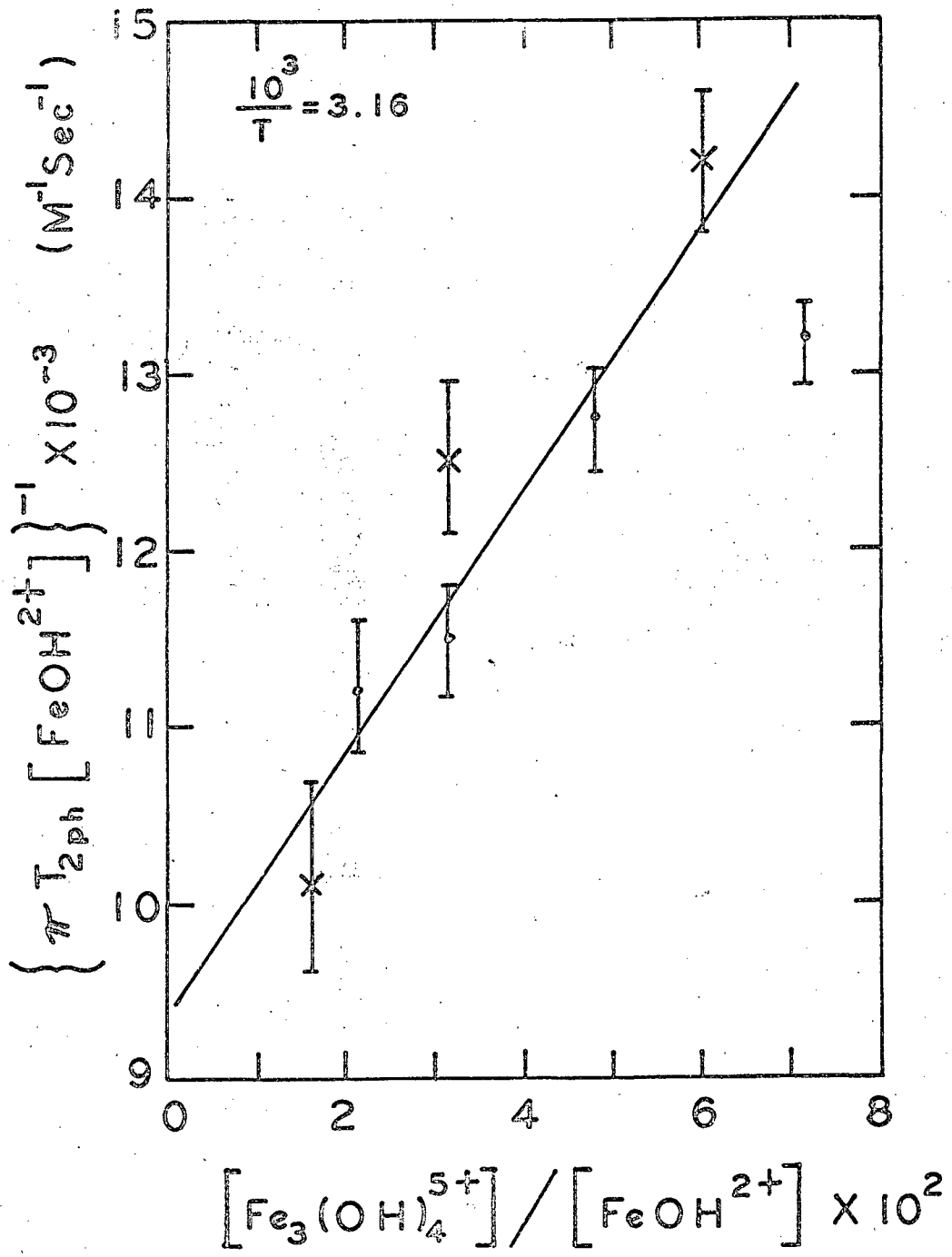

Fig. 8. Dependence of $\{T_{2ph}[FeOH^{2+}]\}^{-1}$ on $[Fe_3(OH)_4^{5+}]/[FeOH^{2+}]$ at 43°C.

• - Solutions 1-4 containing ca 0.2 M Fe(III);

X - Solutions 8-11 containing ca 0.1 M Fe(III).

Table I. H_2O^{17} NMR Linewidths

Solution 1, 8.134 MHz: 0.214 M $Fe(ClO_4)_3$
0.0370 M $HClO_4$
0.114 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.1	3.377	116.5	57.0	187
303.1	3.299	138	48.4	282
310.5	3.221	176.5	41.5	425
318.8	3.137	246	34.5	665
326.9	3.059	363	29.9	1045
333.9	2.995	520	26.5	1550
344.0	2.907	818	21.9	2500
300.0	3.333	111	68.0	135
285.0	3.509	112	79.5	102
280.3	3.568	118	91.0	85
276.4	3.618	127.5	101.5	83
273.1	3.662	138	115	72.5
298.1	3.355	124	54.5	218

Table I. (Cont.)

Solution 2, 8.134 MHz: 0.214 M $Fe(ClO_4)_3$
0.0578 M $HClO_4$
0.114 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
297.1	3.366	108	53.0	173
289.8	3.451	104	67.2	116
302.8	3.303	120	47.8	226
309.3	3.233	147	42.1	330
317.6	3.149	202	35.3	525

Solution 3, 8.134 MHz: 0.213 M $Fe(ClO_4)_3$
0.0781 M $HClO_4$
0.114 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.0	3.378	97	56.5	127
289.2	3.458	99	68.4	96
302.7	3.304	106.5	49.0	181
308.3	3.244	123	43.3	250
316.4	3.161	164	36.5	400

Table I. (Cont.)

Solution 4, 8.134 MHz: 0.2125 M $Fe(ClO_4)_3$
0.0986 M $HClO_4$
0.1135 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.3	3.375	92	56.4	111.5
288.9	3.461	96	68.3	86.5
302.6	3.305	98	49.0	154
309.3	3.233	111.5	42.2	218
317.6	3.149	153	35.3	370

Solution 5, 8.134 MHz: 0.2075 M $Fe(ClO_4)_3$
0.397 M $HClO_4$
0.111 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.0	3.378	76	56.4	61
288.4	3.467	87.5	67.2	63
302.3	3.308	70.5	49.0	67.5
308.6	3.240	67.5	42.2	80
317.1	3.154	73	35.3	120
325.3	3.074	89	30.8	182

Table I. (Cont.)

Solution 6, 8.134 MHz: 0.202 M $Fe(ClO_4)_3$
0.680 M $HClO_4$
0.108 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.4	3.374	72.5	56.4	50.5
288.8	3.463	84	68.4	49
303.0	3.300	65	47.8	54
309.6	3.230	62	41.0	66
317.3	3.152	63.5	35.3	88.5
324.9	3.078	71	30.8	126

Table I. (Cont.)

Solution 7, 8.134 MHz: 0.1975 M $Fe(ClO_4)_3$
0.950 M $HClO_4$
0.1055 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.1	3.377	74	56.4	55
288.8	3.463	84.5	68.4	50
303.2	3.298	67	47.9	60
309.9	3.227	64	41.0	72
317.1	3.154	64	35.3	91
324.9	3.078	68	30.8	116
331.8	3.014	79.5	27.3	165
292.9	3.414	78	60.4	55
283.6	3.526	95	82.0	40.8
278.0	3.597	111	98.0	40.8
274.4	3.644	122	108.5	42.4
337.2	2.966	95	24.0	223

Table I. (Cont.)

Solution 8, 8.134 MHz: 0.1105 M $Fe(ClO_4)_3$
0.0192 M $HClO_4$
0.709 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.1	3.377	110.5	54.5	176
289.1	3.459	102	63.2	122
282.4	3.541	104.5	72.5	100.5
277.9	3.598	110	81.5	89.5

Table I. (Cont.)

Solution 9, 8.134 MHz: 0.1105 M $Fe(ClO_4)_3$
0.0325 M $HClO_4$
0.708 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.5	3.373	93	54.5	121
289.1	3.459	90	63.2	84
284.3	3.517	94	76	56.5
280.3	3.568	99	87	38
275.7	3.627	110	103.5	20.5
302.6	3.305	103	47.3	175
309.3	3.233	124	40.2	263
319.0	3.135	175	33.5	444
329.1	3.039	267	27.5	753

Table I. (Cont.)

Solution 10, 8.134 MHz: 0.110 M $Fe(ClO_4)_3$
0.0538 M $HClO_4$
0.706 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.4	3.374	79.5	54.5	78.5
290.0	3.448	81	65	50.2
302.8	3.303	86	46.2	125
308.8	3.238	100	40.7	186
317.6	3.149	133.	34.1	310

Solution 11, 8.134 MHz: 0.110 M $Fe(ClO_4)_3$
0.075 M $HClO_4$
0.705 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.6	3.372	74	52.8	68
289.2	3.458	78	63.2	46.5
302.8	3.303	77	46.2	96.5
309.4	3.232	85	40.7	139
317.7	3.148	108	33.5	214

Table I. (Cont.)

Solution 12, 8.134 MHz: 0.108 M $Fe(ClO_4)_3$
0.283 M $HClO_4$
0.692 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
296.6	3.372	62.5	53	30
289.2	3.458	72	63.2	27
303.6	3.294	57	46.2	34
309.2	3.234	55	40.7	45
317.7	3.148	57	33.5	74
295.3	3.386	65	55	31.5
288.4	3.467	75	66	28
283.6	3.526	85	72.5	38
279.6	3.577	94	80.4	42.6
277.2	3.608	100	85.5	45.5
274.7	3.640	107	90	53.4

Table I. (Cont.)

Solution 13: 0.375 M $Fe(ClO_4)_3$
1.705 M $HClO_4$
0.730 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
8.134 MHz				
295.4	3.385	98	67	96
291.2	3.434	105	76	84
287.8	3.475	114	82	101
284.0	3.521	121.5	92.5	84
281.1	3.557	132	102	94
278.6	3.589	139.5	109	96
275.7	3.627	150	121	91
308.2	3.245	89.4	50.1	123
313.0	3.195	88.7	45.1	137
316.6	3.159	89.3	41.7	150
320.4	3.121	95.1	39	170
325.9	3.068	104.3	35	218
330.9	3.022	121	30.3	285
335.6	2.980	142	29.3	353
341.1	2.932	182	26.4	489
349.4	2.862	270	23.4	775
274.4	3.644	158	126	101
271.3	3.686	173	139	107

Table I. (Cont.)

Solution 13 (Cont.)

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
267.2	3.743	194	158	113
303.8	3.292	89	55.5	105
308.2	3.245	86	50	113
313.0	3.195	87	45	132
317.4	3.151	87	41.5	143
2.00 MHz				
293.9	3.403	99	68.5	96
261.0	3.830	209*	188	66
272.0	3.676	154.3	134	64

* Sample starts to freeze here so this number is a little high.

Table I. (Cont.)

Solution 14, 0.189 M $Fe(ClO_4)_3$
0.0327 M $HClO_4$
0.101 M $NaClO_4$

T°K	$\frac{10^3}{T}$ °K^{-1}	$\frac{1}{\pi T_2}$ sec^{-1}	$\frac{\eta}{\eta_{H_2O}} \frac{1}{\pi T_{2H_2O}}$ sec^{-1}	$\frac{1}{T_{2p}}$ sec^{-1}
8.134 MHz				
294.6	3.394	125	58	210
300.1	3.333	144	51	292
305.1	3.278	170	46	390
311.9	3.206	209.	39.4	532
2.00 MHz				
293.5	3.407	104.4	60.4	138
304.5	3.284	113.4	46	212
313.4	3.191	141	38	334

Table 2. ESR Linewidths at 9.2 GHz

T°K	ΔH gauss
Solution 13	
299	1140
373	590
Solution 7	
299	900
373	550

Table 3. Chemical Shift at 8.134 MHz
Solution 13

T°K	δ Hz
295.6	546
306	529
315	507
322	486
337	468
348	455

Table 4. Viscosity of Solutions at 25°C
(normal abundance water)

Solution Number	Specific Gravity	Time in Viscometer sec	η/η_{H_2O}
1	1.063	170	1.15
2	1.062	168.2	1.14
3	1.063	168.4	1.14
4	1.064	168	1.14
5	1.078	164.8	1.14
6	1.092	163.4	1.14
7	1.105	162	1.14
8	1.078	158.4	1.09
9	1.079	159.2	1.10
10	1.081	158.8	1.10
11	1.081	158.4	1.09
12	1.085	159.2	1.10
13	1.166	174.6	1.32
H_2O	1	156.5	1.00

Table 5. Slope and Intercepts for Equation 17

$$\frac{1}{T_{2ph}} = a[FeOH^{2+}] + c[Fe_3(OH)_4^{5+}]$$

$\frac{10^3}{1}$	a Hz M^{-1}	c Hz M^{-1}
3.16	9.85×10^3	6.1×10^4
3.24	9.65×10^3	5.9×10^4
3.30	10.1×10^3	4.2×11^4
3.36	9.55×10^3	4.5×10^4
3.44	8.60×10^3	4.45×10^4

Table 6. Concentrations of Species in Solutions

IDENT*	$[FeOH^{2+}]$	$[Fe_2(OH)_2^{4+}]$	$[Fe_3(OH)_4^{5+}]$	$[Fe^{+3}]$	$[H^+]$
191	.046406	.008356	.001058	.147709	.104349
100	.030187	.009158	.001120	.162136	.089984
108	.019981	.009342	.001067	.172134	.079933
124	.008151	.008425	.000750	.186750	.065000
116	.012920	.009081	.000928	.180134	.071794
130	.005723	.007861	.000620	.190694	.060926
136	.003977	.007132	.000490	.194290	.057200
144	.002431	.006204	.000349	.198115	.053233
151	.001559	.005345	.000248	.201006	.050242
157	.001057	.004639	.000180	.203124	.048057
166	.000586	.003697	.000108	.205695	.045413
291	.042767	.007334	.000767	.154263	.118305
200	.027296	.007749	.000757	.168935	.103623
208	.017763	.007636	.000674	.178944	.093530
216	.011259	.007136	.000543	.186840	.085503
224	.006942	.006337	.000402	.193179	.079024
230	.004787	.005683	.000309	.196920	.075189
236	.003277	.005014	.000229	.200007	.072022
244	.001938	.004089	.000145	.203449	.068496
251	.001213	.003356	.000094	.205794	.066099
257	.000806	.002785	.000063	.207437	.064426
266	.000434	.002088	.000033	.209291	.062543
391	.039037	.006233	.000540	.159879	.131761
300	.024569	.006399	.000501	.174130	.117471
308	.015704	.006091	.000417	.183863	.107654
316	.009756	.005454	.000310	.191405	.100005
324	.005900	.004664	.000213	.197133	.094180
330	.003998	.004043	.000153	.200456	.090798
336	.002696	.003459	.000107	.203065	.088142
344	.001561	.002702	.000063	.205847	.085315
351	.000960	.002137	.000038	.207653	.083485
357	.000630	.001737	.000024	.208823	.082301
366	.000331	.001240	.000012	.210154	.080958
416	.008362	.004154	.000178	.195297	.115981
424	.005052	.003535	.000119	.200021	.111198
430	.003379	.002986	.000082	.202905	.108277
436	.002253	.002503	.000055	.205075	.106080
444	.001284	.001893	.000030	.207339	.103791
451	.000784	.001476	.000018	.208712	.102406
508	.004409	.000060	.000000	.202970	.401530
516	.002466	.000436	.000002	.204156	.400346
524	.001374	.000316	.000001	.205491	.399010
530	.000888	.000249	.000001	.206111	.398389
536	.000576	.000197	.000000	.206528	.397972
544	.000319	.000141	.000000	.206898	.397602

Table 6. (Cont.)

IDENT*	$[FeOH^{2+}]$	$[Fe_2(OH)_2^{4+}]$	$[Fe_3(OH)_4^{5+}]$	$[Fe^{+3}]$	$[H^+]$
551	.000191	.000106	.000000	.207097	.397403
608	.002476	.000225	.000000	.199073	.682927
616	.001383	.000163	.000000	.200290	.681710
624	.000767	.000117	.000000	.200999	.681001
630	.000495	.000092	.000000	.201321	.680679
636	.000320	.000072	.000000	.201535	.680465
644	.000177	.000052	.000000	.201719	.680281
651	.000106	.000039	.000000	.201817	.680183
791	.005771	.000242	.000001	.191243	.956257
700	.003000	.000167	.000000	.194165	.953336
708	.001676	.000121	.000000	.195580	.951920
716	.000935	.000092	.000000	.196381	.951119
704	.000520	.000063	.000000	.196854	.950646
730	.000332	.000049	.000000	.197070	.950430
736	.000216	.000039	.000000	.197207	.950293
744	.000119	.000028	.000000	.197326	.950174
751	.000071	.000021	.000000	.197388	.950112
757	.000046	.000016	.000000	.197422	.950078
766	.000024	.000011	.000000	.197455	.950045
836	.003012	.005318	.000517	.095602	.034915
844	.001864	.004741	.000387	.098296	.032091
851	.001214	.004217	.000291	.100277	.030014
857	.000839	.003791	.000225	.101706	.028519
866	.000473	.003123	.000144	.103648	.026496
900	.019418	.004939	.000621	.079340	.064281
908	.012917	.005073	.000589	.085671	.057918
916	.008344	.004909	.000503	.090830	.052672
924	.005238	.004527	.000397	.095017	.048380
930	.003659	.004165	.000318	.097556	.045763
936	.002525	.003736	.000244	.099770	.043474
944	.001526	.003181	.000166	.102114	.041052
951	.000969	.002686	.000113	.103819	.039294
957	.000649	.002274	.000078	.105068	.038010
966	.000353	.001739	.000044	.106538	.036506
1016	.006817	.003323	.000216	.095988	.069129
1024	.004143	.002867	.000150	.099772	.064278
1030	.002821	.002507	.000110	.101935	.062075
1036	.001906	.002158	.000077	.103645	.060332
1044	.001107	.001692	.000045	.105474	.058471
1051	.000682	.001349	.000028	.106636	.057291
1057	.000447	.001090	.000017	.107422	.056496
1116	.005631	.002267	.000097	.099543	.085554
1124	.003331	.001853	.000061	.102780	.082282
1130	.002228	.001564	.000042	.104520	.080522
1136	.001483	.001306	.000028	.105822	.079206
1144	.000844	.000983	.000015	.107144	.077871
1151	.000513	.000764	.000009	.107932	.077077
1216	.001404	.000162	.000001	.106271	.284730

Table 6. (Cont.)

IDENT*	$[FeOH^{2+}]$	$[Fe_2(OH)_2^{4+}]$	$[Fe_3(OH)_4^{5+}]$	$[Fe^{+3}]$	$[H^+]$
1224	.000986	.000186	.000001	.106640	.284361
1230	.000636	.000146	.000000	.107070	.283930
1236	.000413	.000116	.000000	.107355	.283645
1244	.000229	.000083	.000000	.107605	.283395
1251	.000137	.000062	.000000	.107739	.283261
1257	.000088	.000048	.000000	.107815	.283185
1266	.000045	.000033	.000000	.107889	.283111
1391	.005596	.000344	.000001	.368714	1.711287
1300	.002795	.000237	.000000	.371731	1.708269
1308	.001555	.000171	.000000	.373103	1.706897
1316	.000872	.000125	.000000	.373879	1.706122
1324	.000483	.000089	.000000	.374339	1.705661
1330	.000309	.000069	.000000	.374553	1.705447
1336	.000199	.000054	.000000	.374694	1.705306
1344	.000110	.000038	.000000	.374814	1.705186
1351	.000066	.000029	.000000	.374877	1.705123
1357	.000042	.000022	.000000	.374913	1.705087
1366	.000022	.000015	.000000	.374948	1.705052
1416	.012650	.008193	.000875	.157339	.065237
1424	.008045	.007702	.000721	.163388	.059034
1430	.005648	.007204	.000601	.167141	.055160
1436	.003956	.006652	.000486	.170282	.051904
1444	.002413	.005766	.000346	.174016	.048030

* IDENT is keyed for both solution number and temperature.

Example:

solution number 1-14

1024

temperature as $10^3/T$

$\frac{10^3}{T}$	$\frac{10^3}{T}$
91 - 2.91	36 - 3.36
00 - 3.00	44 - 3.44
08 - 3.08	51 - 3.51
16 - 3.16	57 - 3.57
24 - 3.24	66 - 3.66
30 - 3.30	

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