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LA THÈSE A ÉTÉ
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MÖSSBAUER SPECTROSCOPY
OF FERRIC CHLORIDE COMPLEXES AND
THEIR FROZEN SOLUTIONS

by

CLAUDE BORDELEAU, B.Sc., M.Sc.

A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

June 1980

Ce que l'on conçoit bien s'énonce clairement.

Et les mots pour le dire arrivent aisément.

Sans la langue, en un mot, l'auteur le plus divin

Est toujours, quoi qu'il fasse, un méchant écrivain.

NICOLAS BOILEAU

L'art poétique, 1674

The undersigned recommend to the Faculty
of Graduate Studies acceptance of the thesis
"Mössbauer Spectroscopy of Ferric Chloride Complexes
and Their Frozen Solutions"
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ABSTRACT

The initial objectives of determining the composition and structure of ferric chloride complexes present in frozen HCl solutions were met. However, the results obtained are only partly applicable to the room temperature conditions which apply in hydrometallurgical processes using acidic ferric chloride as a leachant. The extraction of Cu-bearing ores by these processes has become increasingly popular in recent years. The efficiency of extraction being dependent on both the ferric ion and acid concentrations, a detailed investigation of the ferric chloride complexes present in these chloride solutions would help to better understand the process and, possibly, to improve it.

The major part of this work consists of the study, by Mössbauer spectroscopy, of the ferric chloride system in a wide range of chloride ion and acid concentrations, as well as at various temperatures. Prior to the measurement of its Mössbauer spectrum, each solution was frozen using a fast or, sometimes a slow freezing rate. Also, many solid iron(II) and iron(III) compounds, among which are the series of ferric chloride hydrates, were studied to afford a basis of comparison with the work on frozen solutions.

The structure of each member in the hydrate series $\text{FeCl}_3 \cdot n\text{H}_2\text{O}$ ($n = 2, 2\frac{1}{2}, 3\frac{1}{2}, 6$) was determined to be a complex cation, $[\text{FeCl}_2(\text{OH}_2)_4]^+$ where the counter anion was either Cl^- or FeCl_4^- . The *cis* configuration of the hexacoordinate cation appeared to be related to an even number of lattice water molecules while the *trans* configuration seemed associated with an odd number of water molecules.

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The magnetically-split spectra of many frozen solutions were processed with a fast Fourier transform method which enabled the separation of individual peaks composing these spectra. Each peak was assigned to a specific ferric complex. The assignments were based on the assumption that, in the ferric hexaquo complex, the internal magnetic field at the iron nucleus decreases linearly with each subsequent water substitution by a chloride ligand.

The complexes $[\text{Fe}(\text{OH}_2)_6]^{3+}$, $[\text{FeCl}(\text{OH}_2)_5]^{2+}$, $[\text{FeCl}_2(\text{OH}_2)_4]^+$ and $[\text{FeCl}_4(\text{OH}_2)_2]^-$ were identified in dilute HCl frozen solutions of Fe(III) ions. The measured amount of each complex was in poor agreement with values calculated from stability constants, possibly due to crystallization during freezing of the solutions. Up to four separate complexes, including $\text{FeCl}_3(\text{OH}_2)_3$, were also found in more concentrated HCl solutions. However, when these frozen solutions solidified as glasses, as a result of either high ionic strength or fast freezing, the agreement between the measured and calculated species distribution appeared to be better.

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I. INTRODUCTION

A. Statement of the problem

The problem of determining the structures of ferric chloride complexes in aqueous solutions has intrigued numerous workers in the past. This problem is of particular relevance in hydrometallurgy. Hydrometallurgical processes have been developed for the recovery of copper from low grade ores as an alternative to existing smelting technologies, thereby eliminating some serious pollution problems (1). For example, a typical procedure for the recovery of copper involves the leaching of copper sulphide ores by ferric ions in acidic media (2). Since most base metal sulphides require a fairly strong oxidizing agent to effect their dissolution, ferric ions are frequently chosen for this purpose (1). The use of trivalent iron avoids the formation of H_2S , as the sulphide ions are further oxidized to elemental sulphur.

It is now generally believed that, in the leaching process, the dissolution of copper from chalcopyrite proceeds in two steps (1). The first step, which is independent of the ferric ion concentration, controls the formation of CuS (which is similar to the natural mineral covellite). During the second step, when both temperature and ferric ion concentration play a very important role, Cu^{2+} or Cu^+ ions are produced together with elemental sulphur. The chemical equation describing the overall

reaction in dilute acid can be illustrated as follows for the mineral chalcopyrite:

where $0 \leq x \leq 1$ (3). Little is known about either the identity of complexes present in such solutions or their structures. It therefore becomes important to investigate in greater detail the questions as to which chloro-complexes of iron(III) are formed in acidic solutions. Complexes of iron(III) which might be expected in aqueous hydrochloric acid solutions include the following:

<u>Ion</u>	<u>Symmetry</u>	<u>Ion</u>	<u>Symmetry</u>
$\text{Fe}(\text{OH}_2)_6^{3+}$	O_h	$\text{Fe}(\text{OH}_2)_4^{3+}$	T_d
$\text{FeCl}(\text{OH}_2)_5^{2+}$	C_{4v}	$\text{FeCl}(\text{OH}_2)_3^{2+}$	C_{3v}
$\text{FeCl}_2(\text{OH}_2)_4^+$	<i>cis</i> C_{2v} ; <i>trans</i> D_{4h}	$\text{FeCl}_2(\text{OH}_2)_2^+$	C_{2v}
$\text{FeCl}_3(\text{OH}_2)_3$	<i>fac</i> C_{3v} ; <i>mer</i> C_{2v}	$\text{FeCl}_3(\text{OH}_2)$	C_{3v}
$\text{FeCl}_4(\text{OH}_2)_2^-$	<i>cis</i> C_{2v} ; <i>trans</i> D_{4h}	FeCl_4^-	T_d
$\text{FeCl}_5(\text{OH}_2)^{2-}$	C_{4v}		
FeCl_6^{3-}	O_h		

Not all of these will in fact be present, and perhaps no more than two or three will be detectable at a time. Depending on the pH and the iron concentration, partly hydrolysed or polymerized complexes, such as $[\text{Fe}(\text{OH})\text{Cl}(\text{OH}_2)_4]^+$, $[(\text{H}_2\text{O})_5\text{Fe}-\text{O}-\text{Fe}(\text{OH}_2)_5]^{4+}$,

and particularly $[\text{Fe}_2(\text{OH})_2(\text{OH}_2)_8]^{4+}$, may also be present.

The study of complex equilibria present in Fe(III) aqueous solutions requires a technique which is both non-disruptive and non-destructive. Mössbauer spectroscopy is such a technique. Other techniques that could be used have proved to be less informative. For example, X-ray diffraction may reveal the presence of one or more complexes in the solutions being investigated. However, it cannot determine with certainty their structures nor can it determine their relative distribution. Furthermore, it is of very limited use when examining dilute solutions since in these the amount of metal ion-water pairs is small compared to that of the water-water pairs. On the other hand, Mössbauer spectroscopy can distinguish between geometrical isomers even in dilute solutions, e.g. *cis* and *trans* isomers of octahedral complexes, provided the solutions can be frozen for measurement of their spectra.

Mössbauer spectroscopy probes directly the electronic interactions at the iron nucleus so that changes in electronic densities are observed when a change in oxidation state occurs, and also when ligands are substituted or assume different arrangements. Thus one can often deduce the oxidation state of iron atoms in solid substrates from measurements of the positions of the resonance peaks. The relative contributions of $4s$ and $3d$ electron populations depend on the degree of σ bonding and $3d-\pi$ back-donation, respectively, and are more difficult to determine separately.

The degree of asymmetry of the coordination cage surrounding the iron determines the magnitude of ΔE , the quadrupole splitting. An ion such as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is cubically symmetric and $\Delta E = 0$, while $\text{FeCl}(\text{H}_2\text{O})_5^{2+}$ has C_{4v} symmetry and $\Delta E > 0$. The symmetries of *cis* and *trans*- $\text{FeCl}_2(\text{H}_2\text{O})_4^+$, C_{2v} and D_{4h} , respectively, are sufficiently different than their ΔE values differ by a factor of two or more.

The objectives of the present study were

- i) to measure the Mössbauer spectra of a large number of crystalline iron(III) chloro compounds for reference purposes.
- ii) to study the Mössbauer spectra of a range of frozen ferric chloride solutions at various temperatures.
- iii) to determine from the above, insofar as possible, the compositions and structures of iron(III)-chloride complexes which may be present in acidic aqueous solutions.

The first of these objectives involved the study of several compounds which had never been measured as well as repetition and confirmation of previous measurements of other compounds. The second involved the detailed analysis of a great many frozen solution spectra measured at a variety of temperatures. These temperatures ranged from 90 K to the melting point or the transition temperature of the solutions - usually between 180 and 210 K. The final objective involved the interpretation of the Mössbauer spectra based on assumptions pertaining to the validity of applying frozen solution data to liquid solution problems.

B. Literature survey

1. Crystalline state

The local symmetry of many complexes can be inferred using data obtained from Mössbauer spectroscopy measurements (4). This type of spectroscopy is especially powerful in assigning bonding properties (5a) and structure (5b) in series of analogous complexes. In addition, conclusive identification of geometrical isomers, although not easy, is often possible. For example, it has been demonstrated that, in octahedral iron(II) low-spin compounds, the quadrupole splitting of the *trans*-MA₂B₄ isomer was approximately double that of the *cis*-MA₂B₄ isomer (5c). This result is in agreement with theoretical calculations of the electric field gradient tensors assuming a point charge model and a zero asymmetry parameter.

A similar correlation has not been done for iron(III) high-spin complexes mainly because of a lack of an appropriate series. However, the relationship between the quadrupole splitting of *cis* and *trans* isomers would still be valid for iron(III) chloro-aqua complexes, $[\text{FeCl}_n(\text{OH}_2)_{6-n}]^{3-n}$, $n = 0 - 6$.

All members in this series, except those for which $n = 3$ and 4, have been isolated as crystalline compounds. Among these, the compound with $n = 1$ has not yet been studied by X-ray diffraction. However, analysis of its electronic spectrum has suggested that this complex shows octahedral symmetry in solution (6). All other solids have been characterized by X-ray crystallography and are listed in Table 1. Octahedral symmetry about the metal

TABLE 1. Structure of iron(III) chloroaqua complexes, $[\text{FeCl}_n(\text{OH}_2)_{6-n}]^{3-n}$

n	Compound	Structure	Ref.
0	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	$[\text{Fe}(\text{OH}_2)_6](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	7
0	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	$[\text{Fe}(\text{OH}_2)_6]_2 \text{ac}-[\text{Fe}(\text{OH}_2)_3(\text{SO}_4)_3]$	8
2	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	<i>trans</i> - $[\text{FeCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$	9
2	$\text{FeCl}_3 \cdot \text{SbCl}_5 \cdot 8\text{H}_2\text{O}$	<i>trans</i> - $[\text{FeCl}_2(\text{OH}_2)_4]\text{SbCl}_6 \cdot 4\text{H}_2\text{O}$	10
5	$\text{K}_2[\text{FeCl}_5(\text{OH}_2)]$	$[\text{FeCl}_5(\text{OH}_2)]^{2-}$	11
5	$(\text{NH}_4)_2[\text{FeCl}_5(\text{OH}_2)]$	$[\text{FeCl}_5(\text{OH}_2)]^{2-}$	12
6	anhydrous FeCl_3	$[\text{FeCl}_6]^{3-}$	13,14
6	$\text{Co}(\text{NH}_3)_6[\text{FeCl}_6]$	$[\text{FeCl}_6]^{3-}$	15

ion is a common characteristic of iron(III) chloro-aqua complexes. This has been corroborated for all complexes that have been studied by Mössbauer spectroscopy (16-20).

Another structurally important family of ferric chloride complexes consists of solids in which the ferric ion assumes tetrahedral symmetry. In most of the compounds isolated the FeCl_4^- anion is stabilized by a bulky cation, e.g. tetrabutyl ammonium ion. However, stable complexes exist in which the cation is either an ammonium ion or one of the alkali metal ions. Where Mössbauer spectra of these complexes have been measured, the observed isomer shift is indicative of a ferric compound with tetrahedral symmetry. In fact, an extensive study has shown that, at 90 K, the isomer shift of octahedral compounds is approximately 0.20 mm/sec greater than that of tetrahedral compounds (21). Mössbauer spectroscopy has also indicated that the FeCl_4^- tetrahedron is slightly distorted in some complexes (19,22,23). This departure from tetrahedral symmetry is reflected by the appearance of a quadrupole splitting, ΔE , in the measured spectra. The greater the distortion, the greater the value of ΔE . X-ray crystallography has confirmed the presence of distortion in these FeCl_4^- tetrahedra (24,25). The distortion is probably due to van der Waals forces between neighbouring atoms.

2. Solutions and frozen solutions

a) Solutions

Numerous authors have studied the formation of iron(III) chloride complexes in various solutions over a temperature range of 18 to 45 °C by potentiometry (26-29), UV and visible spectrophotometry (30-49), Raman spectroscopy (50-53), ion-exchange extraction (54-59), radio-tracer technique (60-67), pressure and temperature jump (68,69), stopped-flow (70-73), electron magnetic resonance (74-75), nuclear magnetic resonance (76), X-ray diffraction (77-79), as well as quasi-elastic neutron scattering (80). The solutions investigated had hydrochloric acid concentrations ranging from dilute (27) to concentrated (32,36).

The results obtained using the physicochemical methods mentioned above show a lack of consensus regarding which species are present in ferric chloride solutions. Nevertheless, in the literature reviewed most workers seem to agree that iron(III) solutions having HCl concentrations of 1 M or less contain only two complexes, those being $[\text{Fe}(\text{OH}_2)_6]^{3+}$, and $[\text{FeCl}(\text{OH}_2)_5]^{2+}$. According to Marcus (81), dilute ferric chloride solutions can be selected where only one type of complex is predominant depending on the hydrochloric acid concentration. These findings are based on ion-exchange and solvent extraction studies which suggest that, up to 0.5 M HCl, Fe^{3+} is predominant. Marcus (81) claims that, between 0.5 and 2 M HCl, the predominant species is FeCl^{2+} , from 2 to 6 M, it is FeCl_2^+ , from 6 to 9 M, it is FeCl_3 , while from 9 to 12 M FeCl_4^- predominates. However, such a

statement is suspicious since the author did not specify how many water ligands were associated with the metal ion, thereby avoiding the problem of determining the structure of these ferric complexes.

Iron(III) is considered to be a hard acid according to the Pearson notation (82). That is, it belongs to the complex-forming metal class "a" which, in solution, forms more stable compounds with the first element of each group in the periodic table. Hard acids (acceptors) bind strongly to hard bases by predominantly electrostatic forces thereby favouring more ionic bonding. As a result, iron(III) forms more stable complexes with chloride ions than with bromide ions, and the stability constant, K_1 , for $[\text{FeCl}(\text{OH}_2)_5]^{2+}$, measured at 25 °C and zero ionic strength is greater than the corresponding K_1 for $[\text{FeBr}(\text{OH}_2)_5]^{2+}$ by approximately one order of magnitude (83). According to spectrophotometric studies (30-49) the value of K_1 for $[\text{FeCl}(\text{OH}_2)_5]^{2+}$, at an ionic strength, μ , of 1.0 and at 25 °C, varies from 3.0 to 4.6 depending on the method of extrapolation.

In the frequently quoted work of Rabinovitch and Stockmayer (32) the measured stability constants should be approached with caution since the authors did not take into account the variation of extinction coefficients with temperature. The same caution should be used when considering the results obtained by Connick and Coppel (40). In a later UV study by Heistand and Clearfield (45) a value of $K_1 = 3.9$ at $\mu = 1.0$ and 25 °C was obtained. This value of the stability constant can be accepted as fairly accurate as it has since been confirmed by more recent studies involving a variety of techniques (42,44,61,67,69,76).

The octahedral species $[\text{FeCl}(\text{OH}_2)_5]^{2+}$ can be described as an inner-sphere complex, a fact which is strongly supported by results from UV (45), NMR (84) and Raman spectroscopy (51). In these and in other kinetic studies the perchlorate anion is used as a supporting electrolyte due to its relative inertness towards ferric ions. It is generally accepted that ClO_4^- does not form inner-sphere complexes with iron(III), as shown by Raman spectroscopy (85) and NMR (86). However, there may be significant outer-sphere interactions in ferric chloride solutions depending on the perchlorate concentration (87). As early as 1952, Sutton recognized the existence of $\text{Fe}^{3+}, \text{ClO}_4^-$ ion pairs in solution (88). Subsequent studies by other workers support this conclusion (89). Schwarz and Dodson (90) recently examined the kinetics of dissociation of ferric chloride complexes by pulse radiolysis and suggested that $\text{Fe}^{3+}, \text{ClO}_4^-$ outer-sphere complexes are present for ionic strengths as low as 1 M. These interactions could be responsible, in part, for the significant differences observed in the literature values of the stability constants.

The investigation methods referred to in the opening paragraph of this section have identified several iron(III) chloride complexes. However, in most instances, there is little certainty about the stereochemistry of these complexes, especially the higher chloro-complexes. This is probably due to the difficulty involved in isolating them in a pure form (91). For example, the neutral species $[\text{FeCl}_3(\text{OH}_2)_3]$, assumed to be of octahedral symmetry, is generally included in equilibrium calculations. Yet, there is no solid evidence

that this species is present in aqueous solutions. Some studies have suggested that there is a rapid octahedral-tetrahedral equilibrium between $[\text{FeCl}_3(\text{OH}_2)_3]$ and $[\text{FeCl}_3\text{OH}_2]$ but none offers conclusive evidence of this effect (46,76).

It is generally assumed that tetrahedral $[\text{FeCl}_4]^-$ is present in acidic solutions since it can be readily extracted from these solutions by organic solvents, such as diethyl ether and nitrobenzene, thereby forming the well-known tetrahedral complex HFeCl_4 (92). It is also known from kinetic studies that, in aqueous solutions, ratios of successive metal ion stability constants, K_1/K_{n+1} , are usually similar in value (93). Since the K_3/K_4 ratio is much bigger than the previous ratios it has been inferred that the tetrachloro complex has a tetrahedral rather than an octahedral configuration. However, this assumption does not take into account the possibility of a rapid equilibrium between the octahedral $[\text{FeCl}_4(\text{OH}_2)_2]^-$ and tetrahedral $[\text{FeCl}_4]^-$ configurations, the latter being favoured in organic solvents. In addition, the information available concerning the extractability of HFeCl_4 into oxygenated solvents does not support the belief that significant amounts of the tetrachloro species are present in aqueous solutions. Indeed, the presence of FeCl_4^- anion in organic solvents could be explained by the existence of a fast equilibrium between the aqueous and organic phases resulting in the successful extraction of this anion from aqueous solutions.

When working with ferric chloride solutions one has to consider the possible formation of higher chloroferrate complexes, especially as the HCl concentration increases. Recent laser-Raman investigations (51-53) have suggested the presence of the species $[\text{FeCl}_5\text{OH}_2]^{2-}$ and

$[\text{FeCl}_6]^{3-}$ in ferric chloride solutions. These solutions consist of concentrated ferric chloride hexahydrate (3.44 M) dissolved in relatively dilute HCl (3 M) as well as concentrated HCl (11.5 M). However, it is unlikely that these species occur in dilute ferric chloride solutions, even in the presence of very high chloride concentrations (77). Hence, these two chloro-iron(III) complexes will not be considered to form to any significant extent in the solutions studied in this project.

b) Frozen solutions

Mössbauer spectroscopy has been used extensively for the investigation of frozen aqueous solutions. However, most of the previous studies have been done on salts of iron(II). Comparatively, very few studies have examined in detail the distribution of ferric chloride complexes in aqueous solutions (91,94-103). This is probably related to the difficulty of interpreting complex iron(III) Mössbauer spectra. Unlike iron(II) spectra, iron(III) spectra often show magnetic hyperfine splitting (hfs) due to the magnetic interaction between the nucleus and the electronic spin. Moreover, the spectra can be affected by relaxation of the electronic spin among the ionic levels.

The data available from Mössbauer studies of frozen ferric chloride solutions are at best contradictory (91,102). Whether or not the highest chloro-complex of iron(III) in concentrated HCl solutions is tetrahedral $[\text{FeCl}_4]^-$ or octahedral $[\text{FeCl}_4(\text{OH}_2)_2]^-$ is still being debated. Plachinda and Makarov (91) have presented evidence which suggests ferric chloride aqueous solutions contain an equilibrium mixture of tetrahedral and octahedral tetrachloro-complexes. The hexacoordinate anion would be the most prominent species in these aqueous solutions whereas, in the course of extraction by an organic solvent, the tetracoordinate anion solubilizes in the organic phase. This would account for the discrepancies observed between the results obtained by Mössbauer and optical spectra.

The same authors have measured Mössbauer spectra of ferric chloride solutions in 1.0 and 4.0 M HCl. Their results show the presence of at least two iron(III) chloride complexes. They suggest that these complexes possess octahedral coordination based on the measured values of the magnetic field, H_n . However, they did not attempt any further identification of the complexes. Similarly, Mørup, Knudsen, Nielsen and Trumpy (102) have suggested that octahedral complexes were present in FeCl_3 aqueous solutions but could not determine whether the ferric ions were coordinated to one, two, or three-chloride ions.

C. The Mössbauer effect

Even though the presence of resonant absorption in optical systems had been known since the beginning of this century, its nuclear counterpart was not observed until 1951 (104). A few years later, the phenomenon of recoilless nuclear resonance was discovered by Rudolf L. Mössbauer (105). A growing number of chemists began to make use of this new technique during the early '60's and its potential in studies of chemical bonding (106), oxidation states (107,108), crystal structure (109-111), lattice dynamics (112), as well as magnetic properties (113) proved enormous. Mössbauer spectroscopy is now well accepted by scientists in all fields and is frequently used to complement work done by other spectroscopic techniques such as NMR, NQR, EPR and X-ray diffraction. Indeed, it is a technique which has a wide range of applications in not only chemistry and physics but metallurgy and geology as well.

1. Nature of the phenomenon

The basis of the Mössbauer effect is that both the energy loss due to nuclear recoil and the Doppler broadening, which is due to thermal motion, can be eliminated under certain circumstances. The effect itself results from the fact that, in a solid, the emitting or absorbing nucleus is not free to move but is instead bound to neighbouring atoms. Upon emission of a gamma-ray, the crystal lattice acting as a whole absorbs the energy due to recoil and, consequently, this recoil becomes negligible. This description of

the Mössbauer effect will be illustrated using ^{57}Fe which is by far the most widely studied nucleus.

The characteristics of the excited ($I^* = 3/2$) and ground states ($I = 1/2$) for an ideal ^{57}Fe nuclide are listed in Table 2 while the nuclear interactions involved in the ^{57}Fe Mössbauer effect are shown in Fig. 1.

Fig. 1. Decay scheme of ^{57}Co , showing the energy levels in ^{57}Fe . The 14.4 keV is the recoilless γ -ray or Mössbauer transition.

In this example, the ^{57}Fe excited state is produced by radioactive decay from a source of long-lived ^{57}Co nuclei. These nuclei decay by electron-capture with high efficiency to the 136.5 keV level of

^{57}Fe , from which 91% of the decays proceed to the 14.4 keV level, which has a half-life of 97.8 nsec. The Mössbauer effect can thus be seen as the recoilless emission and readsorption of the 14.4 keV gamma-ray by an atomic nucleus in a radioactive source. This gamma-ray is then resonantly absorbed by a nucleus of the same kind in an absorber. In an actual Mössbauer experiment, the source is usually moved relative to the absorber in a controlled fashion and the transmitted γ -rays are counted as a function of the relative source velocity (Doppler velocity).

2. Recoil-free fraction and molecular dynamics

As discussed in the previous section, ^{57}Co nuclei decay spontaneously to the excited state of ^{57}Fe which then emits a gamma-ray. Upon emission of this gamma-ray, the law of conservation of momentum requires that the nuclei receive a recoil energy E_R given by

$$E_R = \frac{E_\gamma^2}{2Mc^2} \quad (1.1)$$

where E_γ is the gamma-ray energy, M is the nuclear mass, and c is the velocity of light. The usual value of E_R given for transitions used in Mössbauer spectroscopy is $10^{-2} - 10^{-3}$ eV. It is similar in magnitude to the lattice-vibration phonon energies. These phonon energies are quantized and the recoil energy can only be transferred to the lattice if it corresponds closely to an allowed quantum jump.

TABLE 2. Characteristics of the ^{57}Fe nuclide

Energy of transition	$E_Y = 14.413 \times 10^3 \text{ eV}$
Half-life of excited state	$t_{1/2} = 9.781 \times 10^{-8} \text{ sec}$
Mean-life of excited state	$\tau = 14.111 \times 10^{-8} \text{ sec}$
Natural linewidth ($\Gamma_{\text{nat}} = \hbar/\tau$)	$\Gamma_{\text{nat}} = 4.665 \times 10^{-9} \text{ eV}$
Shift due to recoil	$2E_R = 3.913 \times 10^{-3} \text{ eV}$
Natural linewidth due to Doppler velocity	$v = \frac{2\Gamma_{\text{nat}}}{E_Y} c = 0.194 \text{ mm/sec}$
Debye temperature (best reliable value)	$\Theta_D = 420 \text{ K}$
Recoilless fraction for $\Theta_D = 420 \text{ K}$	$f = 0.79 \text{ at } 300 \text{ K}$ $f = 0.92 \text{ at } 0 \text{ K}$
Nuclear spins	$I^* = 3/2, I = 1/2$
Nuclear g-factors	$g_N^* = -0.103, g_N = 0.18$
Internal conversion coefficient	$\alpha = 8.21$
Absorption cross-section	$\sigma_0 = 2.56 \times 10^{-18} \text{ cm}^2$
Natural abundance	$a = 2.14\%$

Only a fraction f of emission events result in no transfer of energy to the lattice (zero-phonon transitions), where f is characteristic of the chemical form of ^{57}Fe . The mass M of the nucleus in Equation (I.1) is then increased to that of the whole lattice, thereby making E_R effectively zero.

The vibrational characteristics of the solid lattice may be predicted by the Einstein model which has only one vibrational frequency, ω . The transfer of energy to the lattice then takes place in integral multiples of $h\omega$. However, the Einstein model offers only a crude approximation and fails in particular to reproduce the low-temperature behaviour of the specific heat. A better model, suggested by Debye, takes into consideration all frequencies of vibration from $\omega = 0$ to a maximum frequency of $\omega_{\max}$. A characteristic temperature Θ_D known as the Debye temperature is defined by

$$\Theta_D = \frac{\pi \omega_{\max}}{k} \quad (1.2)$$

where k is Boltzmann's constant and $\hbar$ is Planck's constant divided by 2π . In the Debye model the final expression for the fraction f of recoil-free emissions is

$$f = \exp \left\{ - \frac{6E_R}{k\Theta_D} \left[\frac{1}{4} + \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{x dx}{e^x - 1} \right] \right\} \quad (1.3)$$

where T is the absolute temperature and x is the component of the mean-square vibrational amplitude of the emitting nucleus in the solid. For specific cases, the above equation can further be

reduced to:

$$f = \exp \left(- \frac{3E_R}{2k\theta_D} \right) \quad \text{at } T = 0 \text{ K} \quad (1.4)$$

and

$$f \approx \exp \left(- \frac{6E_R T}{k\theta_D^2} \right) \quad \text{for } T \geq \theta_D/2 \quad (1.5)$$

The recoil-free fraction, also called Mössbauer-Lamb fraction, is strongly temperature dependent. The rapid decrease in f at high temperatures proves a limiting factor in many applications of the Mössbauer effect. The fraction f will be greatest for ionic solids at very low temperatures although the Mössbauer effect has been observed in viscous liquids (114). Even if the Debye model is not applicable in all cases e.g. noncubic lattices and lattices with different masses, it still provides a reasonable estimate of the value of f .

The recoil-free fraction f is often referred to as the Debye-Waller factor which is a familiar term in X-ray diffraction. For this technique, the Debye-Waller factor gives the fraction of X rays which are scattered without creating any excitation in the crystal (115). The f factor has the same origin in γ -resonance scattering, although it is expressed in a slightly different form. In other words, the Mössbauer effect provides an alternative way of measuring f .

In the thin absorber approximation[†], and given the assumptions established for Equation (I.5), the absorber recoil-free fraction is directly proportional to the total area, A, of the resonance peak. Under these conditions, the area under the resonance maximum of a Lorentzian curve is adequately given by

$$A = \frac{\epsilon}{2\pi} \Gamma_{\text{exp}} \quad (\text{I.6})$$

where ϵ is the resonance effect magnitude and Γ_{exp} is the full width at half maximum (116). According to Equation (I.5) the temperature-dependence of the resonance area is

$$\frac{d \ln A}{dT} \approx \frac{d \ln f}{dT} \approx - \frac{6E_R}{k\theta_M^2} \quad (\text{I.7})$$

where θ_M is now used instead of θ_D . The characteristic Mössbauer temperature θ_M reflects the strength of the chemical bond binding the Mössbauer atom in the absorber lattice. Following rearrangement of Equation (I.7) θ_M can be expressed by

$$\theta_M = \left[\frac{6E_R}{k} \times \left(- \frac{d \ln A}{dT} \right)^{-1} \right]^{\frac{1}{2}} \quad (\text{I.8})$$

[†] See for example ref. 4, pp. 33 ff.

The slope of the straight line obtained by plotting $\ln A$ versus temperature is directly related to the strength of the intermolecular bonding forces in the solid (116). The smaller the slope the stronger is the bonding of adjacent molecular units in the compound being investigated.

3. Measured parameters

Parameters can be deduced either directly or indirectly from a Mössbauer experiment. Isomer shift, quadrupole splitting, linewidth, magnetic hyperfine splitting, and internal field are examples of parameters which can be derived directly from a spectrum. They reflect the details of the electronic charge and the spin-density distributions. The Debye-Waller factor (recoilless fraction) and the second-order Doppler shift (thermal shift) can, on the other hand, only be determined by carrying out a series of experiments over a broad temperature range. These parameters are very important in studies of lattice dynamics as well as in the elucidation of problems of chemical bonding.

a) Isomer shift

The isomer shift arises from the electrostatic interaction of the nuclear charge with that part of the electronic cloud which is inside the volume of the nucleus. This interaction results in a shift of the unsplit nuclear energy levels in a compound (absorber) relative to their position in a free atom. If the nuclear ground and excited states both have zero radius, their energy difference would be $E_0^* - E_0$. The effect of a finite nuclear radius R is to raise each energy level in relation to its zero radius value, E_0^* or E_0 , thereby giving the energies

$$E^* = E_0^* + \frac{2\pi}{5} Ze^2 R^{*2} |\psi(0)|^2 \quad (1.9)$$

$$E = E_0 + \frac{2\pi}{5} Ze^2 R^2 |\psi(0)|^2$$

where Z represents the atomic number, e , the electronic charge, R^* and R , the radii of the excited and ground states respectively, and $|\psi(0)|^2$, the total S -state electron density at the nucleus (117). The energy of the gamma-ray is then determined to be

$$\begin{aligned} E_\gamma &= E^* - E \\ &= (E_0^* - E_0) + \frac{2\pi}{5} Ze^2 (R^{*2} - R^2) |\psi(0)|^2 \end{aligned} \quad (1.10)$$

The magnitude of $|\psi(0)|^2$ depends both on the electronic configuration and on the chemical environment, and varies from one compound to another.

A Mössbauer experiment can be used to measure the difference in transition energies occurring between a source (electronic density $|\psi(0)_s|$) and an absorber $|\psi(0)_a|$. The isomer shift δ can then be determined as follows:

$$\begin{aligned} \delta &= E_\gamma^a - E_\gamma^s \\ &= \frac{2\pi}{5} Ze^2 (R^{*2} - R^2) \{ |\psi(0)_a|^2 - |\psi(0)_s|^2 \} \end{aligned} \quad (1.11)$$

where the subscripts a and s refer to the absorber and source respectively. Since the actual change between R^* and R is generally very small the above equation is frequently expressed using

$$dR = R^* - R.$$

$$\delta = \frac{4\pi}{5} Ze^2 R \left(\frac{dR}{R} \right) \{ |\psi(0)_a|^2 - |\psi(0)_s|^2 \} \quad (I.12)$$

The isomer shift depends on a nuclear term dR/R and an extranuclear term $\{ |\psi(0)_a|^2 - |\psi(0)_s|^2 \}^\dagger$, which is sometimes referred to as the chemical term.

For any given nuclear transition all the terms in Equation (I.12) are constant with the exception of $|\psi(0)_a|$, so that the isomer shift is directly proportional to the s -electron density at the nucleus. The expression for the isomer shift can therefore be simplified to

$$\delta = K \{ |\psi(0)_a|^2 - C \} \quad (I.13)$$

where K is a nuclear constant and C is a constant characteristic of the source used.

The isomer shift can thus be seen to be directly proportional to the electron density (primarily s electrons) at the nucleus. In the case of ^{57}Fe , the excited nucleus has a smaller radius

[†] Equation (I.12) can also be related to the measured shift in Doppler velocity units, v , by equation $v = (c/E_\gamma \delta)$.

than when in the ground state, and dR/R is negative. Consequently, an increase in s -electron density at the absorber nucleus results in a more negative isomer shift.

Although the wavefunctions for p and d electrons have zero probability at the nucleus, they nevertheless interact indirectly with the nucleus by shielding the s electrons. This means that Mössbauer spectroscopy can be a valuable tool in the study of transition metal complexes, because of the changes in the electronic configurations of these complexes. For example, a ferrous ion ($3d^6$) has a higher $3d$ -electron density than a ferric ion ($3d^5$). One might therefore assume a more negative isomer shift. However, the electron density at the nucleus of the ferrous ion is actually smaller than that of the ferric ion since the extra d electron shields the $4s$ electrons from the nucleus. A ferrous ion will thus show an appreciably larger isomer shift than a ferric ion. Moreover, knowing the value of the isomer shift, it becomes possible in many cases to draw conclusions about the degree of covalent bonding existing in the compound being investigated.

Nevertheless, it is important to note that the observed line shift in a spectrum is not entirely caused by the isomer shift discussed above. The Doppler effect, which is related to the vibrational energy of the lattice, has a further influence on the line shift. Virtually no frequency shift occurs through the first-order Doppler effect. This arises because the period of vibration of the emitting or absorbing nucleus is much shorter than

the nuclear lifetime in the excited state. Therefore the average displacement and velocity of a nucleus are effectively zero.

However, significant frequency shifts are observed through the second-order Doppler effect. The average mean-squared values of the velocity, $\langle v^2 \rangle$, are finite and this average increases in direct proportion to the average kinetic energy (117). Consequently the Mössbauer resonance moves to a more negative velocity, as the temperature is raised and the observed shift is defined by

$$\frac{\delta E}{E_0} = \frac{v_0 - v}{v} = \frac{\langle v^2 \rangle}{2c^2} \quad (1.14)$$

where c represents the velocity of light and E_0 , the γ transition energy. For metallic iron at room temperature this shift amounts to approximately -0.0073 mm/sec per $^{\circ}\text{C}$ while at -193 $^{\circ}\text{C}$ it is reduced to about -0.0022 mm/sec per $^{\circ}\text{C}$ (118).

b) Quadrupole splitting

The isomer shift can only raise or lower the nuclear energy levels. It cannot split them. Further splitting of the nuclear energy levels can only occur through electronic quadrupole or magnetic-dipole interactions.

A nucleus with spin $I > \frac{1}{2}$ has a quadrupole moment, Q , which interacts with the electric field gradient (EFG) q , created at the nucleus by neighbouring electrons, thus resulting in quadrupole splitting. The value of Q is a direct measure of the extent of departure from spherical symmetry at a nucleus. The sign of Q reflects the shape of the nucleus: a negative quadrupole moment means that the nucleus is an oblate (flattened) ellipsoid while a positive quadrupole moment is evidence of a prolate (elongated) ellipsoid.

According to Abragam (119), the Hamiltonian describing the quadrupole coupling can be expressed as

$$\mathcal{H} = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1)] + \eta(I_+^2 - I_-^2) \quad (I.15)$$

using the relation $I_{\pm} = I_x \pm iI_y$,

where I_+ and I_- are respectively quantum mechanical raising and lowering operators of the spin. The asymmetry parameter η is related to the magnitude of the x , y , and z components of the electric field gradient, viz.,

$$\eta = \left(\frac{\delta^2 V}{\delta x^2} - \frac{\delta^2 V}{\delta y^2} \right) / \frac{\delta^2 V}{\delta z^2}$$

$$= (V_{xx} - V_{yy}) / V_{zz} \quad (1.16)$$

where $V_{zz} = eq$ is taken to be the largest value of $|V_{ii}|$ such that $0 \leq \eta \leq 1$. The z axis is then referred to as the major axis, and the x axis as the minor axis. Given $I = 3/2$, the energy levels may be determined by finding the eigenvalues of the Hamiltonian in (1.15).

$$E_Q = \frac{e^2 q Q}{4I(2I-1)} [3m_I^2 - I(I+1)](1 + \eta^{3/2})^{1/2} \quad (1.17)$$

where m_I has two possible values $3/2$ and $1/2$. The quadrupole splitting ΔE_Q , which is written frequently as ΔE , is then given by the difference in the energy levels for these two values of m_I (see Fig. 2).

$$\Delta E_Q = E_Q(3/2) - E_Q(1/2)$$

$$= \frac{1}{2} e^2 q Q (1 + \eta^{2/3})^{1/2} \quad (1.18)$$

If the EFG has axial symmetry ($\eta = 0$) the quadrupole splitting[†] then becomes

[†] The value of the quadrupole splitting is exactly half the value of the quadrupole coupling constant used in nuclear quadrupole resonance (NQR) spectroscopy.

Fig. 2. Nuclear energy levels and the quadrupole splitting. In an electric field gradient the nuclear level with spin $I = 3/2$ is split into two sublevels.

$$\Delta E_Q = \frac{1}{2} e^2 q Q \quad (I.19)$$

Given this information, the resultant Mössbauer spectrum is a symmetrical doublet from which the separation ΔE may be easily measured. However, the sign of the quadrupole splitting cannot usually be obtained since Equation (I.17) contains the square of m_I . Hence the states whose m_I differ only in sign are degenerate. The sign of ΔE can, on the other hand, be determined either by applying a large external magnetic field to the sample, or by looking at the angular dependence of the line intensities in single crystals (114).

The symmetry properties of a crystal can be deduced from the knowledge of what contributes to the EFG. There are two separate interactions which contribute to the EFG. The first is due to the electrons associated with the Mössbauer atom itself and include the group of high-spin (weak crystal field) ferrous compounds of octahedral symmetry. Since their electronic configuration is d^6 , there is one 3d electron outside a half-filled shell of spherical symmetry. Thus, the entire field gradient arises from this electron. The observed quadrupole splitting is usually large and, in most cases, highly temperature dependent. The second interaction is due to neighbouring ions in the crystal. The group of high-spin ferric compounds of octahedral symmetry is a typical example of this contribution. In a weak crystal field, the outer shell configuration of the atom is d^5 . The five 3d electrons do not contribute to the EFG since they are in a half-filled shell having spherical symmetry. Therefore, since the observed quadrupole splitting arises from the disposition of the effective charges on the ligands, and is also temperature independent, it is generally small.

A compound experiencing an electric quadrupole interaction generally gives a spectrum where both lines are of similar intensity. However, line-intensity asymmetry may sometimes result from the following factors or combination of them: crystallite orientation, Goldanskii-Karyagin effect (also called recoilless fraction anisotropy), the spin-spin or spin-lattice relaxation (120). It is possible, however, virtually to eliminate these factors. The problem

of crystallite orientation can be solved by dispersing finely ground samples in Fluorolube grease or any other non-reactive medium. Relaxation effects can be distinguished from the Goldanskii-Karyagin effect by calculating the relative areas of the doublet lines. If the line-intensity asymmetry is due to relaxation effects the peak area ratio is unity whereas if it is due to the Goldanskii-Karyagin effect the area ratio is different from unity.[†]

Hence, from the analysis of the quadrupole splittings observed in Mössbauer spectra conclusions can often be reached concerning the point symmetry at the site of the Mössbauer ion.

[†] See for example ref. 113, pp. 102-107.

c) Linewidth

Ideally, the energy of the γ -ray which results from the transition between the excited and ground states in nuclei should be equal to the energy difference between these two levels. However, while the ground state is stable, and thus has an infinite lifetime and zero uncertainty in its energy (121), the excited state of a source nucleus has a mean life, τ , of a microsecond or less (0.14 μsec for the 14.4 keV radiation in ^{57}Fe), where $\tau = t_{1/2}/0.693$.

The Heisenberg relation states that the shorter the half-life of the excited state, the greater the uncertainty of the γ -ray energy and the broader the resonance line. This results in a spread of the γ -ray energies, thus giving an inherent width of the γ -radiation line. According to the Heisenberg uncertainty principle, $\Delta E \Delta t \geq \hbar$, and the so-called natural linewidth, $\Gamma_{\text{nat}} = \Delta E$, for the excited level can be estimated by setting $\Delta t = \tau$.

$$\Gamma_{\text{nat}}(\text{eV}) = \hbar/\tau = \frac{4.562 \times 10^{-16}}{t_{1/2}(\text{sec})} \quad (1.20)$$

Considering ^{57}Fe , $t_{1/2}$ is 9.781×10^{-8} sec, so that from (1.20),

$$\Gamma_{\text{exp}} = 2\Gamma_{\text{nat}} = 9.32 \times 10^{-9} \text{ eV}$$

In practice however, the observed linewidth is found to be 20% to 30% broader than this value even when thin absorbers are used

(122). For an absorber of finite thickness the effective thickness t is defined as

$$t = n\phi\tau_0 \quad (I.21)$$

where n is the number of resonant atoms per square centimeter, ϕ , the recoil-free fraction, and τ_0 , the absorption cross-section (τ_0 has a value of $2.56 \times 10^{-18} \text{ cm}^2$ for a single ^{57}Fe nucleus). For thickness values currently used in Mössbauer experiments ($1 \leq t \leq 5$) the absorption still very closely approximates a Lorentzian shape. However, the absorption effect at the center of the resonance line increases faster than it does at the wings resulting in a wider observed spectral line which is given by,

$$\Gamma_{\text{exp}} = 2\Gamma_{\text{nat}}(1 + 0.135t) \quad (I.22)$$

Self-resonance in the source matrix also results in additional line broadening but is practically independent of absorber thickness.

The Doppler velocity which defines the experimental line-width can be expressed as

$$v = \left(\frac{2\Delta E}{E_\gamma} \right) c = 0.194 \text{ mm/sec} \quad (I.23)$$

Therefore, it suffices to move the source at small velocities ($> 0.2 \text{ mm/sec}$) in order to sweep over the resonance. The problem of producing uniform velocities, while avoiding any vibrations in

the system, is usually solved by the use of transmission geometry. However, if the actual distance between the source and the detector is significant, there will be further broadening of the linewidth (121). In the case of an uncollimated source, some photons will be travelling at an angle θ to the direction of motion of the source. Equation (I.23) may therefore be transformed to read:

$$v = \left(\frac{2\Delta E}{E_\gamma \cos \theta} \right) c \quad (I.24)$$

Thus, photons that are detected at an angle of e.g. 20° will increase Γ_{exp} by approximately 6%, giving rise to the so-named cosine effect (123).

Other factors such as i) inhomogeneous hyperfine interactions, ii) electronic relaxation and iii) instrumental effect may cause broadened linewidths.

i) Inhomogeneous hyperfine interactions - These usually result if the environment of the emitting atom varies, as it does for sources diffused on stainless steels or other alloys (122). By using sources of ^{57}Co embedded in a palladium matrix, this effect can be avoided and linewidths close to the natural linewidth are observed.

ii) Electronic relaxation - The linewidth is strongly dependent on the electronic relaxation time, τ , when τ is comparable to the nuclear Larmor period (102). In the case of relatively fast relaxation, e.g. $\tau \leq 10^{-9}$ sec, the linewidth decreases with decreasing

τ . However, for very fast relaxation, where $\tau \leq 10^{-11}$ sec, line shapes of natural linewidth are found.

iii) Instrumental effects - These include mechanical vibrations, the finite number of channels in the analyser and a high level of counts. All of these effects can be minimized to a great extent with a carefully designed experiment. For example, mechanical vibrations can be eliminated by enclosing the spectrometer and the detector in a sound-proof box, the spectra resolution improved by using 1024 channels or more, and the level of counts lowered by determining the most efficient distance between the source and the detector.

d) Magnetic hyperfine splitting

Electronic precession rates are much higher than their nuclear counterparts. As a result, the electronic and nuclear spins are usually considered as precessing independently around a common axis of quantization. The nucleus may be regarded as being exposed to magnetic fields undergoing constant changes due to the fluctuating electronic spins. The effective fields seen by the nucleus then result from time-averaging the instantaneous fields produced by the electrons. In the case of fast fluctuations, the magnetic field is averaged to zero because the electronic spin is seen "up" by the nucleus as often as it is seen "down". However, magnetic hyperfine interactions are observed when the electronic relaxation rates are slow compared to the nuclear frequencies, i.e. in the case of slow fluctuations. In the absence of applied external fields, the Hamiltonian for the interaction of the nuclear magnetic dipole moment with a magnetic field H is

$$\mathcal{H}(M1) = -\hbar\gamma_N \mathbf{I} \cdot \mathbf{H} = -\mu H \quad (1.25)$$

where γ_N is the nuclear gyromagnetic ratio in a given state:

$$\hbar\gamma_N = g_N \beta_N = \mu / I \quad (1.26)$$

Here g_N is the nuclear Landé splitting factor, β_N is the Bohr nuclear magneton $e\hbar/2Mc$, and μ is the nuclear magnetic moment. Eigenvalues of this Hamiltonian yield the corresponding Zeeman energy levels:

$$E_m = -\mu H \cdot m / I = -g_N \beta_N H \cdot m \quad (1.27)$$

where m , the nuclear magnetic quantum number, is the component of the nuclear spin I in the z direction. The magnetic field H splits each nuclear level into $(2I + 1)$ equally spaced levels. The transitions between these levels are governed by the selection rules for magnetic-dipole (M1) interactions according to $\Delta m = 0, \pm 1$. The splitting between adjacent levels is $g_N \beta_N H$ and the splitting between the lowest and the highest level is $2g_N \beta_N H \cdot I$ for any given I as indicated in Figure 3.

Fig. 3. Hyperfine magnetic splitting of nuclear energy levels in a magnetic field H .

Figure 3 also shows that the spacing of the levels in the excited state quartet is less than that for the ground state doublet and that the ordering of the levels is reversed. This arises because the nuclear splitting factor for the excited state of ^{57}Fe is smaller than that of the ground state and of opposite sign: $g_N^*/g_N = -0.571$.

For a monocrystalline absorber the magnetic dipole transition probabilities are dependent on the orientation angle θ between the gamma-ray and the symmetry axis. The relative transition probabilities are given by the square of the Clebsch-Gordan coefficients (124) and are summarized in Table 3, together with their angular dependence.

TABLE 3. Relative transition intensities between magnetic hyperfine states in ^{57}Fe .

Transition	Angular dependence	Relative intensities			
		$\theta = 0^\circ$	$\theta = 90^\circ$	Integrated	
I_e	I_g				
$\pm 3/2$	$\pm 1/2$	$3/2(1 + \cos^2\theta)$	3	3/2	3
$\pm 1/2$	$\pm 1/2$	$2\sin^2\theta$	0	2	2
$\pm 1/2$	$\mp 1/2$	$1/2(1 + \cos^2\theta)$	1	1/2	1

Polycrystalline absorbers are made up of randomly oriented magnetic domains for which the angular dependence must be integrated over all orientations. The averaged values of $\sin^2\theta$ and $\cos^2\theta$ are $2/3$ and $1/3$ respectively. Consequently, the six-line hyperfine pattern with relative intensities $3 : 2 : 1 : 1 : 2 : 3$ is observed. In practice, however, the γ -ray radiation can easily be polarized in

the iron foils because of the directional correlation between the internal field and the magnetization (125). The nuclei are then in a preferred orientation with relative intensities $3 : \beta : 1 : 1 : \beta : 3$, where $\beta = 4(1 + 2\cot^2\theta)$ and $0 \leq \beta \leq 4$ (126).

Complex and partially resolved spectra are often observed in the study of ferromagnetic materials. The application of an external magnetic field causes the magnetic domains to line up parallel to this applied field (case of $\theta = 0$). As a consequence, the $\Delta m_I = 0$ transitions vanish and only four transitions are allowed. The resolution of the spectra may thus improve and permit an easier interpretation.

So far, we have only considered the interaction between a pure magnetic field and the excited nuclear levels giving rise to an even spacing of the levels. In the presence of quadrupole interactions these levels are no longer equally spaced as indicated in Figure 4.

The nuclear ground state has no quadrupole effect, hence the spacing of the levels will not be affected. The exact shift in the magnetic sublevels depends on the angle between the magnetic field and the electric field gradient. If the crystal symmetry and the position of the magnetic axes are known, it is usually possible to determine the sign of the quadrupole coupling and hence the sign of the electric field gradient (127).

In the case of an isotropic EFG tensor ($\eta = 0$), at an angle θ with respect to the magnetic axis, the nuclear energy levels are given (127) by a relation similar to Equation (I.18).

Fig. 4. Hyperfine structure plus weak quadrupole interaction with corresponding line patterns.

$$E = -g\beta_N H m_I + (-1)^{|m_I| + \frac{1}{2}} \frac{e^2 q Q}{4} \frac{(3\cos^2\theta - 1)}{2} \quad (1.28)$$

assuming $\mu H \gg e q Q$. The expression for the quadrupole splitting then follows

$$\Delta E_Q = \frac{e^2 q Q}{8I(2I-1)} [3m_I^2 - I(I+1)] (3\cos^2\theta - 1 + \eta \sin^2\theta \cos^2\phi) \quad (1.29)$$

where θ and ϕ are the polar angles that define the direction of the magnetic field H with the crystal axes. When dealing with the excited state of ^{57}Fe , $I = 3/2$ and, assuming $\eta = 0$, Equation (1.29) becomes

$$\Delta E_Q = \frac{e^2 q Q}{8} (3\cos^2\theta - 1) \quad (1.30)$$

e) Internal magnetic field

The measurement of magnetic hyperfine interactions by Mössbauer spectroscopy often provides valuable information concerning the electronic properties of magnetic compounds. Classical theories of atomic structure predict the absence of magnetic hyperfine structure for systems such as Fe^{3+} , whereas in fact, these systems have quite large magnetic fields. Indeed, since they are in the $3d^5$ configuration and ^6S ground electronic state, the $3d$ electrons have zero charge density at the origin (128) and therefore, the observed large H_{eff} at the nucleus is believed to result from what is called the exchange polarization.

As the name "exchange polarization" implies, the spin of the $3d$ electrons interacts with the inner-shell s electrons. This interaction of the inner electrons which have their spins parallel to the $3d$ spin directions is different from the interaction of those which have their spins anti-parallel to the same $3d$ spin directions. The ensuing polarization creates unequal densities at the nucleus for s electrons of opposite spin orientation, $e(|\psi_{s\uparrow}(0)|^2 - |\psi_{s\downarrow}(0)|^2)$. As a result, an effective field is established parallel to S , which has an approximate value of 300 kGauss for iron metal (117).

The internal magnetic field, H_n , is generally considered in terms of three components (129).

$$H_n = H_C + H_L + H_D \quad (1.31)$$

Each individual component is defined as follows,

$$H_C = a(|\Psi_{\uparrow}(0)|^2 - |\Psi_{\downarrow}(0)|^2) \quad (I.32)$$

$$H_L = -2\mu_B \langle r^{-3} \rangle \langle L_z \rangle \quad (I.33)$$

$$H_D = -\frac{1}{2}\mu_B q_z \langle S_z \rangle \quad (I.34)$$

where

$$q_z = \langle r^{-3} \{ (3z^2/r^2) - 1 \} \rangle \quad (I.35)$$

H_C represents the Fermi contact interaction where a is an experimental coefficient and $\Psi_{\uparrow}(0)$ and $\Psi_{\downarrow}(0)$ are the respective magnitudes of the s wavefunctions for spin up and spin down. H_L arises from the coupling of the nuclear spin with the angular momentum of outer electrons. μ_B is the Bohr magneton, r represents the position of electrons relative to the nucleus, and $\langle \rangle$ denotes the average of the $3d$ wavefunctions.

The components of the spin and orbital angular momenta, in units of $\hbar$, are respectively $\langle S_z \rangle$ and $\langle L_z \rangle$. H_D is the dipolar interaction arising from the coupling of the nuclear spin with the moment of the electron spin-density, where q_z is the electric field gradient at the nucleus. For a cubic metal, given the absence of spin-orbit coupling, this dipolar field is strictly zero (128).

For a non-cubic crystal, H_D has a non-zero value. This is due to the asymmetry of the electron spin density (130). However, it is small enough to be neglected for most practical purposes. The orbital-current term, H_L , accounts for approximately 20% or less of the total hyperfine field in iron compounds. Therefore, the dominant contribution to the internal magnetic field at an ^{57}Fe nucleus is that due to the core polarization, H_C .

Watson and Freeman (128) have been able to determine approximate values of H_n arising mainly from the core polarization by applying exchange-polarized Hartree-Fock (EPHF) calculations to various systems in the iron series. As can be seen from Table 4, the $1s$ electrons are less polarized than the $2s$ electrons since these have a greater overlap with the $3d$ electrons. There is considerably more overlap for $3s$ electrons. However, since these electrons lie partially inside and partially outside the $3d$ electrons, the net effect is a predominance of the inner electrons and a positive contribution to the hyperfine field.

Whether or not hyperfine structure will be seen in Mössbauer spectra depends upon the mean spin-flip rate of the electronic transition. These flips are due to electronic relaxation or, above the Curie point, to exchange coupling between neighbouring electron spins. For paramagnetic substances, hyperfine structure can be resolved when the electron spin relaxation rate, ω_e , is comparable to or smaller than the nuclear precessional frequency, $AS/\hbar$, where A represents the hyperfine splitting constant and S , the net spin of

TABLE 4. Individual δ -electron contributions to H_n (kGauss) (Watson and Freeman, ref. 128)

	Mn ²⁺ (3d ⁵)	Fe ³⁺ (3d ⁵)	Fe ²⁺ (3d ⁶)
	H_C	$n\delta\uparrow - n\delta\downarrow$	$n\delta\uparrow - n\delta\downarrow$
1 $\delta\uparrow$	2502840	~ - 30	- 50
1 $\delta\downarrow$	-2502870		- 30
2 $\delta\uparrow$	226670	-1410	-1790
2 $\delta\downarrow$	-228080		-1310
3 $\delta\uparrow$	31210	+740	+1215
3 $\delta\downarrow$	-30470		+790
Total		~ -700	-625

the ion (131). Two possibilities exist to reduce this rate thereby enabling the usual six-line spectrum to be observed. The first possibility consists of lowering the temperature (132) in order to lengthen the spin-lattice relaxation time, T_1 . The second involves the use of magnetically dilute samples (133) in which the spin-spin relaxation time, T_2 , is increased substantially. Both techniques have been employed during this study to obtain a measure of the internal field of ferric complexes in frozen solutions.

Experimentally, Knudsen and Mørup (134) have found that H_n decreases almost linearly without increasing ligand covalency. The introduction of six fluoride ligands in octahedral symmetry around a ferric ion gives a value of 622 kG (135) for the internal field. This result agrees remarkably well with the EPHF calculations.

Ligands less ionic in nature yield smaller H_n values, the order being $F^- > H_2O > O^{2-} > Cl^-$ (23).

It is very difficult to predict quantitatively the way in which a given ligand will affect the hyperfine field at the metal site (136). Many mechanisms which are at play tend to perturb both the charge and the spin densities of the system. Such factors as charge transfer, orbital overlap, covalent bonding, and crystal field effects, e.g. distortions from cubic symmetry, have been shown to reduce the free-ion value of H_n (128). Moreover, for ions like Fe^{2+} , large positive contributions to H_n arise from unquenched orbital angular momentum. Covalent bonding results in additional mixing of the 3d and s orbitals. This tends to delocalize the spin moment of the ion, thereby reducing the effective S associated with the Fe site. Since the Fermi-contact term per unpaired electron, $H_C/2S$, is constant the value of H_n is thus reduced (137).

D. Characteristics of the vitreous state

The present project involves the study of ferric chloride complexes in frozen solutions by Mössbauer spectroscopy. In order to interpret the results obtained by this technique correctly, it is necessary to examine the characteristics of the vitreous state. Supercooling of liquids at low temperatures produces what appears to be a second-order transition. During this transition, the viscous liquids are transformed into hard and brittle, yet amorphous, solids which are designated as glasses (138a). The specific temperature at which this transformation occurs is known as the glass transition temperature, T_g . There is, strictly speaking, no sharply defined glass transition temperature, but rather a range of temperatures over which the observed changes occur. It would probably be better to use the term glass-transition interval (139).

The thorough understanding of the vitreous state requires a knowledge of the relative positions of all the ions or molecules forming a particular glass as well as the forces acting between them. In fact, not every liquid is capable of forming a glass. Whether it will or not is a question concerning crystallization kinetics (140). Many glasses have a high viscosity slightly above the liquidus temperature, the temperature at which a solid crystalline phase is in equilibrium with the liquid. It appears that lack of mobility above the liquidus temperature is the main kinetic factor controlling glass formation. If a substance can be quenched from temperatures

above the liquidus to temperatures below the glass transition, in a shorter time than that required for nucleation and growth of the crystalline phase, glass formation will result (141). Liquids that will likely form glasses are those for which this quenching can be achieved at relatively slow rates approximately $1^{\circ}\text{C}/\text{min}$.

Extensive studies have shown that water, whether in bulk or droplet form, does not freeze to a glass using ordinary rates of cooling (138b). However, rapid quenching of concentrated aqueous electrolyte solutions initially at room temperature usually forms a glass (142). This technique was first introduced by Zachariasen (143) while working on simple crystalline oxides. He used rapid cooling from a melt in order to introduce randomness and produce glasses of unusual structure. The same method can also be used with dilute electrolyte solutions after the addition of a glass-forming agent such as glycerol. In this way, solute segregation is kept at a minimum (144).

Studies by Mössbauer spectroscopy of many rapidly frozen ionic solutions have suggested that the freezing process produces a homogeneous glass (145-47). These studies have assumed that the composition and structure present in the solutions at room temperature would be preserved following quenching and that a homogenous solid solution would grow with the same concentration as that of the liquid phase (148). However, this is not always the case, even when very rapid rates of freezing are employed. As Pearson pointed out (149), the reactivity of an aquametal ion is dependent on the rate of exchange of its coordinated water molecules. Seen in this light,

chromium(III) ions are generally considered inactive with a water exchange rate of $7.5 \times 10^{-6} \text{ sec}^{-1}$ (150), whereas copper(II) ions are among the transition metal ions undergoing the fastest water-water exchange rate ($8.3 \times 10^9 \text{ sec}^{-1}$) (151). By contrast, ferric ions are neither clearly reactive nor clearly inactive. They have an intermediate rate of water exchange established at approximately $2 \times 10^4 \text{ sec}^{-1}$ (151-153). The exchange of a water molecule for a chloride ion in the ferric ion coordination sphere is expressed in the following two steps:

where K_E represents the equilibrium constant describing the encounter between the two species. The first step is controlled by diffusion while the second one is a first order process in which the outer-sphere complex, $\text{Fe}(\text{OH}_2)_6^{3+}, \text{Cl}^-$, is transformed into the final inner-sphere complex (154). Provided steric and electrostatic effects are negligible, the rate-determining step will be the loss of a water molecule with concomitant substitution of the entering ligand into the inner sphere. Moreover, the rate of dissociation of water molecules often increases after the addition of a non-labile ligand with good sigma bond donor capacity, such as Cl^- (155), to the metal ion. Thus, a solution containing various ferric chloride species would undergo faster rates of water exchange than a solution with only hexaquo ferric ions. Since Cl^- ions are better sigma bond donors

than OH^- ions, the rate of water exchange for ferric chloride complexes would probably be around 10^6 sec^{-1} (154). The formation of these complexes, which are in dynamic equilibrium with one another, proceeds through endothermic reactions mainly due to the large positive entropy term. According to the Le Chatelier principle, such endothermic reactions should proceed to a lesser extent at lower temperatures. The rate of ligand exchange could thus possibly be reduced to 10^5 sec^{-1} by the time the temperature of a ferric chloride solution reaches its own freezing point. However, this rate of exchange is still fast enough so that, when the solution finally gets frozen, the species distribution would be different than that prevalent at 25°C .

Crystallization of the solvent is yet another problem which becomes important in the study of dilute aqueous solutions. As a result of diffusion processes taking place during the freezing of the solutions, the solute ions frequently segregate in high-concentration regions having an amorphous or crystalline structure (148). In effect, extensive hydrogen bonding in aqueous solutions precludes inclusion of foreign ions in the ice structure, thus permitting the solvent to crystallize in a virtually pure phase (144). Aqueous solutions can effectively be frozen in about 1 to 8 milliseconds (156, 157) by rapid cooling in liquid nitrogen. However, in spite of this short time, one should note that at -10°C the formation of ice crystals is quite significant since ice crystallizes at a rate of approximately 8 cm/sec (158, 159).

Very high crystallization velocities, in the order of 10^6 cm/sec or greater, are needed to obtain a homogenous distribution of the solute upon freezing the solution (148). If this condition is not met, most of the solute is displaced at the advancing crystalline

phase of the solvent. Thus, in a limited sample volume, the solute is increasingly concentrated in the remaining liquid regions until the temperature is low enough for solidification (146). However, in solutions which do not normally form glasses, the addition of a glass-former reduces or completely inhibits solute segregation even when relatively slow rates of freezing are used. This technique has been employed in this project to measure the value of the internal magnetic field in the case of dilute ferric chloride solutions.

II. EXPERIMENTAL

A. Mössbauer spectrometer

1. Description of the System

The Mössbauer experiments were performed using a constant acceleration spectrometer operating in the usual transmission geometry. Figure 5 shows a block diagram of the experimental arrangement of the Mössbauer spectrometer used in this project. Its various components are also listed in Table 5. A Hewlett-Packard (3300 A) function generator supplied the triangular waveform signal used to power the drive system via an electromechanical transducer. The drive system was built by the Science Workshop at Carleton University.

The linearly changing velocity (constant acceleration) was synchronized to the advance of the address scaler of a Northern Scientific (NS-636) multichannel analyser (MCA) operating in the multiscaling mode. The synchronization was done by triggering the analyser clock with the function generator, so that each channel was open to the correct velocity interval. During the time the system dwelled at a particular channel, the incoming pulses were counted by an arithmetic scaler and added to the numbers that were stored in the memory from the previous counting cycle. Then, the address scaler was advanced to the next channel and the entire process again repeated.

Fig. 5. Block diagram of constant acceleration Mössbauer spectrometer.

TABLE 5. Mössbauer spectrometer components

1. Triangular wave generator (Hewlett-Packard, 3300A)
2. Power amplifier (Hewlett-Packard, 6823A)
3. Mössbauer drive unit (Carleton University, Science Workshop)
4. Mössbauer source, $^{57}\text{Co}(\text{Pd})$ (New England Nuclear Corp.)
5. Mössbauer absorber
6. Variable-temperature cryostat (Janis Research, DT-1954)
7. Temperature controller (Lake Shore Cryotronics, DTC-500)
8. Thermocouple, Silicon Diode (Lake Shore Cryo., DT-500KL)
9. Detector Xe-CO_2 , 2 atm (Reuter-Stokes, RS-P3-1605-261)
10. Preamplifier (Ortec, 109PC)
11. High voltage DC supply (John Fluke, 413C)
12. Pulse amplifier (Ortec, 471)
13. Single Channel Analyser (Ortec, 406A)
14. Oscilloscope Camera (Tektronic, C-12)
15. Multichannel analyser (Northern Scientific, NS-636)
16. Digital readout control (Northern Scientific, NS-421)
17. Teletype (Teletype Corp., 33TC)
18. Sigma-9 computer (Xerox Corp.)

The spectra stored in the MCA in this fashion represent the counting rate as a function of velocity. The Mössbauer spectra were recorded in 1024 channels having velocities between +15 and -15 m/sec, which corresponded to a velocity increment of ca 0.03 mm/sec per channel. This ensured that even the largest magnetic splitting in iron(III) compounds could be measured by the analyser.

A total of four different radioactive $^{57}\text{Co(Pd)}$ sources (New England Nuclear Corp.) were used during the course of this project. Each source had an initial activity of ca 20 mCi and was replaced after approximately one year. The 14.4 keV transition in ^{57}Fe was detected with a Reuter-Stokes (RS-P3-1605-261) gas-proportional counter. This detector was filled with a Xe-CO₂ mixture under 2 atmospheres pressure.

A high-voltage DC source (John Fluke, 413C) was used to supply an operating voltage of approximately 2800 V to the detector. The signal from the detector was then fed into a pre-amplifier (Ortec, 109PC) followed by a pulse amplifier (Ortec, 471). The amplified signal was further directed to a single channel analyser (Ortec, 406A) to ensure that only the counts coming from the 14.4 keV transition were being counted. Furthermore, a sheet of clear Plexiglass was placed directly in front of the detector to enhance the signal-to-noise ratio by eliminating most of the low-energy X-ray radiation. A Plexiglass density of 160 mg/cm² was found adequate for that purpose. The signal was then processed by the MCA in the manner described previously. After completion of a Mössbauer experiment, the output of the stored

spectrum in the MCA was directed to a teletype (Teletype Corp., 33TC) through a readout control unit (Northern Scientific, NS-421). A punched paper tape was also produced to be read later into the computer (Xerox Corp., Sigma-9).

The spectrometer and the detector were housed in a sound-proof and vibration-proof wooden box (160) which was also lined with a 2 mm thick sheet of lead for radiation protection. The spectrometer and detector were both mounted on a 7 mm thick aluminum plate and were positioned 20 cm apart. This distance was selected as being the best compromise between too close, which broadens the linewidth, and too far, which requires longer times of counting for the same spectrum. The absorbers used in this project were always located exactly midway between the source and detector. The ^{57}Co sources were electroplated onto a 4 mm diameter active area of a 12 micron thick palladium foil, which had an overall diameter of 6 mm. They were located at 20 cm from the detector and, given that the detector window was 25 mm in diameter, the broadening of the natural linewidth suffered through the cosine effect was only about 0.6%. For room temperature measurements a thin aluminum plate, fitted with two small clamps, was used to support the sample holders. For frozen solutions study, however, the sample holders were attached to long support rod which was inserted into a variable-temperature cryostat (Janis Research, DT-1954).

2. Velocity calibration

The most appropriate material for calibration is a thin foil of metallic iron. Its use is highly recommended over that of sodium nitroprusside dihydrate (161) especially now that high purity foils are readily obtained. Metallic iron has the added advantage that it covers a large range of velocities, thereby allowing one to check the linearity of the transducer.

The velocity scale of the present system was calibrated with an α -iron foil (99.999% purity, New England Nuclear Corp.) of 25 μ m thickness, containing 0.44 mg cm⁻² ⁵⁷Fe. The calibration constant value, as calculated from the data of Violet and Pipkorn (162), was quite reproducible and did not vary by more than 0.2% over a period of two weeks. The velocity scale linearity was normally within 0.8% in the range -6 to +6 mm/sec.

The positions of the six lines in an iron foil Mössbauer spectrum are as shown in Table 6 where g_0 is the ground-state magnetic splitting and g_1 represents the excited-state splitting. In this project, the calibration constant, k , was calculated from the line positions of the four outermost peaks

$$k = \frac{g_0 + 3g_1}{n_6 - n_1} = \frac{g_0 + g_1}{n_5 - n_2} \quad (II.1)$$

where n_i is the center position of the i th resonance line expressed in channel numbers, thereby giving k in units of velocity per channel.

TABLE 6. Line positions of a metallic iron foil.

Line	Energy ^a	Observed ^b Position (mm/sec)
1	E_0	-5.4823
2	$E_0 + g_1$	-3.2473
3	$E_0 + 2g_1$	-1.0132
4	$E_0 + g_0 + g_1$	0.6624
5	$E_0 + g_0 + 2g_1$	2.8967
6	$E_0 + g_0 + 3g_1$	5.1338

a. theoretical relationship

b. $g_0 = 3.9098$ mm/sec and $g_1 = 2.2342$ mm/sec, quoted with an error of ± 0.0008 mm/sec, are taken from ref. 162.

All isomer shifts are quoted relative to the centroid of the four outermost peaks. The isomer shift and quadrupole splitting of magnetically split spectra can be determined from the following relationships (163):

$$\delta = \frac{n_1 + n_2 + n_5 + n_6}{4} \quad (\text{II.2})$$

$$\Delta E = \frac{n_1 + n_6 - n_2 - n_5}{2} \quad (\text{II.3})$$

The internal field, H_n , of a given compound can also be calculated knowing that, at room temperature, Violet and Pipkorn (162)

found a value of -330.4 kG for H_n of metallic iron which had a maximum splitting of 10.6124 mm/sec. The negative sign simply indicates that the direction of the internal field in metallic iron is opposite to that of an externally applied magnetic field. This relation therefore corresponds to a calibration factor of -31.13 kG per mm/sec.

A linewidth of ca 0.25 mm/sec was found for the two inner resonance lines of metallic iron. This is in good agreement with Violet and Pipkorn's value and also with the value that can be calculated from the lifetime of the excited state, taking into account the sample thickness. If small impurities, usually carbon, are present in the metallic iron foil the calculated velocity constant, k , becomes larger due to a reduced magnetic splitting. The linewidth of the peaks also becomes significantly larger. This particular problem often arises when foils of enriched ^{57}Fe are used for velocity calibrations. As can be seen from Spectrum 1, the asymmetry of the peaks is clearly evident. For this reason, enriched ^{57}Fe foils are not recommended as calibration standards even though they require a much shorter time of counting.

B. Cryogenics

As mentioned previously, the Mössbauer spectra of frozen solutions were measured after these were inserted in a cryostat. The temperature of the sample was monitored with a silicon diode sensor (Lake Shore Cryotronics, DT-500 KL) located on the sample holder, immediately above the frozen solution. The sensor was held in place with a low-melting alloy, Woods metal. Since the sample holders were made of copper, a material of high thermal conductivity, and since the samples were allowed to equilibrate with the surrounding temperature for a minimum of two hours before the beginning of a new Mössbauer spectrum, it was assumed that the measured temperature was that of the sample. The temperature of each sample was held constant over a period of time with a programmable temperature controller (Lake Shore Cryotronics, DTC-500). The samples that were placed in the cryostat were enclosed in an evacuated copper tube which had two windows made of 0.005 inch (127 μm) Mylar foils. The 14.4 keV radiation emanating from the source also had to pass through the two cryostat windows made of 0.003 inch (76 μm) Mylar foils. Liquid nitrogen was used as a coolant for all low-temperature measurements. The frozen solutions were transferred as quickly as possible into the pre-cooled cryostat. The transfers were done in less than 5 seconds, a time short enough not to raise appreciably the temperature of the sample, as observed with the temperature sensor.

C. Computation

1. Description of the program

The Mössbauer spectra were deconvoluted by assuming Lorentzian line shapes superimposed on a parabolic baseline. The analyses were performed using a nonlinear least-squares regression program which had been modified by Dlouhy (160). The successive-approximations method used in this program requires initial estimates of peak position and halfwidth at half height for each peak in a spectrum. A given analysis must also include a convergence criterion specifying the desired degree of accuracy as well as a maximum number of iterations which will be performed by the computer. The program was modified to make it compatible with the present Xerox Sigma-9 computer and the plotting subroutine was rewritten using the standard CALCOMP BASIC SUBROUTINES.

Standard error propagation equations which require the variance in the parameters of best fit were employed to ascertain the error limits on the final Mössbauer parameters. These error limits were routinely given in the computer printout, together with the final parameters after a successful analysis of a spectrum. They were listed as the variance of each parameter which is defined mathematically as the square of the standard deviation. The chi-square, χ^2 , test was used as a criterion of good fit. It involves the minimization of the weighted mean square deviation between the calculated values Y_i^o and the corresponding experimental data points Y_i :

$$\chi^2 = \sum_{i=1}^N \frac{1}{\sigma_i^2} (Y_i^0 - Y_i)^2 \quad (\text{II.4})$$

where N is the total number of data points and σ represents the statistical variation of the count rate of the i th channel of the MCA corresponding to a velocity increment v_i to $(v_i + \Delta v_i)$. An increment of 0.5 channel was commonly used to analyse the Mössbauer spectra. For ease of calculation, Y_i^0 is expressed as the sum of n independent Lorentzian lines with different intensities and halfwidths, these lines being superimposed on a parabolic background:

$$Y_i^0 = Y_{\text{baseline}}^0 - \sum_{i=1}^n \frac{A_i}{1 + \left(\frac{x - p_i}{B_i} \right)^2} \quad (\text{II.5})$$

where A_i , p_i and B_i are the amplitude (peak height), position and halfwidth at half maximum of the i th peak. Here x represents a given channel number and n is the total number of Lorentzian peaks. The term Y_{baseline}^0 represents the parabola and can be written as:

$$Y_{\text{baseline}}^0 = ax^2 + bx + c \quad (\text{II.6})$$

where a , b and c are constants related to the number of peaks and degrees of freedom. The differences between calculated and experimental values were further plotted directly on the line printer for each analysis. This allowed a rapid visual check of the closeness of fit. If all the peaks have been properly assigned the resulting differences

will be randomly scattered on each side of the zero line. This was observed in fact after the compound $(\text{NH}_4)_2\text{FeCl}_5(\text{OH}_2)$ had been correctly analysed with two lines separated by a small quadrupole splitting (Spectrum 2). However, if the same data points are analysed with only one line, the resulting differences show definite regularities (see Figure 6).

Fig. 6. Residual differences for $(\text{NH}_4)_2\text{FeCl}_5(\text{OH}_2)$ analysed with only one line.

In order to consider an analysis as satisfactory, the plot of differences should be statistically featureless to within ± 3 standard deviations. When this condition is met a final plot of the Mössbauer

spectrum can be obtained on the off-line plotter. The relative absorption (%) is customarily plotted against the velocity (mm/sec) where isomer shifts are given with respect to the isomer shift of a pure iron foil standard.

The program also provides the user with the option of applying constraints to the parameters during the optimization process. These three parameters, position, halfwidth and height of the peaks, can be kept constant or be made equal to one another. This feature allows the successful analysis of many spectra for which the convergence criterion could not otherwise be reached. The peak areas can usually be determined with a precision better than $\pm 0.2\%$. However, in the case of closely overlapping peaks, the "precision-of-fit" worsens due to uncertainties in peak positions. Moreover, the assumption that the peak areas are directly proportional to the recoil-free fractions of the various complexes is not entirely exact. Thus, the species distribution values quoted in this project could carry an absolute error up to $\pm 5\%$.

2. Fourier transform

Mössbauer spectra can be readily analysed by computer since they are recorded in digital form. The signal-to-noise ratio is usually high in spectra of iron-containing compounds and the relative absorption are of the order of a few percent. The values of isomer shifts and quadrupole splittings obtained from the analyses of these spectra carry only a small error. However, the recoil-free fraction is sometimes very small ($\leq 0.5\%$) which leads to an imprecise analysis of the Mössbauer parameters.

Such is the case for frozen solutions where only natural iron is used and for solid iron compounds where the Mössbauer atoms are enclosed in a "soft" crystalline matrix, i.e. a matrix where these atoms experience a large recoil due to weak intermolecular bonds.

It is possible to obtain a substantial improvement in the resolution of Mössbauer spectra by using the fast Fourier transform (FFT) technique as was first demonstrated by Stone (164). This technique is rapidly increasing in popularity and several researchers have used it to process Mössbauer spectra (165-72). The fast Fourier technique uses a discrete algorithm developed by Cooley and Tukey (173) which can be made to be a close approximation of the continuous Fourier transform (174). With this algorithm, a transformation may be performed relatively easily and rapidly by a digital computer.

In Mössbauer spectroscopy, the number of counts (γ radiation detected after going through the samples during a given time is recorded as a function

of velocity or more exactly as a function of channel number. The Mössbauer spectrum of the tetrahedral compound, $(\text{Bu}_4\text{N})\text{FeCl}_4$, has been measured at room temperature and is shown in Spectrum 3. The scattering of the experimental points which is clearly evident, results in approximately 10% error in the determination of the isomer shift. This normal Mössbauer spectrum may be referred to as the "time-domain" spectrum for which the Fourier transformation gives a "frequency-domain" spectrum. The frequency spectrum has units that are the reciprocal of those used in the Mössbauer spectrum and consists of two series, the real part of the transform, and the imaginary part. The real output of the fast Fourier transform is represented by a damped cosine wave while the imaginary output takes the form of a damped sine wave. Because the sine wave has characteristics similar to the real output, only the real output need to be used in the inverse Fourier algorithm to transform the frequency-domain back into the "time-domain" spectrum. Thus, if the transformation is performed on 512 data points (channels), the real output will consist of 256 channels. The frequency spectrum of the compound $(\text{Bu}_4\text{N})\text{FeCl}_4$, resulting from the FFT of its Mössbauer spectrum, is shown in Figure 7. This frequency spectrum indicates that the original Mössbauer spectrum is composed mainly of low frequencies having high amplitudes. Although the higher frequencies have low amplitudes, they are still important since they are responsible for the background noise in the original spectrum.

The improved Mössbauer spectrum is obtained by modifying the real output with a smoothing function (usually a rectangular filter).

Fig. 7. Real output of Mössbauer spectrum of $(\text{Bu}_4\text{N})\text{FeCl}_4$ after Fourier transformation.

then using a Fourier transformation of the modified real output. The width of the rectangular filter must be determined carefully since it determines the amount of noise information to be truncated. If the filter width is too narrow, some spectral information will be lost at the same time, thereby resulting in a distorted spectrum. The purpose of the filter is to produce a spectrum with a high signal-to-noise ratio while, at the same time, keeping intact the characteristics of the original spectrum. At present, the appropriate filter width, i.e. the cut-off frequency, can only be determined empirically since

it is highly dependent on the characteristics of a spectrum.

The Mössbauer spectrum of the solid compound $(\text{Bu}_4\text{N})\text{FeCl}_4$ was measured at 298 K. The Mössbauer parameters for both the original spectrum and the Fourier transformed spectra with various cut-off points are listed in Table 7. The smoothed spectrum which is shown in Spectrum 4 corresponds to a cut-off frequency of 20 channels. The 10-channel cut-off produced more smoothing of the raw data and smaller amplitude of the side lobes, however, this was done at the expense of broadening the peak by approximately 25%. By contrast, a filter width of 20 channels was found to cause less distortion of the original spectrum while highly improving its signal-to-noise ratio. The data smoothing technique employing Fourier transformation is thus very useful in eliminating most of the random fluctuations without affecting spectral resolution.

TABLE 7. Mössbauer parameters for $(\text{Bu}_4\text{N})\text{FeCl}_4$ before and after Fourier transformation. ^(a)

δ (mm/sec)	Γ (mm/sec)	ϵ (%)	Cut-off frequency (channel)	$\Delta A^{(b)}$ (relative %)
0.255 ± 0.024	0.51	0.87	Original spectrum	0
0.243 ± 0.005	0.64	0.77	10	+11.2
0.247 ± 0.004	0.54	0.85	15	+ 3.2
0.254 ± 0.004	0.51	0.87	20	+ 0.2
0.257 ± 0.005	0.51	0.87	25	+ 0.7

- a. the original spectrum was measured at 298 K, and the analyses of the transformed spectra were performed on 512 channels.
- b. difference between peak areas of Fourier transformed spectrum and original spectrum.

D. Synthesis and handling of solid samples

The solid absorbers and the ferric ion solutions were prepared with the following reagents: Reagent grade FeCl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$, $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, SOCl_2 , and Certified ACS H_2O_2 (30%), $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, Fe metal, and AlCl_3 obtained from Fisher Scientific Co.; Reagent grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, and Analytical reagent NH_4Cl , concentrated HClO_4 , and K_2CO_3 from BDH Chemicals Ltd.; Reagent grade $\text{Fe}(\text{ClO}_4)_3$, and $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ from Alfa Inorganics Inc.; Reagent grade SbCl_5 , and Reagent ACS concentrated HCl from Allied Chemical Co.; Reagent grade $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, Reagent ACS HF (48%) and NaCl from Anachemia Chemicals Ltd.; Certified ACS DMSO and C_6H_6 from Aldrich Chemical Co.; Reagent grade KCl from J.T. Baker Chemical Co.; Reagent AgNO_3 from Merck and Co.; and enriched ^{57}Fe metal (90.6%) from New England Nuclear Corp.

As a rule, iron compounds were recrystallized before use. The following complexes were synthesized according to published procedures and then used as absorbers: $(\text{NH}_4)_2\text{FeCl}_5(\text{OH}_2)$, $\text{K}_2\text{FeCl}_5(\text{OH}_2)$, $\text{Rb}_2\text{FeCl}_5(\text{OH}_2)$, and $\text{Cs}_2\text{FeCl}_5(\text{OH}_2)$ (12), Cs_3FeCl_6 both yellow and orange form (20), $\text{Co}(\text{NH}_3)_5\text{FeCl}_6$ (15), $(\text{Bu}_4\text{N})\text{FeCl}_4$ (175), *trans*- $[\text{CoCl}_2(\text{en})_2]\text{FeCl}_4$ (176), $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, and $\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (177), *trans*- $[\text{FeCl}_2(\text{OH}_2)_4]\text{SbCl}_6 \cdot 4\text{H}_2\text{O}$ (178), *trans*- $[\text{FeCl}_2(\text{DMSO})_4]\text{FeCl}_4$ (179), *trans*- $[\text{FeCl}_2(\text{DPSO})_4]\text{FeCl}_4$ (180), $[\text{FeCl}(\text{OH}_2)_5](\text{NO}_3)_2$ (6), $[\text{Fe}(\text{CNCH}_3)_6][\text{FeCl}_4]_2$ (181), $\text{Na}_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ (182a), $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ (182b), $\text{Na}_2[\text{Fe}(\text{CN})_5\text{py}] \cdot 3\text{H}_2\text{O}$ (183), $\text{Na}_3[\text{Fe}(\text{CN})_5\text{OH}_2]$ (184), $\text{Ag}_3\text{Fe}(\text{CN})_6$ (185),

β - $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (186), and $\text{K}_2\text{FeF}_5(\text{OH}_2)$ (187). Some preparations were done at the CANMET Division of the Department of Energy, Mines and Resources, courtesy of Dr. D.J. Francis.

Several compounds were hygroscopic or had low melting points. The $2\frac{1}{2}$ and $3\frac{1}{2}$ hydrates of FeCl_3 were especially prone to melt on exposure to air. These were handled under dry nitrogen in a glove bag, and were gently crushed in an agate mortar under low-boiling petroleum ether (30-45°C) to prevent overheating of the samples. The petroleum ether had been previously dried over activated molecular sieves (4A).

For liquid nitrogen measurements, all absorbers were placed between the two thin Mylar foils (0.025 mm) of a gold-plated copper sheet (31 x 10 x 0.7 mm) having a 20 mm hole in its center. Cardboard holders were used sometimes for room temperature measurements. Gold plating of the copper was found to be necessary since the acidic solutions and some of the more hygroscopic solids have a strong tendency to be reduced by the copper, giving rise to false Fe(II) components in the spectra. The thickness of the absorbers was approximately 0.3 mm, and the amount of natural iron in them varied usually between 5 and 10 mg/cm².

E. Preparation and handling of solutions

Aqueous solutions of iron(III) compounds were prepared by dissolving enriched ^{57}Fe metal (90.6%) in concentrated HCl or HClO_4 . After being twice evaporated to dryness, the solutions were oxidized with 30% hydrogen peroxide and made up to volume for storage in the dark. The ionic strength was adjusted by the addition of NaClO_4 . The solutions were injected into a gold-plated cell, similar to those made for solid samples, by using an extra-fine Pasteur pipette. During the course of this project, two different cells were used having maximum capacities of 0.5 and 0.8 ml, respectively. All Mössbauer spectra were measured with the frozen solutions in the larger cell, except where noted.

The solutions were frozen using one of three techniques: the fast-freezing, the gradual freezing, and the slow-freezing technique. The first of these involved the direct immersion of the sample holder as quickly as possible in a bath of liquid nitrogen. For solutions of sufficiently high ionic strength, this method produced frozen solutions with the characteristics of a glass, although with hairline cracks at times. The gradual freezing technique was only used in certain cases to study the effects of glass formation. This method consisted in dipping the sample holder repeatedly in liquid nitrogen, a fraction of a second each time, until the solutions were completely frozen. The slow-freezing technique required a special set-up. The sample holder was held in a large glass test tube which, itself, was suspended over liquid nitrogen. The solutions were cooled by convection through

the glass walls as the test tube assembly was lowered very slowly in liquid nitrogen. The slow freezing process was spread usually over a period of 5-6 hours. Regardless of the freezing technique employed, the freshly frozen solutions were immediately transferred to the cryostat which had previously been stabilized at the temperature of measurement of the Mössbauer spectra.

Those solutions having low ionic strength were also studied after addition of a glass-forming agent. Several glass-forming agents were tested by the following procedure: each was added in various concentrations to a 0.10 M ferric ion solution in 1.0 M perchloric acid, and then rapidly frozen in liquid nitrogen. Ethylene glycol was found to be the most suitable agent since it could form glasses even when added in relatively low concentrations. Other glass-formers, such as methanol and ethanol, required concentrations of up to 60% by volume in order to produce the same effect as ethylene glycol.

III. RESULTS AND DISCUSSION

A. Crystalline Compounds

In order to obtain reference data with which to compare the spectra of frozen solutions, it was necessary to determine the spectra of a number of crystalline compounds of Fe(III) and some of Fe(II). Ferric chloride complexes, which are essentially ionic in character, give positive isomer shift with respect to iron metal. The influence of covalency in these paramagnetic compounds is sometimes difficult to assess. It is thus convenient to examine covalent effects in low-spin compounds where paramagnetic effects are absent. This allows a more extensive calibration of the velocity scale of the Mössbauer apparatus.

1. Low-spin and high-spin compounds

The isomer shift and quadrupole splitting values of selected low-spin compounds are presented in Table 8. Cyanide ligands feature a strong ligand-field which causes spin pairing in ferrous as well as in ferric compounds. Cyanide ligands also increase the electronic density around the iron atoms since the metal 3d orbitals are delocalized on the ligands. Thus, isomer shifts of iron cyanide compounds can be seen to be among the most negative. This fact prompted the use of disodium pentacyanonitrosyl ferrate(II) dihydrate, the so-called sodium nitroprusside, as a reference for the isomer shift of iron compounds in the early years of Mössbauer spectroscopy. A nitrosyl ligand has replaced one cyanide in the nitroprusside ion, thus changing the overall

TABLE 8. Mössbauer parameters for Fe(II) and Fe(III) low-spin compounds.

Compound	90 K		298 K	
	δ (mm/sec)	ΔE (mm/sec)	δ (mm/sec)	ΔE (mm/sec)
(a) Ferrous ion				
1. $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$	0.020	0.0	-0.013	0.0
2. $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$	-	-	-0.072	0.0
3. $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	-0.075	0.0	-0.028	0.0
4. $\text{Na}_3[\text{Fe}(\text{CN})_5\text{OH}_2]$	-	-	0.052	0.768
5. $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$	0.090	0.665	0.041	0.679
6. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$	-	-	-0.240	1.695
7. Mixture of 5 (70.0%)	-	-	0.046	0.674
and 6 (30.0%)	-	-	-0.234	1.682
(b) Ferric ion				
$\text{Na}_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$	-	-	0.021	0.384
$\text{K}_3\text{Fe}(\text{CN})_6$	0.010	0.446	-0.112	0.266
$\text{Ag}_3\text{Fe}(\text{CN})_6$	-0.059	0.823	-0.113	0.731
$\text{Na}_2[\text{Fe}(\text{CN})_5\text{py}] \cdot 3\text{H}_2\text{O}$	-	-	-0.106	1.664

symmetry from O_h to axial C_{4v} . The large quadrupole splitting observed in the Mössbauer spectrum (Spectrum 5) is then mainly due to electron π -donation to the 2p-orbitals of the nitrosyl group. By contrast, the spectra of unsubstituted iron(II) cyanide compounds present only one line because of the regular octahedral geometry.

In order to test the resolution achievable with the spectrometer, the spectrum of a mixture of two iron(II) low-spin compounds was measured. This sample consisted of 30.0% $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ and 70.0% $Na_3[Fe(CN)_5NH_3]$. These percentages are based on the total amount of iron atoms present in the compounds. The isomer shifts and quadrupole splittings obtained for each compound in the mixture are fairly close to the values obtained for the two compounds taken individually. As can be seen in Spectrum 6, the two doublets are easily distinguished. Their respective peak areas were determined from the computer fit of the spectrum. The peak area of the sodium nitroprusside doublet was found to be $33.4 \pm 5.3\%$ of the total. This figure agrees, within the experimental error, with the known value and confirms that the relative composition of a mixture can be determined with reasonable accuracy.

A few iron(III) cyanide compounds were also measured. Since they have one fewer electron than their iron(II) counterparts, their spin quantum number $S = \frac{1}{2}$. Therefore, compounds having a regular octahedral symmetry present a quadrupole splitting, as seen in Table 8. This characteristic is very valuable in trying to distinguish between ferrous and ferric low-spin compounds since they often have similar isomer shifts.

2. Ferric chloride hydrates

The series of crystalline hydrates $\text{FeCl}_3 \cdot n\text{H}_2\text{O}$ ($n = 2, 2\frac{1}{2}, 3\frac{1}{2}, 6$) were first made in 1892 by Roozeboom (188) through a study of the ferric chloride-water phase diagrams. The hexahydrate ($n = 6$) has been studied crystallographically by Lind (9a) and found to consist of *trans*- $[\text{FeCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$: a D_{4h} structure with two lattice water molecules. A study by infrared spectroscopy (189) has shown that the dihydrate ($n = 2$) consists of both a tetrahedral and octahedral ion and should be written as *trans*- $[\text{FeCl}_2(\text{OH}_2)_4][\text{FeCl}_4]$. Recently, the hemipentahydrate ($n = 2\frac{1}{2}$) has been studied by X-ray crystallographic methods (190) and was found to depart from the *trans* configuration and is instead *cis*- $[\text{FeCl}_2(\text{OH}_2)_4][\text{FeCl}_4] \cdot \text{H}_2\text{O}$. A structural study of the hemiheptahydrate ($n = 3\frac{1}{2}$) has not yet been reported in the literature, possibly due to its high hygroscopicity and low melting point.

Mössbauer spectra of all members of this series have been measured at 90 K to confirm and extend structural understanding of ferric chloroaqua complexes in the solid state (191). The spectra are given in Spectra 7-10 for the four hydrates $n = 2, 2\frac{1}{2}, 3\frac{1}{2}$ and 6, respectively. Clearly evident in Spectrum 10 are two peaks constituting a quadrupole split pair. Spectra 8-10 show the four peaks of two quadrupole doublets. The results obtained for the centre shifts and quadrupole splittings of these compounds are given in Table 9. Also summarized in Table 9 are the stereochemical assignments indicated by the Mössbauer data.

TABLE 9. Mössbauer parameters[†] for the hydrates $\text{FeCl}_3 \cdot n\text{H}_2\text{O}$ measured at 90 K

n	δ (mm/sec)	ΔE (mm/sec)	Assignment	Structural formula
6	0.580	0.871	$\text{trans}[\text{FeCl}_2(\text{OH}_2)_4]^+$	$\text{FeCl}_2(\text{OH}_2)_4\text{Cl} \cdot 2\text{H}_2\text{O}$
2	0.509	0.799	$\text{trans}[\text{FeCl}_2(\text{OH}_2)_4]^+$	$\text{FeCl}_2(\text{OH}_2)_4\text{FeCl}_4$
	0.409	0.240*	$[\text{FeCl}_4]^-$	
2½	0.585	0.302	$\text{cis}[\text{FeCl}_2(\text{OH}_2)_4]^+$	$\text{FeCl}_2(\text{OH}_2)_4\text{FeCl}_4 \cdot \text{H}_2\text{O}$
	0.380	0.380*	$[\text{FeCl}_4]^-$	
3½	0.575	0.256	$\text{cis}[\text{FeCl}_2(\text{OH}_2)_4]^+$	$\text{FeCl}_2(\text{OH}_2)_4\text{FeCl}_4 \cdot 3\text{H}_2\text{O}$
	0.354	0.308*	$[\text{FeCl}_4]^-$	

* Note that these tetrahedra are all distorted.

† See reference 191.

The centre shift, δ , of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is 0.580 mm/sec and is in keeping with the expected values for octahedral Fe(III) compounds.[†] The high quadrupole splitting value, ΔE , of 0.871 mm/sec is indicative of a large electric asymmetry, such as that present in an octahedral *trans* configuration. The asymmetry of linewidth and surface area of the two peaks is still evident at 90 K, although they become symmetric at 1.8 K, as was shown first by Wignall (192). The asymmetry is well explained by Thrane and Trumpy (193) in terms of combined spin-spin interaction and the Goldanskii-Karyagin effect. The temperature dependence of the recoil-free fraction was studied in view of obtaining a measure of the strength of intermolecular bonding forces in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The data are listed in Table 10 and a plot of $\log A$ against temperature is given in Figure 8. The isomer shift and Mössbauer effect decrease regularly with the rise in temperature. The quadrupole splitting, however, is practically constant and does not vary by more than 4%. The variation of peak area for both peaks of the doublet was plotted against temperature. As expected, both straight lines obtained from a least-squares fit of the data give very similar slopes. From these, the average Mössbauer temperature was calculated as 238 ± 8 K with a maximum lattice frequency, ν_{max} , of $166 \pm 5 \text{ cm}^{-1}$. Since the smaller the slope the stronger the bond between adjacent molecular units (116), the present value indicates relatively strong intermolecular bonds. This is in keeping with results obtained from the structure determination of crystalline $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (9).

[†] See for example J. Danon, in ref. 113, pp. 246-7.

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TABLE 10. Mössbauer parameters for solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at various temperatures.

T (± 0.5 K)	δ (± 0.009 mm/sec)	ΔE (± 0.015 mm/sec)	ϵ (± 0.1 %)	$A \times 10^{-5}$ (a),(b) (± 0.016)		log A (± 0.002)	
				1st peak	2nd peak	1st peak	2nd peak
90	0.547	0.872	5.8	9.506	6.699	5.978	5.826
150	0.502	0.889	5.6	8.281	5.945	5.918	5.774
200	0.446	0.907	5.0	7.127	5.166	5.853	5.713
250	0.395	0.884	4.4	6.547	4.590	5.816	5.662

(a) Peak area normalized to 24 h counting

(b) First and second peak correspond to the more negative and the more positive peaks, respectively

Fig. 8. Plot of peak area vs temperature for solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

It was shown then that the crystal was stabilized by hydrogen bonding between solvate water molecules and adjacent octahedral cations in addition to the electrostatic attraction between oppositely charged ions. The value of the lattice frequency also agrees well with a strong IR vibration measured by Adams and Lock (194).

The dihydrate compound $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, shows isomer shift and quadrupole splitting values very similar to those of the hexahydrate, indicating again the presence of a D_{4h} *trans* configuration. The Mössbauer spectrum of the dihydrate also shows an additional doublet. A value of 0.409 mm/sec observed for δ , coupled with a value of 0.240 mm/sec for ΔE , strongly suggests (195) that this part of the compound is the anionic species FeCl_4^- . This tetrahedral unit should give a single line, and the quadrupole splitting suggests that the tetrahedron is distorted. This is to be compared with quadrupole splittings values of 0.30 mm/sec and 0.2 mm/sec for NaFeCl_4 (22) and $(\text{Ph}_4\text{As})\text{FeCl}_4$ (23), respectively, where each has been shown to consist of a distorted tetrahedron by X-ray analysis (24,25). A ΔE value of 0.45 mm/sec was also found for the tetrahedral LiFeCl_4 (19). Given no other influence, this seems to indicate a roughly inverse correlation of ΔE with the sizes of the four cations: Li^+ , Na^+ , $\text{trans}-[\text{FeCl}_2(\text{OH}_2)_4]^+$, and Ph_4As^+ with ΔE values of 0.45, 0.30, 0.240, 0.2 mm/sec, respectively. The most reasonable configuration for the dihydrate, then, is *trans*- $[\text{FeCl}_2(\text{OH}_2)_4][\text{FeCl}_4]$. Again, the *trans* configuration is in keeping with conclusions derived earlier from infrared measurements (189).

The two intermediate hydrates ($n = 2\frac{1}{2}, 3\frac{1}{2}$) seem to show somewhat different spectra. Each gives a doublet whose isomer shift is characteristic (195) of the tetrahedral FeCl_4^- , where the doublet indicates a distortion of the tetrahedron. The ΔE value for the other doublet in each spectrum is relatively small, viz. 0.302 mm/sec for the $2\frac{1}{2}$ hydrate and 0.256 mm/sec for the $3\frac{1}{2}$ hydrate. The values indicate greater likelihood of a *cis*-dichloro than a *trans*-dichloro configuration. A recently published study (190) of the crystal structure of the $2\frac{1}{2}$ hydrate corroborates this finding and shows an unambiguous *cis* configuration. The crystal lattice also contains a distorted tetrahedron of FeCl_4^- and a single water molecule of hydration.

The distorted tetrahedral configuration is also borne out by the present Mössbauer data. The ΔE value of 0.380 mm/sec, which seems rather high, suggests an influence of the crystal packing. A close examination of the crystal structure confirms this hypothesis. The crystal shows a layered structure, with one plane consisting of FeCl_4^- anions and an equal number of water molecules, while the alternate planes each consist of $\text{FeCl}_2(\text{OH}_2)_4^+$ cations.

The data for the $3\frac{1}{2}$ hydrate seem unambiguous as well. The hexacoordinate iron(III) is identified by its isomer shift value of 0.575 mm/sec. Its value of 0.256 mm/sec for the quadrupole splitting is clearly not consistent with the *trans* configuration, and is well within the range expectable for the cation *cis*- $[\text{FeCl}_2(\text{OH}_2)_4]^+$. The tetrahedral FeCl_4^- likewise is distinct and easily assigned from the isomer shift. The ΔE value of 0.308 mm/sec suggests that the crystal

packing is less asymmetric in this compound, although unfortunately nothing is known about its crystallography.

Each compound in the series of four ferric chloride hydrates has one element in common: an octahedral cation, $[\text{FeCl}_2(\text{OH}_2)_4]^+$, the octahedron changes its configuration from *trans* to *cis* and back again. The reasons for this transformation are at present obscure. The effect of the availability of lattice water for binding or hydration of the anion seems significant. Szymański (190) has shown the lattice water to be hydrogen bonded to two chlorine atoms of the FeCl_4^- anion, thus contributing to the distortion of the tetrahedron, even though these two chlorines subtend an angle of 110.6° at the iron atom. The lattice water molecules seem not to interact strongly with the octahedra.

It is interesting to regard all these hydrates as being derived from a $[\text{FeCl}_2(\text{OH}_2)_4]^+$ cation, where the anion can be Cl^- , FeCl_4^- or SbCl_6^- (196), and to consider then that the number of water molecules associated with each cation is the deciding factor for its configuration, as is shown in Table 11. One sees that the $[\text{FeCl}_2(\text{OH}_2)_4]^+$ cations which are in a *trans* configuration are all associated with even numbers of lattice water molecules, while odd numbers seem to go along with a *cis* configuration. Whether this observation represents a cause or an effect is at present difficult to say.

TABLE 11. Configuration of several compounds $[\text{FeCl}_2(\text{OH}_2)_4]\text{X} \cdot n\text{H}_2\text{O}$,
where X is a counter anion, Cl^- , FeCl_4^- or SbCl_6^- .

Compound	Formulation	n	Configuration
$\text{FeCl}_3 \cdot \text{SbCl}_5 \cdot 8\text{H}_2\text{O}$	$[\text{FeCl}_2(\text{OH}_2)_4]\text{SbCl}_6 \cdot 4\text{H}_2\text{O}$	4	<i>trans</i> (196)
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	$[\text{FeCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$	2	<i>trans</i> (9)
$\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$	$[\text{FeCl}_2(\text{OH}_2)_4][\text{FeCl}_4]$	0	<i>trans</i> (189)
$\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	$[\text{FeCl}_2(\text{OH}_2)_4][\text{FeCl}_4] \cdot \text{H}_2\text{O}$	1	<i>cis</i> (190)
$\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$	$[\text{FeCl}_2(\text{OH}_2)_4][\text{FeCl}_4] \cdot 3\text{H}_2\text{O}$	3	<i>cis</i>

3. Other ferric compounds

A number of other compounds of Fe(III) were measured, both chloro and aquo complexes, with a view to building up a background of numerical information for comparison with the frozen solution data. The results of these measurements at 90 K and 298 K are given in Table 12. It will be noted that the symmetric O_h and T_d compounds, containing $FeCl_6^{3-}$, $[Fe(OH_2)_6]^{3+}$ and $FeCl_4^-$, have symmetrical electric fields and thus show no quadrupole splitting. This is particularly interesting for the ferric nitrate and perchlorate complexes, which may be written as $Fe(NO_3)_3 \cdot 9H_2O$ and $Fe(ClO_4)_3 \cdot 9H_2O$ and could thus be regarded as analogous to $FeCl_3 \cdot 6H_2O$. However, the analogy is not confirmed by the Mössbauer spectra, so that such conjectural structures as $[Fe(NO_3)_2(OH_2)_4]NO_3 \cdot 5H_2O$ are ruled out by the absence of a quadrupole splitting.

Similarly, the five $FeCl_4^-$ compounds reported in Table 12 seem also to be electrically symmetrical. It is not yet understood why these compounds promote regular tetrahedra, except for the fact that each of the cations is relatively bulky. By contrast, the compounds mentioned earlier, for which Li^+ , Na^+ and $(Ph_4As)^+$ serve as cations, all have distorted $FeCl_4^-$ ions. There are two separate Fe(III) units in compounds 14 and 15, one octahedral and the other tetrahedral as shown by the X-ray structure (197). One would then expect both a doublet and a singlet to appear in the Mössbauer spectrum.

However, only the $FeCl_4^-$ singlet seems to be present. Possibly, the recoil-free fraction of the octahedral unit is so small

TABLE 12. Mössbauer parameters for some Fe(III) chloro and aqua complexes.

Compound	90°K		298 K		Ref.
	δ (mm/sec)	ΔE (mm/sec)	δ (mm/sec)	ΔE (mm/sec)	
1. $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ (78°K)	0.605 0.60	0.0 0.0	0.493 --	0.0 --	(15)
2. $(\text{NH}_4)_2[\text{FeCl}_5(\text{OH}_2)]$	0.580 --	0.381 --	0.475 0.48	0.303 0.30	(19)
3. $\text{K}_2[\text{FeCl}_5(\text{OH}_2)]$	0.593 --	0.200 --	0.452 0.44	0.213 0.16	(19)
4. $\text{Rb}_2[\text{FeCl}_5(\text{OH}_2)]$	--	--	0.47	0.33	
5. $\text{Cs}_2[\text{FeCl}_5(\text{OH}_2)]$	--	--	0.47	0.00	
6. $\text{K}_2[\text{FeF}_5(\text{OH}_2)]$	0.589	0.472	0.463	0.490	
7. <i>cis</i> - $[\text{FeF}_4(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}$	0.561	0.428	0.429	0.401	
8. <i>trans</i> - $[\text{FeCl}_2(\text{OH}_2)_4]\text{SbCl}_6 \cdot 4\text{H}_2\text{O}$	0.618	0.535	0.380	0.708	
9. $[\text{FeCl}(\text{OH}_2)_5](\text{NO}_3)_2$	0.582	0.407	0.400	0.699	
10. $[\text{Fe}(\text{OH}_2)_6](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	0.533 --	0.0 --	0.337 0.35	0.0 --	(16)
11. $[\text{Fe}(\text{OH}_2)_6](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	0.525 0.46	0.0 0.0	0.294 --	0.0 --	(17)
12. $(n\text{-Bu}_4\text{N})[\text{FeCl}_4]$	0.388 --	0.0 --	0.260 0.351	0.0 0.0	(196)
13. <i>trans</i> - $[\text{CoCl}_2(\text{en})_2][\text{FeCl}_4]$	0.378	0.0	0.243	0.0	
14. <i>trans</i> - $[\text{FeCl}_2(\text{DMSO})_4][\text{FeCl}_4]$	0.384	0.0	0.264	0.0	
15. <i>trans</i> - $[\text{FeCl}_2(\text{DPSO})_4][\text{FeCl}_4]$	0.392	0.0	--	--	
16. $[\text{Fe}(\text{CNCH}_3)_6][\text{FeCl}_4]_2$ $\begin{cases} \text{Fe}^{3+} \\ \text{Fe}^{2+} \end{cases}$	0.368 1.330	0.0 0.604	0.252 1.175	0.0 0.299	
17. Mixture of 1 (51.0%) and 13 (49.0%)	-- --	-- --	0.481 0.246	0.0 0.0	

as to prevent it from showing up.

The temperature dependence of the recoil-free fraction was also determined for the solid $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$. The Mössbauer parameters are given in Table 13 and the plot of $\log A$ vs temperature is shown in Figure 9. While the isomer shift and recoil-free fraction decrease monotonically with the increase in temperature, the linewidth at half-maximum changes only slightly, suggesting that an intermediate rate of relaxation is taking place. The Mössbauer temperature was determined to be 192 ± 3 K, for which ν_{max} is equal to 134 ± 2 cm^{-1} . This value of Θ_{m} is smaller than that obtained for $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. It probably reflects the fact that no significant hydrogen bonding exists in crystalline $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$, thus accounting for weaker intermolecular bonds.

The spectrometer's resolution was again checked, this time with a mixture of ferric high-spin compounds which consisted of 51.0% $\text{Co}(\text{NH}_3)_6\text{FeCl}_6$ and 49.0% $[\text{CoCl}_2(\text{en})_2]\text{FeCl}_4$. The Mössbauer spectrum (Spectrum 11) shows two largely overlapping singlets. Nevertheless, the computer analysis with two peaks is better than that with only one peak since the average mean-square residual (AMSR) dropped by more than 15 points in the former case. A lower value of AMSR is usually indicative of a closer fit to the experimental data. Similar isomer shifts were obtained for both the compounds in the mixture and the compounds measured separately. The peak area of $\text{Co}(\text{NH}_3)_6\text{FeCl}_6$ was normalized to account for this compound's higher recoil-free fraction and found equal to $52.9 \pm 4.0\%$, thus agreeing with the known value.

TABLE 13. Mössbauer parameters for solid $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$
at various temperatures.

T (± 0.5) K	δ (± 0.010) mm/sec	Γ (± 0.01) mm/sec	ϵ (± 0.1) %	$A \times 10^{-5} \text{ (a)}$ (± 0.015)	$\log A$ (± 0.002)
90	0.525	1.16	8.2	2.193	5.341
150	0.514	1.14	7.7	2.038	5.309
120	0.496	1.12	6.8	1.960	5.292
135	0.468	1.07	6.6	1.862	5.270
150	0.453	1.10	6.1	1.742	5.241
165	0.434	1.19	5.8	1.641	5.215
180	0.411	1.24	5.2	1.574	5.197

(a) peak area normalized to 24 h counting.

Fig. 9. Plot of peak area vs temperature for solid $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$.

In summary, we can portray the values of isomer shift and quadrupole splitting at low temperatures for the range of monomeric iron(III) chloroaqua compounds as in Table 14.

TABLE 14. Ranges of δ and ΔE values for iron(III)
chloroaqua compounds at 90 K.

Ion	δ (mm/sec)	ΔE (mm/sec)
$[\text{Fe}(\text{OH}_2)_6]^{3+}$	0.53	0.0
$[\text{FeCl}(\text{OH}_2)_5]^{2+}$	0.58	0.4
$[\text{FeCl}_2(\text{OH}_2)_4]^+$ <i>cis</i>	0.58	0.25-0.30
<i>trans</i>	0.5-0.6	0.80-0.87
$[\text{FeCl}_3(\text{OH}_2)_3]$	*	*
$[\text{FeCl}_4(\text{OH}_2)_2]^-$	*	*
$[\text{FeCl}_5(\text{OH}_2)]^{2-}$	0.59	0.2-0.3
$[\text{FeCl}_6]^{3-}$	0.60	0.0
$[\text{FeCl}_4]^-$	0.38-0.40	0.0

*Compounds not available for study.

B. Frozen solutions

As was discussed in the previous section, Mössbauer spectroscopy often yields valuable information concerning the type of bonding in solids. It can also be applied to the study of frozen solutions and numerous authors have used it to study phenomena such as hydrolysis (198), electron exchange (199), magnetic ordering (200), speciation of complexes (134), liquid to glass transition (201), diffusion (100), as well as magnetic relaxation (102). In order that molecular motion be inhibited, the solutions are kept in a frozen state during the measurement of their spectra. Indeed, in solutions which are kept at room temperature, the solutes are relatively free to move around. This motion combined with the great amount of recoil that the Mössbauer atoms experience upon emission of a gamma ray, totally prevents any resonance effect from taking place.

1. Effect of the conditions of freezing

The fast-freezing technique as described in the Experimental part, is most commonly used to remove motional and recoil effects occurring in liquid solutions. Alternatively, the solutes can be adsorbed on a solid matrix, e.g. an ion-exchange resin (58).

It is generally assumed that the freezing process does not perturb the distribution nor the structure of the complexes present in solution at room temperature (202). In order for this assumption to be valid, phenomena such as eutectic formation and crystallization of solvated salts must be avoided. Ruby, Tseng, Cheng and Li (145).

found that a rapid cooling rate of about 10^4 °C/sec, as achieved by the fast-freezing technique, was adequate to prevent segregation of ions in Sn(IV) solutions. However, all the aqueous solutions studied by these authors had relatively high ionic strengths and were thus more likely to form glasses at high freezing rates than were aqueous solutions with low ionic strength (203). Metal ion segregation often occurs in dilute aqueous solutions that are being frozen, even for cooling rates of up to 10^4 °C/sec. There is evidence from Mössbauer (201,204) and EPR (145) studies that the freezing process alters the distribution of metal ions complexes in aqueous solutions having low ionic strength.

In the course of this project, it was found that rapid freezing of Fe(III) solutions of up to 3-4 M ionic strength produced crystallization of the samples. The colour of the frozen solutions varied between white and yellow and all were completely opaque. On the other hand, rapid freezing of solutions with an ionic strength greater than 4 M resulted in the formation of glasses, as was shown by their transparent and vitreous aspect. The addition of up to 40% glycerol to the solutions of low ionic strength produced similar glasses.

2. Dilute perchloric acid solutions

The solutions investigated were prepared as was described in Section II. They all contained sufficient acid to prevent the possible hydrolysis of iron (205). The first series of Mössbauer spectra were

recorded at several temperatures for solutions containing 0.10 M ferric ions dissolved in 1.0 M perchloric acid. The effect of increasing iron(III) concentration was studied at two different temperatures. The parameters obtained from computer analyses of the spectra are listed in Table 15.

a) Comparison with solid compounds

Several factors emerge from these data. For example, the linewidths are approximately ten times greater than those normally obtained in solid compounds. As a consequence, very precise resolution of spectra is difficult and it cannot be claimed, without any doubt, that quadrupole splitting is absent. In the absence of chloride ions, however, only one ferric species is expected in acidic solutions: the octahedral $[\text{Fe}(\text{OH}_2)_6]^{3+}$ cation (206,207). Therefore, there should not be any quadrupole splitting since this cation is of high spin and is cubically symmetric. The observed isomer shifts are also indicative of an octahedral species and the values are fairly close to those obtained for the ferric hexaquo ion present in the solid compounds $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ (see Table 12). This again is in keeping with the belief that only $[\text{Fe}(\text{OH}_2)_6]^{3+}$ is present in dilute perchloric acid solutions.

b) Influence of relaxation

The broad linewidths observed may be the result of various relaxation processes. In the case of a paramagnetic ion, spin-lattice and spin-spin relaxations have to be considered. The former type of

TABLE 15. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 1.0 M HClO₄ at various temperatures.

T (± 0.5 K)	δ (± 0.010 mm/sec)	Γ (± 0.02 mm/sec)	ϵ (± 0.1 %)	A x 10 ⁻⁶ (a) (± 0.012)	log A (± 0.006)
-90.0 b,e)	0.544	3.41	6.8	1.225	6.088
105.0	0.538	3.46	6.4	1.176	6.070
120.0	0.525	3.56	6.5	1.074	6.031
135.0	0.546	3.64	6.1	1.025	6.011
150.0	0.507	3.65	5.9	1.006	6.002
165.0	0.497	3.68	5.7	0.913	5.960
180.0 c)	0.502	3.58	5.1	0.883	5.946
90.0 d,e)	0.506	3.93	10.6	-	-
180.0 d)	0.464	4.08	9.2	-	-

(a) peak area normalized to 24 h counting

(b) Average of six measurements

(c) Average of three measurements

(d) Solutions with an iron concentration of 0.34 M

(e) The magnetic field at the nucleus, H_n , was determined as 580 ± 10 kG

relaxation involves lattice phonons and, as a rule, will slow down with decreasing temperature, thereby increasing the linewidths until magnetic hyperfine splitting occurs. Since the results in Table 15 do not show any significant variation of linewidth upon changing the temperature, the influence of spin-lattice relaxation is probably negligible. The other process, spin-spin relaxation, involves a mutual spin-flip between neighbouring ions i.e. it consists of simultaneous transitions among their eigenstates (102). Because the spins are on neighbouring ions, the relaxation is strongly concentration-dependent and will become slower as the distance between ferric ions increases. Unlike spin-lattice relaxation, spin-spin relaxation is not temperature-dependent and thus, is the most likely mechanism responsible for the broad linewidths observed in the Mössbauer spectra of dilute perchloric acid solutions. Under the condition where the electron spin relaxation time is much longer than the nuclear Larmor precession time ($\tau_s \gg \tau_L$) a non-vanishing hyperfine interaction is present at the nucleus and a hyperfine spectrum with sharp lines is expected (208). The splitting of nuclear energy levels collapses to an average value if $\tau_s \ll \tau_L$ and, as a result, the spectra present a sharp singlet or doublet. According to the shape of the spectra listed in Table 15, the value of the spin-spin relaxation time lies somewhere in between these two extremes i.e. between very short and very long. We can therefore assume that the conditions are such that $\tau_s \ll \tau_L$, which would allow an estimate of the electron relaxation time to be made, i.e. $10^{-8} \text{ sec} \leq \tau_r \leq 10^{-10} \text{ sec}$ (209).

In the case of the 0.34 M Fe(III) frozen solution, τ_r can be estimated from the broad linewidth resulting from the relaxation between the $S_z = \pm 5/2$ electronic levels. For fast relaxation rates, a simple two-level relaxation model (210) gives a broadening, Γ , which is related to the relaxation time:

$$\tau_r = \frac{\hbar \Gamma}{\Delta^2}$$

where $\hbar$ is Planck's constant divided by 2π , Γ represents the full width at half maximum of the broad line, and 2Δ is the splitting between the two levels i.e. the maximum splitting in the Mössbauer spectrum. This treatment yields an approximate relaxation time of 0.62 nsec, to be compared with a spin-spin relaxation time of 0.4 nsec for solid ferric ammonium alum (211) which is known to consist of a ferric hexaquo complex. This qualitative agreement is a further confirmation of the spin-spin relaxation interpretation of Mössbauer line broadening in the frozen solutions.

It is important to point out another characteristic in the Mössbauer spectra of the dilute perchloric acid solutions. The measured linewidths are approximately 50% larger than those obtained with crystalline ferric nitrate or ferric perchlorate enneahydrates. However, according to Morup and Thrane, (209) the average distance between ferric ions in these ferric hexaquo complexes is approximately 7-8 Å. This would mean that the ferric ion distance is even longer in the frozen solutions, possibly as a result of crystallization taking

place during cooling of the solutions. Indeed, even with the fast freezing technique, the dilute absorbers did not solidify as homogeneous glasses. They were white in colour and completely opaque.

c) Effect of concentration and freezing rate

When solutions of higher concentration in ferric ions were studied under the same conditions, the observed overall appearance of their Mössbauer spectra was very similar. Like the spectra of 0.10 M Fe(III) solutions, they had a poorly resolved hyperfine structure at 90 K. A representative spectrum of the more concentrated solution is shown as Spectrum 12. The value of the internal magnetic field, H_h , was almost identical for the concentrated and dilute solutions and established to be 580 ± 10 kG. The lack of precision in this value is due to poor resolution of the lines. Nevertheless, the value is in good agreement with other values reported for the ferric hexaquo species, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, (91,97,98,102,200,209,212-14).

The solutions of 0.10 M in ferric ions were frozen under two different conditions: fast freezing and gradual freezing. For these two conditions, the spectra measured at 90 K showed only little difference. The linewidths did not vary by more than 5% and the isomer shifts were within 0.03 mm/sec. A similar behaviour was observed for solutions with 0.34 M ferric ions. The fact that the rate of freezing had virtually no effect on the Mössbauer spectra is not unexpected in this case since crystallization takes place at a much faster rate than the actual freezing of the bulk of the solution

(5-10 sec). What is interesting, is the comparison between the 90 K spectrum of the dilute (0.10 M) and the less dilute (0.34 M) solution measured after fast freezing. They both feature a broad absorption line and a poorly resolved hyperfine structure. Here the resemblance ends. The linewidth is approximately 20% larger for the 0.34 M frozen solution and the hyperfine structure is slightly more visible. This is contrary to what theory predicts when spin-spin interactions are the main source of relaxation (209). One would expect a smaller linewidth for the central peak and a smaller intensity for the hyperfine peaks for increasing concentration of ferric ions, as a result of the decreasing distance between them. The observed behaviour is not fully understood. Nevertheless, a few possible explanations may be examined:

1. some other relaxation mechanism may be at work, namely spin-lattice. It is unlikely, however, since this mechanism is not concentration dependent.
2. different ferric complexes with different relaxation times may be formed upon freezing of the solutions. There was enough acid in the solutions to make the ferric hexaquo complex the only probable one.
3. crystallization of the solutions may be producing variable-size clusters of ferric ions.

The third alternative is more probable because it implies a random variation of the ferric ion concentration. Even though the Mössbauer spectra of the dilute and less dilute solutions are different,

their dissimilarities are not in proportion to their difference in initial concentrations. The relaxation times, which can be estimated from the measured linewidths, differ by less than 20%. Similarly, Ohya and Ono (200) have found that variation of the initial concentration by as much as 80 times had almost no effect on the relaxation time. This fact suggests that regions of almost constant concentration are dispersed in the frozen solution. With regards to the 0.34 M solution, the freezing process could have isolated the ferric ions into regions where the Fe-Fe distance is greater on the average than than existing in the 0.10 M solution. This would insure a slightly longer relaxation time, thus resulting in a more resolved hyperfine structure.

d) Lattice dynamics

The Debye temperature of the lattice, also called the Mössbauer temperature, has been calculated from the temperature dependence of the total area of the absorption line for the 0.10 M ferric perchlorate solution. A valid approximation used here is that the peak area, A , is directly proportional to the recoilless fraction (116). After normalization of the peak area to a 24-hour counting period, a plot of $\log A$ versus temperature yields a relatively straight line from which $\Theta_M = 192 \pm 6$ K. The data are listed in Table 15 and a plot of these is presented in Figure 10. The Mössbauer temperature value is in good agreement with the value ($\Theta_M = 185$ K) obtained by Mørup and Thrane (209) for the solid $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. This solid compound

Fig. 10. Plot of peak area vs temperature for 0.10 M Fe(III) in 1.0 M HClO₄ frozen solution.

and our frozen ferric perchlorate solution both feature the $[\text{Fe}(\text{OH}_2)_6]^{3+}$ ion and thus, the calculated Θ_M should be characteristic of this ferric complex. As was discussed previously, Mössbauer nuclei are not in a completely static environment, but rather are vibrating in the lattice sites. The mode of these vibrations depends on the nature of the chemical bonding between the Mössbauer atom and the lattice. Therefore, the Mössbauer temperature will reflect the strength of the intermolecular forces in the absorber. The maximum frequency of these vibrations can be calculated, and a value of $\nu_{\text{max}} = 133 \pm 4 \text{ cm}^{-1}$ has been found for the frozen solution. This frequency value is well into the range where the frequencies of lattice vibrations have been found in other ferric-aquo complexes (189,194).

Finally, the melting point of the frozen solutions, both dilute and less dilute, was estimated as $195 \pm 5 \text{ K}$. The estimate was done by taking the frozen solution outside the cryostat and looking for signs of thawing of the frozen material as the sample holder was slowly warmed up. The value of 195 K is consistent with the observed change in the Mössbauer effect of the spectra measured both below and above this temperature. The recoilless fraction decreased by approximately half its value when the temperature was raised from 180 K to 190 K, and it decreased to virtually zero when the temperature reached 200 K.

3. Concentrated perchloric acid solutions

The Mössbauer spectra of dilute Fe(III) solutions in concentrated perchloric acid were measured at 90 K. Several ferric ion concentrations were investigated under fast and slow conditions of freezing. The Mössbauer parameters for these frozen solutions are presented in Table 10. The solutions having concentrations of 0.10 M in ferric ion were also studied at different temperatures and the results are listed in Table 17.

a) Effect of concentration and freezing rate

The rapid freezing of the solutions with ferric ion concentrations of 0.04 M and 0.08 M produced a transparent glass striated by cracks. Each of these solutions gave a Mössbauer spectrum for which a faint, yet still visible, hyperfine splitting was observed. The shape of the spectra appeared to be independent of the rate of freezing and the mean average value of the internal field was determined to be 572 ± 5 kG. Typical spectra for the fast and slow freezing rate are presented in Spectrum 13 and 14, respectively. As expected the spectra show the presence of only one magnetically split species which can be reasonably assumed to be $[\text{Fe}(\text{OH}_2)_6]^{3+}$. In addition, a Fe(II) doublet is seen present in small amounts. A recent ^{35}Cl NMR relaxation study (215) examining the interaction of perchlorate ions with ferric ions in aqueous solutions showed that there were no significant interactions of the perchlorate anions with the metallic cations for ferric ion concentrations up to 0.5 M. The same conclusion was reached in a

TABLE 16. Mössbauer parameters for dilute Fe(III) frozen solutions in 9.4 M HClO₄ at 90 K.

[Fe ³⁺] (M)	δ (± 0.02 mm/sec)	ϵ (± 0.1 %)	H_n (± 5 kG)	Conditions of freezing
(a) 0.04	0.52	0.5	567	fast
(a) 0.08	0.52	1.5	574	fast
(a) 0.08	0.50	1.2	571	fast
(a) 0.08	0.55	1.4	570	slow
0.08	0.53	2.9	575	fast
0.08	0.51	2.6	568	slow
0.08	(b) 0.426 ± 0.007	4.2	none	fast, after 18 hours, at 250 K
(a),(c) 0.08	0.49	1.6	579	fast
(a) 0.10	(d) 0.531 ± 0.025	2.1	none	fast
(a) 0.10	0.54	1.9	575	gradual
(a) 0.10	0.54	1.8	574	slow

(a) Smaller sample holder

(b) Full width at half-maximum, Γ , is 1.54 mm/sec

(c) Ferric ions dissolved in 4.7 M HClO₄

(d) $\Gamma = 3.53$ mm/sec

TABLE 17. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 9.4 M HClO₄ at various temperatures.

T (± 0.5 K)	δ (± 0.025 mm/sec)	Γ (± 0.05 mm/sec)	ϵ (± 0.1 %)	A x 10 ⁻⁵ (a) (± 0.014)	log A (± 0.002)
90 ^{b)}	0.537	3.58	2.1	7.261	5.861
120	0.510	3.48	1.9	6.457	5.810
150	0.482	3.55	1.9	5.916	5.772
180 ^{b)}	0.455	3.69	2.0	5.202	5.716
200	0.426	3.80	1.8	4.898	5.690

(a) peak area normalized to 24 h counting

(b) Mean average of three different solutions

Raman spectroscopy study of $\text{Fe}(\text{ClO}_4)_3$ solutions for which the ferric ion concentrations ranged from 0.3 to 2.0 M (51). Moreover, an investigation of fairly concentrated ferric perchlorate solutions (216) using the X-ray scattering technique, showed very little presence of an outer-sphere Fe-ClO_4 complex. Therefore, the solutions containing ferric ions in concentrated perchloric acid should contain solely the octahedral hexaquo ferric complex. This is supported both by the observed isomer shift and internal field values which are typical of that complex.

On the other hand, Mössbauer spectra for the solution with a higher ferric ion concentration, 0.10 M, were dependent on the freezing rate. When the solution is frozen gradually or very slowly, its physical aspect is very similar to the frozen solution resulting from fast freezing of the more dilute solutions, i.e. a vitreous material with a multitude of tiny cracks. The Mössbauer spectra associated with these features all present a magnetic splitting. The value of the internal field is again characteristic of the ferric hexaquo species. By contrast, the transparent and colourless material produced by fast freezing of the solution did not show any magnetic splitting. However, the single peak visible in Spectrum 15 is still broadened by relaxation. In these fast frozen solutions, the ferric ions appear to be slightly closer to one another, thus having a shorter spin-spin relaxation time and causing the disappearance of the hyperfine splitting (217). This behaviour is not unexpected as the ferric ion concentration for these solutions is at least 25%

greater than the other solutions studied in Table 16.

A solution having a ferric ion concentration of 0.08 M was rapidly frozen in liquid nitrogen, heated slowly up to 250 K and kept at this temperature for 18 hours, then, rapidly frozen in liquid nitrogen, and finally, the spectrum measured at 90 K. The process was repeated twice, each time giving the same result. The hyperfine splitting was no longer visible, the six-line pattern having coalesced into a single, sharp peak (see Spectrum 16). The two small lines on both sides of this peak are due to some Fe(II) present. The isomer shift of the central peak, although lower than the value for ferric hexaquo ion, is characteristic of a Fe(III) species.

The molecular motion of the this frozen solution was studied in order to identify the complex or complexes which were present. A plot of $\log A$ versus temperature is shown in Figure 11 and the data are presented in Table 18. The least squares fitting to a straight line gave a Mössbauer temperature, θ_M , of 209 ± 7 K. This value, which is approximately 10% greater than that obtained for crystalline $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$, indicates stronger intermolecular bonds in the frozen solution. Moreover, the linewidth value of 1.54 mm/sec observed for the ferric peak suggests the presence of a fast relaxation mechanism. This faster relaxation is most likely due to a shorter Fe-Fe distance which would mean that the sample treatment has altered the distance of closest approach. It has also, apparently, altered the structure of the ferric ion complex according to the decrease in isomer shift value.

TABLE 18. Mössbauer parameters for 0.08 M Fe(III) frozen solutions in 1.0 M HClO₄.

T (± 0.5 K)	δ' (± 0.007 mm/sec)	Γ (± 0.01 mm/sec)	ϵ ($\pm 0.04\%$)	$A \times 10^{-6}$ (a) (± 0.013)	log A (± 0.003)
90 ^{b)}	0.426	1.54	4.2	1.026	6.011
120	0.405	1.43	3.9	0.905	5.960
150	0.397	1.34	3.4	0.843	5.926
180	0.381	1.28	3.0	0.769	5.887

(a) peak area normalized to 24 h counting

(b) Average of two measurements

Fig. 11. Plot of peak area vs temperature for 0.08 M Fe(III) in 9.4 M HClO₄ frozen solution.

The more negative isomer shift strongly suggests a more covalent complex and, assuming only one type of ligand, the presence of tetrahedral aquo complex, $[\text{Fe}(\text{OH}_2)_4]^{3+}$, could explain the measured parameters. However, this hypothesis is unlikely, even though metal ions with d^5 electronic configuration have zero crystal field stabilization energy in either O_h to T_d symmetry. The bulk of evidence confirms that metal ions assume an octahedron structure whenever oxygen-donor ligands are involved. Another hypothesis would be that the partially melted solution at 250 K underwent restructuration upon second freezing and produced a type of "polymeric Fe(III) unit" with water molecule bridges. This kind of bonding would increase the effective $4s$ electron density at the iron nucleus and explain the observed isomer shift. It would also be consistent with the molecular dynamics results which indicate stronger intermolecular bonding than that of ferric hexaquo monomolecular complex. This second hypothesis is fairly reasonable considering the previous thermal history of the sample.

The 0.08 M ferric solution was further studied in 4.7 M perchloric acid, and the Mössbauer spectrum, measured at 90 K, is shown in Spectrum 17. From this experiment, it can be seen that there is no significant difference between the concentrated and the more dilute acid solutions. Thus, it appears that ferric ion concentration is a more important factor than acid concentration in determining the shape of the Mössbauer spectra.

b) Effect of temperature

The Mössbauer spectrum of the 0.10 M ferric solution was measured at five different temperatures. As can be seen from Table 17 all spectra feature a single, broad absorption line. The measured isomer shift decreases regularly with the increase in temperature. This change in isomer shift value has the appropriate magnitude expected from classical second-order Doppler effect and amounts to ca 0.001 mm/sec per degree. The large linewidth values indicate the ferric ions are undergoing an intermediate rate of relaxation. Each ferric ion is not distant enough from its nearest neighbours in order to produce the characteristic six-line magnetic splitting. However, the hyperfine structure would likely be made visible by further cooling of the frozen solution to liquid helium temperature since then, the spin relaxation time would be sufficiently long to present a static magnetic field at the iron nucleus.

The molecular motion of the 0.10 M frozen solution was studied by integrating the area under the resonance line of the Mössbauer spectrum at each temperature. A plot of $\log A$ versus temperature is shown in Figure 12. The Mössbauer temperature, Θ_M , calculated from the slope was found equal to 195 ± 3 K. The maximum frequency of the Mössbauer nuclei vibrating in the lattice was, $\nu_{max} = 135 \pm 3 \text{ cm}^{-1}$. These values of Θ_M and ν_{max} are very similar to the values obtained for the dilute perchloric acid solution. This fact gives further support to the conclusion that $[\text{Fe}(\text{OH}_2)_6]^{3+}$ is present in both the dilute and concentrated perchloric acid solutions.

Fig. 12. Plot of peak area vs temperature for 0.10 M Fe(III) in 9.4 M HClO₄ frozen solution.

4. Dilute hydrochloric acid solutions

a) Effect of freezing rate

Solutions containing 0.10 M Fe(III) ions dissolved in 1.0 M HCl were frozen under various conditions and their Mössbauer spectra measured at several temperatures. The Mössbauer parameters derived from computer analysis of their spectra are listed in Tables 19 and 20. A separate parameter, R, defined in Figure 13, was used to estimate the degree of resolution of the magnetic hyperfine splitting in each spectrum. This parameter expresses the intensity of absorption in the magnetically split peaks compared with the absorption in the unsplit central peak. Note that this is the inverse of the parameter used by Ohya and Ōno (200).

Fig. 13. Mössbauer spectrum of 0.10 M Fe(III) in 1.0 M HCl at 90 K indicating definition of parameter R.

TABLE 19. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 1.0 M HCl using different freezing rates.

T (± 0.5) K	δ (± 0.006) mm/sec	Γ (± 0.05) mm/sec	ϵ^a (± 0.1) %	H_n (± 5) kG	Conditions of freezing	R
90 ^{b)}	-	4.66	4.2	581,566,555,518	fast	0.85
90 ^{b)}	-	4.74	4.0	582,567,558,520	slow	0.82
90	0.557	2.41	5.1	545	gradual	0.25
150	0.542	2.24	4.4	-	gradual	-
180	0.533	1.26	5.5	-	gradual	-
90 ^{c)d)}	-	4.80	2.4	576,550,521	gradual	0.89
150 ^{d)}	0.535	2.33	2.8	-	gradual	-
180 ^{d)}	0.520	1.20	4.9	-	gradual	-

a) These values refer to the widths and recoil-free fraction of each central peak

b) Average of five different measurements

c) Average of two measurements

d) Sample partially covered with aluminum disk

TABLE 20. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 1.0 M HCl at various temperatures (fast freezing).

T (± 0.5) K	δ (± 0.015) mm/sec	Γ (± 0.05) mm/sec	ϵ (± 0.1) %	H_n (± 5) kG	R
90	-	4.71	4.3	583,565,556,516	0.83
120	0.556	4.48	4.0	541	0.54
150	0.540	2.68	3.1	-	-
180	0.518	1.38	7.6	-	-
150 ^{a)}	0.522	2.80	3.8	543	0.35
120 ^{a)}	0.553	4.36	4.9	536	0.59
90 ^{a)}	0.550	4.69	5.2	534	0.74

a) Spectra measured during the cooling down cycle after 20 hours at 250 K.

At both the fast and slow freezing rates, the frozen samples were yellowish in colour, opaque and without any cracks. As can be seen from Table 18, similar spectral parameters were obtained for the two rates of freezing. The measured degrees of resolution of magnetic hfs were small and almost identical, thus indicating that solvent crystallization probably occurred in each case. In this respect, the frozen HCl solutions exhibited the same behaviour as the dilute perchloric acid solutions in that they were independent of the freezing rate. The presence of magnetic hfs in the former case indicate a longer relaxation time than that observed in the latter case. This suggests that more than one ferric complex was present in the HCl solutions. As pointed out by Marups and Knudsen (103), longer relaxation times should exist when neighbouring ions have different energy splittings due to a difference in their crystal field interactions.

Fourier transformation of the original 90 K spectrum obtained with a fast freezing rate clearly showed the presence of four different ferric species (Spectrum 18). Following the estimation of the magnitude of each internal field, the four species have been tentatively assigned the following structures: $[\text{Fe}(\text{OH}_2)_6]^{3+}$, $[\text{FeCl}(\text{OH}_2)_5]^{2+}$, $[\text{FeCl}_2(\text{OH}_2)_4]^+$, and $[\text{FeCl}_4(\text{OH}_2)_2]^-$. This is based on the assumption that the value of the internal field for the ferric hexaquo complex would decrease approximately linearly with each subsequent substitution of a water ligand by a chloride ligand. A list of calculated values of magnetic fields is presented in Table 21. Such a correlation has already been established in the case of ferric fluoride solutions (134).

TABLE 21. Calculated[†] values for internal magnetic field of iron(III) chloroaqua complexes.

Ion	H _n (kGauss)
Fe(OH ₂) ₆ ³⁺	580
FeCl(OH ₂) ₅ ²⁺	564
FeCl ₂ (OH ₂) ₄ ⁺	549
FeCl ₃ (OH ₂) ₃	534
FeCl ₄ (OH ₂) ₂ ⁻	518
FeCl ₅ (OH ₂) ²⁻	502
FeCl ₆ ³⁻	487
FeCl ₄ ⁻	470

[†]Calculations based on assumption of linear decrease of magnetic field upon chloride complexation.

Furthermore, a detailed Raman study made by Sharma (52) indicated the presence of monochloro, dichloro and tetrachloro complexes in a 3 M HCl solution of 1.2 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. However, this study did not specify whether the tetrachloro complex was tetrahedral or octahedral.

It is interesting to note that the species $[\text{FeCl}_3(\text{OH}_2)_3]$ does not seem to be present in the fast frozen solution. From calculations of species distribution using the equilibrium constants measured by Lister and Rivington (37) and Marcus (55), one would expect to find approximately 5% of this species at 25 °C. However it is likely that a shift of room temperature equilibria would occur during the freezing process. The absence of the neutral trichloro complex may be explained by the well-known *trans* effect. This effect, as described by Basolo and Pearson (218), is a kinetic phenomenon through which a ligand influences the rate of exchange of the group *trans* to itself. Therefore, after substitution of one water molecule by a chloride ligand in ferric hexaquo complex, there would be greater tendency to form a *trans*-dichloro than a *cis*-dichloro complex. Further substitution would not likely stop at three Cl^- ligands due to the *trans* effect and the complex *trans*- $[\text{FeCl}_4(\text{OH}_2)_2]^-$ would result.

There was a significant amount of ferric tetrachloride in the frozen solution although its presence was not predicted by the calculations. After computer analysis of the Mössbauer spectrum, the composition of the frozen solution was estimated as 18% hexaquo, 50%

monochloro, 20% dichloro, and 12% tetrachloro ferric complexes. Both the calculations and experimental results indicate that the bulk of the solution consists of mono and dichloro complexes. Moreover, the tetrachloro complex has unambiguous octahedral coordination at the metal ion since a tetrahedral species would show a much smaller magnetic field. As was pointed out in the Introduction, controversy still exists about the true structure of ferric tetrachloride in dilute acidic solutions. If one favours the hypothesis that a rapid equilibrium exists between $[\text{FeCl}_4(\text{OH}_2)_2]^-$ and FeCl_4^- in aqueous solutions (91), it follows that the equilibrium is markedly displaced towards the hexacoordinate anion during the freezing process since this was the only structure detected in the Mössbauer spectrum.

The 0.10 M Fe(III) solutions were also studied after gradual freezing. Following this process, Mössbauer spectra were observed where the magnetic splitting was barely visible (Spectrum 19) and the resolution parameter had decreased by a factor of three. Furthermore, the measured absorption intensities were significantly higher. These results can be related to the physical appearance of the frozen solutions which were completely opaque with a darker yellow area in the center of the sample. It appears that the process of gradual freezing had concentrated the ferric ions in the solution. Consequently, there should also exist regions of comparatively lower Fe(III) concentration within the sample.

In order to test this hypothesis, solutions of ferric chloride in dilute HCl were frozen gradually down to 90 K. A small aluminum disk,

approximately 2 mm in thickness, was then centered on the outside of the sample holder so that it covered about one-third of the surface area. Next, Mössbauer spectra were measured at 90 K (see Spectrum 20) and at two higher temperatures. The same results were obtained in a duplicate run and thus, were not likely an artifact of the procedure. The extent of the observed magnetic splitting was similar to that of the fast frozen solutions while the recoil-free fractions were reduced to about half of their previous values. This suggests that ferric ions found in the periphery of the gradually frozen samples have a concentration similar to those in the bulk of the fast frozen solutions. It follows that the Fe(III) concentration in the central portion of the gradually frozen solutions should be higher. Thus, in the absence of an aluminum disk, the Mössbauer parameters obtained for the gradually frozen solutions probably represent a combination of the parameters observed for the three chloro-ferric species observed in the fast frozen solutions. In the former case, computer analysis could resolve only one magnetic splitting with a value of $H_n = 545$ kG. However, when these solutions were covered with an aluminum disk, the Mössbauer spectrum showed clearly the presence of three magnetically split species after Fourier transformation. These three species are not the same as those observed in either fast or slow frozen solutions. The measured internal field values could be assigned to the following ions: $[\text{Fe}(\text{OH}_2)_6]^{3+}$, $[\text{FeCl}_2(\text{OH}_2)_4]^+$, and $[\text{FeCl}_4(\text{OH}_2)_2]^-$ in the proportion 18%, 60% and 22%, respectively. The amount of the third species is still approximately the same as that found in fast frozen solutions

but the dichloro complex has now become the main complex and the monochloro complex could not be detected. As mentioned earlier, the absence of odd numbers of Cl^- substituents may be explained by the *trans* effect. The slower rate of freezing has likely shifted the complex ferric chloride equilibrium and, thus, has altered the relative distribution of species in solution. In an earlier X-ray study, Lind (9a) had concluded that the dichloro species should be the predominant species, in line with the structure found in crystalline $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

b) Effect of temperature

The temperature of 0.10 M Fe(III) solution, which had previously been fast frozen, was slowly raised and Mössbauer spectra were measured at various temperatures up to 180 K (see Table 20) after which the temperature was raised to 250 K and kept there for approximately 20 hours. The temperature was then lowered and Mössbauer spectra measured at three different temperatures during the cooling down cycle.

The 90 K spectrum in the warming up cycle again showed the presence of monochloro, dichloro and tetrachloro complexes. However, the 90 K spectrum measured during the cooling down cycle showed a single hyperfine splitting which had an intermediate internal field value and a measured isomer shift characteristic of a ferric high-spin complex. These results may be explained in one of two ways. Either the three species have rearranged their structures into a single one or, less likely, the separate hyperfine structures are no longer discernible because of increased spin-spin relaxation due to concentration of the sample (102). The fact that the Mössbauer spectrum

still showed only one magnetic splitting after Fourier transformation (Spectrum 21) tends to support the first hypothesis. The internal field value thus points to the neutral complex $[\text{FeCl}_3(\text{OH}_2)_3]$ as the species responsible for the observed hfs. This would represent an interesting transformation from the combination of three ferric chloride complexes to a single complex upon heating the frozen solutions.

5. Concentrated hydrochloric acid solutions

a) Effect of acid concentration

The Mössbauer spectra of 0.10 M Fe(III) solutions in varying concentrations of hydrochloric acid were measured at 90 K. The Fourier transformed spectra for these frozen solutions between 2.0 and 12.0 M HCl are grouped together in Fig. 14 (plot in Fig. 14a) and the Mössbauer parameters derived from these are listed in Tables 22 and 23.

Up to and including 4.0 M HCl, the frozen solutions were yellow in colour and completely opaque as a result of crystallization whereas the solutions between 6.0 and 12.0 M HCl solidified as a transparent, glassy material. Although all the solutions were yellow, the 12.0 M HCl was much darker than the others. Concurrently, the hfs resolution parameter increased steadily from 1.0 to 6.0 M and decreased thereafter until the 12.0 M HCl concentration was reached.

The results obtained may be explained if we consider these solutions as a two-component system, $H_2O - HCl$, in which the ferric salt is an added microcomponent acting as a probe (100). Upon crystallization the ferric ions are concentrated in a separate phase and the magnetic hfs disappears as a result of the ferric ions being closer together and undergoing faster spin-spin relaxation. Thus, hyperfine splitting should be more apparent in solutions which have a greater tendency of forming a glass upon cooling i.e. when these solutions approach the region of eutectic composition. As

TABLE 22. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in HCl of varying concentrations at 90 K.

[HCl] (M)	ϵ ($\pm 0.1\%$)	H_n (± 5 kG)					R
		a	b	c	d	e	
2.0	2.8	564	550	537	-	-	1.2
4.0	2.7	568	547	535	-	474	1.3
6.0	1.6	568	549	538	-	469	2.1
9.4	2.4	-	543	-	522	478	1.9
12.0	2.2	-	545	-	516	478	1.4

(a-e) have been assigned the structures $[\text{FeCl}(\text{OH}_2)_5]^{2+}$, $[\text{FeCl}_2(\text{OH}_2)_4]^+$, $[\text{FeCl}_3(\text{OH}_2)_3]$, $[\text{FeCl}_4(\text{OH}_2)_2]^-$ and $[\text{FeCl}_5]^-$, respectively.

TABLE 23. Relative distribution (%) of ferric species for 0.10 M Fe(III) in HCl of varying concentrations at 90 K.

Species	[HCl] (M)				
	2.0	4.0	6.0	9.4	12.0
$\text{FeCl}(\text{OH}_2)_5^{2+}$	26	14	12	-	-
$\text{FeCl}_2(\text{OH}_2)_4^+$	41	52	49	42	28
$\text{FeCl}_3(\text{OH}_2)_3$	33	23	19	-	-
$\text{FeCl}_4(\text{OH}_2)_2^-$	-	-	-	36	45
FeCl_4^-	-	11	20	22	27

Fig. 14. Mössbauer spectra of 0.10 M Fe(III) in HCl (2.0 - 12.0 M) at 90 K.

Fig. 14a. Plot of distribution of ferric chloride complexes in HCl (1.0 - 12.0 M).

this region is located between 7.5 and 8.6 M HCl for the system $\text{H}_2\text{O-HCl}$ (140), the prediction that the resolution parameter would be smaller on either side of this range is thus confirmed experimentally.

Unlike the 1.0 M HCl solution, the 2.0 M and 4.0 M HCl solutions contained the species $[\text{FeCl}_3(\text{OH}_2)_3]$. No octahedral tetrachloro or hexaquo complexes were detected. In each of these solutions, $[\text{FeCl}_2(\text{OH}_2)_4]^+$ was the predominant complex. In addition the 4.0 M HCl solution showed the presence of approximately 10% tetrahedral FeCl_4^- . Although the measured composition of these solutions does not exactly match the distribution calculated from equilibrium constants, it gives a reasonable estimate of which species are present at 90 K. An NMR study of ferric chloride solutions done in this department (218) have indicated that the mono- and dichloro ferric complexes were important components of these solutions at room temperature. The width of the measured signal further suggested that the dichloro complex probably had D_{4h} symmetry, i.e. *trans*- $\text{FeCl}_2(\text{OH}_2)_4^+$. Also on the basis of linewidth values, the presence of *fac*- $\text{FeCl}_3(\text{OH}_2)_3$ was ruled out although a small amount of *mer*- $\text{FeCl}_3(\text{OH}_2)_3$ could have accounted for the observed results.

As pointed out in the Introduction, only a few Mössbauer studies have dealt with ferric chloride solutions and these were unable to distinguish more than two ferric species in this range of HCl concentrations. From the Mössbauer spectrum of 0.10 M Fe(III) in 4.0 M HCl, Plachinda and Makarov (91) measured two magnetic splittings. Although these authors did not attempt to determine the species identification nor their relative distribution the quoted H_n values indicate the presence of mono- and dichloro ferric complexes.

An interesting comparison can be made between the 4.0 M

and 6.0 M HCl solutions. Despite the fact that the former appeared to have crystallized while the latter had formed a glass, the same ferric species were found in each solution. The relative distribution of mono-, di- and trichloro ferric complexes was also similar but the amount of FeCl_4^- had almost doubled in the 6.0 M solution. For this solution, the higher acidity or chloride concentration is probably responsible for shifting the ferric chloride equilibrium towards this anion although the influence of the freezing process cannot be excluded.

With ever increasing HCl concentration, the amount of mono- and trichloro ferric complexes decreased gradually and these complexes had completely disappeared in the 9.4 M solution. They were replaced by a new species, $[\text{FeCl}_4(\text{OH}_2)_2]^-$, which accounted for more than a third of the total absorption. A similar situation was observed in the 12.0 M HCl solution in which the octahedral ferric tetrachloride made up approximately half of the total.

These findings concerning the composition of ferric chloride solutions at high HCl concentrations contradict the view, which is widely held in the literature, that only tetrahedral FeCl_4^- exists in these solutions (33,35,36,76,78,79) and may be explained in the following manner. The literature interpretation has relied partially on similarities between UV spectra of solid tetrachloroferrate(III) salts and ferric chloride solutions, and partially on the ease of extraction of FeCl_4^- from aqueous solutions by organic solvents. Since Fe(III) ions have a d^5 electronic configuration and a zero crystal field stabilization energy between octahedral and tetrahedral symmetry, these two structures are probably not distinguishable by UV spectroscopy. Moreover, as was discussed in the Introduction, a highly favourable distribution coefficient of the tetrahedral

anion may account for its successful extraction.

Some authors have analysed their results in terms of both the octahedral and tetrahedral species. On the basis of an X-ray study of concentrated ferric chloride solutions (ca 5 M) in both water and 6 M HCl, Brady, Robin and Varimbi (79) concluded that the neutral water solution contained mainly $[\text{FeCl}_4(\text{OH}_2)_2]^-$ ions while a significant amount of FeCl_4^- was also present in the acidic solution. A recent X-ray study (219) indicated the presence of $[\text{FeCl}_2(\text{OH}_2)_4]^+$ in less concentrated ferric chloride solutions (ca 2 M) but did not find any octahedral ferric tetrachloride. Consequently, this project represents the first attempt to measure quantitatively the distribution of ferric chloride species in dilute solutions (0.1 M) of variable acid concentrations.

b) Effect of temperature and freezing rate

The Mössbauer spectra of frozen solutions between 2.0 and 12.0 M HCl were measured at 180 K and their parameters are presented in Table 24. The 9.4 M HCl solution was also measured at various temperatures after both slow and fast freezing and the Mössbauer parameters are given in Table 25.

The measured linewidths, which remained almost identical up to 6.0 M HCl, decreased by about 15% at 9.4 M and by 20% at 12.0 M HCl. However, the most significant aspect was the steady decline of the recoil-free fraction up to and including 6.0 M HCl. The increase observed in the 9.4 M solution, followed by a decrease at 12.0 M, suggests a direct correlation with the formation of a glass in the

TABLE 24. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in HCl of varying concentrations at 180 K.

[HCl] (M)	δ $\left(\pm 0.006\right)$ mm/sec	Γ $\left(\pm 0.03\right)$ mm/sec	ϵ $(\pm 0.1\%)$
2.0	0.549	1.34	4.5
4.0	0.558	1.34	3.9
6.0	0.550	1.36	2.0
9.4	0.542	1.16	3.2
12.0	0.570	1.07	2.7

TABLE 25. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 9.4 M HCl at various temperatures (slow and fast freezing).

T (± 0.5 K)	δ (± 0.004 mm/sec)	Γ (± 0.03 mm/sec)	ϵ ($\pm 0.1\%$)	$A \times 10^{-5a)}$ (± 0.012)	log A (± 0.003)
90	0.557	1.18	3.8	5.873	5.769
120	0.560	1.20	4.0	5.224	5.718
150	0.552	1.04	3.6	5.057	5.704
180	0.549	0.91	3.3	4.228	5.626
210	0.488	1.15	1.4	4.011	5.603
90 ^{b)}	-	-	2.4	15.320	6.185
150 ^{b)}	0.536	1.45	1.7	9.996	5.998
180 ^{b)}	0.542	1.16	3.2	9.722	5.960
210 ^{b)}	0.497	1.06	1.8	7.123	5.853

a) peak area normalized to 24 h counting

b) Spectra measured after fast freezing

H₂O-HCl phase diagram. The ferric chloride solutions were still frozen at 180 K and the variation of spectral parameters with increase in acidity was similar to that observed at 90 K. However, it was not possible to identify positively which species was or were present at 180 K: A single peak was observed for every solution even after Fourier transformation of the Mössbauer spectra. In each case, the isomer shifts were indicative of an octahedral ferric complex although no trend appeared among the values.

Unlike the fast freezing rate which gave a transparent glass, slow freezing of the 9.4 M HCl solution produced a yellow, opaque solid. The Mössbauer spectrum associated with the latter conditions was also strikingly different, showing a complete disappearance of the hyperfine splitting. However, the single peak observed at 90 K appeared to have a quadrupole splitting after Fourier transformation and the measured isomer shift was characteristic of an octahedral ferric species. At any rate, this splitting is considered small (≤ 0.25 mm/sec) and rules out the possibility of being associated with the ion *trans*-[FeCl₂(OH₂)₄]⁺. According to the δ and ΔE ranges outlined in Table 14, the Mössbauer spectrum could be assigned one of four structures: [FeCl(OH₂)₅]²⁺, *cis*-[FeCl₂(OH₂)₄]⁺, [FeCl₃(OH₂)₃], or *cis*-[FeCl₄(OH₂)₂]⁻, although the first one is an unlikely candidate in a concentrated HCl solution. Any of the last three species, or combination of these, agree with the measured parameters and further identification was not possible based on the data available.

A gradual decrease in the recoil-free fraction was observed when the temperature was raised. The log of the peak area was plotted against the temperature for the slowly frozen solutions as well as for the fast frozen solutions to allow comparison between the two cooling rates (see Figure 15). In the first case, the Mössbauer temperature was determined to be 205 ± 8 K and, in the second case, a value of $\theta_m = 149 \pm 7$ K was found. The higher θ_m value measured suggests again that crystallization occurred using the slow freezing rate, thus creating stronger intermolecular bonding. Nevertheless, each value was lower than that obtained for crystalline $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ where the octahedral iron units are linked together through hydrogen bonding.

Fig. 15. Plot of peak area vs temperature for 0.10M Fe(III) in 9.4 M HCl (slow and fast freezing).

6. Mixed acid solutions

a) Dilute acid

i) Effect of chloride concentration

Solutions of 0.10 M Fe(III) ions in 1.0 M HClO₄ were mixed in various proportions with solutions of 0.10 M Fe(III) ions in 1.0 M HCl and the new solutions were frozen rapidly in liquid nitrogen. Their Mössbauer spectra were measured at 90 K and the analysed parameters are listed in Table 26. The Fourier transformed spectra for these solutions are shown in Figure 16 and the measured species distributions are presented in Table 27 (plot in Figure 16a).

Rapid freezing of these solutions produced a crystallized, opaque solid, as may be expected from their low ionic strengths. The white colour observed for the 1.0 M HClO₄ frozen solution was replaced by a yellow colour which gradually deepened as the chloride concentration was increased. This change, which is paralleled by a higher resolution of hyperfine splitting (see Figure 16), is due to the ever increasing amount of ferric chloride species formed in the solutions. For each concentration, the Mössbauer spectrum was analysed using one central peak to allow easy comparison with the lower end-member of the series. The initial decline in linewidth levelled off at 0.60 M chloride concentration and remained approximately constant up to 1.0 M. The decrease in the recoil-free fraction was, however, more pronounced. This reflects the greater proportion of Mössbauer atoms undergoing fast spin relaxation as [Cl]⁻ was increased.

TABLE 26. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 1.0 M $\text{H}(\text{Cl}, \text{ClO}_4)$ at 90 K.

$[\text{Cl}^-]$ (M)	δ $\left(\pm 0.010 \right)$ mm/sec	Γ $\left(\pm 0.02 \right)$ mm/sec	ϵ ($\pm 0.1\%$)	R
0.0 ^{b)}	0.544	3.41	6.8	0.0
0.10	0.563	3.48	6.0	0.29
0.30	0.559	2.99	5.4	0.37
0.60	0.569	2.72	4.8	0.50
0.80	0.523	2.66	4.2	0.75
1.0	0.545	2.71	3.3	0.85

a) Values which refer to spectra analysed with one central peak

b) Average of six different measurements

TABLE 27. Relative distribution (%) of ferric species for 0.10 M Fe(III) in 1.0 M H(Cl,ClO₄) at 90 K.

Species	[Cl ⁻] (M)					
	0.0	0.10	0.30	0.60	0.80	1.0
Fe(OH ₂) ₆ ³⁺	100	32	27	30	20	18
FeCl(OH ₂) ₅ ²⁺	--	40	43	37	41	50
FeCl ₂ (OH ₂) ₄ ⁺	--	28	30	33	24	20
FeCl ₄ (OH ₂) ⁻	--	--	--	--	15	12

Fig. 16. Mössbauer spectra of 0.10 M Fe(III) in 1.0 M acid of varying chloride concentration at 90 K.

Fig. 16a. Plot of distribution of iron(III) complexes in 1.0 M $HClO_4$ (Cl^- varying from 0 to 1.0 M).

The presence of three different species, four for the last two solutions in Table 27, was revealed by the Fourier transformation of each 90 K spectrum. The measured internal magnetic fields were assigned to the octahedral hexaquo, monochloro, dichloro and tetrachloro ferric complexes. A curve-fitting of the transformed spectra gave the relative distribution of each complex (Table 27) with a relative precision of between 5 and 10%. The species distribution may be calculated using literature values of equilibrium constants at room temperature. However, this calculation predicts that more than two-thirds of the ferric species should be in the form of hexaquo ferric ions. The measured value was only about one-third of the total. Moreover, the measured amount of dichloro complex exceeded the calculated value by six times. Furthermore, the calculations overestimated the importance of hexaquo and dichloro ferric species in 0.30 and 0.60 M $[Cl^-]$ solutions, respectively, while the amount of dichloro and hexaquo was underestimated in these same solutions. Therefore, it appears that, at ambient temperature, these solutions favour the presence of lower chloroferric complexes. It is difficult to ascertain to which extent the lowering of temperature promotes higher chloroferric complexes since crystallization of the solutions could stabilize these species more than others. Each effect, i.e. lower temperature and crystallization, certainly plays a role in the determination of the final distribution of ferric complexes in frozen solutions.

The measured amounts of the hexaquo and monochloro Fe(III) species in the 0.80 M $[Cl^-]$ solutions are roughly the same as the

calculated values. However, the measured amount of the dichloro complex was only half the calculated value. In addition, 15% of a fourth species, determined to be octahedral ferric tetrachloride, was found in this solution, even though the calculations did not predict its presence. A similar species distribution, having a slightly higher proportion of monochloro and dichloro complexes, was measured for the 1.0 M solution. Given the low availability of chloride ions in these dilute solutions, it is remarkable that $[\text{FeCl}_4(\text{OH}_2)_2]^-$ was present at all. Finally, there is no question that the measured magnetic splitting is due to an octahedral species, and not to $[\text{FeCl}_4]^-$, because of the relatively large difference in internal field values between these two species. Thus, the adoption of octahedral rather than tetrahedral symmetry is probably dependent on the activity of H^+ ions since $[\text{FeCl}_4]^-$ became prevalent in more concentrated HCl solutions. An earlier study based on spectrophotometric and X-ray evidence, had also proposed that the octahedral-tetrahedral transformation was caused by H^+ ions (81).

ii) Effect of temperature and vitrifying agent

The Mössbauer spectra of the solutions studied in Part i were also measured at 180 K and the results are shown in Table 28. Each solution had previously been fast frozen.

All of the spectra obtained consisted of a single line, broadened by electronic relaxation. With each addition of Cl^- ion, the relaxation process became more efficient and the linewidth

TABLE 28. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 1.0 M H(Cl,ClO₄) at 180 K.

[Cl ⁻] (M)	δ $\left(\pm 0.009 \right)$ (mm/sec)	Γ $\left(\pm 0.01 \right)$ (mm/sec)	ϵ ($\pm 0.1\%$)
0.0 ^{a)}	0.502	3.58	5.1
0.10	0.517	3.42	4.9
0.30	0.528	3.15	5.4
0.60	0.506	2.85	6.0
0.80	0.515	1.55	7.3
1.0	0.518	1.38	7.6

a) Average of three different measurements

decreased steadily up to and including the 0.60 M solution. Past this Cl^- concentration, there was a sudden decline in linewidth which decreased by another 10% at 1.0 M HCl concentration. This abrupt change suggests that there was probably a new species present in solution which increased the relaxation rate. Since this change also coincided with the appearance of an octahedral ferric tetrachloride complex in the 90 K spectra, this species could be responsible for the linewidth decrease observed at 180 K.

In order to study the dilute acid solutions without the problem of solvent crystallization, a given amount of glass former was added to several of them. Both ethylene glycol and glycerol were tried. The former was found to be more adequate, i.e. a smaller amount was needed to produce the glassy material. The solutions were rapidly frozen and the Mössbauer spectra measured at 90 K. Typical spectra are presented in Figure 17 and the magnetic field of each observed species, together with their relative distribution, are given in Table 29.

The addition of 40% ethylene glycol to 0.10 M Fe(III) in 1.0 M HClO_4 resulted in a glassy solid for which the Mössbauer spectrum is shown in Figure 17 (number 1). The only detectable species had a magnetic splitting of 574 kG which is characteristic of the ferric hexaquo species observed in other vitreous absorbers (102,103,213). Following addition of 20% glycerol (number 2, Fig. 17) to 0.10 M Fe(III) in 1.0 M HClO_4 containing 0.015 M $[\text{Cl}^-]$, the frozen solution was opaque and appeared homogeneous. The resulting Mössbauer spectrum showed a partially resolved magnetic splitting.

TABLE 29. Internal field values for 0.10 M Fe(III) frozen solutions in 1.0 M H(Cl,ClO₄) with added glass former at 90 K.

Vitrifying Agent (%)	[Cl ⁻] (M)	H _n (±5 kG)			Relative distribution (%)		
40	0.0	574	-	-	100	-	-
20 ^{a)}	0.015	571	551	519	71	23	6
50 ^{a)}	0.015	572	548	500	68	20	12
40	0.030	578	-	498	91	-	9
40 ^{b)}	0.030	573	-	507	83	-	17
40	0.070	575	-	502	85	-	15
40	0.25	573	-	505	78	-	22

a) Glycerol was used instead of ethylene glycol

b) Temperature cycling from 90 K to 250 K and back to 90 K

Fig. 17. Mössbauer spectra of 0.10 M Fe(III) in 1.0 M HClO₄ with added glass former at 90 K.

Three different species were detected after Fourier transformation. These were assigned the following structures: $[\text{Fe}(\text{OH}_2)_6]^{3+}$, $[\text{FeCl}_2(\text{OH}_2)_4]^+$ and $[\text{FeCl}_4(\text{OH}_2)_2]^-$. The *trans* effect is probably responsible for the notable absence of ferric complexes with odd numbers of Cl^- ligands. As expected, ferric hexaquo ion was the predominant complex. There was, however, approximately eight times more of the dichloro complex than calculated. Furthermore, a surprising 6% of the tetrachloro complex was measured. The evidence of crystallization in the sample is probably sufficient to explain the observed discrepancies. When 50% glycerol was added to the same solution, complete hfs resolution was obtained (number 3, Fig. 17). Once again, three species were detected. However, the third one had a smaller H_n value than that previously measured. The reduced magnetic field value indicates the presence of a ferric complex having more covalent bonding than $[\text{FeCl}_4(\text{OH}_2)_2]^-$ and, according to Table 21, the species $[\text{FeCl}_5(\text{OH}_2)]^{2-}$ could give rise to such a value. However, the presence of this species is not expected in these low chloride concentrations. More likely, there may exist some form of "glycerol-ferric chloride" complex due to the high concentration of the vitrifying agent. The effective 4s electronic density, which would be reduced in such a complex, would account for the observed lower H_n value.

The addition of ethylene glycol to Fe(III) solutions of higher chloride concentration (0.030 to 0.25 M) produced very similar results. In each case, two species were found. The first one was ferric hexaquo ion and the second one had an average H_n value of 503 KG, which is close to the value measured for the 50% glycerol solution. This suggests that partial bonding exists between Fe(III) ions and the vitrifying agent, thus, explaining the observed value of internal magnetic field. Number 4

in Figure 17 represents a typical spectrum. The relative amount of the second species increased rapidly as the chloride concentration increased. In one instance, this amount almost doubled when the Mössbauer spectrum was measured at 90°K after the temperature had previously been raised to 250 K for about 15 minutes. These observations suggest that the presence of octahedral ferric tetrachloride is more probable and that it was responsible for the second magnetic splitting observed in the last four solutions of Table 29.

b) Concentrated acid

i) Effect of chloride concentration

Varying amounts of chloride ion were added to solutions of 0.10 M Fe(III) ions in 9.4 M HClO₄, and the solutions were subsequently frozen rapidly in liquid nitrogen. The Fourier transformed Mössbauer spectra are grouped together in Figure 18 and the spectral parameters are listed in Table 30.

With the addition of 0.005 M Cl⁻, the concentrated perchloric acid solution changed from a colourless to a very pale yellow solution. When frozen, the solution was transparent and vitreous, like the pure HClO₄ solution. The resulting Mössbauer spectrum did not present magnetic splitting and was similar to that of the pure HClO₄ solution. The measured linewidth for the chloride solution was approximately 5% smaller than for the HClO₄ solution. The almost identical isomer shift suggests that the same ferric species, namely [Fe(OH₂)₆]³⁺, was present in each case. Due to the high ionic strength, one would expect to see some monochloro or dichloro Fe(III) complexes. However, none were detected, within the limits of uncertainty of the apparatus.

TABLE 30. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 9.4 M HClO₄ at 90°K.

[Cl ⁻] (M)	ϵ ($\pm 0.1\%$)	R	H_n (± 5 kG)				Relative distribution (%)			
0.0 ^{a)}	2.1	0.0	none				100	-	-	-
0.005 ^{b)}	2.0	0.0	none				100	-	-	-
0.010	1.3	0.82	575	-	524	476	28	-	37	35
0.010 ^{c)}	1.1	0.0	none				-	-	-	-
0.050	1.2	0.95	571	549	522	478	21	17	33	29
0.100	1.3	0.96	573	544	518	472	18	24	27	31

a) Linewidth, $\Gamma = 3.53$ mm/sec

b) Linewidth, $\Gamma = 3.38$ mm/sec

c) Spectrum measured after 18 hours at 200 K ($\Gamma = 2.97$ mm/sec)

Fig. 18. Mössbauer spectra of 0.10 M $Fe(III)$ in 9.4 N $HClO_4$ with varying chloride concentration at 90 K.

The solution to which 0.010 M chloride ion was added solidified upon freezing to a transparent glass slightly more yellow than the previous solution. The existence of magnetic splitting was very apparent in the 90 K Mössbauer spectrum and the resolution parameter was similar to that observed for the 1.0 M HCl solution. The three different magnetic splittings which were identified in the Fourier transformed spectrum are believed to arise from the following species: $[\text{Fe}(\text{OH}_2)_6]^{3+}$, $[\text{FeCl}_4(\text{OH}_2)_2]^-$ and $[\text{FeCl}_4]^-$. As may be seen from Table 30, almost three-quarters of the iron atoms are in the form of ferric tetrachloride complexes. In an earlier study, Friedman (35) determined that more than 90% of the iron in dilute (0.68 M) ferric chloride solutions in concentrated HCl was present as FeCl_4^- . More recently, Brady, Robin and Varimbi (79) concluded that the amount of FeCl_4^- in strongly acid solutions of FeCl_3 did not depend upon the Cl^- ion concentration. These authors also found that, in a 5 M FeCl_3 aqueous solution, the $[\text{FeCl}_4(\text{OH}_2)_2]^-$ species made up almost 75% of the total ferric ions. In this project, it is worth noting that both $[\text{FeCl}_4(\text{OH}_2)_2]^-$ and $[\text{FeCl}_4]^-$ were present in the concentrated HClO_4 solutions while $[\text{FeCl}_4]^-$ was absent in the dilute HClO_4 solutions. This observation may be qualitatively explained by the strong dehydrating action of the perchlorate ions (41). These ions could effectively remove the two water molecules from the first coordination sphere of the metal ions, thus stabilizing the tetrahedral ferric tetrachloride species.

After exposure of the 0.010 M Cl^- solution to a temperature (200 K) above the glass transition temperature, an irreversible change took place. The homogeneous glass developed a white, opaque circular section on the outer ridge of the cell, while the yellow center section

became semi-transparent. Magnetic hfs was absent from the Mössbauer spectrum and the measured isomer shift was that of Fe(III) ions with octahedral symmetry in the presence of Cl^- ions. The large linewidth prevented a more precise identification of the iron coordination to be done.

Both the 0.050 M and the 0.100 M Cl^- solutions produced a pale yellow transparent glass upon freezing. In each case, the Mössbauer spectrum revealed the presence of four ferric species. Three of these had internal field values similar to those calculated for the 0.010 M Cl^- solution, while the fourth species was determined to be $[\text{FeCl}_2(\text{OH}_2)_4]^+$. As was expected, the relative amount of the ferric hexaquo complex decreased markedly as the Cl^- concentration was increased. However, the dichloro complex now constituted almost a quarter of the total ferric species. The increased amount of this species was obtained at the expense of the tetrachloro complexes which were reduced by about 20%. Therefore, it appears that in concentrated acid the tetrachloro complexes are more stable than the dichloro complex. The limited availability of chloride ions in the 0.010 M Cl^- solution probably explains why the dichloro complex was not detected.

ii) Effect of temperature

The series of solutions described in the previous sub-section were warmed slowly up to 200 K and the Mössbauer spectra measured at this temperature. The Mössbauer parameters are presented in Table 31.

Since the 0.005 M Cl^- solution had shown only one species at 90 K, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, the spectrum at 200 K was very similar to the pure

TABLE 31. Mössbauer parameters for 0.10 M Fe(III) frozen solutions in 9.4 M HClO₄ at 200 K.

[Cl ⁻] (M)	δ (± 0.015) mm/sec	Γ (± 0.05) mm/sec	ϵ ($\pm 0.1\%$)
0.0	0.426	3.80	1.8
0.005	0.438	3.71	1.9
0.010	0.513	1.64	2.2
0.050	0.509	2.61	2.1
0.100	0.527	2.03	1.7

9.4 M HClO_4 solution. However, there was a sudden increase in the observed isomer shift for the 0.010 M Cl^- solution, together with an even more abrupt decline in linewidth. These observations indicate that other ferric species, which enhance the relaxation process e.g. ferric chloride complexes, were present in this solution.

An increase in the isomer shift was also noted for both the 0.050 M and the 0.100 M Cl^- solutions. However, their linewidth values were both higher than those measured for the previous solution. The more positive isomer shifts values observed are consistent with the higher percentage of ferric chloride complexes at 90 K. However, the measured distribution of species is not likely to have remained the same at 200 K given the noted physical change in the frozen samples. Thus, it is not possible to identify which ferric chloride species are responsible for the resonant absorption in the 200 K spectra. As regards the 0.010 M Cl^- solution, the recrystallization which occurred upon heating the sample simply created a higher concentration of Fe(III) ions. This explains the much smaller linewidth and higher recoil-free fraction.

IV. CONCLUSION

The results obtained in this project have shed some light on several aspects of the study of ferric chloride complexes. Numerous Mössbauer spectra of iron compounds in the solid state were determined in order to facilitate the identification of the species present in acidic iron(III) chloride solutions. Many of these compounds have been measured here for the first time. The well-known series of ferric chloride hydrates was also studied by Mössbauer spectroscopy. The structure of each of the compounds was determined to be a complex cation, $[\text{FeCl}_2(\text{OH}_2)_4]^+$, together with an appropriate anion which could be either Cl^- or FeCl_4^- . The configuration of the cation appeared to be related to the number of lattice water molecules trapped inside the solid. Whenever there was an even number of water molecules the hexacoordinate cation was *cis* while the *trans* configuration was always associated with an odd number of water molecules.

In this project, several iron(III) solutions were studied under a variety of conditions. It was shown that the structure of rapidly frozen solutions can only correspond to that of liquid solutions under certain specific conditions which are highly dependent on the composition of the solution, the freezing rate, and the nature of the components.

Whenever the solutions were dilute in iron and of low ionic strength, they did not solidify as homogeneous glasses when cooled rapidly, indicating that crystallization had taken place. Consequently,

it cannot be assumed that the relative distribution of various complexes present in solution at room temperature remained the same after freezing, nor can it be assumed that these complexes retained their original structure. Nevertheless, some conclusions may be drawn from these experiments. The dilute ferric perchlorate solutions produced similar spectra whether they were quickly or slowly frozen. For each set of conditions, a single peak, broadened by relaxation, was observed and the species, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, was identified. Unlike these solutions, the concentrated ferric perchlorate solutions solidified into a glass and gave Mössbauer spectra where magnetic hyperfine splitting was well resolved. The measured values of internal magnetic field and isomer shift were very similar to those observed in solid compounds where $[\text{Fe}(\text{OH}_2)_6]^{3+}$ is known to be present. Thus, the same ferric hexaquo complex was identified in both the dilute and the concentrated perchlorate solutions. One frozen solution of dilute Fe(III) in 9.4 M HClO_4 , which had been melted and frozen again showed complete disappearance of the previously observed hyperfine splitting. The measured spectral parameters were indicative of the presence of some form of water-bridged, polymeric Fe(III)-aquo complex. This species was considered more likely to be responsible for the observed spectrum than the tetrahedral species $[\text{Fe}(\text{OH}_2)_4]^{3+}$, especially when considering the thermal history of the sample.

Solutions of Fe(III) ions in dilute HCl were frozen using both a fast and a slow freezing rate. The resulting Mössbauer spectra were almost identical in each case. With the help of a data treatment method, namely the fast Fourier transform, it was possible

to distinguish four different complexes in the spectra:

$[\text{Fe}(\text{OH}_2)_6]^{3+}$, $[\text{FeCl}(\text{OH}_2)_5]^{2+}$, $[\text{FeCl}_2(\text{OH}_2)_4]^+$ and $[\text{FeCl}_4(\text{OH}_2)_2]^-$.

The structural assignments were performed by measuring the different hyperfine splittings (internal magnetic field) in a given spectrum with the assumption that the internal field at the Fe(III) nucleus decreases linearly with each subsequent chloride complexation.

The relative amount of each complex was measured and compared with values calculated from the stability constants published in the literature. There was poor agreement between the two sets of values, possibly due to crystallization of the solutions. Also, the rate of reaction between Cl^- ions and the various ferric chloride complexes is still fast at temperatures slightly above the freezing point of the solutions.

Thus, the measured values of species distribution would probably not be the same as the calculated values at 25°C , even without taking into account the problem of crystallization..

Gradual freezing of these dilute HCl solutions was shown to have produced two different areas within the sample. The first area was the central portion of the sample enriched in Fe(III) ions, while the second one was the periphery with a lower concentration of ferric ions. The relative distribution of ferric species achieved with this rate of freezing was different from that obtained with either the fast or the slow freezing rate. It appears that the gradual freezing has allowed a different ferric chloride equilibrium to form before quenching it in the frozen solution.

The study of dilute Fe(III) solutions in HCl of increasing concentration made it possible to identify three and, in some cases,

four different complexes. The species $[\text{FeCl}(\text{OH}_2)_5]^{2+}$, $[\text{FeCl}_2(\text{OH}_2)_4]^+$ and $[\text{FeCl}_3(\text{OH}_2)_3]$ were present in solutions with up to 6.0 M HCl. Tetrahedral $[\text{FeCl}_4]^-$ was also found in every solution higher than 4.0 M HCl. However, this species was only present with $[\text{FeCl}_2(\text{OH}_2)_4]^+$ and $[\text{FeCl}_4(\text{OH}_2)_2]^-$ at HCl concentrations of 9.4 and 12.0 M. Similarly, relatively high amounts of ferric tetrachloride complexes were found in 9.4 M HClO_4 solutions which had Cl^- ion concentrations less than 0.10 M. Therefore, high H^+ ion concentration appears to be a more important factor than high Cl^- ion in stabilizing the higher iron(III) chloro complexes.

The effect of adding a vitrifying agent to dilute HCl solutions was also investigated. While this succeeded in producing glasses instead of crystallized solutions, it was felt that the initial ferric chloride equilibria had been altered by this procedure. Unless Fe(III) solutions already have a high ionic strength and, thus, readily freeze to a glass, the measured distribution of species in the frozen solutions would not be representing room temperature conditions.

In summary, a close connection between the physical appearance of the frozen solutions and their Mössbauer spectra has been shown to exist. By comparison with spectra of solid compounds, valuable information was derived concerning the coordination of ferric ions in acidic solutions. The ability to use Fourier transformation with complex Mössbauer spectra, as described in this work, should help the development of a better understanding of chemical and physical processes involved in the leaching of ores by ferric chloride.

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APPENDIX

MÖSSBAUER SPECTRA

1 - 21

SAMPLE: Iron foil enriched Fe-57 FER52ST

SAMPLE: (NH₄)₂FeCl₅(OH₂) 155 mg T=90 K NH₄FE

SAMPLE: Cn-Bu4N]FeCl4 11 mg Fe/cm² T=298 K FECL4B

SAMPLE: (n-Bu₄N)FeCl₄ 11 mg Fe/cm² T=298 K FECL4B20

SPECTRUM 4

SAMPLE: $\text{Na}_2(\text{Fe}(\text{CN})_5\text{N}_3) \cdot 2\text{H}_2\text{O}$ 10 mg Fe/cm² T = 298 K NPN3

3 3

OF / DE

SAMPLE: $\text{Na}_2(\text{Fe} < \text{CN} > 5\text{N}0).2\text{H}_2\text{O}$ (30.0%) + $\text{Na}_3(\text{Fe} < \text{CN} > 5\text{NH}_3)$ (70.0%) T=298 K NA3NA2

SAMPLE: $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ $T=90 \text{ K}$

SAMPLE: $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$ T=90 K

SAMPLE: $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$ T=90 K

SAMPLE: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ T=90 K

SAMPLE: (C₉NH₃>6)FeCL6 (51.0%) + (CoCL2<en>2)FeCL4 (49.0%) T=298 K CL4CL6

SAMPLE: Fe(CLD04)3 0.34M IN HCL04 1.0M T=90 K FE4S

SAMPLE: 0.08M Fe(III) in 9.4M HCL04 T=90 K FECLF

SAMPLE: 0.08M Fe(III) in 0.4M HCL04 T=90 K FECL04L5

SAMPLE: 0.10M Fe(III) in 9.4M HCL04 T=90 K FEHR

SAMPLE: 0.08M Fe(III), in 9.4M HCL04 T=90 K CL3M9AA

SAMPLE: 0.08M Fe(III) in 4.7M HCL04 T=90 K FECL04L2

SAMPLE: 0.10M Fe(III) in 1.0M HCL T=90 K 60CLFE

SAMPLE: 0.10M Fe(III) in 1.0M HCL T=90 K FECLK

SAMPLE: 0.10M Fe(III) in 1.0M HCL T=90 K AI disk FECL160

SAMPLE: 0.10M Fe(III) in 1.0M HCL T=90 K FECLH60

END

1 5 1 2 8 1

FIN