MASTER

**MÖSSBAUER STUDY OF DIFFUSION
IN LIQUIDS**

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MOSSBAUER STUDY OF DIFFUSION
IN LIQUIDS

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of
Purdue University

by
Anuar Abras

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LIST OF SYMBOLS

Symbol	Name
Sample A	Generic term denoting a solution of ferrous chloride dissolved in dry glycerol with no water added. In general, curves associated to this solution are labelled A.
Sample B	Sample A + 5% of pure water (by weight). In general, curves associated to sample B are labelled B.
Sample C	Sample A + 10% of pure water (by weight). In general, curves associated to sample C are labelled C.
η	Viscosity
D	Diffusion coefficient.
R	Radius of diffusing entity.
T	Absolute temperature.
k	Boltzmann constant.
$\hbar$	Planck's constant divided by 2π .
c	Velocity of light.
$\text{\AA}$	Angstrom.
E_0	Transition energy of a nuclear decay.
Γ_N	Natural linewidth of the Mössbauer resonance.
C_o, C_{av}	Average concentration of the isotope (Fe^{59}) before and after the diffusion takes place.

Symbol	Name
τ_N	Mean life of a nuclear state.
v	Relative velocity between source and absorber in a Mössbauer experiment, taken as positive when absorber moves toward the source.
A_T	Total area under Mössbauer absorption line.
f	Recoil-free fraction.
QS	Quadrupole splitting.
IS	Isomer shift.
$ n\rangle$	Eigenstate of the lattice.
Θ_M	Mössbauer characteristic temperature within the Debye approximation.
$\vec{\kappa}$	Gamma ray wave vector.
$G_S(\vec{r}, t)$	Self correlation function.
τ_0	Mean time for remaining in the oscillatory state.
τ_1	Mean time for diffusing by translation.
$\sigma_a(E)$	Absorption cross section.
$\Delta\epsilon$	Incremental broadening of the observed Mössbauer line.
τ_j	Mean time between atomic jumps (equal to τ_0 in the sudden jump model and equal to τ_1 in the continuous diffusion model).

ABSTRACT

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MOSSBAUER STUDY OF DIFFUSION IN LIQUIDS. Major Professor:
James G. Mullen.

The diffusive motion of ferrous ions in glycerol and glycerol-water solutions is studied by Mössbauer, diffusion, and viscosity measurements. The three solutions investigated are prepared by dissolving ferrous chloride in pure glycerol and adding small amounts of hydrochloric acid to prevent precipitation. The solution A corresponds to a dry (99⁺%) glycerol as a solvent. The solutions B and C are obtained by adding respectively 5% and 10% of pure water (by weight) to the solution A. This viscosity, η , of glycerol and the three solutions is measured between 0°C and 100°C. The temperature dependence of η is found to follow an empirical relation based on the Arrhenius relation as modified by T. A. Litovitz. A tracer-capillary method is used to measure the diffusion coefficient, D , for sample A. For this sample the values of D (in cm^2/sec) are $(3.67 \pm 0.25) \times 10^{-8}$ at $T = (318 \pm 1)^\circ\text{K}$, $(3.16 \pm 0.04) \times 10^{-7}$ at $T = (359 \pm 1)^\circ\text{K}$ and $(6.94 \pm 0.11) \times 10^{-7}$ at $T = (372.5 \pm 1.0)^\circ\text{K}$. A rough measurement of D was also made for sample C at $T = 296^\circ\text{K}$. The Einstein-Stokes relation is consistent with the measured values of η and D , and gives for the diffusing particle an average radius equal to $(3.9 \pm 0.4) \overset{\circ}{\text{A}}$, which is comparable to the radius of

a glycerol molecule. The Mössbauer parameters (linewidth, area, quadrupole splitting, and isomer shift) are reported from 130°K to 250°K. For all three samples the spectra show a symmetrical doublet characteristic of Fe^{2+} . The diffusional broadening is observed above the glass-liquid transition temperature, approximately 185°K, 175°K and 170°K for samples A, B and C, respectively. We can quantitatively explain the temperature dependence of the broadening of the Mössbauer resonance, by assuming that the diffusion of Fe^{2+} in general is caused by two mechanisms, where the first is based on a simple continuous diffusion model associated with the Einstein-Stokes relation, and the second is based on an activated jumping process similar to solid state diffusion. For the continuous part of the diffusion our results are in quantitative agreement with the Singwi-Sjölander theory, with the coefficient of proportionality between theory and experiment agreeing to within 20%. The broadening of the Mössbauer line is observed to vary linearly with respect to $(-\ln f)$ and QS, where f is the recoil-free fraction and QS is the quadrupole splitting of the Mössbauer spectrum. A phenomenological explanation for this first effect has been given by Jensen. The second is explained by postulating that the effect of diffusion on the quadrupole splitting is to reduce the average electric field gradient at the nucleus in proportion to the diffusivity.

I. INTRODUCTION

In 1958 R. L. Mössbauer (1) observed for the first time the recoilless absorption and emission of gamma rays by nuclei found in a crystal. Because the recoil energy of a nucleus in resonant absorption or scattering experiments is several orders of magnitude greater than the natural line-width of the emitted gamma ray, the recoil energy shifts the absorption and emission lines so that resonance cannot occur. Some methods to compensate for the recoil energy loss had been used, such as doppler shifting the gamma ray, either by means of thermal motion or high speed rotation. A new method was discovered by Mössbauer as a consequence of his experiments on nuclear resonance fluorescence with Ir^{191} . In an attempt to decrease the residual scattering, Mössbauer cooled both source and absorber expecting a decrease in effect. Instead, the resonance scattering increased. Following a suggestion by Jensen, he could interpret this new effect based on Lamb's theory of resonant neutron scattering. Thus, Mössbauer showed that there is a finite probability that a nucleus will emit or absorb a gamma ray, without a change in the phonon states of the crystal. In this case the recoil momentum is transferred to the entire solid and the loss of energy by the gamma ray due to the recoil

process is negligible in comparison to the minimum gamma ray linewidth required by the uncertainty principle.

The nucleus most commonly used in Mössbauer studies is Fe^{57} , which occurs naturally with a relative abundance of 2.2 percent in all iron. It is also the daughter of Co^{57} , which decays by electron capture. The 14.4 keV gamma ray emitted by $\text{Fe}^{57\text{m}}$ during the transition from the first excited state to the ground state is used in Mössbauer resonance absorption experiments. It has a natural linewidth of $4.67 \times 10^{-9} \text{ eV}$. If the nucleus were allowed to recoil freely, the energy carried away by the nucleus upon emission of the 14.4 keV gamma ray would be about 10^{-3} eV , far greater than the natural linewidth of the 14.4 keV level.

In a typical Mössbauer experiment a relative velocity, v , between the source and absorber is introduced which causes a doppler shifting of the gamma ray energy given by $\frac{v}{c} E_0$, where c is the velocity of light, and E_0 is the transition energy of the nuclear gamma ray. In this way, the 14.4 keV gamma ray can be doppler shifted over a range of energy 100 times the natural linewidth by a relative velocity of only 1 cm/sec.

An important consequence of the Mössbauer effect in Fe^{57} is that the gamma ray linewidth is typically smaller than the characteristic energy splittings of nuclear levels in crystalline fields, and, therefore, Mössbauer spectroscopy (2) permits a direct observation of these interactions.

Because the nucleus possesses a magnetic dipole moment and an electric quadrupole moment its energy level will be split by interaction with a magnetic field and an electric field gradient, respectively. The 14.4 keV line of Fe^{57} consists of a transition from spin $3/2$ to $1/2$, which results in a doublet in the presence of an electric field gradient. The monopole interaction between the nucleus and electron density at the nucleus produces a shift in the centroid of the Mössbauer spectrum. This isomer shift is proportional to the total electron density at the nucleus, which is directly related to the valence of the ion. Isomer shift measurements can be used to distinguish between Fe^{2+} and Fe^{3+} , for instance. The Mössbauer spectra (3) examined in this thesis, were all doublets having isomer shifts and quadrupole splittings characteristic of Fe^{2+} ions.

In 1960 K. S. Singwi and A. Sjölander (4) extended the self correlation formalism, proposed by L. Van Hove (5), to the resonance absorption of the gamma rays. Through a self correlation function, $G_s(\vec{r}, t)$, which may be defined as the probability that an atom will undergo a displacement $\vec{r}$ in a time interval t , they showed that recoil-free fraction, spectrum lineshape, and linewidth, for an emitter, or absorber, in any physical phase, could be related to the dynamics of the emitting or absorbing nuclei. By assuming that a particle alternately performs an oscillatory motion for a mean time τ_0 , and then diffuses by continuous

translation for a mean time τ_1 , Singwi and Sjölander explicitly treat two limiting cases, $\tau_1 \gg \tau_0$ and $\tau_0 \gg \tau_1$. One can summarize the results predicted for a nucleus moving in two idealized limits as follows:

i) A continuous diffusion model, or Brownian motion (as in a liquid) when $\tau_1 \gg \tau_0$. This leads to a broadening of the Mössbauer spectrum with no change in the basic Lorentzian lineshape, and no reduction in overall recoil-free fraction from that expected in the absence of diffusion. The broadening (in energy units) is given by $\Delta\epsilon = 2\hbar\kappa^2 D$, where $\hbar$ is Planck's constant divided by 2π , $\vec{\kappa}$ is the wave vector of the gamma ray, and D is the diffusion coefficient.

ii) A sudden-jump approximation analogous to solid state diffusion when $\tau_0 \gg \tau_1$. If the nucleus jumps instantaneously between fixed sites, with no correlation between one jump and the next, a broadening of the spectrum is predicted. The theoretical lineshape is shown to remain Lorentzian, and the recoil-free fraction to follow the usual Debye-Waller temperature dependence.

The first reported measurements of diffusion effects by the Mössbauer technique were published in 1963 by Bunbury et al. (6) and Craig and Sutin (7), studying the Fe^{57} resonance in glycerol, which in the liquid phase is very viscous at low temperature. The data of Bunbury et al. were explained by an assumption of both continuous and sudden-jump diffusivity effects in the ratio of about one to three,

whereas Craig and Sutin were able to explain their results purely in terms of a continuous diffusion model, where the ratio of temperature to viscosity was calculated from extrapolated values of the viscosity, and the Einstein-Stokes relation was assumed to relate diffusivity and viscosity. A number of features in the two experiments differed and may have served as the reason for the discrepancies. Craig's experiment used Co^{57} in glycerol and gave a minimum linewidth much greater than expected from the uncertainty relation. Also, possible complications associated with K-capture prior to the emission of the 14.4 keV line could not be ruled out.

Bunbury et al., on the other hand, were looking at Fe^{3+} resonances with large admixtures of Fe^{2+} due to poor chemical processing. The Fe^{3+} resonance is complicated to analyze because the quadrupole splitting of the Fe^{57} level is of the same order as that of the expected minimum linewidth at low temperatures. This is a serious complication as a temperature dependent quadrupole splitting would make it uncertain what reference linewidth should be subtracted from the observed linewidths to obtain the incremental broadening. To get around these difficulties and resolve the experimental questions we tried looking at the Mössbauer effect in many liquids (some of which are described in Appendix A), and found that Fe^{2+} in glycerol was the most satisfactory in that it gave a minimum linewidth of about

0.4 mm/sec only twice that of the ideal linewidth predicted by the uncertainty relation.

Another motivation for the present experiment had to do with a desire to quantitatively compare the Singwi-Sjölander theory with experiment in the continuous diffusion limit. An earlier measurement by Knauer and Mullen (8) had shown that for solid state diffusion of iron in copper and gold, there is a serious quantitative discrepancy between the experimental line broadening and that predicted by the jump model of the Singwi-Sjölander theory. We wanted to see what kind of quantitative comparison could be made with the Singwi-Sjölander theory in the continuous diffusion limit. Also, to check whether the measured broadening of our Mössbauer spectra depended on viscosity as found by Craig and Sutin (7), we varied the viscosity of our glycerol samples by dilution with water, as well as by systematically changing the temperature.

Champeney and Woodhams (9) have also investigated molecular motion in liquids using Mössbauer scattering. They were not able to get a satisfactory comparison with several models, which have been proposed for liquid diffusion. In order to try to resolve these difficulties, we felt that more precise measurement would be required with much more data to check on errors and reproducibility.

We have been able to achieve this improved accuracy and to make a more detailed and quantitative comparison

between theory and experiment. Another purpose to the experiment was to measure the viscosity and classical diffusivity of our specimens directly to allow a comparison which would not permit sample variations to confuse the interpretation.

Recently Jensen (10) has studied liquid diffusion using the Mössbauer effect for Fe^{57} in propane-(1.3)-diol. Similar to the earlier studies of Knauer and Mullen (11), he found a rapid fall off in the recoil-free fraction in the region where diffusion broadening occurred, which he explained in terms of a phenomenological theory, predicting a line broadening proportional to the logarithm of the recoil-free fraction. The recoil-free fraction has also been carefully measured in the present study and a comparison with Jensen's description will be given in Section V.

II. THEORY

A. Lineshape of Mössbauer Resonance

In this section we will give a brief discussion of the main steps one can follow to derive the lineshape of the Mössbauer resonance. Consider an interacting system consisting of nuclei-bound in a lattice. Let us assume that when a nucleus makes a transition from state A to state B, the lattice simultaneously makes a transition from state n to state m. The transition matrix element, corresponding to the absorption of a photon, can be written as

$$\langle Bm | H | An \rangle, \quad (II.1)$$

where H is the interaction Hamiltonian between the radiation field and the charged particles of the nucleus. This Hamiltonian can be expressed (4) as

$$H = \sum_j c a_{\vec{k}}^{\dagger} \exp(i\vec{k} \cdot \vec{r}_j), \quad (II.2)$$

where c is a constant, $a_{\vec{k}}^{\dagger}$ is the creation or destruction operator for a photon of wave vector $\vec{k}$ and $\vec{r}_j$ is the position of the j^{th} nucleon. By separating the position coordinates $\vec{r}_j$ into the center of mass coordinate $\vec{r}$ and relative coordinates $\vec{r}_j - \vec{r}$ one can write relation (II.2) as

$$H = \exp(i\vec{k} \cdot \vec{r}) \sum_j c a_{\vec{k}}^{\dagger} \exp[i\vec{k} \cdot (\vec{r}_j - \vec{r})]. \quad (II.3)$$

The first factor in equation II.3 is the interaction operator for transitions of the nuclear center of mass due to recoil of the nucleus when a photon is absorbed, and the factor $\exp[i\vec{k} \cdot (\vec{r}_j - \vec{r})]$ is the operator governing transitions of the nucleus neglecting recoil. Thus, the transition matrix element, given by equation II.1, can be expressed as a product of two matrix elements, one corresponding to the change in the internal state of the nucleus and the other corresponding to a change in the state of the collective motions of the center of masses. If only a single transition is allowed for the nucleus the first matrix element is a constant, and it can be shown (4,12) that the absorption cross section per nucleus for a photon of energy E in a multiphonon process is given by

$$\sigma_a(E) = \frac{\sigma_o \Gamma_N^2}{4} \sum_{n,m} g_n \frac{|\langle n | \exp(i\vec{k} \cdot \vec{r}) | m \rangle|^2}{(E - E_o + \epsilon_n - \epsilon_m)^2 + (\Gamma_N/2)^2}, \quad (\text{II.4})$$

where Γ_N is the natural linewidth of the nuclear level, E_o is the transition energy of the nucleus, ϵ_n and ϵ_m are, respectively, the energies of the states $|n\rangle$ and $|m\rangle$ of the lattice, σ_o is the resonance absorption cross section, g_n is a statistical weight factor of the lattice state $|n\rangle$ and $|\langle n | \exp(i\vec{k} \cdot \vec{r}) | m \rangle|^2$ gives the probability of exciting the lattice from state $|n\rangle$ to state $|m\rangle$.

The Mössbauer resonance is characterized by a zero-phonon process in which only terms $n=m$ of equation II.4 are considered. This implies for the absorption cross section

a Lorentzian function given by

$$\sigma_a(E) = \frac{\sigma_o \Gamma_N^2}{4} \frac{f}{(E-E_o)^2 + (\Gamma_N/2)^2}, \quad (\text{II.5})$$

$$\text{where } f = \sum_n g_n |\langle n | \exp(i\vec{k} \cdot \vec{r}) | n \rangle|^2 \quad (\text{II.6})$$

is the recoil-free fraction, giving the fraction of photons absorbed in a zerophonon process. It can be shown for an ideal thin absorber that f is proportional to the area under the curve.

If a magnetic field or an electric field gradient is present at the nucleus, then more than one transition will occur. By working out the nuclear matrix element, and assuming that the natural linewidth is independent of the particular sublevel of the nuclear state, it can be shown (13) that the Mössbauer spectrum is given by a sum of Lorentzians centered so as to reflect the Zeeman and quadrupole splitting of the nuclear levels.

It can be seen from equation II.6 that the recoil-free fraction depends in detail on the phonon spectrum, and gives a technique to study those parameters related with the lattice dynamic properties. For a system in which interatomic forces are harmonic, we can show (14) that

$$f = \exp(-\kappa^2 \langle x^2 \rangle), \quad (\text{II.7})$$

where x is the displacement from equilibrium of the absorbing nucleus in the direction of $\vec{k}$. The average of x^2 is both a

quantum mechanical average over the normal modes of vibration and an ensemble average at an equilibrium temperature T . From equation II.7 we can see that the Mössbauer effect increases as the temperature decreases, since $\langle x^2 \rangle$ decreases with decreasing T . The temperature dependence of f is given by the temperature dependence of $\langle x^2 \rangle$, which depends on details of the model used. For example, for a harmonic system within the Debye approximation (15),

$$f(T) = \exp\left[-\frac{3R'}{2k\theta_M} \left(1 + 4\frac{T^2}{\theta_M^2} \int_0^{\theta_M/T} \frac{y dy}{\exp(y)-1}\right)\right], \quad (\text{II.8})$$

where $y \equiv \frac{\hbar\omega_c}{kT}$, and ω_c is the frequency of the harmonic oscillator, k is Boltzmann's constant, $R' = E_0^2/2Mc^2$ is the recoil energy of a nucleus of mass M , c is the velocity of light, and θ_M is the Mössbauer characteristic temperature, which may be different from the Debye temperature depending on the binding of the Mössbauer ion and the host ions. The expression in equation II.8 can be simplified for two limiting cases:

i) In the low temperature limit $T \ll \theta_M$ we have

$$f(T) \approx \exp\left[-\frac{3R'}{2k\theta_M} \left(1 + \frac{2\pi^2 T^2}{3\theta_M^2}\right)\right]. \quad (\text{II.9})$$

ii) In the high temperature case ($T > \frac{\theta_M}{2}$), where the lattice energy approaches its classical limit ($\hbar\omega_c \ll kT$), we have $f(T) \approx \exp\left(-\frac{6R'}{k\theta_M^2} T\right)$. (II.10)

In Section II.C we will discuss how the diffusive motion of Mössbauer nuclei can alter the lineshape and affect the Mössbauer parameters, linewidth, and recoil-free fraction.

B. Basic Equations from Diffusion Theory

In this section we would like to discuss three basic relations which will be used in subsequent discussions. They are

$$D = \frac{\langle x^2 \rangle}{2\tau}, \quad (\text{II.11})$$

$$D = \frac{kT}{6\pi R\eta} \quad (\text{II.12})$$

and

$$D = D_1 + D_2. \quad (\text{II.13})$$

The first of these expressions relates the mean square displacement of an atom in a time τ to the diffusion coefficient, D . It was originally derived by Einstein (16), and for cubic solids where D is isotropic, we can relate D to the individual atomic displacement, r_o , by $D = \frac{r_o^2}{6\tau_j}$, where τ_j is the mean time between atomic displacements.

Equation II.12 is the Einstein-Stokes relation for the diffusivity of a hard sphere of radius R diffusing in a viscous medium of viscosity, η , and at a temperature T . Variations on the proportionality constant in this relation have been proposed due to rotational friction effects (17) and other effects (18). We shall always use it in the form shown, although we shall take R to be an effective radius,

which is slightly smaller than that found from the molecular volume, as was considered by Robinson-Stokes (18).

Equation II.12 can be derived from simple arguments originally due to Einstein and Stokes. For a particle diffusing in a liquid at temperature, T , the diffusion coefficient is related to the frictional resistance, ρ , imparted to the particle by the liquid, through an expression given by $D = \frac{kT}{\rho}$, as was first shown by Einstein (16). Stokes showed (19) that for a sphere of radius R moving in a continuous liquid of viscosity, η , $\rho = 6\pi R\eta$. By combining these two relations we obtain the desired equation II.12.

The third relation expresses the diffusion coefficient for ions diffusing by two independent mechanisms. In our discussion (Section V), we shall require this relation to explain the temperature dependence of the observed Mössbauer line broadening. This relation is easily derived for the one dimensional case.

Let $P_1(x_1)$ be the probability that an ion will displace a distance x_1 due to mechanism 1, and $P_2(x_2)$ be the probability of a displacement x_2 due to mechanism 2. If either mechanism operated independently we would have

$$P_1(x_1) = (4\pi D_1 t)^{-1/2} \exp(-x_1^2/4D_1 t) \text{ and}$$

$$P_2(x_2) = (4\pi D_2 t)^{-1/2} \exp(-x_2^2/4D_2 t),$$

which follows from the basic diffusion equation (16) or from the central limit theorem (20). We can show from basic

probability theory that if both mechanism 1 and 2 are operative, then

$$P_T(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} du \exp(-iux) \int_{-\infty}^{\infty} dx_1 P_1(x_1) \exp(iux_1) \int_{-\infty}^{\infty} dx_2 P_2(x_2) \exp(iux_2).$$

Substituting $P_1(x_1)$ and $P_2(x_2)$ in $P_T(x)$ and performing the integration we obtain

$$P_T(x) = [4\pi(D_1 + D_2)t]^{-1/2} \exp[-x^2/4(D_1 + D_2)t],$$

where $P_T(x)$ is the probability of moving a distance x in time t . This implies the desired equation II.13, which has also been used by Bunbury et al. (6), for analyzing diffusive motions in glycerol.

C. Diffusional Broadening of the Resonance Line

In section II.A, we discussed the lineshape of a Mössbauer spectrum for nuclei bound in a crystalline lattice performing harmonic vibrations. It was found that as the temperature increased the recoil-free fraction decreased, and the lineshape of the absorption cross section remained Lorentzian with the same ideal natural linewidth. Here we are interested in how these theoretical predictions would change if we raised the temperature such that the Mössbauer nuclei had a sufficiently rapid diffusive motion, either hopping from one lattice site to another or diffusing continuously, to alter the basic Mössbauer parameters, such as linewidth and area.

The first treatment of this problem was given by Singwi-Sjölander (4), who extended to the Mössbauer resonance problem a convenient formalism introduced by L. Van Hove (5) to study the dynamical behavior of solids. In this formalism the absorption cross section is expressed in terms of a self correlation function $G_s(\vec{r}, t)$, which may be expressed (5) as

$$G_s(\vec{r}, t) = \langle \int d\vec{r}' \delta(\vec{r} + \vec{r}(0) - \vec{r}') \delta(\vec{r}' - \vec{r}(t)) \rangle, \quad (\text{II.14})$$

where $\vec{r}(t)$ is the vector position of a particle at time t and $\langle \dots \rangle$ means a statistical average at temperature T . A simple interpretation can be given to $G_s(\vec{r}, t)$ if we perform the integration of equation II.14 at $t=0$. This leads to $G_s(\vec{r}, 0) = \delta(\vec{r})$, which gives the initial probability of finding the particle at $\vec{r}$. Singwi-Sjölander (4) have shown that the absorption cross section given by equation II.4 can be written, for a single line, as

$$\sigma_a(E) = \frac{\sigma_o \Gamma_N}{4\hbar} \int_{-\infty}^{\infty} \int \exp[i(\vec{k} \cdot \vec{r} - \omega t) - (\Gamma_N/2\hbar)|t|] G_s(\vec{r}, t) d\vec{r} dt \quad (\text{II.15})$$

where $\hbar\omega = E - E_o$. This expression shows that the calculation of $\sigma_a(E)$ depends on the knowledge of the self correlation function. In the Singwi-Sjölander theory $G_s(\vec{r}, t)$ has been treated in two limiting cases by assuming that a particle oscillates about its equilibrium position for a mean time τ_0 , and then diffuses by translation for a mean time τ_1 , and so on.

case i) For $\tau_1 \gg \tau_0$ the self correlation function can be found (4) from the diffusion equation given by

$$\frac{\partial C(\vec{r}, t)}{\partial t} = D \nabla^2 C(\vec{r}, t), \quad (\text{II.16})$$

where $C(\vec{r}, t)$ is the concentration of diffusing material, and is proportional to $G_s(\vec{r}, t)$. The solution of equation II.16, for an initial δ -function distribution C is a Gaussian function and

$$G_s(\vec{r}, t) \sim C(\vec{r}, t) = (4\pi Dt)^{-3/2} \exp(-r^2/4Dt). \quad (\text{II.17})$$

From equation II.17 and equation II.15 we get the essential lineshape dependence by performing the integration. The explicit result with all the factors included is

$$\sigma_a(E) = \frac{\sigma_o \Gamma_N}{4} f \frac{(\Gamma_N + 2\hbar\kappa^2 D)}{(E-E_o)^2 + 1/4(\Gamma_N + 2\hbar\kappa^2 D)^2}, \quad (\text{II.18})$$

where f is the recoil-free fraction.

case ii) For $\tau_0 \gg \tau_1$, Singwi - Sjölander assume that a particle, after it stays on a given lattice site for a time τ_0 , can suddenly jump to a new lattice position in a time interval small compared to τ_0 , as might be expected for a solid, for instance. With no correlation between one jump and the next, $\sigma_a(E)$ is found to be

$$\sigma_a(E) = \frac{\sigma_o \Gamma_N}{4} f \frac{[\Gamma_N + 2\hbar/\tau_0(1-\alpha)]}{(E-E_o)^2 + 1/4[\Gamma_N + 2\hbar/\tau_0(1-\alpha)]^2}, \quad (\text{II.19})$$

where $\alpha = \int \exp(i\vec{k} \cdot \vec{r}) h(\vec{r}) d\vec{r}$ and $h(\vec{r})$ is the probability of finding the particle at position $\vec{r}$ after a single jump, if

it was at the origin before jumping. The diffusion coefficient, D , is related to τ_0 through the relation

$$D = \frac{1}{6\tau_0} \int r^2 h(\vec{r}) d\vec{r}. \quad (\text{II.20})$$

These results indicate that, for both diffusion mechanisms, the Mössbauer resonance is a Lorentzian with a broadening due to diffusion given by

$$\Delta\varepsilon = 2\hbar\kappa^2 D \quad (\text{II.21})$$

for a continuous model, and

$$\Delta\varepsilon = \frac{2\hbar}{\tau_0} (1-\alpha), \quad (\text{II.22})$$

which is by equation II.20 also proportional to the diffusion coefficient, for the sudden-jump approximation. For a monocrystalline case α will generally average to a small number, and it will be neglected in subsequent discussion. The expressions given by equation II.21 and equation II.22 can be summarized in a convenient way suggested by Mullen and Knauer (8), in which the broadening of the Mössbauer line is characterized by the ratio of the broadening to the natural linewidth, Γ_N , through the relation

$$\frac{\Delta\varepsilon}{\Gamma_N} = \sigma(\kappa^2 \tau_N) D, \quad (\text{II.23})$$

where σ is a dimensionless constant which is model-dependent. For the two models discussed one can write: $\sigma = 2$ for all

examples of the continuous diffusion model and $\sigma \approx 0.04$ for Fe^{57} diffusion in the sudden-jump approximation, for solids where the atomic displacement is of the order of $3 \text{ \AA}$. The Singwi-Sjölander theory predicts a temperature dependence for the recoil-free fraction given by

$$f = \exp(-\kappa^2 \hbar^2 / 8MkT). \quad (\text{II.24})$$

From this expression we can see that the recoil-free fraction increases as the temperature increases, contrary to what has been experimentally observed (10,21). This peculiar temperature dependence to f results from the assumed gas model. In a liquid we might expect a broadening described by equation II.21, but $f(T)$ certainly would not be described by equation II.24. This point has been discussed very recently by Jensen (10), who claimed, by studying the Mössbauer effect and the molecular diffusion in propane-(1,3)-diol, that the recoil-free fraction is related to the diffusion coefficient through an expression given by

$$D = \frac{\langle x^2 \rangle_{\text{bound}}}{\tau_J} = \frac{-\ln f}{\kappa^2 \tau_J}, \quad (\text{II.25})$$

where $\ln$ means the natural logarithm, and τ_J is a relaxation time. In his phenomenological model, Jensen derives equation II.25 using the velocity autocorrelation formalism suggested by Rahman, et al. (22). This model starts with a self correlation function, derived by Van Hove (5) for a harmonic systems (cubic and monatomic crystals)

and for a gas, given by

$$G_s(\vec{r}, t) = [2\pi\gamma(t)]^{-3/2} \exp[-r^2/2\gamma(t)], \quad (\text{II.26})$$

where $\gamma(t)$ relates to the mean square displacement as a function of time. $\gamma(t)$ is treated as a complex function defined in terms of a velocity autocorrelation function given by $\langle V(0) \cdot \vec{V}(t) \rangle$, where $\vec{V}(t)$ is the velocity of a particle at time t . $\gamma(t)$ has an asymptotic value related to the diffusion coefficient given by

$$\gamma_\infty(t) = 2D|t| + C, \quad (\text{II.27})$$

where C is a complex function. Inserting equation II.26 in equation II.15 and taking into account equation II.27 we obtain $\sigma_a(E)$, after performing the integration over t . This is the same expression for the broadening as given in equation II.18 from the Singwi-Sjölander analysis, except there is a small addition asymmetric term, whose magnitude is negligible under the condition $\frac{2\hbar\kappa^2 D}{4kT} \ll 1$, which is satisfied in all observable Mössbauer measurements.

Jensen's approach mainly differs from that of Singwi-Sjölander in the treatment of the recoil-free fraction. Staying within the harmonic approximation (see equation II.7) Jensen writes

$$f = \exp \left(-\kappa^2 \frac{\text{Re}C}{2} \right). \quad (\text{II.28})$$

By postulating

$$\text{Re} \langle \vec{V}(0) \cdot \vec{V}(t) \rangle = \exp(-|t|/\tau_J) \text{Re} \langle \vec{V}(0) \cdot \vec{V}(t) \rangle_{\text{bound}}, \quad (\text{II.29})$$

Jensen shows that

$$\frac{\text{Re}C}{2} = \langle x^2 \rangle_{\text{bound}} = D\tau_J. \quad (\text{II.30})$$

It is interesting to compare equation II.30 with equation II.11. Clearly Jensen's τ_J must be of the order of $(\langle x^2 \rangle_{\text{bound}}/r_o^2)\tau_j \sim 10^{-2} \tau_j$. This "relaxation time", τ_J , is between the jump relaxation time, τ_j , and the characteristic time of a lattice vibration. From equation II.7 and equation II.30 we get

$$D = \frac{-\ln f}{\kappa^2 \tau_J}. \quad (\text{II.31})$$

Unfortunately, $\langle \vec{V}(0) \cdot \vec{V}(t) \rangle_{\text{bound}}$ and the "relaxation time" τ_J are not clearly defined within the theory, although equation II.30 indicates it is connected with the bound oscillations, thus, coupling the bound to the unbounded motions. Since $\Delta\epsilon \propto D$, we would expect $\ln(\frac{\Delta\epsilon}{\Gamma_N})$ to be proportional to $-\ln f$.

Several criticisms of this theory can be made. First equation II.29 is not justified, and hardly seems self-evident. Also, to accept the harmonic approximation is doubtful, because when diffusion effects occur an atom of necessity has large amplitude oscillations which preclude the validity of the harmonic approximation. In fact one might well hope that a proper treatment of the anharmonic effects would account for the rapid fall off in f observed by Knauer and Mullen (11) and Jensen (10). For a comparison of equation II.31 with our experimental results, see Section V, figure 12.

III. EXPERIMENTAL TECHNIQUES

A. Sample Preparation

In the preparation of the samples the cleanest crystals of commercial ferrous chloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, (Baker Analyzed Reagent and Mallinckrodt Analytical Reagent) were selected. These crystals were dissolved in glycerol (certified A.C.S., Fisher Scientific Co., dry 99.2%) in the proportion of 1 gram of the salt for 15 grams of the solvent. This particular composition was chosen to get a desirable concentration of iron for the Mössbauer measurements. In terms of molarity, 1 gram of salt/15 gram of solvent corresponds to about 0.42 M (molar) at room temperature. Because of the high viscosity of the glycerol and low solubility of ferrous chloride in glycerol at room temperature, a flask of the mixture was kept in a water bath at 70°C , for about one week in order to have the salt completely dissolved. During this process, small amounts of hydrochloric acid (Reagent A.C.S.) were added which made the pH of the solution between about 2 and 3. The reason for adding acid was that previous preparation of similar solutions showed possible precipitation or oxidation, within approximately one week after the preparation. Initially, a fresh solution, which did not have HCl added, was faint green and showed a sharp doublet characteristic of

Fe^{2+} . Aging would take place, however, as evidenced by an increasing transparency with time, and the Mössbauer spectra evolved a complex pattern superposed onto the usual Fe^{2+} doublet. It was found that this aging effect could be eliminated by adding a small quantity of hydrochloric acid ($\text{pH} \approx 2.5$).

In these experiments several examples were prepared, particularly of type A, to verify the reproducibility of the data. In samples where tracer diffusion measurements were made, using $\text{Fe}^{59}\text{Cl}_2$, the Mössbauer spectra agreed very well with the non radioactive samples, discussed in detail in Section III.C. Because several samples were made, and because we also measured the diffusivity and viscosity of our samples, natural iron was used throughout instead of enriched Fe^{57} . Although our weight concentration was about 7% of the solvent weight, we only observed $\sim 15\%$ increase in viscosity for our samples compared to those with no salt added.

The sample A which we nominally label as dry may have had 3 to 4 percent water. This resulted from the fact that even the driest vacuum pumped glycerol, used as a starting solvent has about 1% water, while the salt added $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ contributed another 2 or 3 percent water. Weighing the sample before and after heating to dissolve the salt indicated that additional water was not acquired during this operation.

To verify that the dissolved salts dispersed in glycerol, and did not form colloids, two samples were prepared by

dissolving different salts in glycerol. Ferrous chloride and ferrous ammonium sulfate were dissolved in separate glycerol solutions, and the temperature dependence of the Mössbauer parameters (linewidth, quadrupole splitting, and recoil-free fraction) were found to be identical within the experimental errors, indicating that the salts were indeed dispersed (21). These results are given in Appendix B.

Approximately two liters of the ferrous chloride-glycerol solution were prepared, from which two other solutions were obtained by adding 5% and 10% of distilled and de-ionized water (by weight), respectively, to the dry sample solution. It is convenient to label the three solutions as follows:

Solution A is the solution with no water added, although it may contain 3-4 percent of water by weight,

Solution B is solution A + 5% of water (by weight) and

Solution C is solution A + 10% of water (by weight).

The stability of the solutions regarding possible crystallization was checked by taking subsequent Mössbauer runs over intervals of months. The water content in the solutions was monitored periodically by measuring the specific gravity.

Rough thermal analyses were carried out and they showed that our salt carrying samples, like pure glycerol, are liquid-glass substances, with a glass-liquid transition temperature of approximately 185°K, 175°K and 170°K for solutions A, B and C, respectively. The absence of sharp

changes in the derivative of the warmup curve supports the expected results that our samples did not have any crystalline phases in the temperature interval investigated.

The samples used in the Mössbauer experiments were encapsulated and set up according to the following procedure. The sample holders, illustrated in Figure 1(a), consisted of annular plexiglas rings (I) which were sealed at both ends with thin plexiglas disks (M). Two calibrated copper-constantine thermocouples (H), protected by thin pyrex tubing (O), were permanently sealed inside of the holders to monitor the temperature at the center and at the edge of a sample. To improve physical contact between thermocouples and solution, a small amount of silicone grease (N) was introduced in the tubing (O). The holders were filled by injecting the solution (L) with hypodermic needles through a small hole (J) in the side of the ring, which was sealed with epoxy (K). By means of this technique all Mössbauer samples were completely air tight preserving the initial characteristics of the solutions. Mössbauer spectra taken with these samples gave very reproducible results, independent of aging or temperature cycling.

To detect any possible convective current due to thermal gradients, some special samples were prepared following the procedure described above, except for the inclusion of either a porous foam disk or plastic powder inside the plexiglas walls. Placing the sample in such a

fine grained structure would guarantee that macroscopic hydrodynamic motion of the solution could not take place. The plastic powder used was the organic compound Methyl Methacrylate (polymerized), with particles of about 100-600 microns in diameter. The comparison between broadening of samples with and without foam (or plastic powder) were identical within the experimental errors. This showed that no convective current was present, and in subsequent experiments no foam or plastic powder was used.

B. Mössbauer Measurement

1. Spectrometry

Most of the data were obtained with a constant velocity spectrometer (23). A Gaertner microscope slide is the drive mechanism of this instrument on which either the source or absorber can be mounted. In the present experiments the source was moved because the absorber was inside a heavy dewar, whose weight was too great to be carried by the drive assembly. Thus, a 30 mCi single-line Mössbauer source, Co^{57} in palladium matrix, supplied by New England Nuclear, was mounted on the spectrometer slide and kept at room temperature for all runs.

A synchronous A.C. motor was mounted on a separate table to avoid vibration. Power was transferred to the slide through a Metron variable speed reducer by means of a convenient arrangement of pulleys and elastic belts. The slide

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A synchronous A.C. motor was mounted on a separate table to avoid vibration. Power was transferred to the slide through a Metron variable speed reducer by means of a convenient arrangement of pulleys and elastic belts. The slide

was driven at a constant speed, with alternatively positive and negative velocities of nearly equal magnitude. Two microswitches reversed the direction of the motion of the slide. The data recording scalers were switched on and off by two other microswitches located before the motor reversing switches. Using five scalers, we recorded the number of gamma rays detected while the slide is moving in a given direction, the time spent in the counting period, and the total number of trips at a given speed. From the data collected in the scalers, both count rate and velocity were calculated from the distance to time ratio.

The relative source-absorber velocities are obtained automatically through a programmed paper tape and an optical sensor incorporated into a spectrometer. The basic idea of this automation involves the use of a teletype tape wound on two spools. The velocities are programmed by perforating the tape at points which correspond to the desired velocities. After each counting period at a given velocity, the tape is electronically advanced, thereby changing the ratio of the metron speed reducer. This advance continues until the light beam on the tape is interrupted by the next hole in the tape. The light beam causes a sudden decrease in the resistance of the optical sensor generating a pulse which commands the speed control motor to stop. Data are collected for both positive and negative velocities until a desired statistical precision

is obtained. The information accumulated in the scalers is then printed out and the speed changer is automatically set for the next speed according to the programmed tape. The scalers are reset, and data accumulation resumes at this new speed. This process repeats itself automatically until the entire spectrum has been scanned.

As mentioned before, the data recording scalers were controlled by two switches for both directions of the motion of the slide. Because of the intrinsic mechanical behavior of these switches, the distance from the detector at which the scalers are turned on and off, was found to be different for opposite directions of the motion of the slide. Were the start-stop positions identical the average distance between the source and detector would be identical and no correction would be required. This small difference in travel distance represented a serious problem for our moving source experiments because of the $1/r^2$ dependence of the intensity of the gamma rays, where r is the distance between source and detector. This caused a slight (0.4%), but non-trivial, displacement of the baseline for positive as compared to negative velocity data. Thus, a correction factor was worked out and expressed in terms of measured geometrical parameters. The details are discussed in Appendix C.

2. Temperature Measurement and Control

Mössbauer measurements were done in a Texas Instrument dewar model CLF-1. As shown in Figure 1(b), the absorber (G)

(b)

(a) FRONT VIEW
SAMPLE HOLDER

Figure 1. Dewar, heater and sample holder assembly used in Mössbauer measurements.

Components: A) dewar surface, B) dewar window, C) O-ring, D) spacer between coolant and heater, E) copper holder, F) circular heater element, G) absorber, H) thermocouple, I) plexiglas ring, J) hole for injecting solution, K) epoxy, L) solution, M) plexiglas cover, N) silicone, and O) pyrex protecting tubing.

was mounted on a copper holder (E) which had a circular heater element (F). By separating this heater from liquid nitrogen coolant, by means of a convenient arrangement of copper and plexiglas spacers (D), it was possible to vary the temperature of the sample in the desired interval from 120°K to 250°K. The spacers and the copper holder were carefully made such that the internal alignment between absorber (G) and the windows (B) of the dewar could be routinely achieved by mounting the whole assembly on the surface (A) of the dewar. Using the three degrees of freedom of the detector, dewar, and source, the external alignment was easily obtained.

Temperature regulation was achieved by using a solid state temperature controller series 540, manufactured by Barber-Colman Co. Two copper-constantan thermocouples (H) were placed inside of the sample. Both of these thermocouples agreed to within 1.5°K below 200°K, and 0.5°K above 200°K, indicating a maximum thermal gradient of about 1°K across the active portion of the sample used for resonance absorption measurements.

C. Viscosity Measurement

1. Method

The viscosity of the sample solutions and pure glycerol was measured using calibrated Cannon-Fenske Viscometers, supplied and certified by United Scientific Co. The method

used is a standard procedure using inexpensive equipment. It deals with the determination of the kinematic viscosity, by measuring the time of flow of a fixed volume of liquid at a given temperature through a calibrated and shaped glass tubing. The kinematic viscosity (in centistokes) is given by the product of the flow time (in second) times the viscometer constant (in centistokes/second). The dynamical viscosity or absolute viscosity (in centipoise) is given by the product of the kinematic viscosity (in centistokes) times the density (in g/cm^3), at the temperature of the experiment.

A clean and dry viscometer was filled with a fixed volume of the solution and placed in a constant temperature water bath. Precaution was taken to avoid air bubbles in the solution. After thermal equilibrium has been reached, the solution was allowed to flow freely, and the flow time was measured by means of a stop watch, graduated in divisions representing 0.2 sec. The temperature was measured by a calibrated thermocouple in direct contact with the sample, but not in the region which would interfere with the flow rate. At least five runs were taken for each temperature, and the average flow was used to calculate the kinematic viscosity. The reproducibility of the flow time interval was better than 0.5% for intervals greater than 2 minutes and better than 1% for intervals between 1 and 2 minutes.

2. Density

As was mentioned in the preceeding discussion, the dynamic viscosity is given by the product of the kinematic viscosity times the density, at the temperature of the experiment. In this section we will describe the method used to obtain the density of our salt bearing glycerol samples. Since it was possible to measure mass much easier and with more accuracy than volume, the density was obtained through the specific gravity measurements. From the definition of density it follows that $d_L(T) = d_W(T) \frac{m_L}{m_W}$, where $d_L(T)$ and $d_W(T)$ are the densities of a given liquid and water, respectively, at temperature T . m_L and m_W are the masses of the liquid and water, respectively. Since $d_W(T)$ is well known, the density of glycerol used in the preparation of the solution, and the density of the solutions A, B, and C was obtained by weighing samples on a Mettler balance, using a 25 cm³ specific gravity bottle, supplied by E. H. Sargent and Co. At 22.5°C, for instance, the densities of the pure glycerol and solution A were found to be (in g/cm³) (1.260±0.009) and (1.290±0.010), respectively. The same technique was used to obtain the density of solutions A, B, and C at 0°C, where water was replaced by ethanol. For example, the density of the solution A was found to be (1.304±0.026) at 0°C. For other temperatures the density was extrapolated assuming a linear temperature dependence. This assumption is justified, because the

dissolved salt only slightly changed the density of the solvent, and it has been verified experimentally, that this type of temperature dependence holds for undoped glycerol above -62°C .

D. Diffusivity Measurement

1. Method

The diffusion coefficient of Fe^{2+} in glycerol and in glycerol-water solutions was measured by a capillary method (25). This method is based on a solution of the diffusion equation, $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$, for a cylindrical capillary under the following boundary conditions:

- i) at $t=0$ the concentration of the isotope inside of the capillary is uniform, i.e., $C=C_0$ for $0 \leq x \leq L$.
- ii) For all time t the concentration of the isotope at the top of the capillary is maintained equal to zero. This expression is given by (26)

$$\frac{C_{av}}{C_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \{ (2n+1)^{-2} \exp[-\frac{(2n+1)^2}{4L^2} Dt] \},$$

where C_0 and C_{av} are the average concentration of the isotope before and after the diffusion takes place, L is the length of the capillary, t is time of diffusion from the capillary, and D is the diffusion coefficient. By measuring C_0 , C_{av} , t and L , and using a numerical solution of the above equation, one can obtain D .

In this tracer technique, an open-ended capillary with uniform bore contains the radioactive tracer. The radioactive solution is allowed to diffuse into a very large quantity of identical but nonradioactive solution, which is gently stirred to keep the concentration of tracer equal to zero at the top of the capillary. The stirring rate cannot be too rapid or convective currents introduce large errors in the measured diffusion coefficient (27). These errors can be minimized by minimizing the stirring rate consistent with the boundary condition ii), and by minimizing the capillary diameter within the limitations of being able to place the radioactive solution in the capillary without having gas bubbles in the solution.

Capillaries with different lengths, ranging between 1 and 3 cm and inner diameters varying from .55 mm to 2.0 mm were obtained from commercial pyrex tubing. The open end was ground to have a rounded shape to reduce turbulence upon immersion. The other end was ground flat and cemented on a brass or plexiglas base, as shown in Figure 2(a). The length and inner diameter were measured by calibrated traveling microscope within 10^{-2} mm. For each run the bath solution (tracer-free) had a volume of approximately 400 cm³, and it was extracted from the same preparation used for carrying out Mössbauer experiments. The tracer solution was prepared using Fe⁵⁹ supplied by New England Nuclear in a chemical form FeCl₃ in 0.5N·HCl. The conversion of ferric

to ferrous ions was based on following reactions:

It was found that the ratio of approximately $\text{Fe}^0/\text{Fe}^{3+} = 10$ assured the complete reduction of ferric ions. The excess of Fe^0 was converted to Fe^{2+} by adding diluted hydrochloric acid. The whole reduction process was conducted in hydrogen atmosphere, because of the fast oxidation of ferrous ions in air. Chemical tests using potassium thiocyanate showed no presence of ferric ions after metallic iron had been completely dissolved. Also Mössbauer spectra taken with these samples showed only Fe^{2+} in the resonance spectra. Convenient portions of this ferrous radioactive solution were added to the solutions A and C to have both active and inactive solutions with approximately the same pH, concentration of ions and density (27). A high intensity radioactive standard was prepared, which was used to normalize the measured concentration of the tracer in each capillary, and thereby compensate for half life decay and possible electronics drift in the counting apparatus. Details of the counting technique will be given in section III.D.2. Before each run precautions were taken to avoid gas bubbles in both bath and tracer solutions. The capillaries were filled with tracer solution by means of hypodermic needles.

As shown in Figure 2(b), a beaker (E) with a nonradioactive solution (L) is placed on a brass support (C) in an

(a) DETAILS OF CAPILLARY

0 $\frac{1}{2}$ 1
SCALE IN INCHES

Figure 2. Arrangement used in the diffusion experiment.

Components: B) brass cylinder container, C) brass support, E) pyrex beaker, F) plexiglas cover, G) stirrer, H) motor, I) capillary holder, J) pyrex protecting tubing, K) thermocouple, L) tracer-free solution, M) tracer solution, and N) rubber band.

oil bath. Through holes on a plexiglas cover (F) four holders (I) were brought into this solution with a vertical orientation, each of them supporting a capillary clamped with a rubber band (N). The capillaries were symmetrically distributed around a central stirrer (G) rotated by a motor (H). After measuring the net radioactivity of the tracer in each capillary (to be described in section III.D.2), each capillary was suspended in the beaker so that the open end was just above the level of the bath solution until thermal equilibrium was attained. All capillaries were then carefully submerged permitting the diffusion of radioactive iron from the top of the capillary tube. Temperature was set and uniformity maintained by means of a heater, oil bath, and styrofoam insulation arrangement. Two calibrated thermocouples (K), protected by thin pyrex tubing (J), were used to monitor the temperature of the bath solution. The difference between their readings, at various locations, was no greater than 1°C , which was within the fluctuation observed during the run. After a predetermined time interval had elapsed, the capillaries were removed, carefully washed, externally, and then the amount of the remaining radioactive tracer Fe^{59} in each capillary was measured. Capillaries with inner diameter above .82 mm and stirring rates over 1 rpm gave spuriously large values of the diffusion coefficient, as evidenced by a diffusivity which decreased as the diffusion time interval

increased. This shows that convective currents were entering the capillary interior in violation of the assumed boundary condition (ii). The optimum condition was obtained with a stirring rate of approximately 1 rpm and capillaries with inner diameter 0.55 mm. Within this condition it was possible to reproduce the diffusion coefficient at a given temperature for capillaries with different lengths with various diffusion anneal time intervals, as will be shown in section IV.B. (See Table 3).

2. Scintillation Counter

The average concentration of the tracer before and after diffusion took place was measured counting the 1.098 and 1.289 MeV gamma rays emitted by the Fe^{59} . The counting system, schematically shown in Figure 3(a), consisted of a Harshaw scintillation counter, with a 3 x 3 inches NaI(Tl) crystal, and standard counting electronics. A standardized geometry, reproducible within 2%, was obtained by means of the arrangement shown in Figure 3(b). The scintillation detector was mounted in a fixed position inside of a lead cylinder shield, with 1 inch wall thickness. On the removable cap, a plexiglas base was mounted, which would accomodate precisely capillaries with standardized base size. The radioactive decay of the tracer and any possible electronic drift of the counting system during the diffusion experiment, were taken into account by the normalization procedure using a standard source. Both standard and

Figure 3. (a) schematic tracer counting system, and
 (b) detail of source and scintillation arrangement.

capillary were counted long enough to achieve the required statistics, and background corrections were made in each measurement.

IV. RESULTS AND DATA ANALYSIS

A. Viscosity Measurements

The results of the viscosity measurement are shown in Table 1. They were calculated from the relation $\eta = ctd$ at a given temperature, as discussed in section III.C. Since c (viscometer constant) and t (flow time) were known within 1%, and d (density) within 3%, the errors in η are considered to be less than 5% of measured values.

To obtain the viscosity of our glycerol-salt solutions in the temperature region where Mössbauer broadening was observed, we measured the viscosity in a convenient temperature interval from 0°C to 100°C, and then extrapolated our results to lower temperatures, using a well established semi-empirical method due to T. A. Litovitz (28,29). In this method the viscosity is considered as an activated process, but having a temperature dependence of hydrogen bonding. The explicit form of η is taken as

$$\eta(T) = \alpha \exp(\beta/T^3), \quad (\text{IV.1})$$

where α is a constant preexponential factor, and β is referred as an "activation energy constant", where the effective activation energy is considered as β/T^2 . The values of α and β were calculated from our measured $\eta(T)$ using a standard least squares computer program. These

Table 1. Experimentally Measured Viscosity of the Glycerol and Ferrous Chloride in Glycerol and in Glycerol-Water Solutions.

T (°K)	η (poise)			
	Glycerol	Solution A	Solution B	Solution C
273.0	119.0	161.8	-	-
284.7	-	-	-	5.62
285.4	-	-	11.68	-
286.0	28.0	37.25	-	-
290.5	-	-	-	3.38
291.5	-	-	6.54	-
292.0	-	20.17	-	-
294.5	-	-	5.21	2.52
295.0	11.8	-	-	-
295.5	-	14.64	-	-
302.0	-	8.47	-	-
303.0	-	-	-	1.40
303.5	-	-	2.56	-
310.8	-	-	1.54	-
311.3	-	3.92	-	-
311.5	-	-	1.46	-
311.8	3.05	-	-	-
312.0	-	-	-	0.779
314.0	2.68	-	-	-
319.5	-	2.34	-	-
319.7	-	-	-	0.519
322.5	1.50	-	-	-
325.0	-	-	-	0.402
326.6	-	-	0.623	-
328.0	-	-	0.577	-
328.7	-	1.28	-	-
330.5	0.943	-	-	-
332.5	-	-	-	0.277

values for our pure glycerol and samples characterized by A, B, and C are given in Table 2. The errors given in Table 2 are determined purely from the statistical analysis and do not necessarily include small systematic errors, such as a possible 1°K error in the absolute temperature. These values are thought to give a good representation of the relative errors, and when comparison was made with published values of η for glycerol and glycerol-water solutions (24) the agreement was excellent. The errors in α and β were used to make an error analysis of the average error in η in the temperature interval 200°K to 400°K , and these values are shown in the last column of Table 2. It should be noted that the extrapolated errors for samples B and C are about 15%.

Table 2. Viscosity Parameters

Sample	$\alpha \times 10^3$ (poise)	$\beta \times 10^{-9}$ $^{\circ}\text{K}^3$	Average Errors in η
Glycerol	1.80 ± 0.04	0.2257 ± 0.0005	3%
A	1.91 ± 0.06	0.2308 ± 0.0008	5%
B	1.73 ± 0.09	0.2043 ± 0.0015	15%
C	1.78 ± 0.07	0.1854 ± 0.0011	14%

A comparison of the data with the best fit using Equation IV.1, and the parameters of Table 2 is shown in Figure 4 for samples A, B, C, and pure dry glycerol. Curve E is given for comparison and it shows a fit of Equation IV.1 to measured viscosities of a 90% glycerol-water solution, based on the data of Dalton (24).

It should be noted comparing curves in Figure 4 that, from A compared to D and C compared to E, the main effect of adding $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is to raise the viscosity by about 15%, while maintaining practically the same temperature dependence to η . In the subsequent data analysis we shall use the actual values of $\eta(T)$ for the samples containing the salt added. In our analysis however, the slope in Figure 4 is the quantity usually used and it is only slightly affected by the presence of the added salt.

B. Tracer Diffusion Measurements

The results of our diffusion measurements are summarized in Table 3. These results represent diffusion runs ranging from 15 to 30 days using 0.55 mm diameter capillaries. The standard deviation in each value of the diffusion coefficient, D , reflects experimental errors from the counting geometry, measured time, and length of the capillaries. These errors do not include systematic errors such as a possible 1°K error in the temperature, and less than 2% in the measured C_{av} caused by the washing out of the tracer solution from the capillary when dipped in the bath solution and during the run. Therefore, the errors quoted for D may be greater than shown in Table 3. The magnitude of the 2% counting error will be significantly amplified for runs where the drop in activity $(1 - \frac{C_{av}}{C_o})$ is small. In the worst case ($T = 318^\circ\text{K}$), we believe this effect is about 10%. It was

Figure 4. Temperature dependence of measured viscosity of A sample A, B sample B, C sample C, D glycerol, and E 90% glycerol-water solution, data from reference (4), fitted to equation IV.1.

Table 3. Experimentally Measured Diffusion Coefficient of Samples A and C.

SAMPLE A					
Anneal Time (sec)	T (°K)	Capillaries		Fractional Activity Drop	D (cm ² /sec)
		No.	L (cm)		
1.99x10 ⁶	318+ <u>1</u>	1	1.86	.17	(3.82+ <u>.38</u>)x10 ⁻⁸
		2	2.23	.13	(3.55+ <u>.36</u>)x10 ⁻⁸
		3	2.21	.14	(3.64+ <u>.54</u>)x10 ⁻⁸
		Average		(3.67+ <u>.25</u>)x10 ⁻⁸	

1.55x10 ⁶	359+ <u>1</u>	1	1.95	.40	(2.94+ <u>.07</u>)x10 ⁻⁷
		2	1.94	.41	(3.20+ <u>.07</u>)x10 ⁻⁷
		3	2.23	.36	(3.33+ <u>.10</u>)x10 ⁻⁷
		4	2.43	.33	(3.17+ <u>.10</u>)x10 ⁻⁷
Average		(3.16+ <u>.04</u>)x10 ⁻⁷			

7.78x10 ⁵	372.5+ <u>1.0</u>	1	2.19	.37	(6.61+ <u>.12</u>)x10 ⁻⁷
		2	1.97	.41	(6.63+ <u>.20</u>)x10 ⁻⁷
		3	2.40	.35	(7.20+ <u>.20</u>)x10 ⁻⁷
		4	2.10	.41	(7.31+ <u>.30</u>)x10 ⁻⁷
Average		(6.94+ <u>.11</u>)x10 ⁻⁷			

SAMPLE C					
1.64x10 ⁶	296+ <u>2</u>	1	2.17	.13	(3.91+ <u>.39</u>)x10 ⁻⁸
		2	2.36	.12	(3.65+ <u>.37</u>)x10 ⁻⁸
		3	2.20	.10	(2.57+ <u>.26</u>)x10 ⁻⁸
		4	2.43	.11	(3.31+ <u>.30</u>)x10 ⁻⁸
Average		(3.36+ <u>.21</u>)x10 ⁻⁸			

found for sample C that the viscosity of the bath solution at the end of the experiment was about 40% smaller than its initial value. This decrease in viscosity can be explained by assuming that the sample picked up about 3% water during the diffusion run. Considering hygroscopic character of the solution and the difficulties of keeping the diffusion container completely air tight for the long time interval over which the experiment was run, this result is not surprising. Thus, when comparing the D value with viscosity, via the Einstein-Stokes relation we use an average value for the viscosity equal to 80% of the initial measured value at this temperature for sample C. The errors for this case are hard to estimate and might be quite large.

Lower temperature runs were not carried out for our dry glycerol sample A because the diffusivity became so small that the diffusion time was prohibitively large. Also, higher temperature runs were not compatible with the apparatus used. Only one measurement was made with sample C because we had no method of controlling possible changes in water content at elevated temperatures.

The measured values of D and η were used to test the validity of the Einstein-Stokes relation $D = \frac{kT}{6\pi R\eta}$ (see Equation II.12). For sample A, the values of the constant $\frac{k}{6\pi R} = \frac{D\eta}{T}$ in units of erg/°K.cm are

$$(2.90 \pm 0.75) \times 10^{-10} \text{ at } T = 318^\circ\text{K}$$

$$(2.55 \pm 0.05) \times 10^{-10} \text{ at } T = 359^\circ\text{K, and}$$

$(2.98 \pm 0.07) \times 10^{-10}$ at $T = 372.5^\circ\text{K}$.

Within the experimental errors the Einstein-Stokes relation is consistent with the data, giving an average value for $\frac{k}{6\pi R}$ equal to $(2.81 \pm 0.25) \times 10^{-10}$ erg/ $^\circ\text{K}\cdot\text{cm}$. Using this value, an estimate value for the radius of the diffusing entity is found to be $(2.61 \pm 0.23) \overset{\circ}{\text{A}}$. It has been observed (18) that the Einstein-Stokes relation (Equation II.12) is applicable for particles with radius greater than approximately $5 \overset{\circ}{\text{A}}$, but gives a radius smaller than the radius of the actual diffusing entity when applied to particles with radius less than the radius estimated from the molecular volume. A correction factor, f_c , is proposed by Robinson-Stokes (18) for particles with radii between 2 and $5 \overset{\circ}{\text{A}}$, based on their studies of ionic diffusion in aqueous solutions. The same reference gives $f_c = 1.5$ for a radius equal to $2.61 \overset{\circ}{\text{A}}$. Therefore, the estimated radius of the diffusion entity of the solution A, based on the measured diffusivity, from 318°K to 373°K , is $R = (3.92 \pm 0.35) \overset{\circ}{\text{A}}$.

Assuming the validity of the Einstein-Stokes relation for sample C, and taking for the viscosity 80% of its initial value, as pointed out earlier, the radius is found to be $R = (4.28 \pm 0.65) \overset{\circ}{\text{A}}$, after the Robinson-Stokes correction is applied. The values of R for both samples A and C suggest that probably the diffusing entity is the same for all three solutions A, B, and C, and has an average radius $(3.9 \pm 0.4) \overset{\circ}{\text{A}}$, which is about 30% greater than the radius of the glycerol

molecule, $3 \overset{\circ}{\text{A}}$, estimated from the molecular volume.

If we assume that the diffusion constant, D , is proportional to T/η in the region where diffusivity measurements were made, then we can fit D as a function of T with the aid of Equation IV.1. The result is

$$D = \gamma T \exp(-\beta/T^3), \text{ where}$$

$$\gamma = (1.52 \pm 0.46) \times 10^{-7} \text{ cm}^2/\text{sec.}^\circ\text{K}, \text{ and}$$

$$\beta = (0.232 \pm 0.009) \times 10^9 (\text{}^\circ\text{K})^3.$$

It should be noted that the value of β is identical, within the experimental errors, to the value obtained from the direct viscosity measurements for sample A, as shown in Table 2.

C. Mössbauer Measurements

The data output obtained from the constant velocity spectrometer were treated by a flexible non-linear regression, least-squares computer program, which initially calculated the velocity of the source and the relative transmission of the 14.4 keV gamma rays through a stationary absorber. Next, the relative transmission was corrected for a geometrical effect discussed in section III.B.1 and Appendix C., and when necessary, corrected for radioactive decay of the source. Then, velocity and corrected relative transmission were fitted to a sum of Lorentzian lineshapes, described by the following expression,

$$A(v) \equiv \frac{I(\infty) - I(v)}{I(\infty)} = \frac{A_1 \Gamma_1 / 2\pi}{(v-v_1)^2 + \Gamma_1^2 / 4} + \frac{A_2 \Gamma_2 / 2\pi}{(v-v_2)^2 + \Gamma_2^2 / 4},$$

where $I(\infty)$ is transmitted gamma ray intensity at Doppler velocity far removed from the resonant peak velocity, $I(v)$ is the measured transmission intensity as a function of velocity, v , A_T is the total area under the curve and is equal to $A_1 + A_2$, Γ_1 and Γ_2 are the full linewidths at half maximum of first and second peak, and v_1 and v_2 are the velocities of the first and second maxima, respectively. Spectra were fitted such that the sum of the squares of the residuals was a minimum. The fitting program supplied the best estimate values of the Mössbauer parameters and their standard errors, calculated by using statistical techniques. The errors quoted for the Mössbauer parameters include only these statistical errors. The number of counts taken at each velocity ranged between 2×10^5 and 2×10^6 , depending on the percent effect at the maximum. Roughly, the number of counts accumulated was such that the statistical errors were about 5% of the absorption at the maximum. Systematic errors due to vibration, thermocouple calibration error, etc., were investigated and considered small compared to the statistical errors, resulting from the limited number of counts at each velocity. Thus, we believe that the quoted standard errors are representative of the real experimental errors.

A representative set of Mössbauer spectra for absorbers of type A, B, and C as a function of temperature, are shown in Figures 5, 6, and 7, respectively. The solid lines

Figure 5. Temperature dependence of $^{57}\text{Mö}$ ssbauer spectra for sample A. Source was Co^{57} in palladium.

Figure 6. Temperature dependence of ^{57}Co Mössbauer spectra for sample B. Source was Co^{57} in palladium.

Figure 7. Temperature dependence of ^{57}Co Mössbauer spectra for sample C. Source was Co^{57} in palladium.

represent the fitted Lorentzian curves to the experimental data. Within the experimental errors they are symmetrical doublets with the same linewidth, area, and percent absorption for each peak. Although the data suggest some possible deviation from Lorentzian lineshape the effects are small and believed within the experimental errors. The best estimate of the Mössbauer parameters with their standard errors are summarized in Tables 4, 5, and 6, where Γ is the average value of the linewidth of the two peaks, A_T is the total area under the curve, $QS = v_1 - v_2$ is the quadrupole splitting, and $IS = (v_1 + v_2)/2$ is the isomer shift relative to palladium. The spectra for each of the three solutions can be identified as due to Fe^{2+} ions from the IS (≈ 1.1 mm/sec) and QS (≈ 3 mm/sec), since the typical ferrous ion (30) has an IS between 1.0 and 1.5 mm/sec, with QS between 2 to 4 mm/sec.

From the measured linewidths given in Tables 4, 5, and 6, we can calculate the incremental broadening of the Mössbauer line, $\Delta\epsilon = \Gamma - \Gamma_M$. The width of our line without diffusion, Γ_M , was taken as an average of the measured low temperature widths below the glass-liquid transition temperatures of 185°K, 175°K and 170°K for samples A, B, and C, respectively. The values of Γ_M , in mm/sec, are (0.409 ± 0.004) , (0.391 ± 0.005) and (0.385 ± 0.005) for samples A, B, and C, respectively. In Table 7, we show the results of this calculation, where the relative broadening, $\Delta\epsilon/\Gamma_N$, and

Table 4. Experimentally Measured Mössbauer Parameters for Sample A.

T (°K)	Γ (mm/sec)	A_T	V_1 (mm/sec)	V_2 (mm/sec)	QS (mm/sec)	IS (mm/sec)
122.5	.410 $\pm$.007	.1664 $\pm$.0020	2.775 $\pm$.003	-.482 $\pm$.002	3.257 $\pm$.004	1.147 $\pm$.002
160.2	.409 $\pm$.007	.1405 $\pm$.0017	2.737 $\pm$.003	-.479 $\pm$.003	3.216 $\pm$.004	1.129 $\pm$.002
181.0	.411 $\pm$.008	.1255 $\pm$.0018	2.712 $\pm$.004	-.483 $\pm$.003	3.195 $\pm$.005	1.115 $\pm$.003
193.0	.422 $\pm$.009	.1215 $\pm$.0018	2.700 $\pm$.004	-.480 $\pm$.003	3.180 $\pm$.005	1.110 $\pm$.003
211.3	.461 $\pm$.011	.1060 $\pm$.0020	2.657 $\pm$.006	-.460 $\pm$.004	3.117 $\pm$.007	1.099 $\pm$.003
221.0	.478 $\pm$.012	.0957 $\pm$.0018	2.629 $\pm$.006	-.454 $\pm$.005	3.083 $\pm$.008	1.088 $\pm$.004
226.5	.517 $\pm$.013	.0911 $\pm$.0018	2.614 $\pm$.007	-.444 $\pm$.005	3.058 $\pm$.009	1.085 $\pm$.005
232.5	.544 $\pm$.015	.0809 $\pm$.0018	2.587 $\pm$.008	-.439 $\pm$.006	3.026 $\pm$.010	1.074 $\pm$.005
237.0	.607 $\pm$.015	.0795 $\pm$.0016	2.571 $\pm$.007	-.426 $\pm$.006	2.997 $\pm$.009	1.073 $\pm$.005
241.8	.671 $\pm$.018	.0691 $\pm$.0018	2.551 $\pm$.009	-.419 $\pm$.007	2.970 $\pm$.011	1.066 $\pm$.006
245.5	.837 $\pm$.026	.0661 $\pm$.0018	2.513 $\pm$.012	-.385 $\pm$.011	2.898 $\pm$.016	1.064 $\pm$.008
249.5	.986 $\pm$.023	.0595 $\pm$.0013	2.513 $\pm$.010	-.365 $\pm$.009	2.878 $\pm$.013	1.074 $\pm$.007
251.3	1.075 $\pm$.023	.0542 $\pm$.0010	2.485 $\pm$.010	-.342 $\pm$.009	2.827 $\pm$.013	1.072 $\pm$.007
254.5	1.365 $\pm$.032	.0497 $\pm$.0011	2.444 $\pm$.014	-.296 $\pm$.012	2.740 $\pm$.018	1.074 $\pm$.009

Table 5. Experimentally Measured Mössbauer Parameters for Sample B.

T (°K)	Γ (mm/sec)	A_T	V_1 (mm/sec)	V_2 (mm/sec)	QS (mm/sec)	IS (mm/sec)
120.0	.383 $\pm$.006	.1344 $\pm$.0016	2.797 $\pm$.003	-.470 $\pm$.002	3.267 $\pm$.004	1.164 $\pm$.002
152.5	.398 $\pm$.007	.1205 $\pm$.0016	2.768 $\pm$.003	-.474 $\pm$.003	3.242 $\pm$.004	1.147 $\pm$.002
178.5	.409 $\pm$.007	.1068 $\pm$.0014	2.729 $\pm$.004	-.476 $\pm$.003	3.205 $\pm$.005	1.127 $\pm$.003
197.5	.423 $\pm$.009	.0946 $\pm$.0015	2.704 $\pm$.004	-.470 $\pm$.003	3.174 $\pm$.005	1.117 $\pm$.003
209.5	.446 $\pm$.009	.0851 $\pm$.0013	2.682 $\pm$.005	-.458 $\pm$.003	3.140 $\pm$.006	1.112 $\pm$.003
219.5	.488 $\pm$.010	.0787 $\pm$.0012	2.642 $\pm$.005	-.446 $\pm$.004	3.088 $\pm$.006	1.098 $\pm$.003
225.0	.514 $\pm$.011	.0722 $\pm$.0012	2.636 $\pm$.006	-.437 $\pm$.005	3.073 $\pm$.008	1.100 $\pm$.004
230.0	.571 $\pm$.015	.0641 $\pm$.0013	2.628 $\pm$.007	-.423 $\pm$.005	3.051 $\pm$.009	1.102 $\pm$.005
233.5	.602 $\pm$.016	.0592 $\pm$.0013	2.585 $\pm$.008	-.413 $\pm$.006	2.998 $\pm$.009	1.086 $\pm$.005
236.5	.693 $\pm$.015	.0548 $\pm$.0010	2.580 $\pm$.007	-.407 $\pm$.006	2.987 $\pm$.009	1.087 $\pm$.005
240.0	.798 $\pm$.018	.0516 $\pm$.0010	2.563 $\pm$.008	-.391 $\pm$.008	2.954 $\pm$.011	1.086 $\pm$.006
243.4	1.047 $\pm$.028	.0451 $\pm$.0011	2.530 $\pm$.013	-.355 $\pm$.011	2.885 $\pm$.017	1.088 $\pm$.008
246.0	1.255 $\pm$.039	.0397 $\pm$.0011	2.520 $\pm$.019	-.349 $\pm$.014	2.869 $\pm$.011	1.086 $\pm$.011
249.0	1.553 $\pm$.056	.0369 $\pm$.0013	2.449 $\pm$.016	-.289 $\pm$.019	2.738 $\pm$.025	1.080 $\pm$.012
250.0	1.64 $\pm$.12	.0321 $\pm$.0021	2.488 $\pm$.054	-.291 $\pm$.038	2.779 $\pm$.066	1.099 $\pm$.033

Table 6. Experimentally Measured Mössbauer Parameters for Sample C.

T		A _T	V ₁	V ₂	QS	IS
(°K)	(mm/sec)		(mm/sec)	(mm/sec)	(mm/sec)	(mm/sec)
133.0	.386 _± .007	.1183 _± .0016	2.791 _± .003	-.470 _± .003	3.261 _± .004	1.161 _± .002
152.5	.384 _± .007	.1094 _± .0013	2.786 _± .003	-.472 _± .002	3.258 _± .004	1.157 _± .002
179.5	.408 _± .007	.0972 _± .0013	2.752 _± .004	-.468 _± .003	3.220 _± .004	1.142 _± .003
196.0	.429 _± .010	.0881 _± .0014	2.718 _± .005	-.461 _± .004	3.179 _± .006	1.129 _± .003
210.5	.464 _± .011	.0763 _± .0014	2.684 _± .006	-.445 _± .004	3.129 _± .008	1.120 _± .004
221.3	.513 _± .014	.0647 _± .0014	2.648 _± .007	-.430 _± .005	3.078 _± .009	1.109 _± .005
224.0	.526 _± .013	.0616 _± .0012	2.634 _± .007	-.423 _± .005	3.057 _± .009	1.106 _± .005
226.8	.561 _± .016	.0550 _± .0012	2.625 _± .008	-.421 _± .006	3.046 _± .009	1.102 _± .005
230.7	.648 _± .018	.0496 _± .0011	2.600 _± .009	-.408 _± .007	3.008 _± .011	1.096 _± .006
233.0	.732 _± .023	.0497 _± .0014	2.600 _± .011	-.388 _± .009	2.988 _± .014	1.106 _± .007
237.0	.971 _± .026	.0444 _± .0011	2.548 _± .013	-.356 _± .011	2.904 _± .017	1.096 _± .009
240.0	1.203 _± .030	.0423 _± .0009	2.535 _± .014	-.343 _± .010	2.878 _± .017	1.096 _± .009
242.0	1.388 _± .049	.0365 _± .0011	2.531 _± .021	-.300 _± .018	2.831 _± .028	1.116 _± .014

Table 7. Relative Diffusional Broadening and Viscosity as Function of T.

Sample A			Sample B			Sample C		
T (°K)	$\Delta\epsilon/\Gamma_N$	η (poise) *	T (°K)	$\Delta\epsilon/\Gamma_N$	η (poise) *	T (°K)	$\Delta\epsilon/\Gamma_N$	η (poise) *
193.0	.13 $\pm$.10	1.66x10 ¹¹	178.5	.18 $\pm$.09	6.85x10 ¹²	179.5	.24 $\pm$.09	1.49x10 ¹¹
211.3	.53 $\pm$.12	8.11x10 ⁷	197.5	.33 $\pm$.11	5.66x10 ⁸	196.0	.45 $\pm$.11	8.80x10 ⁷
221.0	.71 $\pm$.13	3.70x10 ⁶	209.5	.57 $\pm$.11	7.69x10 ⁶	210.5	.81 $\pm$.12	7.69x10 ⁵
226.5	1.11 $\pm$.14	8.08x10 ⁵	219.5	1.00 $\pm$.11	4.25x10 ⁵	221.3	1.32 $\pm$.15	4.80x10 ⁴
232.5	1.39 $\pm$.16	1.80x10 ⁵	225.0	1.26 $\pm$.12	1.06x10 ⁵	224.0	1.45 $\pm$.14	2.59x10 ⁴
237.0	2.03 $\pm$.16	6.44x10 ⁴	230.0	1.85 $\pm$.16	3.40x10 ⁴	226.8	1.81 $\pm$.17	1.42x10 ⁴
241.8	2.69 $\pm$.19	2.36x10 ⁴	233.5	2.17 $\pm$.17	1.62x10 ⁴	230.7	2.70 $\pm$.19	6.46x10 ³
245.5	4.40 $\pm$.27	1.13x10 ⁴	236.5	3.10 $\pm$.16	8.79x10 ³	233.0	3.57 $\pm$.24	4.14x10 ³
249.5	5.93 $\pm$.24	5.43x10 ³	240.0	4.18 $\pm$.19	4.55x10 ³	237.0	6.02 $\pm$.27	1.99x10 ³
251.3	6.84 $\pm$.24	3.68x10 ³	243.4	6.74 $\pm$.29	2.45x10 ³	240.0	8.41 $\pm$.31	1.19x10 ³
254.5	9.83 $\pm$.33	2.29x10 ²	246.0	8.88 $\pm$.40	1.58x10 ³	242.0	10.31 $\pm$.51	8.54x10 ²
			249.0	11.94 $\pm$.58	9.65x10 ²			
			250.0	12.8 $\pm$ 1.2	8.25x10 ²			

* These values are extrapolated from our experimental values, as discussed in Section IV.A.

the extrapolated viscosities are given for each temperature, where the Mössbauer spectrum was observed. At low temperatures the error in the broadening is quite large, because $\Delta\epsilon$ is the difference in two linewidths which are nearly of the same magnitude.. It should be mentioned that the subtracted minimum width, Γ_M , will in part contain a term involving the "finite thickness" correction, which will decrease as the probability of recoil-free absorption decreases and as the temperature increases. We have not included this correction, although we estimate that it does not change sufficiently to significantly alter the uncorrected incremental broadenings given in Table 7.

V. DISCUSSION

Since the Singwi-Sjölander (4) theory predicts that the broadening of the Mössbauer line should be proportional to the diffusivity (equation II.23), and since the Einstein-Stokes relation predicts a diffusivity proportional to T/η (equation II.12), we might expect a plot $\Delta\epsilon/\Gamma_N$ versus T/η to be linear, as was apparently confirmed by Craig and Sutin (7). Our results are shown in Figure 8 and it is clear that a simple linear relation does not give a satisfactory representation to our data. Although our results are in reasonable agreement with those of Champeney and Woodhams (9), as shown in Figure 8E, particularly considering that they were looking at the Fe^{3+} resonance, and, thus, their system differed significantly from our own, they are in marked contrast to those of Craig and Sutin (Figure 8D). We cannot offer a compelling explanation for this discrepancy, although it could be associated with the fact that they used a Co^{57} doped solution of glycerol, and the atomic relaxation effects following the emission of Auger electrons might have complicated the interpretation of their data. Since their minimum width was about 5 times greater than the minimum expected from the uncertainty principle, some complicating feature was present in their study which was not in ours.

It should also be noted that curves A, B and C in Figure 8 are clearly distinguished. If the simple Einstein-Stokes relation and the Singwi-Sjölander theory were both adequate to describe our system, we should expect these three curves to be superimposed in a single straight line.

In Figure 9 we have plotted the broadening of the Mössbauer line as a function of $1/T$. In the low temperature region the curves approach an Arrhenius relation. If we assume that the diffusion consists of two distinct mechanisms, which are statistically independent, then in accordance with our discussion in the theory (Section II.B), we would expect $D = D_1 + D_2$. We are able to give a very satisfactory fit to our data, as evidenced by the solid lines shown in Figure 9, by assuming that D_1 is due to continuous diffusion, so that $D_1 \propto \Delta\epsilon_1/\Gamma_N = A_1 T \exp(-\beta/T^3)$, where the latter expression is derived from the Litovitz equation IV.1, and D_2 is an activated diffusion process, such as occurs in solid state diffusion, and is described by an Arrhenius temperature dependence, i.e., $D_2 \propto \Delta\epsilon_2/\Gamma_N = A_2 \exp(-E/kT)$. The three parameter least squares fit to the data, with appropriate weighting factors to account for the difference in error bars in the data, give the values of A_1 , A_2 and E shown in Table 8. It should be emphasized that β was not allowed to vary in this calculation, but was taken directly from the curves fitted to the measured viscosity, i.e., the values used were the same as shown in Table 2.

Figure 8. Dependence of diffusional broadening on viscosity.

Figure 9. Temperature dependence of the diffusional broadening for samples A, B, and C.

Table 8. Broadening Parameters for the Relation

$$\Delta\epsilon/\Gamma_N = A_1 T \exp(-\beta/T^3) + A_2 \exp(-E/kT).$$

Sample	$A_1 \times 10^{-4}$ (°K) ⁻¹	$A_2 \times 10^{-5}$	E (eV)
A	2.58 ± .23	4.50 ± 5.52	.252 ± .025
B	1.65 ± .10	2.40 ± 3.38	.234 ± .028
C	1.52 ± .08	.13 ± .19	.176 ± .029

The fit to the data is excellent and the correctness of this interpretation is augmented by a comparison with the results of Larsson et al. (31), who measured diffusion in glycerol by means of neutron scattering experiments. Although they fitted his data to a sum of Arrhenius relations, the slopes in the low and high temperature regions are quite similar to the values we obtain by our Mössbauer studies. The difference in the temperature of the bend in our curve and his could be explained by the fact that the diffusing entity in our case contains Fe⁵⁷. This discrepancy will be reduced in any event if we plot $\ln D$ versus $1/T$ from our data. This cannot be done, however, as insufficient diffusivity data is available to determine σ for the jump part of the diffusivity. The difference in the magnitude of the D values cannot be explained so easily, although the mass difference would account for some of this discrepancy.

The present measurements afford an opportunity to measure σ (equation II.23) in the continuous diffusion

limit. In an earlier work Knauer and Mullen (8) had found a serious discrepancy in σ in the sudden-jump (4) limit corresponding to solid state diffusion, which has led to a reformulation of the theory (32, 33) to include effects of Bardeen-Herring correlation.

We now wish to compare $\Delta\epsilon_1$ with the measured diffusivity in the high temperature region, where the continuous component to the diffusivity is dominant, with the predictions of the Singwi-Sjölander theory in the continuous diffusion limit, $\tau_1 \gg \tau_0$. We can do this by extrapolating $\Delta\epsilon_1/\Gamma_N$ to the temperature where we made tracer measurements of the diffusivity by means of the tracer-capillary technique (Section III.D), and then calculating σ at those temperatures from the relation, equation II.23, $\Delta\epsilon/\Gamma_N = \sigma(\kappa^2\tau_N)D$. This procedure gives the values of σ shown in Table 9. The average value of $\sigma = 2.24 \pm .13$ is in excellent agreement with the theoretically expected value $\sigma = 2.0$.

We were not able to get sufficient tracer diffusion data for samples type B and C to permit this same type of

Table 9. Calculated Values of σ For Sample Type A.

T (°K)	σ
318	$2.16 \pm .24$
359	$2.54 \pm .23$
372.5	$2.02 \pm .18$

comparison. If we do use the values of D measured for sample C at 296°K, we can show that to within the accuracy that we know the average viscosity, we may write, for fixed temperature

$$\frac{D_C}{D_A} = \frac{\eta_A}{\eta_C}, \quad (V.1)$$

which implies that the form of the Einstein-Stokes relation holds in this temperature region, and that the effective radius R of the diffusing entity is essentially constant. In Section IV.B we discuss in greater detail this assumption and show that for sample A the radius of the diffusing entity is comparable with that of a glycerol molecule, as calculated from the molecular volume. Thus, assuming the constancy of the radius of the diffusing entity relation (V.1), and the analogous relation for sample type B, we find $\sigma = 1.30 \pm .16$ and $\sigma = 1.23 \pm .15$ for samples B and C, respectively. If we use the directly measured D value for sample C (Table 3) we obtain $\sigma = 1.35 \pm .11$. The small difference between the two values (1.35 vs. 1.23) indicates that the assumption of a constant radius for the diffusing entity is valid to within about 10%. Although the statistical errors indicate a deviation from the value in the Singwi-Sjölander theory, we think that these statistical errors are smaller than the real errors for case B and C because the error in diffusivity probably is greater than shown in Table 3. We regard the excellent agreement with theory for sample A, for which we had the best diffusion data, as

strong evidence that this continuous limit of the theory is a satisfactory description of the continuous part of the diffusion motion in glycerol. Even taking into account the values of σ for samples B and C, we still find a value of σ in reasonable harmony with theory. The mean value of σ for all three samples is 1.6, which is only 20% below the expected value of 2.0. We regard this as excellent agreement in view of the uncertainties in determining the diffusion coefficient for samples B and C.

We have found that in the temperature region where diffusion is occurring there is a very rapid fall off in the recoil-free fraction. Neglecting changes in the "finite thickness" correction, the recoil-free fraction is proportional to the area under the Mössbauer resonance absorption curve (see Section II.A). A plot of $\ln A_T$ vs. T is shown in Figure 10 for our samples A, B, and C. The curves follow the expected linear dependence predicted by the Debye model below the glass-liquid transition temperature until we reach a temperature of about 200°K, where diffusion effects are observed. In this region we find that the fall off in f is much more rapid, and the effect is similar to earlier (8) results for Fe^{57} in Cu and Au.

In the linear region the values of the Mössbauer characteristic temperature were calculated from equation II.10, and found to be 170°K, 172°K and 177°K for samples A, B, and C, respectively. The absolute errors are

Figure 10. Temperature dependence of the area under Mössbauer resonance for samples A, B, and C.

probably within about 10°K , and the relative errors are of order 2°K . Errors from the changes in "finite thickness" correction and the linear approximation (equation II.10) have not been included. These values are comparable with the Mössbauer characteristic temperature for glycerol found from neutron scattering experiments (34) ($\Theta_M \approx 150^\circ\text{K}$).

In section II.C we discussed Jensen's phenomenological theory which proposes that the broadening of the Mössbauer line should be proportional to $\ln f$ even though both $\Delta\epsilon$ and f have a complicated temperature dependence. A plot of $\Delta\epsilon/\Gamma_N$ vs $-\ln f$ is given in Figure 11. The data can be represented reasonably well by two straight lines in the low and high temperature regions with intercepts at 235°K , 233°K , and 227°K for samples A, B, and C, respectively. The superposition of curves A and B at high temperatures and B and C at low temperatures, is probably statistically fortuitous. The linearity between the diffusion broadening and $\ln f$ would imply from Jensen's analysis that the vibratory and jumping motions are not independent. The possibility of an alternative explanation of the rapid fall off of $\ln f$ in the temperature region where diffusion is occurring, such as anharmonic effects (35), cannot be ruled out, particularly in view of the limited precision of the quantities involved in the plot of Figure 11.

In Figure 12 we show a plot of the quadrupole splitting (QS) as a function of temperature. Again we see a very

Figure 11. Correlation between Mössbauer line broadening and recoil-free fraction.

Figure 12. Temperature dependence of the quadrupole splitting for samples A, B and C.

rapid fall off in the temperature interval above the glass-liquid transition temperature where diffusion broadening effects were observed. This suggested that a plot of $\Delta\epsilon/\Gamma_N$ vs. QS might also yield a linear relation, which is well confirmed in Figure 13. Again the turning points in the linear relations 233°K, 232°K and 225°K for samples A, B and C, respectively, are comparable to those from the curve in Figure 11. We fitted $\Delta\epsilon/\Gamma_N = B_1 - B_2(QS(T)/QS(T_0))$ with our general least squares program, and the parameters B_1 and B_2 are given in Table 10. The small error limits are indicative of the high degree of linearity in both the low and high temperature regions.

Although the temperature dependence of the quadrupole splitting for Fe^{2+} in ionic salts has been studied by Ingalls (36), his analysis does not seem adequate to explain our results, which deal with the same ferrous ion in glycerol. Ingalls considered the splitting of the energy levels of the ferrous ion caused by the crystalline field and assume that the thermal transition times between levels ($10^{-9} - 10^{-11}$ sec) are smaller than the quadrupole splitting precession time ($\sim 10^{-8}$ sec). Based on this assumption the quadrupole splitting is expressed as a function of temperature through a Boltzmann distribution for occupancy of the split levels. His results predict, for $FeCl_2 \cdot 4H_2O$, a decreasing in the quadrupole splitting of $\sim 10\%$ for an increasing in temperature from about 80°K to 330°K, and

Figure 13. Correlation between Mössbauer line broadening and quadrupole splitting for samples A, B, and C.

Table 10. Parameters Fit to Figure 13.

Sample	B_1		B_2	
	Low Temp. region	High Temp. region	Low Temp. region	High Temp. region
A	26.4 ± 2.7	100.3 ± 7.3	25.8 ± 2.6	94.0 ± 6.4
B	25.4 ± 2.4	134.6 ± 6.4	25.1 ± 2.3	126.1 ± 5.6
C	24.9 ± 1.4	138.3 ± 1.2	24.7 ± 1.3	130.1 ± 10.8

agree with the experimental results. Below the glass transition temperature we also observed a similar gradual reduction in the quadrupole splitting, which could probably be explained by Ingall's approach. In our study, however, where the same salt was used, we have observed a sudden 12% decrease in the quadrupole splitting over only a 50°K increase in temperature in the region where diffusion occurred. This strongly supports the view that the diffusive motions are contributing to the rapid fall off in the quadrupole splitting.

A simple explanation for this observation can be given if we assume that the time average electric field gradient diminishes proportional to the diffusivity or rate of jumping, i.e., the electric field gradient reduces in proportion to the jumping frequency, or $\Delta\epsilon/\Gamma_N$. The change in slope again reflects, by this analysis, a change in the dominant diffusion mechanism from sudden jump to continuous, as we go from low to high temperatures.

It should be mentioned that in general the problem of calculating time dependent relaxation effects of hyperfine structure is very involved (37,38). For this case, however, where the hyperfine splitting is large compared to the natural linewidth of the isomeric level, it appears that the effect of diffusion on the quadrupole splitting is quite simple. A more detailed theoretical analysis, however, would be desirable.

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APPENDICES

Appendix A

Search For a Suitable Ferric Salt
For Mössbauer Diffusion Studies

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Search For a Suitable Ferric Salt For Mössbauer Diffusion Studies

In this appendix we will give a brief qualitative discussion of some of the ferric systems, in which we tried to study the diffusion broadening using the Mössbauer effect. These systems were prepared by dissolving ferric compounds either in water or in glycerol. The main reason for this search was to find a single line absorber having a narrow linewidth at low temperature having a convenient QS, i.e. either much larger or smaller than Γ_N . Obviously, it would be the ideal situation for studying the diffusion broadening. Some of the ferric samples we tried are given below:

- a) $\text{FeCl}_3 \cdot 13\text{H}_2\text{O}$
- b) $\text{FeCl}_3 \cdot 13\text{H}_2\text{O} \cdot (.8\text{HClO}_4)$
- c) $\text{FeCl}_3 \cdot 20\text{H}_2\text{O}$
- d) $\text{HFeCl}_4 \cdot (9.67 \text{ H}_2\text{O})$
- e) $\text{Fe}(\text{NO}_3)_3 \cdot 20\text{H}_2\text{O}$
- f) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in glycerol
- g) $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in glycerol

Unfortunately, all ferric solutions studied showed, among other disadvantages, either a complex Mössbauer spectrum or a not well resolved doublet with very small, but not negligible, quadrupole splitting. An example is given in Figure A1 which shows the Mössbauer spectra for the samples, a, c, d, and g, taken at $T = 90^\circ\text{K}$. In the spectrum (a) one can

Figure A1. Mössbauer spectra for some ferric compound solutions taken at 90°K. Source was Co^{57} in palladium.

see slight evidence for a small quadrupole splitting. Assuming a single line with Lorentzian shape for this spectrum, the linewidth is found to be $\Gamma = .98 \frac{\text{mm}}{\text{sec}}$, which is very broad (5 times the minimum expected by the uncertainty relation) at $T = 90^\circ\text{K}$. The spectrum c shows a non-Lorentzian lineshape. In the spectrum d a reasonable doublet could be resolved, giving $QS \approx .39 \text{ mm/sec}$, $\Gamma_1 \approx .57 \text{ mm/sec}$ and $\Gamma_2 \approx .51 \text{ mm/sec}$. The only studied ferric solutions showing a well resolved quadrupole splitting is illustrated in the spectrum g. Assuming a Lorentzian lineshape it was found $QS \approx .46 \text{ mm/sec}$ and $\Gamma_1 = \Gamma_2 \approx .47 \text{ mm/sec}$.

The difficulties with systems having QS smaller or comparable with Γ_N are that, for the diffusion broadening studies, one has to know precisely how Γ is affected by the QS as a function of temperature. This is a complex matter, and no studies have been found in the literature. Based on these difficulties the ferric samples were discarded and our investigations focused on ferrous systems, specifically, ferrous chloride which gave us symmetrical doublet with a large, well resolved quadrupole splitting ($\sim 3 \text{ mm/sec}$) and a narrow linewidth ($\sim .40 \text{ mm/sec}$) at low temperature. With this absorber the lines were all well resolved, even at the highest temperature studied. The low temperature linewidth was near enough to be minimum predicted by the uncertainty relation to give accurate incremental broadening when it was subtracted from the

measured linewidth in temperature region where we observed diffusion broadening.

Appendix B

Comparison of Mössbauer Spectra
for $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
Dissolved in Glycerol

Appendix B

Comparison of Mössbauer Spectra for $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$
and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ Dissolved in Glycerol

The Figure B1 shows a representative set of Mössbauer spectra taken for the two samples containing ferrous chloride and ferrous ammonium sulfate. The Mössbauer parameters (linewidth, Γ , recoil-free fraction, f , and quadrupole splitting QS) were studied as a function of temperature. It was found that the diffusional broadening $\Delta\epsilon/\Gamma_N$, f and QS had identical temperature dependence for both samples, within the experimental errors. This showed that these salts were indeed dispersed in glycerol and did not form colloids.

Figure B1. Temperature dependence of Mössbauer spectra for ferrous chloride and ferrous ammonium sulfate dissolved in glycerol. Source was Co^{57} in palladium.

Appendix C

Geometrical Correction for the Constant Velocity Spectrometer

Appendix C

Geometrical Correction for the Constant Velocity Spectrometer

In the constant velocity spectrometer two microswitches A and B control the operation of data recording scalers for both directions of the motion of the slide.

Let L_A represent the mean distance from the source to the detector when switch A starts the counting scaler for motion in the AB direction, and let L_B represent the mean distance from the source to the detector when switch B stops the counting scaler for motion in the AB direction. For the opposite direction of motion let L'_B and L'_A represent similar starting and stopping position, respectively, for motion in the BA direction. Since the difference in start and stop position is small compared to L_A , L_B , L'_A , or L'_B we may define increments δL_A and δL_B by the relations

$$\begin{aligned}\delta A &= L_A - L'_A \\ \delta B &= L_B - L'_B.\end{aligned}\tag{C.1}$$

For a given constant velocity v , of the source the scalers record a counting rate which is averaged over the distance traveled by the slide. The intensity of the gamma ray detected at time t is given by

$$I = A/r^2,\tag{C.2}$$

where r is the distance between source and detector. For one trip, the average intensity in AB direction is

$$\langle I \rangle_{AB} = \frac{1}{T} \int_0^T I dt = \frac{1}{T} \int_0^T A dt / r^2, \quad (C.3)$$

where $T = \frac{L_B - L_A}{v}$. Writting $r = L_A + vt$ and performing the integration in (C.3) we have

$$\langle I \rangle_{AB} = \frac{A}{L_A L_B}. \quad (C.4)$$

Similarly for BA direction we have

$$\langle I \rangle_{BA} = \frac{A}{L'_A L'_B} \quad (C.5)$$

We found experimentally that $L_A > L'_A$ and $L_B > L'_B$, always. Therefore, $\langle I \rangle_{AB} > \langle I \rangle_{BA}$ which causes a systematic intensity shift of the Mössbauer spectra in one side of the zero velocity respect to the other.

We renormalized the intensity of the counting in the AB direction from the relation

$$\langle I \rangle_{AB, \text{correct.}} = r \langle I \rangle_{AB, \text{measured}}, \quad (C.6)$$

where r is a predetermined correction factor, which can be measured in the absence of the Mössbauer absorber, in which case it is given by

$$r = \frac{\langle I \rangle_{BA}}{\langle I \rangle_{AB}}, \quad (C.7)$$

which from (C.4) and (C.5) can be written as

$$r = \frac{L_A L_B}{L'_A L'_B}. \quad (C.8)$$

Because the detector is not an ideal point object, L_A , L_B , L'_A , and L'_B are not easily measured. We can relate them, however, to the measured intensities via the relations

$$I_A = A/L_A^2, I_B = A/L_B^2, I'_A = A/L'^2_A, \text{ and } I'_B = A/L'^2_B, \quad (\text{C.9})$$

where I_A is the intensity of a source at L_A from the detector, with similar definitions for the other intensity quantities.

From (C.9), r can be expressed as

$$r = \left(\frac{I'_A I'_B}{I_A I_B} \right)^{1/2}. \quad (\text{C.10})$$

Although (C.10) would have sufficed for finding the correction r , we utilized a slightly different procedure involving difference in the L values, which are easily measured. If we define

$$D_{BA} = L'_B - L'_A \quad (\text{C.11}),$$

and utilize (C.1) we can show that

$$r = 1 + \frac{\delta A}{D_{BA}} (\alpha - 1) + \frac{\delta B}{D_{BA}} \left(\frac{\alpha - 1}{\alpha} \right) + \frac{\delta A \delta B}{D_{BA}^2 \alpha} (\alpha - 1)^2, \quad (\text{C.12})$$

where $\alpha^2 = \frac{I'_A}{I'_B}$. Since $(\alpha - 1) \ll 1$, the last term of (C.12) is much smaller compared to the others and it was neglected. Thus, we were able to normalize the intensity difference for AB and BA motion, from measured parameters δA , δB , D_{BA} and α .

Although r was only 0.004, it was important in calculating accurate linewidths and areas under the Mössbauer absorption curve. A check on this procedure was provided by the two lines in the observed spectra. When the

correction was made there was always excellent agreement between the widths and area under the two peaks of the observed doublet.