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BY NUCLEAR MAGNETIC RESONANCE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

ELVE MONTEIRO DE CASTRO, B.S.

******

The Ohio State University

1964

Approved by

[Signature]

Adviser

Department of Physics
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The difficulties involved in writing a Ph. D. dissertation are not only attending the classes, passing the examinations and running the experiments. This is the part that depends almost only on the candidate's effort. The other part, of as much importance but many times neglected or misunderstood, depends upon a great number of friends that indirectly but decisively help with their warm friendship, technical assistance and financial support.

It is an unsurpassable task to enumerate the names of all the collaborators, and I will not attempt to do it. Those names which are not here noted are nevertheless undeletable from my memory.

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In my country, Brazil, I am greatly indebted to several official organizations which granted me at one time or another scholarships, comple-
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VITA

I, Elve Monteiro de Castro, was born in Minas Gerais, Brazil, November 9, 1932. I received my primary and secondary education during eleven years in the public schools of Belo Horizonte. Then I was admitted to a five-year course in Electronics Engineering in the Instituto Tecnológico de Aeronáutica, São José dos Campos, São Paulo, under the auspices of the federal government. During 1958 the French government, through the "Service de Cooperation Technique," granted me a one-year scholarship in the Institut Fourier, Grenoble, France. During 1959 and 1960 I was Assistant Professor of Nuclear and Atomic Physics in the Instituto de Pesquisas Radiativas da Escola de Engenharia da Universidade de Minas Gerais, Belo Horizonte, Brazil.

While at Ohio State University, which I entered in the spring of 1961, I held the position of Research Assistant in the Low Temperature Laboratory.

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ERRATUM

The numerical value of the radio frequency field $H_1$ throughout the whole dissertation is too large by a factor of 2. The value that is given is the amplitude of the oscillating linear polarized field $A \cos \omega t$ in the rf coil, whereas in the analysis the value used is the amplitude of the rotating field $H_1$, which differs from $A$ by a factor of 2.
ABSTRACT

Solid mixtures of H$_2$ - D$_2$ were studied in several concentrations by NMR with a broad line spectrometer (CW) and the pulsed technique. The experiments with pure n-H$_2$ at 10 Mc/s were in good agreement with the results published in the literature by other workers. At 4.2°K the resonance line is narrower than a gaussian, has a linewidth of 5.7 gauss and is slightly asymmetric at an rf field $H_1 \approx 15$ mgauss. At 1.10°K the $\lambda$-splitting of the H$_2$ resonance line shows the center line, two side peaks and the two humps at 3.2, 39.8 and 76 gauss separation measured from peak to peak, respectively. When the pulsed technique was used at 20 Mc/s, beats were observed after the 90° pulse at 4.2°K, and $T_1$ of pure n-H$_2$ was measured using a 180°-90° pulse sequence. A plot of the recovery of the largest beat against time interval $\tau$ gave $T_1 \approx 480$ and 390 msec for the two extreme slopes of the plot. At 1.10°K a series of beats was observed and interpreted as resulting from the $\lambda$-splitting. A simple calculation associates the period of these beats with the 40.3 gauss separation observed in CW measurements.

The experiments with pure n-D$_2$ at 2.6 Mc/s show no $\lambda$-splitting above 1.10°K. The linewidth at 4.2°K was 1.66 gauss from peak to peak and very asymmetric compared with the n-H$_2$ line. The $\lambda$-splitting of D$_2$ was found below 2°K using an enriched sample of D$_2$ containing 80% para/ortho. The side peaks were 76.8 Kc/s apart.
Mixtures of normal H\textsubscript{2} with normal D\textsubscript{2} behaved very much like mixtures of ortho and para H\textsubscript{2}. Concentrations above 95\% H\textsubscript{2}/D\textsubscript{2} show the same type of \(\lambda\)-splitting as pure H\textsubscript{2}, and no significant change in the splitting distances was observed. The temperature \(T_\lambda\) of the transition decreases as the H\textsubscript{2} concentration decreases. At 10\(^\circ\)K the resonance line is simple with a small broad tail of similar shape and amplitude in all concentrations. At 4.2\(^\circ\)K the peak to peak linewidth fits the formula (where \(x\) is the concentration of H\textsubscript{2}):

\[
<\Delta H^2>_{\text{mix}}^{1/2} = <\Delta H^2>_{\text{pure}}^{1/2} \left\{ x + k(1-x) \right\}^{1/2}
\]

obtained from a calculation of the rigid lattice second moment for protons in a homogeneous solid H\textsubscript{2} - D\textsubscript{2} mixture where \(k\) is equal to 0.021. The broad tail at 4.2\(^\circ\)K has larger amplitude for samples with lower concentrations of H\textsubscript{2}. Below 4.2\(^\circ\)K the tail increases very much in amplitude; the lineshape becomes composite and almost resolved at the lower concentrations of H\textsubscript{2}. This composite line can be due to phase separation or quenching of the rotation of the ortho-H\textsubscript{2} molecules. The second interpretation is more likely to be true because the transition occurs very quickly when temperature is lowered rapidly, and the lineshape does not change with time over several hours of observation. In general, the conclusions of Kogan et al. regarding isotopic phase separation (J. Exptl. Theoret. Phys. USSR 34, 238, 1958) were not confirmed.

Finally, in all concentrations it was observed that the linewidth narrows with increasing the rf field H\textsubscript{1}. If these results are compared with the theory...
due to Provotorov (J. Exptl. Theoret. Phys. USSR 41, 1582, 1961), one obtains $T'$ (the longitudinal relaxation time characteristic of the return to the equilibrium distribution of the dipolar energy) to be about $0.4 \ T_1$. 
CHAPTER I

INTRODUCTION

The possibility of isotopic ordering or phase separation in solids has been predicted theoretically by Prigogine and co-workers and by Montroll and Potts. In particular they predicted that the effect would be significant in solid solutions of the hydrogen isotopes and in \( \text{He}^3 - \text{He}^4 \) mixtures because the effect is due to the predominance of the zero point energy in the description of the solid. Recently experimental evidence for isotopic ordering in solid solutions of \( \text{He}^3 \) in \( \text{He}^4 \) has been provided by Edwards, McWilliams and Daunt in specific heat measurements below 1°K. This result encouraged the undertaking of the work reported in this dissertation on an experimental investigation of the possibility of similar effects in solid \( \text{H}_2 - \text{D}_2 \) mixtures. Following a suggestion put forward by Daunt, it was decided to attack the problem by observation of nuclear magnetic resonance in \( \text{H}_2 \). In the temperature region in which the solid mixture is "rigid," i.e., below the linewidth broadening temperature, occurring below the solidus line, it was suggested that isotopic phase separation should become evident in the occurrence of composite resonance lines consisting of broad and narrow parts, the broad part coming from hydrogen surrounded by hydrogen and the narrow part coming from
hydrogen surrounded largely by deuterium. We therefore undertook an extensive investigation of NMR in $\text{H}_2 - \text{D}_2$ solid mixtures at low temperatures.

The existence of phase separation, nevertheless thermodynamically favorable, will be strongly dependent on a dynamical process, like diffusion, permitting the system to relax toward the lower states.
CHAPTER II

THERMODYNAMICS OF PHASE SEPARATION

A brief outline of the main reasoning leading to theoretical predictions of phase separation in mixtures, like the phase separation found in liquid$^1$ and solid$^2$ mixtures of He$^3$ - He$^4$ follows in the next sections.

A. Guggenheim's Theory

Guggenheim$^3$ in 1952 tried to describe the thermodynamic properties of condensed phases using a lattice model, i.e., a lattice partition function. The energies which appear in this partition function are those of the particles at rest in their equilibrium positions in the lattice.

The basic assumptions that define the strictly regular solution are the following:

a. The motions of the molecules reduce to oscillations about their respective equilibrium positions in the lattice.

b. The total partition function can be factored into two parts: one referring to the internal motions of the molecule and the other concerned with simple translation of the molecule.

c. The lattice is treated as rigid, i.e., no change in intermolecular distance results from a change in composition.
d. Each molecule occupies a single lattice point.

Using the above conditions, a critical temperature $T_c$ can be derived for a binary mixture of molecules of type A and B. The simplest approximation consists of a replacement of the quantity $N_{AB}$ (the number of AB pairs of nearest neighbors) by $N^*_{AB}$ (the number of AB pairs in a random mixture). This "zeroth approximation" yields the result

$$T_c = \frac{W}{2R}$$

(1)

for a 50-50 mixture, where $W$ is the heat of mixing and $R$ the universal gas constant. The value of $W$ can be obtained from experimental data, for instance, of vapor pressure curves.

B. Montroll and Potts

Montroll and Potts$^4$ studied the effect of defects on lattice vibrations for one-dimensional chains, and an example is given for a three-dimensional lattice (simple cubic lattice). Three kinds of disturbances into the perfect lattice are considered:

a. Impurity is the replacement of a normal lattice particle by a foreign atom.

b. Interstitial is defined as a normal or impurity atom inserted between normal lattice points.

c. Hole is the omission of an atom in the normal lattice.

The interaction of two defects as a function of their distance of separation is calculated for the range of very low temperature. It is found
that the attraction between two mass defects (in one dimension) is proportional to the cube of their distance of separation, and in a cubic lattice the effect of a localized defect mode diminishes with the distance as \( r^{-1} \exp(-Ar) \). They conclude that the attraction between light isotope defects in a system of a heavy isotopic species leads to a clustering tendency for the light isotope at very low temperatures and therefore one would expect an ordering into two phases.

C. Prigogine's Theory

Prigogine\(^5\) extended the considerations of Guggenheim to include the zero point energy of each pure component.

In order to have a better understanding of his results and the other theories as well, we will review a few important definitions.

a. Changes of thermodynamic properties at constant pressure and temperature are called thermodynamic functions of mixing and denoted by a superscript \( \text{M} \). For instance, for a binary mixture

\[
G^\text{M} = G(p, T, n_1, n_2) - G^0_1 (p, T, n_1) - G^0_2 (p, T, n_2)
\]  

(2)

is the change of the Gibbs free energy due to the mixing. The term \( G^0 \) is the Gibbs free energy of pure component. \( T, p \) and \( n_i \) are temperature, pressure and number of moles of each component.

Using molar quantities

\[
g^\text{M} = g(p, T, x_2) - x_1g^0_1 (p, T) - x_2g^0_2 (p, T)
\]  

(3)

where \( x_i \) is the mole fraction of the ith component.
In a similar way we define the other thermodynamic functions of mixing.

b. A solution will be described as perfect if the Gibbs free energy of mixing takes the following simple form:
\[ g^M = RT (x_1 \ln x_1 + x_2 \ln x_2) \]
(4)

The enthalpy of mixing, which is the heat of mixing, if we neglect the term \(-V\Delta p\) in the first law: \(dQ = dH - V\Delta p\), is
\[ h^M = -T^2 \frac{\partial g^M}{\partial T} \]
(5)

and the volume of mixing,
\[ v^M = \frac{\partial g^M}{\partial p} \]
(6)

both vanish for a perfect solution, and these properties may be used to test the validity of perfect solutions for a given mixture.

In general we can say that in a perfect solution all thermodynamic functions of mixing except those containing the entropy are zero.

c. For a perfect solution the chemical potential \(\mu\) is
\[ \mu_i = \mu_i^0 (T, p) + RT \ln x_i \]
(7)

Deviations from the laws of a perfect solution may be expressed formally by introducing the activity coefficient \(\gamma_i\) in the expression of the chemical potential of the perfect solution. Thus, we obtain the chemical potential of the actual solution as:
\[ \mu_i = \mu_i^0 (T, p) + RT \ln \gamma_i x_i \]
(8)
By the same way, it is easy to prove that the Gibbs free energy of mixing of an actual binary solution will be

\[ g^M = RT \left( x_1 \ln \gamma_1 x_1 + x_2 \ln \gamma_2 x_2 \right) \]  

(9)

and so on.

d. The difference between a thermodynamic function of mixing for an actual system and the value corresponding to a perfect solution at the same T, p and composition is called the thermodynamic excess function, denoted by superscript \( E \).

Let us calculate the excess Gibbs free energy, for example:

\[ g^E = g^M - RT \left( x_1 \ln x_1 + x_2 \ln x_2 \right). \]  

(10)

Substituting the actual \( g^M \) from equation (9),

\[ g^E = RT \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right) \]  

(11)

As we see, the excess function permits a direct representation of the deviation from the laws governing a perfect solution.

Equation (11) shows also that the Gibbs free energy can be deduced from the determination of the activity coefficients, generally from vapor pressure measurements.

The excess enthalpy (the heat of mixing at constant pressure per mole of solution) can be deduced from direct measurements.

The excess entropy is

\[ T s^E = h^E - g^E \]  

(12)

The excess volume is deduced from the change of the activity coefficients with pressure:
\[ \nu E = -RT \left( x_1 \frac{\partial \ln \gamma_1}{\partial p} + x_2 \frac{\partial \ln \gamma_2}{\partial p} \right) \] (13)

e. For a binary mixture to be stable and not to separate into two phases, the following thermodynamic condition has to be satisfied.\(^6\)

In Figure 1, \( g \) is plotted as a function of \( x_2 \). Curve (a) is convex downwards, the above inequality is satisfied, and the system is stable. The curve of type (b) is convex upwards between \( x_2' \) and \( x_2'' \). The system ceases to be stable and separates into two phases of concentration, \( x_2' \) and \( x_2'' \).

A critical temperature (or consolute point) \( T_c \) is found from the condition:

\[ \left( \frac{\partial^2 g}{\partial x_2^2} \right)_c = 0 \] (15)

Using equations (3) and (10) in (15), we obtain

\[ RT_c = -x_1 x_2 \frac{\partial^2 g}{\partial x_2^2} \] (16)
The whole problem of calculating the critical temperature $T_c$ in the
"perfect solution" model is then reduced to calculating the excess Gibbs free
energy.

The fact that the thermodynamic conditions of phase separation are
satisfied does not mean that the system will undergo such a transformation in a
reasonable time. If $T_c$ is in the solid range of temperatures, the existence of
a dynamical process, like diffusion, is very important to permit the system to
relax and accommodate itself in the lower energy states. If this relaxation
time is too long, instead of having an ordered state, a glassy type of solid may
be formed.

Another condition for phase separation, still in this dynamical
aspect of the problem, is the nucleation studied by Turnbull. He found that
to form a seed, or a first sphere of the separated phase, with radius larger
than a certain critical radius, equivalent to a sphere of about one hundred
molecules, energy is required.

f. Now, still following Prigogine, we will calculate the excess
Helmholtz free energy $f^E$ for two isotopes, A and B, with:

\[ x_A, x_B, \text{ the molar fractions of the pure isotopes;} \]
\[ v_A, v_B, \text{ the molar volumes of the pure isotopes;} \]
\[ m_A, m_B, \text{ their respective masses. Assume } m_A < m_B. \]
\[ v, \text{ the molar volume of the mixture for given values of } p \text{ and } T. \]
\[ \text{Suppose } v_A \geq v \geq v_B. \]
We may split the mixing process in two parts:

I - We first compress at constant $T$ the pure isotope $A$ to the molar volume $v$. Similarly we apply a "negative pressure" to $B$ in order to bring it to volume $v$. The corresponding change in the free energy per mole $f_\text{I}$, in this first part is:

$$f_\text{I} = x_A \left[ f_A(v) - f_A(v_A) \right] + x_B \left[ f_B(v) - f_B(v_B) \right].$$  \hspace{1cm} (17)

Then we express the free energy of each component $f_A$ and $f_B$ as a power series in the difference between $v$ and the molar volume of the pure component as:

$$f_A(v) = f_A(v_A) + \frac{1}{2} f_A''(v - v_A)^2 + \ldots$$ \hspace{1cm} (18)

where

$$f'' = \left( \frac{\partial^2 f}{\partial v^2} \right)_T, \text{ at } p = 0.$$  

After rearranging terms, we replace $v$ by

$$v = x_A v_A + x_B v_B$$

neglecting the excess volume $v^E$, and we find:

$$f_\text{I} = \frac{1}{2} x_A x_B (v_A - v_B)^2 \left( x_A f_A'' + x_B f_B'' \right)$$  \hspace{1cm} (19)

Usually the above expression vanishes when the volume is independent of the masses. This is, however, not at all the case for light isotopes where the volume depends strongly on the masses, which is the essential nature of the quantum effects considered by Prigogine.

II - Now, in the second part, the two isotopes are mixed at molar volume $v$. Then Prigogine calculates the excess free energy $f_\text{II}$ involved in
this process, what he calls the "harmonic oscillator model," and he finds a negligible contribution to $f^I$. That is why we will not describe it here in more detail.

Now, from the definition of the thermodynamic function of mixing, $f^M$, the definition of the excess function, $f^E$, and using equation (17) as the excess free energy, i.e., neglecting $f^{II}$, we obtain:

$$f(v, T) = x_A f_A(v, T) + x_B f_B(v, T) + R T (x_A \ln x_A + x_B \ln x_B)$$

(20)

from which we can derive all other thermodynamic properties of the mixture. Prigogine derives the excess volume and then the excess free energy and he finds:

$$f^E = \frac{1}{2} x_A x_B (v_A - v_B)^2 f''$$

(21)

where

$$f'' = x_A f_A'' + x_B f_B''$$

(22)

$f''$ is related to the compressibility and molar volume, i.e.,

$$f'' = - \frac{\partial P}{\partial v} = \left( - \frac{1}{v} \frac{\partial v}{\partial p} \right)^{-1} > 0$$

(23)

Thus, the excess free energy in equation (21) is positive and has exactly the same value obtained in equation (19). This indicates that at sufficiently low temperatures we shall have a phase separation due to quantum effects.

In the case of vanishing external pressure, Helmholtz and Gibbs free energy are the same. Then substituting equation (21) and (22) in equation (16), with $x_A = x$ and $x_B = 1 - x$, we have:
\[ T_c = \frac{x}{R} (v_A - v_B)^2 \left[ (3x^2 - 5x + 2) f''_B - (3x^2 - 4x + 1) f''_A \right] \]  

(24)

In the case of non-vanishing external pressure he obtains:

\[ g^E = \frac{1}{2} x_A x_B (v_A - v_B)^2 f'' \]  

(25)
i.e., the same equation (21) but now the values of \( v_A, v_B \) and \( f'' \) will be different. They will be functions of the pressure.

**TABLE 1**

**THERMAL PROPERTIES OF SOLID H\(_2\) AND D\(_2\) AT 4.2°K AFTER WOOLLEY ET AL.**

<table>
<thead>
<tr>
<th>Component</th>
<th>( v ) cm(^3)/mole</th>
<th>( f'' ) cal mole cm(^{-6})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A normal H(_2)</td>
<td>22.65 ± 0.01</td>
<td>1.6 ± 0.5</td>
</tr>
<tr>
<td>B normal D(_2)</td>
<td>19.56 ± 0.01</td>
<td>2.7 ± 0.1</td>
</tr>
</tbody>
</table>

From the above table, \( T_c \approx 2.5°K \) for \( x = 1/2 \).

**D. Lifshitz and Stepanova Theory**

Another approach, used by Kogan et al.,\(^9\) to predict phase separation of light isotopes is due to Lifshitz and Stepanova.\(^10\) They had set forth previously\(^11\) a method for the study of the vibration spectrum of solid solutions of isotopes. Then they applied the method to the determination of the spectral density of solutions in the presence of long range order. From it Kogan\(^9\) and his associates were able to obtain the critical temperature of a mixture:

\[ T_c = \epsilon^2 \theta_D \]  

(26)
\[ \epsilon = \Delta m/m, \text{ and } \theta_D \text{ is the Debye temperature (}\theta_D = 85^\circ \text{K for H}_2\text{). They did not explain, however, how the above equation was derived from Lifshitz' and Stepanova's theory, and we mention it here only to point out the agreement between the theoretical value so obtained of } T_c \approx 16.4^\circ \text{K for a 50-50% mixture of } \text{H}_2 - \text{D}_2 \text{ and the experimental result they reported.}

E. Coldwell-Horsfall Theory

One of the most recent theoretical results on phase separation is due to R. A. Coldwell-Horsfall.\(^{12}\) She obtained a general expression for the free energy of an isotopically disordered lattice when cubic and quartic harmonic terms are retained in the expansion of the potential energy of the lattice in powers of the nuclear displacements. The difference \(\Delta E\) between the ground state energy of the disordered system and that of the separated isotopes is calculated for \(\text{H}_2 - \text{D}_2\) and \(\text{He}^3 - \text{He}^4\). Some results are as follows:

\[ \Delta E = 2.5 \text{ cal/mole for } x = 50\% \text{ } \text{H}_2 \]
\[ \Delta E = 0.36 \text{ cal/mole for } x = 57\% \text{ } \text{He}^3. \]

F. Comments

The main criticism on applying Guggenheim's work to light isotopes is that he does not take into account the zero point energy, which is very important in these cases.

Prigogine took the zero point energy into consideration, but the expansion in power series done in equation (18) is not justified in some instances, as was pointed out by Drs. J. G. Daunt and A. K. Sreedhar.\(^{13}\)
A new approach to circumvent this difficulty using an extrapolation of pressure was put forth by Simon and Bellemans. The conclusions now depend on this extrapolation to negative pressures of the heaviest isotope, and this may lead to very inaccurate results. Nevertheless one gets very good agreement, after this correction, with the experimental results of Bellemans for the excess Gibbs free energy. This experiment was very carefully done at 22°K, and he found at the boiling curve:

\[ G^E = 6.2 \times (1 - x) \text{ cal/mole}, \]  

and at the dew curve:

\[ G^E = 6.8 \times (1 - x) \text{ cal/mole}, \]  

for \( \text{H}_2 - \text{D}_2 \) mixtures and where \( x \) is the molar fraction of \( \text{H}_2 \).

We cannot comment on the result of Kogan et al. because they do not describe how they got equation (26) from Lifshitz and Stepanova’s theory.

Finally, the work of Coldwell-Horsfall is in one dimension and assumes long range order.

The experimental evidence on the above theories will be discussed in the next chapter.
CHAPTER III

RELEVANT DATA ON LIGHT ISOTOPES

This chapter summarizes the more important experimental results obtained in mixtures of He\(^3\) - He\(^4\) and H\(_2\) - D\(_2\). Particular emphasis will be put on the values of excess Gibbs free energy, heat of mixing, transition temperatures and diffusion coefficients. Other recent summaries of some of these properties are found in White and Knobler,\(^{15}\) De Bruyn Ouboter\(^{16}\) and Taconis and De Bruyn Ouboter.\(^{17}\)

A. Liquid He\(^3\) - He\(^4\) Mixtures

Phase separation in liquid He\(^3\) - He\(^4\) mixtures was found by Walters and Fairbank\(^1\) and later by several authors.\(^{16, 18, 19}\) They all found a critical temperature around \(T_c = 0.8^\circ K\) (for a 50-50% mixture), using different methods of measurement. Walters and Fairbank used NMR, Zinov'eva and Peshkov used a visual method, and Sydoriak and Roberts measured the vapor pressure.

The excess Gibbs free energy fits the regular solution model result very well below \(1^\circ K\),\(^{20, 21}\)

\[ G_E = W x (1 - x) \]  

(29)

if \(W/R\) is taken to be \(1.54^\circ K\).
The heat of mixing was measured by De Bruyn Ouboter\textsuperscript{16} for all concentrations of the mixture in the range of temperatures between 0.5 and 1.7°K. They used an indirect method and got good agreement with the direct method used by Sommers et al.\textsuperscript{22} The heat of mixing is always positive in the above range of temperatures and its numerical value is given by Ouboter.\textsuperscript{16}

B. Solid He\textsuperscript{3} – He\textsuperscript{4} Mixture

Phase separation of solid mixtures of He\textsuperscript{3} – He\textsuperscript{4} was observed by Edwards, McWilliams and Daunt\textsuperscript{2} in specific heat measurements at a critical temperature given by:

\[
T_c = \frac{\Delta E}{k} \frac{\frac{1}{2} - x}{\ln\left[\frac{1}{x} - 1\right]}
\]

with the parameter $\Delta E/k = 1.51°K$ adjusted for the best fit of the data ($x$ is the molar fraction of He\textsuperscript{4}). The above expression can be derived from a Bragg-Williams type model\textsuperscript{15} or a regular solution model (see Prigogine and Defay\textsuperscript{6}, p. 249). It is also interesting to note that the maximum value of $T_c$ from equation (30) for a 50-50% mixture is: $(T_c)_{\text{max}} \approx 0.38°K$ in very good agreement with the value obtained from equation (1), noticing that $W = \Delta E/2$.

C. Diffusion Rates

The total activation energy $E_a$ for diffusion can be considered as the energy necessary to remove an atom from its lattice position and an additional energy to move it through the crystal. The self-diffusion coefficient $D$, when
thermally activated, is connected with $E_a$ at a temperature $T$ by an Arrhenius type equation:

$$D = D_0 \exp \left[ -\frac{E_a}{kT} \right]$$ (31)

In liquid He$^3$ Garwin and Reich$^{23}$ found that $D$ is thermally activated in the range 0.5° up to 4°K. Hart and Wheatley$^{24}$ confirmed this result and found also that $D$ has a minimum value of $5 \times 10^{-5}$ cm$^2$/sec around 0.5°K. At lower temperatures $D$ increases continuously as $T^{-3/2}$ in good agreement with the Landau theory of a Fermi liquid.$^{25}$ On the whole $D$ in liquid He$^3$ is large and phase separation, if energetically favorable, will occur quickly.

In solid He$^3$ Reich$^{26}$ measured $D$ and he summarized his results in the following manner: (1) Near the melting point and down to about 1°K $D$ follows equation 31; (2) $E_a$ increases with increasing density; (3) The value of $D$ at the melting curve is approximately constant and has the value $D = 1.5 \times 10^{-7}$ cm$^2$/sec; (4) The value of $D_0$ is independent of density and has a value $D_0 = 3.5 \times 10^{-5}$ cm$^2$/sec; (5) The value of $E_a/k$ is proportional to the melting temperature and has the value, in degrees Kelvin, $E_a/k = 5.2T_M$; (6) At the lowest density, as the temperature is lowered, $D$ is observed to become constant, independent of the temperature.

At 0.6°K the self diffusion is $3 \times 10^{-8}$ cm$^2$/sec. This number is very large for a solid and that is probably why Edwards et al.$^2$ were able to detect the phase separation of solid He$^3$ - He$^4$ mixtures. If otherwise, $D$ follows the Arrhenius equation, we might expect a value of the order of $10^{-14}$ to $10^{-16}$ cm$^2$/sec and then phase separation would be nearly impossible.
There is an interesting yet completely different line of thought as follows: We assume the diffusion in solid He³ is thermally activated and therefore Reich's result is wrong. The addition of He⁴ to He³ changes the diffusion radically, i.e., He⁴ diffuses but not He³ (Edwards et al. experiment). Presently there is no way of measuring the He⁴ diffusion other than by the Edwards et al. experiment itself.

D. Phase Diagrams of H₂ – D₂

Kogan et al. have studied H₂ – D₂ solid mixtures by X-ray scattering and by a technique they call "thermal analysis" and have interpreted their results as indicative of isotopic phase separation below 16.4°K. We reproduce in Figure 2 their phase diagram.

![Phase Diagram of H₂-D₂](image)

**Figure 2**

H₂-D₂ Phase Diagram after Kogan et al.
The thermal analysis was essentially the following: The mixtures were prepared from pure isotopes, condensed into a calorimeter cooled with liquid hydrogen kept at reduced pressure by a vacuum pump and then frozen. After the pump was stopped, the mixture was allowed to warm up slowly over the temperature interval from 14° to 19°K. During the crystallization of mixtures in the concentration range 26-52% of hydrogen by volume, the presence of peritectic regions was established visually at T = 16.4°K, in very good agreement with equation (26). Comparison of the thermal analysis data with the results of X-ray patterns at 4.2°K enabled them to determine the approximate limits of the two phase region.

E. Existing NMR Data on Hydrogen Isotopes

1. Ortho- and Para Hydrogen

Because protons are particles of spin 1/2 which obey Fermi statistics, their total wave function, the product of a spin function and a rotational function, must be antisymmetric with respect to interchange of particles.

The spin function is symmetric in the triplet state $I = 1$ and antisymmetric in the singlet state $I = 0$. For molecules in the triplet state, the rotational functions are antisymmetric, i.e., $J$ (total angular momentum) is odd; for molecules in the singlet state $J$ is even.

There are several reasons for believing that the intermolecular forces are particularly weak in solid hydrogen. One of the arguments is the smallness of the heat of fusion, suggesting that the molecule can rotate almost freely in
the solid. Another indication is the existence in liquid hydrogen of Raman frequencies in good agreement with those calculated from the energies of rotation of the free molecule. This implies that the theoretical behavior of solid hydrogen is very similar to that of a gas of non-interacting hydrogen molecules providing the intermolecular interactions are treated as weak perturbations.

At low temperature the extreme slowness of the transitions between the singlet and triplet states (about 1% per hour) because of the weakness of the intermolecular magnetic forces permits us to consider the molecules in the singlet and triplet states as two different species labelled para-hydrogen and ortho-hydrogen respectively. The extreme slowness of this ortho-para conversion (even though very favorable energetically) is due to the fact that the system must eject one quantum of orbital angular momentum and one quantum of nuclear spin simultaneously. The combined system of nuclear spins and lattice is practically incapable to absorbing these quanta by itself. If one desires to enhance this conversion, one uses a catalyst such as oxygen, which has a large paramagnetic moment and is capable of undergoing a mutual spin flip with the ortho hydrogens.

It is the existence of the ortho molecules in this metastable state of equilibrium that makes possible the observation of the magnetic resonance in solid hydrogen. If thermal equilibrium could be reached (quickly), the molecules would be all in the lower state \( J = 0, I = 0 \). Since this state has neither spin or orbital magnetic moment, no resonance could be observed.
In the absence of catalytic action, the ratio of ortho- to para-states at low temperature is essentially the same as it was at room temperature, namely 3:1 (normal hydrogen), which is the ratio of the statistical weights of the two spin states.

Since the spin of the deuteron is one, it obeys Bose statistics. The total wave function must now be symmetric with respect to interchange of particles implying that the only permissible states are combinations where both J and I are even or both J and I are odd. As before, the relative abundance at high temperatures of the different species is simply determined from the statistical weights of the spin states, as shown in Table 2.

**TABLE 2**

**STATES AND RELATIVE ABUNDANCE OF D₂**

<table>
<thead>
<tr>
<th>Classification</th>
<th>J</th>
<th>I</th>
<th>Abundance (at high temperature)</th>
<th>No. of Spin States</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Ortho</td>
<td>0</td>
<td>2</td>
<td>55</td>
<td>5</td>
</tr>
<tr>
<td>Para</td>
<td>1</td>
<td>1</td>
<td>33</td>
<td>3</td>
</tr>
</tbody>
</table>

2. Hatton and Rollin Experiment

The pioneer work on NMR (nuclear magnetic resonance) of hydrogen and deuterium was done about 15 years ago by Hatton and Rollin. They measured $T₁$ (spin-lattice relaxation time) and the linewidth, w, of hydrogen
in the range of temperature between 1° and 20°K. The results are summarized in the table below.

**TABLE 3**

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>20.0</th>
<th>14.0</th>
<th>11.0</th>
<th>4.2</th>
<th>1.85</th>
<th>1.3</th>
<th>1.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁ (sec)</td>
<td>0.02</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>w (gauss)</td>
<td>0.1</td>
<td>0.1</td>
<td>1.0</td>
<td>8.0</td>
<td>10.0</td>
<td>50.0</td>
<td>50.0</td>
</tr>
</tbody>
</table>

The above measurements have been repeated in recent years with improved accuracy, but these are adequate to show the existence of three distinct regions:

a. For the liquid and also for the solid just below the triple point, the width of the line is extremely small (≈ 0.1 gauss) which probably is due to inhomogeneities in the applied magnetic field in these observations.

b. Between 11° and 10°K there is a rapid increase of the width to about 8 gauss (later found to be about 5.4 gauss) with no substantial subsequent changes down to about 1.7°K.

c. At 1.5°K a further considerable change begins and, at the lowest temperature attained in these experiments (1°K), there is a very broad resonance with two peaks separated by about 50 gauss (later found to be about 40 gauss with two humps separated by about 75 gauss).
3. Reif and Purcell Experiment

The fine structure found by Hatton was later studied by Reif and Purcell,\(^3\) using a recording meter technique. This gives a much better accuracy than the large modulation amplitude (where the line is displayed in an oscilloscope) used by Hatton. Reif obtained the derivative of the absorption line. In this method\(^4\) the linewidth \(\Delta\) is measured from peak to peak and his results are these:

At 4.2°K the resonance line is simple. The linewidth is 18 Kc/s (or 4.23 gauss, because for protons 1 gauss corresponds to 4.257 Kc/s). Below 1.5°K the center line has \(\Delta_0 = 19.6\) Kc/s (or 4.6 gauss) and it becomes flanked by two side peaks and two humps, apart by \(\Delta_1 = 170\) Kc/s (or 40 gauss) and \(\Delta_2 = 328.1\) Kc/s (or 77 gauss).

Another very important result found by Reif is the rf (radio frequency) saturation behavior of \(\text{H}_2\) and HD at 4.2°K. The linewidth shows the rather unexpected behavior of decreasing as the rf field is increased beyond 0.05 gauss rms, the point where saturation begins to set in. He did not find a satisfactory explanation for this phenomenon. This will be discussed in more detail in the appendix. He did an experiment with solid \(\text{D}_2\) also but obtained

\(^4\)We use the following notation: Call the linewidth, \(w\), between the half amplitude points of the absorption line \((X'')\) and \(\Delta\), the linewidth from peak to peak in the derivative of the absorption line \((\text{d}X''/\text{d}H)\). See Figure 5 and Plate III for illustration. In case of a gaussian resonance line, \(w = \sqrt{3/2} \Delta\).
no fine structure above 1.16°K. This will be discussed later also in Chapter VI. Another detail in the Reif and Purcell paper is how the observed lineshape can be explained quantitatively by the magnetic dipole interaction of the two protons in a hydrogen molecule, provided one takes into consideration the effect of the crystalline potential responsible for lifting the rotational degeneracy of the ortho-molecules in the solid. This subject is also discussed in detail by Abragam.

4. Pure Hydrogen in Different Ortho/Para Concentration

Sugawara et al. did an experiment in pure hydrogen with different ortho/para concentrations. The results at 4.2°K are in good agreement with Reif and Purcell. The width $\Delta_0$ of the line is 5.4 gauss for normal hydrogen and decreases with falling ortho concentration. $\Delta_0$ was nearly constant in the range 1.6 to 10°K. At about 1.5°K the side peaks and humps appeared at separations $\Delta_1 = 39.5$ and $\Delta_2 = 75.5$ gauss respectively. At 63% ortho-hydrogen the center line has $\Delta_0 = 5.6$ gauss at 4.2°K and the side peaks appeared at 1.22°K with the same value of $\Delta_1$.

Their results for the concentration dependence of the transition temperature are in reasonably good agreement with the data of Hill and Ricketson obtained from specific heat measurements (see Figure 3). The figure shows the temperature $T_\lambda$ and concentration where the side peaks appear in NMR and where a $\lambda$-type anomaly appears in specific heat measurements. Below 59% ortho-hydrogen no fine structure side peaks nor specific heat $\lambda$
Figure 3

Transition Temperature versus Ortho/para Concentration of H₂

anomalies were found above 1.17°K. The linewidth Δ₀ was found to decrease more of less continuously with the ortho concentration at 4.2°K as shown in Table 4.

TABLE 4

LINEWIDTH VERSUS ORTHO CONCENTRATION OF H₂
AT 4.2°K

<table>
<thead>
<tr>
<th>Ortho H₂ %</th>
<th>75</th>
<th>70</th>
<th>67</th>
<th>63</th>
<th>59</th>
<th>55</th>
<th>34</th>
<th>16</th>
<th>11</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ₀ (gauss)</td>
<td>5.4</td>
<td>5.1</td>
<td>5.6</td>
<td>5.6</td>
<td>5.2</td>
<td>5.0</td>
<td>3.3</td>
<td>1.6</td>
<td>1.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>
In the interval 59 to 34% ortho-hydrogen the linewidth at 1.17°K was about the same as at 4.2°K but the flanks of the resonance line spread. Below 34% a kind of fine structure composed of a narrow and wide line was shown at 1.17°K. The width of the wide line was about 8 or 9 gauss at 1.2°K. These effects are shown in Figure 4, reproduced from Sugawara et al.

They explain their experimental results in essentially the same manner as Reif and Purcell (see page 24), except that they arbitrarily introduce a narrowing factor \( f(\rho) \) in the calculation of the line shape. They found empirically the different forms of \( f(\rho) \) at low and high temperatures and for low and high ortho concentration that gave the best approximation to the experimentally obtained lineshape.

In a subsequent paper Sugawara studied the effect of rf saturation upon the linewidth and lineshape of normal \( \text{H}_2 \). His findings were: the linewidth decreased with increasing rf power and different portions of the line (broad and narrow) saturated at different rates. He attempted to explain the experimental lineshape in terms of a model in which \( T_1 \) was not a unique time constant but was a function of the resonance frequency of a given spin group in the dipolar broadened line. This point will be discussed further in Chapter IV.

5. Translational Diffusion

The linewidth transition in \( \text{H}_2 \) near 10°K discovered by Hatton and Rollin was subsequently studied in more detail by Rollin and Watson. The sudden increase in linewidth as the temperature was reduced was attributed to
Figure 4

Derivatives of the Resonance Absorption Lines at Several Ortho-Hydrogen Concentrations (after Sugawara et al. \textsuperscript{31})
59% ORTHO-H₂
T = 4.2 °K

34% ORTHO-H₂
T = 4.2 °K

11% ORTHO-H₂
T = 4.2 °K

59% ORTHO-H₂
T = 1.19 °K

34% ORTHO-H₂
T = 1.19 °K

11% ORTHO-H₂
T = 1.20 °K
a restriction of the translational motion of the molecules (i.e., reduced molecular diffusion). This effect is observed at about 10°K for $\text{H}_2$ and 12.5°K for $\text{D}_2$. The activation energy was observed to be approximately 350 cal/mole for $\text{H}_2$ (for several ortho-para concentrations) and 550 cal/mole for normal $\text{D}_2$.

It is interesting to note that these values are considerably larger than the respective heats of vaporization (180 cal/mole and 275 cal/mole). The observed width for $\text{H}_2$ at the conclusion of the transition is 5.6 gauss whereas the width in $\text{D}_2$ is 1.8 gauss. Rollin and Watson also point out that according to their calculations the spin-spin interaction between all neighboring ortho molecules can account for only 3.5 gauss of the observed width of 5.6 gauss in $\text{H}_2$. It is also reasonable to assume that no appreciable contributions to the linewidth will be made by intra-molecular proton-proton interactions or by interactions between the ortho $\text{H}_2$ spin and the internal magnetic field set up by molecular rotation. The rapid averaging of these interactions brought about by the nearly free rotation of the ortho molecules leads to no net contribution to the linewidth. To explain the discrepancy between the calculated value and observed value of the linewidth, they suggested that the ortho molecules may have a tendency to cluster together. This type of phase separation of ortho and para hydrogen was first suggested by Pauling. Later Reif and Purcell said they were not able to explain the anomalous narrowing of the linewidth of $\text{H}_2$ and HD with increasing rf power, unless they assumed regions in the sample with different relaxation time and linewidth.
Myer Bloom measured diffusion, $T_1$ and $T_2$ ($T_2$ is the spin–spin relaxation time) in solid $H_2$ in the region of temperatures below the melting point. He found the diffusion to be thermally activated with an activation energy ($E_a$) equal to $380 \pm 20$ cal/mole in the range $10^\circ$ to $14^\circ$K and $D_0$ equal to $10^{-3}$ cm$^2$/sec. $T_1$ was found to be temperature independent in the range from 11 to $14^\circ$K and equal to about 0.22 sec. His result for $T_1$ is in good agreement with the theoretical calculation of Moriya and Motizuki who found:

$$T_1 = 0.361 c^{1/2} \text{ sec.}$$

(32)

where $c$ is the fraction of ortho-hydrogen molecules.

6. Linewidth and Lineshape of Hydrogen

Recently Dickson and Meyer studied solid hydrogen and deuterium under high pressures by NMR techniques, using a Robinson oscillator with a very low rf level ($H_1 = 6 \times 10^{-3}$ gauss). They found the hydrogen line to be narrower than a gaussian, as is shown in Figure 5. It shows the absorption resonance line of 71% ortho-hydrogen at $4.2^\circ$K and at normal density ($\rho$), and for comparison also shows a gaussian line of approximately the same area and same width $w$. An empirical relation was obtained between $w$ and the second moment $M_2$ for samples at different densities ($\rho$) and ortho concentration ($c$). It was found quite generally that

$$w = (2.95 \pm 0.15) M_2^{1/2} \text{ h/ g} \beta \text{ (gauss)}$$

(33)
Figure 5

Absorption Resonance Line of 71\% Ortho-Hydrogen at 4.2°K

Compared to a Gaussian Line of Same Area (after Dickson and Meyer\textsuperscript{37})
GAUSSIAN

$\Delta H (\text{Gauss})$

$\chi''$

$w$
where $\beta$ is the nuclear magneton and $g$ is the corresponding Lande factor. The coefficient 2.95 is to be compared with 2.0 for a gaussian line. Using an equation that they derived for $M_2$ from the Van Vleck theory of moments, assuming that the ortho and para molecules are distributed uniformly throughout the lattice and combining with equation (33) they obtained:

$$w = 6.5 \, c^{1/2} \, \rho / \rho_0$$

(34)

From the above equation a linewidth of 5.63 gauss is obtained for normal hydrogen in good agreement with the experimental results in the literature.

They found also that for a given ortho-hydrogen concentration the transition temperature (from the state of free rotation to that of hindered rotation) $T_\lambda$ is proportional to the square of the density ($\rho$).

About deuterium it is interesting to note that their observed lineshape was asymmetric even at the lowest rf level of the Robinson oscillator and was more similar to a gaussian curve than the corresponding shape in hydrogen. The linewidth data fit the following expression:

$$w = 1.6 \, \rho / \rho_0 \, \text{gauss}$$

(35)

and no evidence for a $\lambda$-splitting was found above 1.5°K.

Recent specific heat measurements on samples artificially enriched in para-deuterium composition$^{39}$ disclosed a $\lambda$-transition similar to the one observed in hydrogen (with sufficient ortho concentration).
F. Our Program of Work

In view of the theoretical predictions, the success of the solid $\text{He}^3 - \text{He}^4$ experiments and the fascinating results of Kogan et al.\textsuperscript{9} our program was to study the dynamics of possible phase separation in mixtures of $\text{H}_2 - \text{D}_2$. Using NMR, both broad line spectrometer and pulsed techniques, we measured $T_1$, $T_2$, linewidth and lineshapes, and determined whether the observed transition was of long range or short range order from the magnitude of the local fields.
CHAPTER IV

THEORIES OF NUCLEAR MAGNETIC RESONANCE

A. Bloembergen-Purcell-Pound Theory†

In a slow passage experiment (the time to sweep the line is large compared with both $T_1$ and $T_2$), a steady-state situation is realized when one considers the combined system of nuclear spins plus lattice. The coupling between the spin system and the lattice is characterized by the spin-lattice relaxation time $T_1$. In hydrogen the dominant relaxation mechanism is the modulation of the interaction between molecules by the rotational motion of the molecules.

The imaginary component of the radio frequency susceptibility ($\chi''$) characteristic of the energy absorption in a steady-state situation can be calculated by equating the amount of energy transferred per unit time to the lattice from the spin system, $H_0(M_0 - M_z)/T_1$, to the amount of energy absorbed per unit time by the spins $(2\omega \chi''H_1^2)$. Thus the calculation of $\chi''$ reduces to the calculation of the relative departure of the z magnetization from

†The development of BPP theory presented here is basically due to Redfield.
its equilibrium value, as shown in the equation below:

$$\chi'' = \frac{M_0 H_0 (M_0 - M_z)}{2\omega H_1^2 T_1 M_0}$$  \hspace{1cm} (36)$$

where $\omega$ is the frequency of the applied radio frequency (rf) field $H_1$ and $H_0$ is the dc magnetic field, in the z direction. $M_0$ is the static value of the magnetization $\vec{M}$, i.e., $M_0 = \chi_0 H_0$, and $M_z$ is the z component of $\vec{M}$. The assumptions of Bloembergen, Purcell and Pound are relatively simple:

a. The spin-lattice interaction tends to relax the spins to their equilibrium state in a time $T_1$.

b. The spins interact strongly with one another so that the energy absorbed at one frequency of the dipolar broadened line is quickly transferred to all the spins whether or not they are in a local field exactly corresponding to the applied rf frequency.

c. The complex rf susceptibility is proportional to the difference in population of the nuclear spin levels and is not affected by the presence of the rf field except in so far as the spin level populations are.

These assumptions are all in keeping with the following oversimplified calculation relating the relative departure of the magnetization to the transition probability in the presence of the rf field and the spin-lattice relaxation time. We assume that the sample has a magnetization $M_0 = \chi_0 H_0$ parallel to the applied magnetic field (in equilibrium) which implies that the off-diagonal elements of the density matrix are zero and the diagonal elements unequal.
Let us apply these considerations to a two level system with energies $E_a$ and $E_b$ and populations $N_a$ and $N_b$. In the presence of an applied radio frequency field of appropriate frequency one must consider two mechanisms for relaxation: First, the populations $N_a$ and $N_b$ return to their equilibrium (no rf field) values $(N_a)_0$ and $(N_b)_0$ with a time constant $T_1$ due to the interaction of the spin system with the lattice degrees of freedom. In the processes the energy of the spin system is not conserved but the energy of the spin system plus the lattice energy is conserved. Second, the radio frequency field induces transitions between the two levels $a$ and $b$. The expression for the transition probability per unit time $W$ can be obtained from the "Golden Rule" from time-dependent perturbation theory.

$$W_{ab} = \frac{2\pi}{\hbar} |<b|V|a>|^2 \rho(\Delta E)$$

$$V = -\vec{\mu} \cdot \vec{H}_{rf} = -\mu_x H_1 \cos \omega t - \mu_y H_1 \sin \omega t$$

$$W_{ab} = \frac{2\pi \gamma_{11}^2 H_1^2}{4} |<m| I_+ |m - 1>|^2 \frac{g(\omega)}{\hbar}$$

$$W_{ab} = \frac{\pi \gamma_{11}^2 H_1^2}{2} [ (I + m)(I - m + 1) ] g(\omega)$$

Therefore $W_{ab} = W_{ba} = W$.

We write the gain-loss equation for the populations $N_a$ and $N_b$ keeping the above relaxation mechanism in mind:

$$\frac{d}{dt} N_a = WN_b - WN_a - \frac{N_a - (N_a)_0}{T_1}$$

$$\frac{d}{dt} N_b = WN_a - WN_b - \frac{N_b - (N_b)_0}{T_1}$$
The steady-state solution of these equations is:

\[ N_b - N_a = \frac{N_a - (N_a)_o}{WT_1} \]

\[ N_a - N_b = \frac{N_b - (N_b)_o}{WT_1} \]

which leads to:

\[ N_a - N_b = \frac{(N_a)_o - (N_b)_o}{1 + 2WT_1} \]  \hspace{1cm} (39)

The magnetization in the z direction is simply related to the difference in population of the levels:

\[ <M_z> = \text{Trace} \left( (M_z)_{op} \rho_{op} \right) \text{ where } (M_z)_{op} = \gamma \hbar I_z \]

\[ = \sum_{m m'} \gamma \hbar <m | I_z | m'> <m' | \rho | m> \]

\[ = \gamma \hbar \sum_{m m'} m \delta_{m m'} <m' | \rho | m> \]

\[ = \gamma \hbar \sum_m m \rho_{m m} = \gamma \hbar (m_a N_a + m_b N_b) \]

but \( m_a = -m_b = 1/2 \) for the case chosen:

\[ <M_z> = \gamma \hbar \left( \frac{1}{2} \right) (N_a - N_b) = \gamma \hbar \left( \frac{1}{2} \right) \frac{(N_a)_o - (N_b)_o}{1 + 2WT_1} = M_z \]

Define \( M_o = \left[ (N_a)_o - (N_b)_o \right] \gamma \hbar \left( \frac{1}{2} \right) \) so that \( M_z = M_o/1 + 2WT_1 \) and finally the departure of \( M_z \) from its equilibrium value is given by:

\[ \frac{M_o - M_z}{M_o} = \frac{2WT_1}{1 + 2WT_1} \]  \hspace{1cm} (40)

Thus substituting equation (40) into equation (36) yields the following expression for the rf susceptibility:
\[
X''(\omega) = \frac{M_0 H_0}{2 \omega H_1 T_1} \left\{ \frac{2WT_1}{1 + 2WT_1} \right\} = \frac{X_0 \omega_0 \pi g(\omega)}{1 + 2\pi(\gamma H_1)^2 T_1 g(\omega)}
\]  
(41)

where $\omega$ has been replaced by its value at resonance $\omega_0$ and $T = 1$ for the case of $H_2$. If $g(\omega)$, the shape function describing the resonant absorption is replaced by a Lorentz shaped curve, one obtains the same expression for $X''(\omega)$ as obtained from the Bloch equations. Equation (41) and the equation obtained by assuming that $g(\omega)$ is a Lorentz curve

\[
g(\omega) = \frac{T_2}{\pi} \frac{1}{1 + (\Delta \omega)^2 T_2^2}
\]

(42)

\[
X'' = \frac{X_0 \omega_0 (1/2) T_2}{1 + (\Delta \omega)^2 T_2^2 + (\gamma H_1)^2 T_1 T_2}
\]

are the equations used to determine $T_1$ in steady-state experiments. The additional broadening is measured as a function of increasing $H_1$ and $T_1$ is determined.

\section*{B. The Phenomenological Equations of Bloch}

To derive the Bloch equations more assumptions have to be made. The starting point is the torque equation:

\[
\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H}
\]

(43)

for a system of free spins with magnetization $\vec{M}$ in an homogeneous field $\vec{H}$. Second, in the dc magnetic field $H_0$, the $z$ magnetization tends towards its
equilibrium value $M_z = M_0 = \chi_0 H_0$ in a time $T_1$ (spin-lattice or longitudinal relaxation time) given by the equation:

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

(44)

Third, if by any means there is a transversal component of the magnetization, it will decay in a time $T_2$ (transversal or spin-spin relaxation time) due to spin-spin interaction, given by the equations:

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2}, \quad \frac{dM_y}{dt} = -\frac{M_y}{T_2}$$

(45)

Fourth, (the superposition assumption) in the presence of an applied field (dc and rf fields) the motion due to relaxation can be superposed on the motion of the free spins, i.e.,

$$\frac{dM}{dt} = \gamma M \times H - \frac{M_{x|} + M_{y|}}{T_2} - \frac{(M_z - M_0)^k}{T_1}$$

(46)

where $\hat{i}, \hat{j}$ and $\hat{k}$ are the unit vectors in the laboratory co-ordinate system.

The steady-state solution of the Bloch equations (46) in a reference system rotating with angular velocity $\omega$ around the $z$ direction is:

$$\tilde{M}_x = \frac{\Delta \omega \gamma H_1 T_2^2}{1 + (T_2 \Delta \omega)^2 + \gamma^2 H_1^2 T_1 T_2} M_0$$

(47)

$$\tilde{M}_y = \frac{\gamma H_1 T_2}{1 + (T_2 \Delta \omega)^2 + \gamma^2 H_1^2 T_1 T_2} M_0$$

(48)

$$M_z = \frac{1 + (\Delta \omega T_2)^2}{1 + (T_2 \Delta \omega)^2 + \gamma^2 H_1^2 T_1 T_2} M_0$$

(49)
where: $\tilde{M}_x$ and $\tilde{M}_y$ (also called $u$ and $v$ respectively) are the transversal components of $M$ in the rotating frame; $\Delta \omega = \omega - \omega_0$ and $\omega_0 = -\gamma H_0$; $\gamma$ is the gyromagnetic ratio.

The rf field $H_1$ is applied in the $x$ direction giving $H_x = 2H_1 \cos \omega t$. It can be seen that BPP theory gives the same magnetization, in the case of a Lorentzian lineshape, as the steady-state solution of Bloch equations.

C. Redfield Theory of Saturation

To account for anomalous behaviour under rf saturation in Cu and Al (i.e., it was observed that $\chi'$ and $\chi''$ saturated at significantly different rf levels diametrically opposed to BPP and the Bloch equations), Redfield made one rather far-reaching assumption: namely that the spin system could be described by a temperature (the spin temperature) in a reference system rotating at the rf frequency. Upon transformation to this reference frame the Hamiltonian

$$\mathcal{H} = -\hbar \omega_0 I_z + \frac{\mu H_1}{2} (I_+ e^{i\omega t} + I_- e^{-i\omega t}) + \mathcal{H}_{\text{dipole}}$$

becomes

$$\tilde{\mathcal{H}} = \hbar \Delta \omega I_z + \frac{\mu H_1}{2} (I_+ + I_-) + \sum_{m=-2}^{2} H_m e^{i \omega m t}$$

where $H^0$ is the secular part of the dipole-dipole interaction (the part of the dipole interaction that commutes with $I_z$) and $\Delta \omega = \omega - \omega_0$. The argument usually put forward is that by this transformation one has traded a time-dependent radio frequency field for a time-dependent dipole-dipole interaction. It should be pointed out, however, that the time dependence carried by the
dipole interaction is present in terms that are "off resonance" (since $\Delta \omega$ is the resonance frequency in the rotating frame) whereas the original time dependence was carried by a term "on resonance" namely the applied rf field. Since the time dependent terms are "off resonance," they are usually discarded leaving a Hamiltonian in the rotating system, $\mathcal{H}$, that is time independent.

Redfield argues that under these conditions the spin system will evolve toward a canonical distribution in the rotating system and thus will be describable by a spin temperature. Using this major assumption and postulating the usual coupling between the spin system and the lattice, he obtains the following expression for the dispersion component of the complex susceptibility:

$$
\chi' = \frac{M_0 \gamma (\omega_0 - \omega)}{2 \left[ (\omega_0 - \omega) + \gamma^2 [H_1^2 + 2(\delta H)^2] \right]} = \frac{M_0 \chi}{2H_1} \quad (52)
$$

where $\delta H$ is of the order of the rms magnetic field at a nucleus due to its neighbors (or approximately the half-width of the resonance line). As before, one finds the value of $\chi''$ from energy consideration since the procedure that leads to the above expression for $\chi'$ predicts zero absorption in the region of strong saturation. The value obtained by Redfield is:

$$
\chi'' = \frac{\gamma^2 [H_1^2 + 2(\delta H)^2]}{2 \left[ (\omega - \omega_0)^2 + \gamma^2 [H_1^2 + 2(\delta H)^2] \right]} T_1 H_1^2 \omega \quad (53)
$$

Thus one expects a Lorentz shaped line with $T_2 = \gamma^2 [H_1^2 + 2(\delta H)^2]^{-1}$. 
D. Recent Developments

In 1962 Provotorov\textsuperscript{42} published the results of a calculation of both the real and imaginary components of the complex susceptibility. His calculation follows the same lines as the Redfield theory with one major difference: When absorption of energy occurs for a value of $\Delta \omega = \omega - \omega_0 \neq 0$, this absorption is accompanied by a change $\hbar \Delta \omega$ in the dipole–dipole energy, leading to a limitation in the absorbing capability of the spin system. Redfield considers only absorption at $\Delta \omega = 0$. The expression derived by Provotorov (again using energy considerations) is:

$$
\chi'' = \frac{\mu^2 I_{oz}}{2\hbar} \cdot \frac{\pi g(\Delta \omega)}{1 + \pi T_1 \gamma^2 \hbar^2 I_1 g(\Delta \omega) \left\{ 1 + \frac{\hbar^2 \Delta \omega^2 T_1'}{\hbar^2 T_1} \right\} } \tag{54}
$$

where $T_1'$ is the longitudinal relaxation time characteristic of the return to the equilibrium distribution of the dipole–dipole energy following the absorption of a $\Delta \omega \neq 0$ quantum,

$$
\overline{H_0^2} = \frac{\text{Tr}(H^0)^2}{\text{Tr}I_z^2} \sim (\mu H_{\text{loc}})^2 \tag{55}
$$

The other symbols are conventional. In the limit of high rf field $\chi''$ will be of the Lorentz shape, independent of the lineshape $g(\Delta \omega)$ and proportional to $1/H_1^2$ as in BPP theory:

$$
\lim_{H_1 \to \infty} \chi'' = \frac{\mu^2 I_{oz}}{2\hbar T_1 \gamma^2 H_1^2} \cdot \frac{1}{1 + (\Delta \omega \tau)^2} \tag{56}
$$

where $\tau^2 = \frac{\hbar^2 T_1'}{\hbar^2 T_1}$. 
CHAPTER V

EQUIPMENT AND EXPERIMENTAL TECHNIQUE

A. Equipment

The equipment used in the experiments is of two different types: a broad line steady state spectrometer and a pulsed NMR spectrometer. By now both of these types of spectrometers have been intensively discussed in literature but nevertheless block diagrams will be presented with a complete list of model numbers of the units that are commercially available.

1. Pulsed Nuclear Magnetic Resonance Equipment

A conventional pulsed NMR apparatus is described by Hahn. The one used is shown in Figure 6. Its principal parts are:

Waveform generator, Tektronix Type 162. This unit produces one sawtooth waveform that will trigger the pulse generators and one pulse that triggers the oscilloscope at the beginning of the sawtooth waveform.

Two pulse generators, Tektronix Type 163, connected in parallel. These generators give two rectangular pulses with variable amplitude, width and time interval (τ).

Pulse amplifier and inverter, General Radio Type 1219-A. This unit amplifies and inverts the two rectangular pulses to about -200 volts.
Figure 6

Block Diagram of the Pulsed Apparatus
Pulsed oscillator, Arenberg Ultrasonic Laboratory Model PG-650 C. This is a high rf power pulsed oscillator that oscillates in the range 0.5 Mc/s to 60 Mc/s. Its output is matched through a coaxial cable in the rf sample coil in the magnetic field.

The magnet is made by Newport Instruments, Type E, 7" wide with an air gap of 2-3/8". The magnet power supply is a "Precision Magnet Power Supply," Model HS-1365 from Harvey-Wells Corporation. The dc current is adjustable from 0 to 65 amperes and regulated to better than 1 part in $10^5$.

The rf amplifier is a LEL (Linear Equipment Laboratory) Model IF-2515 for 10 Mc/s, or Model IF-1876 for 20 Mc/s. The amplification gain is of the order of $10^5$ at a fixed frequency and has a bandwidth which is approximately 10% of the center frequency.

A voltage power supply, Kepco Model 103, was used to provide the B+ and filament of the LEL amplifier.

A 6 volt storage battery with a low impedance potentiometer (46 ohms) was used to bias the grid of the LEL amplifier to about -4 volts. This grid voltage controls the gain of the amplifier.

A Tektronix Oscilloscope (Type 545A) with Type L plug-in was used to display the resonance signal.

A Hewlett-Packard Oscilloscope Camera (Model 196A) was used to photograph the displayed resonance. As a rule Polaroid film (PolaPam 200, Type 42) was used in the camera.
2. Broad Line Spectrometer

When this dissertation was started, the spectrometer was a NUMAR (Nuclear Magnetics Corporation) Model S-1. After successive modifications we ended up with a good spectrometer but with very little resemblance to the original NUMAR S-1. The first modification was a substitution of NUMAR's phase shift oscillator by a Hewlett-Packard audio oscillator, Model 200 CDR, which was also used to modulate the dc magnetic field ($H_0$). Later a replacement was made of the whole lock-in amplifier and the modulator unit of NUMAR by the lock-in amplifier, Model JB-4 of PAR (Princeton Applied Research). The final version of the spectrometer (see Figure 7) is:

A rf oscillator and detector unit of the Pound-Watkins type. This oscillator generates the rf voltage which is applied to the rf coil (field $H_1$) around the sample and detects a change in the level of this voltage when NMR absorption occurs. The oscillator itself is a cathode-coupled radio frequency oscillator. The oscillator unit also contains two stages of rf amplification, a hard tube detector, a differential amplifier and a long time constant dc feedback path. This feedback stabilizes the amplitude of the oscillator as it is tuned over the complete frequency range.

A resonance line is scanned by continuous variation of the rf frequency through the Larmor frequency. This can be done by a motor driving the variable condenser of the oscillator. A very slow sweep rate can be obtained using a set of reducing gears coupling the motor and the condenser. Type SM
Figure 7

Block Diagram of the Broad Line Spectrometer
and CA Hurst synchronous motors were used with speeds of 1 rpm, 1/2 rpm and 1/3 rpm. A proton resonance line at 10 Mc/s could be scanned as slow as 10 Kc/s/min, but a typical number used is 80 Kc/s/min. For deuteron resonances at 2.6 Mc/s the sweep rate could be as slow as 4 Kc/s/min.

The signal that comes out of the oscillator unit is already rf detected. It can now be recorded in the following three different ways:

a. If the signal comes from a very narrow resonance line, like the resonance of a liquid, it goes through an audio amplifier to the oscilloscope vertical input. In this case the dc field (H₀) is modulated with a signal of amplitude much larger than the linewidth of the resonance.

b. If the signal comes from a very broad resonance line, like the resonance of a solid, the derivative of the absorption line (dX''/dH) can be observed if the lock-in amplifier and phase sensitive detector are used.

c. The absorption line (X'') can be recorded if the output signal of the lock-in amplifier is integrated. The integrator used was the "Magnetometer type J" from Newport Instruments. It has an integrating circuit made with a dc amplifier Solartron type AA 1023. In order to match the magnetometer with the lock-in amplifier the output dc level of operation of the latter was shifted from -6 volts to zero (ground level).

The recorder used to plot the resonance lines was an X-Y Moseley Autograf, Model 2D-2. The X axis was used as the internal time base and at 20 seconds/inch. The time base calibration had an error of less than 5% of
full scale. This was our main source of error in linewidth measurement. If use is made of the mark generator of NUMAR to calibrate the time base during the display of one resonance, then a much better accuracy is obtained for that particular resonance line.

The mark generator is a 100 Kc/s crystal oscillator loosely coupled to the rf oscillator. It gives very well defined marks each 100 Kc/s. Using the scanning rate of 80 Kc/s/min, the marks appear around 96 mm apart, which was used most of the time (for hydrogen).

3. The Cryostat

The cryostat is composed of the following parts: two dewars, the probe, the mixing system and the associated vacuum pumps. All of these parts are illustrated in Figures 8 through 11 and Plate I.

The cooling system has one outer nitrogen dewar (77°K) around the inner helium dewar. The inner dewar was used for liquid hydrogen or helium. As will be described later, the condensation of hydrogen was easily achieved in the sample at 4.2°K without a hydrogen dewar. Both dewars are inside the narrow air gap of the magnet (2-3/8") as shown in Figure 8.

The probe, seen in Figure 9, has the following main parts: the top flange, the transmission line, the sample filling tube and the sample container. The top flange, shown in Figure 10, is a disc that vacuum seals the top of the inner dewar and has the appropriate holes and electrical connectors. The transmission line is electrically similar to RG-11 coaxial cable but with the
Figure 8

Cross-sectional View of the Dewars, Magnetic Field and Probe
LEGEND FOR FIGURE 8

A - Resistance Thermometer
B - Sample Tubing
C - Coaxial Line
D - Top Flange
E - Streamline Tee
F - "O" Rings
G - Stopcock
H - Dewar
I - Neoprene Washers
J - Brass Shims (0.005" thick)
K - Nitrogen Dewar
L - Helium Dewar
M - Plexiglass Disc
N - Magnet, 2.397 ± 0.002" Air Gap (Newport Instruments)
O - Helmholtz Coils
P - rf Coil

Dimensions are in inches.
TO STOKES PUMP
Figure 9

Detailed View of the Probe
A - AMPHENOL
B - KOVAR SEAL
C - CUPRO NICKEL-307
D - COAXIAL TRANSMISSION LINE
E - TEFLOM INSULATOR
F - PILOT TUBE
G - HELIUM TRANSFER PORT
H - TOP FLANGE (6.5" x 0.25")
I - SAMPLE TUBING (CUPRO NICKEL-307)
J - BRASS BUSHING (THREADED)
K - TEFLOM CONTAINER
L - RF COIL
M - TEFLOM SPACER DISC
N - RESISTANCE THERMOMETER
Figure 10

Top view of the Flange
6 equally spaced 1/4-20 holes for Allen head screws.
copper braid and inner conductor substituted by cupro-nickel 30% tubing. This reduces the heat leak to a very satisfactory level. In its design the most important consideration was the achievement of a high Q at the amplifier input. Three typical Q's at 10 Mc/s when measured at the terminals of the coil, terminals of the transmission line outside the dewar, and terminals of the transmission line inside the dewar (at room temperature) are respectively: 150, 80 and 50. The last Q reduction is due to eddy currents induced in the silver coating of the dewar. The sample tubing is also made of cupro-nickel 30%. It connects the mixing chamber or vacuum pumps to the sample container. The sample container was made of teflon and threaded to a brass bushing. Dimensions and details can be seen in Figure 9. Attached to the bottom of the container was a teflon disc to center the sample in the dewar and reduce vibrations. Cemented to the outside of the teflon container is a carbon resistor for temperature measurements. All these details can be seen in Plate I.

Figure 11 and its associated legend describe the gas mixing system. The hydrogen and deuterium gases were bought in commercial cylinders from The Matheson Company, Inc. Deuterium came in a 6" x 21" cylinder with a pressure of 225 psi, which is equivalent to 100 liters at atmospheric pressure. The factory purity analysis reveals:
Plate I

Detailed View of Components of the Probe

Top Flange
Electrical Connectors
Kovar Seal
Transmission Line
Brass Bushing
Carbon Resistor
Figure 11

The Mixing System and Pumps
LEGEND OF FIGURE 11

$V_1$ Temescal 1/2" Bellows Valve
$V_2$ Hills McCann 1/2" Ball Valve
$V_3$-$V_6$ Whitey 1/4" Ball Valve
$V_7$-$V_8$ Pressure Regulator
$V_9$ Circle Seal Check Valve
$V_{10}$ Hoke Toggle Valve
$V_{11}$-$V_{12}$ Bypass Hoke 1/4" Needle Valve
$V_{13}$ Superior 1" Packless Line Valve
<table>
<thead>
<tr>
<th>Impurity</th>
<th>Analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen deuteride</td>
<td>0.6</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.06</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.002</td>
</tr>
<tr>
<td>Argon</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

Hydrogen came in a standard size K cylinder with a pressure of about 2,000 psi, which is equivalent to a volume of 194 cu. ft. (5,500 liters) at atmospheric pressure. The purification was made by electrolysis of brine solution. A typical factory analysis is:

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>8 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>400 ppm</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1 ppm</td>
</tr>
</tbody>
</table>

Both hydrogen and deuterium before being mixed passed through a hydrogen deoxo catalytic purifier, made by Engelhard Industries, Inc. The gases are then admitted to a mixing chamber. In the chamber the partial pressures are measured by a Heise Gauge, made by Heise Bourdon Tube Company.

The rotary pumps used are "duo seal" made by W. M. Welch Manufacturing Company. The diffusion pump was made by Distillation Products, Type VMF 260-R. The helium bath pump was a Stokes pump, Model 212,
475 rpm and 5 HP motor. The vacuum produced by the diffusion pump was measured by a "Discharge Vacuum Gauge" (Type GPH-100A) from Consolidated Vacuum Corporation. The vacuum produced by the Stokes pump was measured by a thermocouple vacuum gauge (Type 501) from NRC Equipment Corporation. The helium vapor pressure was measured by a double manometer of mercury and oil. This manometer was used to measure the bath temperature, using the 1958 helium scale of temperature, and also to calibrate the carbon resistor. The resistance of the carbon resistor was measured by a Volt-Potentiometer manufactured by Leeds and Northrup.

B. Technique

In this section we will describe the technique used in performing the various experiments, the preparation of samples, how to measure the various parameters like temperature, linewidth, relaxation times, etc.

1. Generalities

A typical experiment was performed in the following manner: During overnight all vacuum pumps were left running. The Stokes pump could give a vacuum of a few microns of mercury in the helium dewar. The diffusion pump, pumping the sample line, usually evacuated it to about $10^{-6}$ mm of mercury. The mixing chamber was pumped by a rotary pump. The inner jacket of the helium dewar was flushed with air and pumped out after each experiment. A small amount of air was left in to make the thermal contact between the outer and inner dewars at the higher temperatures. In the morning pre-cooling of
the helium dewar was made by transferring nitrogen to the outer dewar and
filling the inner dewar with helium gas to atmospheric pressure. In less than
one hour the inner dewar was pre-cooled to about 80°K. Then the desired
partial pressures of the gases (hydrogen and deuterium) were measured in the
mixing chamber. It was always made in such a way that the total pressure of
the mixture was of the order to 25 psi. Then, with all the electronics on and
tuned to the exact position of the resonance, the mixture was admitted to the
sample container and liquid helium transfer started. It was possible to transfer helium so slowly that the resonance could be seen growing in the oscillo-
scope (large modulation); or, in the case of the pulsed system, not only the
resonance (after the 90° pulse), but many times the echo itself could be seen.
This was adopted as the criterion for a good condensation. After the liquid
line was fully seen in the oscilloscope, the dewar was completely filled with
helium. Then the liquid bath was pumped from 4.2°K down to about 1°K, as
slowly as desired, controlling the vapor pressure by the adjustment of the
needle valves in the Stokes pump line and watching the mercury level in the
manometer or the resistance of the carbon resistor. The same procedure was
used with liquid hydrogen as a bath (20°K - 10°K), except that for safety a big
rotary pump was used instead of the Stokes. This pump had its exhaust outlet
connected to the outside of the building through a long hose.

A few experiments were made in the temperature range 4.2°K to 10°K.
For these the charcoal method of Rose-Innes and Broom was used. A
plastic cylinder of 7" x 1-1/4" was fixed around the rf coil, carbon resistor
and evanohm heater, containing 37 grams of activated charcoal of 6-14 mesh. The top of the plastic cylinder was covered with cotton. The temperature was measured with the carbon resistor only (100 ohms at room temperature) calibrated by use of the two constant formula of Clement and Quinnell.45

2. NMR Technique with Broad Line Spectrometer

After the sample was condensed, the modulation amplitude was reduced to a fraction of the resonance linewidth (order of 0.37 gauss peak to peak at 30 cps). Later the modulation frequency was changed to 47 cps, which gave a better signal to noise ratio, but approximately the same amplitude was maintained. The amplitude of modulation was observed by measurement of the voltage induced in a small search coil of known area. The search coil had 5,000 turns of wire, AWG 42, with 16 layers, total resistance of 2,466 ohms and total area of $19.1 \times 10^3$ cm$^2$. At the center of the modulation coil and at a frequency of 29.8 cps we obtained for the modulation amplitude

$$\Delta H = 19.1 \text{ v (gauss peak to peak)}$$

where v is the induced voltage (in volts peak to peak), measured with an oscilloscope at the terminals of the search coil.

The same could not be done to measure the rf field $H_1$ in the rf coil. In this case the voltage was simply measured (with the high impedance probe of the oscilloscope) across the rf coil and knowing the number of turns, area and frequency, an estimation was made of the order of magnitude of $H_1$ in the center of the coil. The relative measurements of $H_1$ are nevertheless much
better because the NUMAR oscillator had a meter graduated from 0-100 that measured the rf level of oscillation with an accuracy of about 1%. With the rf coil used in most of the proton resonance experiments, at 10 Mc/s, the rf level could be varied in the range 15 to 150 mgauss. The above-mentioned coil had 13 turns, length 1/2", diameter 1/4" and inductance of 1.4 μhenry. The sample inside the coil occupies 0.4 cm³, i.e., about 1/4 the volume of the sample container shown in Figure 9. The one shown in Figure 9 was used in the experiments with deuterium sample.

There are several important conditions to be satisfied in order to record a true resonance line (or its derivative) in a broad line spectrometer. The first was already mentioned, i.e., the amplitude of modulation must be small compared with the linewidth (at 4.2°K the hydrogen line has about 5.4 gauss and the deuterium line has about 1.6 gauss linewidth). The second condition is concerned with the steady-state solution of Bloch's equations. It requires a slow passage through the resonance line. In more quantitative terms it requires the time of passage to be large compared with both $T_1$ and $T_2$. Using the 80 Kc/s/min scanning rate, which is equivalent to about 4 seconds to sweep the hydrogen line at 4.2°K, the above conditions are in general satisfied, in the solid region. Finally, the conditions require an homogeneous magnetic field. The field inhomogeneity across the sample volume has to be small compared with the linewidth. The magnet was not very homogeneous, but good enough for experiments with solid hydrogen. As it will be shown in the next chapter, the inhomogeneity across the sample volume was of the order of 140 milligauss.
There are also conditions concerning the proper operation of the lock-in phase sensitive detector, the integrator, etc., that will not be discussed here because they are explained in the instruction manuals.

With this equipment operated as described above, it was possible to measure the linewidth, lineshape and saturation behavior of the absorption resonance line as well as its derivative, for all mixtures of \( H_2 - D_2 \) below 10\(^\circ\)K.

3. NMR Technique with Pulsed Apparatus

The pulsed technique is very powerful and also a versatile method of studying important properties of liquids and solids like \( T_1, T_2, \) diffusion, etc. Due to the extensive and detailed literature published on the subject it seems unnecessary to make more than a short summary of the basic concepts and the principal results. The versatility of the method resides in the large combinations of number of pulses, width, relative position and time interval between the 90 and 180 degree pulses.

A sample containing magnetic nuclei is placed in a dc field \( H_0 \) and subjected to short pulses of the rf field \( 2H_1 \cos \omega_0 t \), orthogonal to \( H_0 \). Here \( \omega_0 \) is the Larmor precession frequency of the nuclei in the field \( H_0 \); i.e., \( \omega_0 = \gamma H_0 \), and \( \gamma \) is equal to \( 2.67 \times 10^4 \) sec\(^{-1}\) gauss\(^{-1}\) for protons. Initially \((t = 0)\) the sample is magnetized in the \( z \) direction, chosen to be the \( H_0 \) direction. After the application of one rf pulse of duration (width) \( t_w \), the magnetization rotates through an angle

\[
\theta = \gamma H_1 t_w
\] (57)
which is called a "θ pulse." Here two conditions are required: \( t_w \ll T_2 \) and 
\( H_1 \) larger than the field inhomogeneity and linewidth. The second condition was
easily accomplished in the experiments. For the 180° pulse used, \( t_w = 15 \mu \text{sec} \),
which gave \( H_1 = 78.5 \) gauss. The other condition \( t_w \ll T_2 \) is not satisfied
because at 4.2°K for instance, for hydrogen, \( T_2 (T_2 \approx \frac{1}{\gamma \Delta_0} ) \) is equal to 7 \( \mu \text{sec} \).
This is not too serious, however. It means that some relaxation occurs during
the pulse. From all possible "θ pulses" the 90° and 180° are the more
important. They are obtained by tuning the width \( t_w \) to give a first maximum
signal after the 90° and a first minimum signal after the 180° pulse. If now
these two pulses are displayed together, with the 90° pulse leading the 180° by
a time interval \( \tau \), an echo will be seen at a time \( 2\tau \) from the first pulse (see
Figure 7) provided \( \tau \ll T_2 \). This last condition does not permit echoes to be
seen in solid hydrogen.

There are several ways of measuring \( T_1 \). The one used here consists
of applying a 180° pulse followed by 90° a time \( \tau \) later. Then a plot is made of
the height of the resonance following the 90° pulse against the time \( \tau \). The
height is given by:46

\[
h(\tau) = h_{\text{max}} \left[ 1 - 2 \exp \left( - \frac{\tau}{T_1} \right) \right]
\]

i.e., \( |h(\tau)| \) goes from \( h_{\text{max}} \) at \( \tau = 0 \), through zero at \( T_1 = \frac{T_{\text{null}}}{\ln 2} \), to \( h_{\text{max}} \)
again at \( \tau = \infty \). A straight line with slope \( 1/T_1 \) is obtained if we plot
\( \ln \left[ 1 - \frac{h(\tau)}{h_{\text{max}}} \right] \) against \( \tau \). This is what is done in Figure 13. The value of \( h \) at
τ = ∞, i.e., -h_{\text{max}} is used as the normalizing factor. The value of \(1 - \frac{h(\tau)}{h_{\text{max}}}\)
at \(\tau = 0\) is not 2 like it should be from equation (58), because the condition
\(t_w << T_2\) was not satisfied. This more realistic condition will be considered
in Chapter VII.
CHAPTER VI

PRESENTATION OF EXPERIMENTAL DATA

The data will be presented in a series of 17 figures and 4 plates summarizing more than one hundred experiments. Most of the results are concerned with the more recent experiments since they were done with improved equipment. Only a small fraction of the data taken by pulsed technique will be presented, since they lie outside the main scope of the dissertation, except for the measurements of $T_1$, the spin lattice relaxation time.

A. Pulsed Technique Data

Pulsed techniques (principally spin echoes) were used to determine the solidus line of $\text{H}_2 - \text{D}_2$ mixtures for a few concentrations. The signal to noise ratio of the echoes was very good, as is shown in Plate II-A at 19°C for a mixture of 72%. The horizontal sweep was $X = 1$ msec/cm and the vertical axis $Y = 0.5$ v/cm. The Larmor frequency was 10 Mc/s. Liquid hydrogen was used as a bath and the temperature was determined by a manometer, using the vapor pressure curve of equilibrium hydrogen. When the sample solidifies, the echo amplitude decreases sharply due to the rapid decrease of $T_2$ upon solidification. A plot of echo amplitude against temperature is shown in Figure 12 for an $\text{H}_2 - \text{D}_2$ mixture with 40% $\text{H}_2$. A solidification temperature of 15.7°C
Plate II

A - View of an Echo
B - T$_2$ of the Magnet
C - Beats after 90° Pulse
D - Series of Beats due to $\lambda$-splitting of Hydrogen
A) View of an echo at 72% H₂/H₂ + D₂
X = 1 msec/cm
T ≈ 19°K

B) T₂ of the magnet
X = 50 μsec/cm
Y = 0.5 v/cm

C) Beats after 90° pulse in pure H₂
X = 20 μsec/cm
T = 4.2°K

D) Beats after 90° pulse in pure H₂
X = 5 μsec/cm
T = 1.1°K
Figure 12

Echo Amplitude Versus Temperature
was found in very good agreement with White and Gaines.\textsuperscript{47} Pulsed methods were also used to measure T$_2$ of the magnet with a sample of pure liquid hydrogen whose T$_2$ is so long due to rotational averaging of the local fields that the resultant decay time for the x-y component of the magnetization is dominated by magnetic field inhomogeneities (T$_2^*$). Plate II-B shows the exponential decay after a 90° pulse with X = 50 \( \mu \)sec/cm and Y = 0.5 v/cm. The picture was taken during a slow helium transfer at about 18°K and from it T$_2$ = 135 \( \mu \)sec was obtained, which is equivalent to an inhomogeneity \( \Delta H = 280 \) milligauss at about 5 kilogauss (20 Mc/s) across a sample of 0.4 cc. All the experiments with the broad line spectrometer were made at 10 Mc/s, therefore, with an inhomogeneity of about 140 mgauss.

At 4.2°K T$_1$ of pure H$_2$ was measured by the 180°-90° sequence of pulses, i.e., measuring the recovery of the M$_z$ magnetization to the equilibrium condition. It was surprising to see a kind of Lowe\textsuperscript{48} beat after the 90° pulse, as if the sample were a single crystal. In two other experiments the same beats were observed. When \( \tau \) (time interval between the 180° and 90° pulses) was increased the height h(\( \tau \)) of the first beat decreased, vanished at \( \tau_{null} \approx 160 \) msec and increased again to the maximum value at \( \tau \) infinite. The beats are seen in Plate II-C. The 90° pulse has 7.2 \( \mu \)sec width and the scale in the X axis is X = 20 \( \mu \)sec/cm. In Figure 13 a plot of \( 1 - \frac{h(\tau)}{h_{max}} \) versus \( \tau \) is shown. T$_1$ was found to be \( \sim 390 \) msec in one region of the curve and \( \sim 480 \) msec in the other. It was found also that h(\( \tau \)) satisfies an equation of the type:
Figure 13

$T_1$ of Pure Hydrogen at 4.2°K
PURE HYDROGEN
T = 4.2 °K
f₀ = 20 MCPS
\[ h(\tau) = h_{\text{max}} \left[ 1 - k \exp \left( -\frac{\tau}{T_1} \right) \right] \] (59)

where \( h_{\text{max}} \) is the value of \( h \) at \( \tau \) infinite (not at \( \tau \) equal to zero), with \( k = 1.4 \) for \( T_1 \approx 480 \) and \( k = 1.55 \) for \( T_1 \approx 390 \) msec. Then, after the temperature was lowered to about 1.1°K, a series of beats were obtained after the 90° pulse as shown in Plate II-D. The scale is \( X = 5 \mu \text{sec}, Y = 1 \text{v/cm} \) and the 90° width is 8 \( \mu \text{sec} \). The average period of the beats was found to be 11.6 \( \mu \text{sec} \) which corresponds (after Fourier transformed, see Chapter VII) to \( \Delta_1 = 40.3 \) gauss, in good agreement with the side peaks of the \( \lambda \)-splitting obtained in pure \( \text{H}_2 \) from the broad line spectrometer shown in Plate III.

**B. Line Splitting in Hydrogen and Deuterium**

An experiment with pure normal hydrogen was recorded by means of the broad line spectrometer as a check of its performance at a Larmor frequency of 10 Mc/s. The results shown in Plate III confirmed the well-known \( \lambda \)-splitting values published in the literature.\(^{27, 29, 30, 31}\) The plate is a detailed view of the splitting at 1.1°K. A few similar experiments were performed on mixtures of \( \text{n-H}_2 \) and a small amount of \( \text{n-D}_2 \). The results were essentially the same for all mixtures between 100\% and about 95\% of \( \text{H}_2 \). The only significant difference is that the temperature where the \( \lambda \)-splitting occurs decreases with the hydrogen concentration and it is around 1.1°K at 95\%. The experiments with pure normal deuterium at a Larmor frequency of 2.63 Mc/s show no splitting above 1.1°K. At 4.2°K the linewidth \( \Delta \) is 1.66 gauss. The
Plate III

λ-splitting of Hydrogen
PURE HYDROGEN
T = 1.10 °K
H_z = 15 mGauss
Mod: 380 mGauss
at 47 CPS

\[ \Delta_0 = 3.2 \text{ Gauss} \]
\[ \Delta_1 = 39.8 \text{ }\]
\[ \Delta_2 = 76.0 \text{ }\]

SCALE: 96 divisions = 100 KCPS
lineshape at the lowest rf level was much more asymmetric than the corresponding one for hydrogen. All these results are in good agreement with Dickson and Meyer.\textsuperscript{37}

Several previous unsuccessful attempts had been made by nuclear magnetic resonance techniques\textsuperscript{29, 25, 31} to observe a cooperative transition in solid deuterium analogous to the $\lambda$-type anomaly in solid hydrogen. Recent heat capacity measurements by Grenier and White\textsuperscript{49} demonstrated the existence of such a cooperative transition in solid $D_2$ above 1.5°K providing the para $D_2$ ($I = 1, J = 1$) concentration was in excess of 60%. We\textsuperscript{50} have made nuclear resonance studies of enriched para $D_2$ samples (with concentration of about 80%) and have observed the splitting of the resonance line in $D_2$ below 2°K. Figure 14 shows the derivative of the resonance line at 4.2°K, and Figure 15 shows how it splits. The side peaks appeared 76.8 Kc/s apart in good agreement with a calculation made by Reif and Purcell.\textsuperscript{30}

C. Lineshape and Linewidth

From now on all the experimental results shown were obtained observing the proton resonance due to ortho-hydrogen (pure or in a mixture with deuterium) at a Larmor frequency of 10 Mc/s and recorded in the broad line spectrometer previously described. All the concentrations mentioned will refer to concentration of normal $H_2$ in mixture with normal $D_2$. Figures 16, 17 and 18 show one side of the derivative of the absorption resonance line for several different concentrations at about 10°K, 4.2°K and 1.1°K respectively.
Figure 14

Derivative of the Absorption Resonance Line of

Pure Enriched Deuterium at 4.2°K
PURE DEUTERIUM
81 % p-D₂
T = 4.2 °K
H₀ = 15 mgauss
Mod: 350 mgauss
at 47 CPS
Figure 15

Splitting of Deuterium Resonance Line at 1.2°K
PURE DEUTERIUM
84 % p-D₂
T = 1.2 °K
H₁ ≈ 15 mgauss
Mod: 350 mgauss
at 47 CPS
It is interesting to observe that there is no significant difference in the tails of the several concentrations at around 10°K (Figure 16). The tail becomes more pronounced at 4.2°K (Figure 17) for concentrations below 50% and becomes very significant at 1.1°K. Pure hydrogen shows no splitting at 1.1°K in Figure 18-A because it had a low ortho/para concentration (it was recorded about six hours after condensation). For very small concentrations of H₂ the resonance line is almost resolved in a broad line of about 12 gauss peak to peak and a very narrow line in the center. The linewidth of the broad part of the resonance line is not very sensitive to a change of concentration (12 gauss) but the narrow part becomes so skinny for lower concentrations that it resembles the derivative of a Dirac delta function at the origin. The linewidth peak to peak of the narrow part of the line is shown in Figure 28 as a function of concentration for both low and high rf levels at 4.2°K. It was noticed also that the line becomes more asymmetric as the concentration decreases. It was not difficult to record a resonance line with 1.8% of normal H₂. Figures 19, 20 and 21 show one side of the absorption resonance line in the same range of temperature and concentration as Figures 16, 17 and 18. They are not strictly an integration of Figures 16, 17 and 18 because many of them were obtained in a different run, nevertheless under the same experimental conditions. Figures 22 and 23 show the change in the shape of \( \frac{d\chi''}{dH} \) and \( \chi'' \) for a fixed concentration (40%) at three different temperatures (10°K, 4.2°K and 1.1°K). Plate IV is a photograph of the derivative of a resonance line as it is actually recorded. It was obtained from a mixture of 18.4% H₂ at about 1.17°K.
It shows also the marks of the "Mark Generator" at an interval of 300 Kc/s. The generator marks at each 100 Kc/s, but it was turned off during an interval of about 250 Kc/s around the resonance line to preserve its actual shape. The rf level used was the minimum possible and a small asymmetry is still noticed.

It was not easy to determine the temperature where the linewidth becomes composite because the change is very slow. Plate V is a photograph of a series of resonance lines in the transition region. The legend gives the temperature of each curve from 4.2°K to 2.10°K, as it was measured with the double manometer. Below 50% it is practically impossible to find where the transition occurs, mainly because even at 4.2°K the curves have already a broad tail in the noise level. At 50% (shown in Plate V) it seems to occur at curves 19 or 20. If the temperature is lowered to 1.1°K, a curve like 22 in Plate V will become like curve B in Figure 18. At concentrations higher than 60% the transition is better defined. Figure 24 shows the transition temperatures found as described above and plotted against concentration. It shows also the temperature of phase separation predicted by Prigogine (equation 24) and by Bellemans from equation 28.

Figure 25 shows the linewidth (w) plotted against temperature in the range 1°K to 10°K for several different concentrations. The linewidth is nearly constant above 4.2°K at all concentrations and increases below 4.2°K. The curve shown for 20% was obtained in two different experiments: one below and the other above 4.2°K.
Figure 16

Derivative of the Absorption Resonance Line at
Several Concentrations of Hydrogen at \( \sim 10^7 \)K
CONCENTRATION

\[
\left( \frac{H_2}{H_2 + D_2} \right) \% \quad T(\text{oK})
\]

- 4.9 % - 9.6
- 40 % - 10.9
- 60 % - 9.2
- 90 % - 9.6

r.f. = 17 mgauss
Mod: 350 mgauss
at 47 CPS
Figure 17

Derivative of the Absorption Resonance Line at

Several Concentrations of Hydrogen at 4.2°K
CONCENTRATION

\[ \frac{H_2}{H_2 + D_2} \] %

- ▽ - 100 %
- ○ - 40 %
- ⭕ - 20 %
- ▼ - 10 %

T = 4.2 °K
r.f. = 17 mgauss
Mod: 350 mgauss
at 47 CPS

\[ \frac{d^2}{dH^2} \] NORMALIZED

\( \Delta H \) (gauss)
Figure 18

Derivative of the Absorption Resonance Line at

Several Concentrations of Hydrogen at 1.1°K
CONCENTRATION

\( \frac{H_2}{H_2 + D_2} \% \)

A - 100 %
B - 50 %
C - 40 %
D - 30 %
E - 10 %

\[ T = 1.1 \, ^\circ K \]
\[ r.f. = 17 \, \text{mgauss} \]
\[ \text{Mod: 350 mgauss} \]
\[ \text{at 47 CPS} \]
Figure 19

Absorption Resonance Line at Several Concentrations of Hydrogen at ~10°K
CONCENTRATION

\[
\left( \frac{H_2}{H_2 + D_2} \right) \%
\]

T(°K)

- \( \circ \) 4.9 % - 9.6
- \( \circ \) 40 % - 9.8
- \( \triangledown \) 60 % - 8.9
- \( \triangledown \) 90 % - 9.6

r.f. = 17 mgauss
Mod: 350 mgauss
at 47 CPS
Figure 20

Absorption Resonance Line at Several Concentrations of Hydrogen at 4.2°K
CONCENTRATION
\( \left( \frac{H_2}{H_2 + D_2} \right) \% \)

- \( \bullet \) 10 \%
- \( \circ \) 20 \%
- \( \triangledown \) 40 \%
- \( \triangle \) 100 \%

\[ T = 4.2 \, ^\circ K \]
\[ r.f. = 17 \, mgauss \]
\[ M = 350 \, mgauss \] at 47 CPS

\( \Delta H(\text{gauss}) \)
\( \chi^\prime \text{NORMALIZED} \)
Figure 21

Absorption Resonance Line at Several Concentrations of Hydrogen at \(~1.1^\circ\)K
CONCENTRATION

\( \left( \frac{H_2}{H_2 + D_2} \right) \% \)

- • - 10 %
- ○ - 20 %
- ▼ - 40 %
- ▼ - 100 %

\( T = 1.1 \, \text{°K} \)

r.f. = 17 mgauss

Mod: 350 mgauss

at 47 CPS
Figure 22

Derivative of the Absorption Resonance Line (40%) at Several Temperatures
\[ \frac{H_2}{H_2 + D_2} = 40\% \]

\[ \text{r.f.} = 17 \text{ mgauss} \]

\[ \text{Mod.} = 350 \text{ mgauss at 47 CPS} \]
Figure 23

Absorption Resonance Line (40%) at Several Temperatures
CONCENTRATION
\[ \frac{H_2}{H_2 + D_2} = 40\% \]

r.f. = 17 mgauss
Mod: 350 mgauss
at 47 CPS
Plate IV

Derivative of a Resonance Line with 18.4% H$_2$ at 1.17°K
\( \frac{H_2}{H_2+D_2} = 18.4 \% \)

\( T = 1.17 \, ^\circ K \)

\( H_1 \equiv 15 \, \text{mGauss} \)

Mod: 350 mGauss

at 30 CPS
Plate V

Derivatives of Absorption Resonance Line (50%) at Several Temperatures
<table>
<thead>
<tr>
<th>Figure</th>
<th>T °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>4.08</td>
</tr>
<tr>
<td>3</td>
<td>3.95</td>
</tr>
<tr>
<td>4</td>
<td>3.86</td>
</tr>
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Figure 24

Transition Temperature $T_c$ Versus Concentration
Figure 25

Linewidth $w$ versus Temperature for Several Concentrations of Hydrogen
D. Saturation Behavior

The next three figures summarize the data obtained in the study of saturation. The rf energy could be varied by a factor of 100, i.e., $H_1$ varied roughly from 0.015 gauss to 0.15 gauss. Figure 26 shows the variation of the linewidths $\Delta$ and $\omega$ (see footnote on page 23) with the rf field for several different concentrations. For lower concentrations both linewidths are practically constant. For higher concentrations, up to pure normal hydrogen, they both decrease with rf increasing. This rather abnormal behavior for pure $H_2$ was first pointed out by Reif and Purcell. Figure 27 shows the variation of the normalized amplitude of $\chi''$ and of $\frac{dx''}{dH}$ (from peak to peak) with the rf field for concentrations of 10%, 40% and 100%. The figure also shows that the data fit better a $1/H_1$ curve (for any concentration) than the expected $1/H_1^2$ in the region of high rf field. Finally Figure 28 shows the linewidth $\Delta$ (peak to peak) at 4.2°K plotted against the hydrogen concentration in both low and high rf field. It is interesting to note that the experimental result agrees very well with a calculation of the rigid lattice second moment for protons in a homogeneous solid $H_2 - D_2$ mixture. The heavy line, at low rf field, in Figure 28 is given by:

$$<\Delta H^2>^{1/2}_{\text{mix}} = <\Delta H^2>^{1/2}_{\text{pure}} \left[ x + k(1-x) \right]^{1/2}$$ (60)

where $x$ is the $H_2$ concentration and where

$$k = \frac{4}{9} \left( \frac{\gamma_{D_2}}{\gamma_{H_2}} \right)^2 I_{D_2} (I_{D_2} + 1)/I_{H_2} (I_{H_2} + 1)$$ (61)

The value of $k$ averaged over all $D_2$ spin states is 0.021.
Figure 26

Linewidths $w$ and $\Delta$ versus rf Field for Several Concentrations of Hydrogen at 4.2°K
\[ \frac{H_2}{H_2 + D_2} \% \]

(a) \[ \Delta(\text{gauss}) \]

(b) \[ w(\text{gauss}) \]

10 arbitrary units = 0.015 gauss of \( H_1 \)
Figure 27

Amplitude of the Resonance Line and Its Derivative Versus

rf Field for Several Concentrations of Hydrogen
$\frac{H_2}{H_2 + D_2} \%$

- $\bullet$ - 10
- $\circ$ - 40
- $\times$ - 100

$1/H_1^2$

$1/H_1$

$T = 4.2 \, ^{\circ}K$

$\chi''$ normalized

$10$ arbitrary units $\approx 0.015$ gauss of $H_1$. 

r.f. (arbitrary units)
Figure 28

Linewidth $\Delta$ versus Concentration of Hydrogen

at Low and High rf Fields at 4.2°K
SECOND MOMENT CALCULATION

\[ \Delta H(\text{Full Width}), \text{Gauss} \]

- \( H_L \approx 0.015 \text{ gauss} \)
- \( H_L \approx 0.15 \text{ gauss} \)

\[ X_{H_2} \]
A. **Pulsed Technique Results**

The pulsed method used to study H$_2$ - D$_2$ mixtures in the range 20-10°K could be good enough to determine the solidus line, as shown in Figure 12 for a 40% mixture. The temperature of the hydrogen bath was obtained by measuring its vapor pressure with a simple mercury manometer. The accuracy was not very good in the region below 14°K. No anomaly that could be interpreted as characteristic of the phase separation (found by Kogan et al.⁹) was observed. This negative result was later confirmed by the broad line spectrometer experiments.

Pulsed methods were also used to measure $T_1$ at 4.2°K in pure H$_2$ using the recovery method of two pulses. $T_1$ was found to be 0.39 sec in one region and 0.48 sec in another region of the curve (see Figure 13). The fact that $k$ (see equation 59) was not equal to 2 means that $M_(t=0)$ was not equal to $-M_0$ because the width $t_W$ was not much less than $T_2$, as usually required. This can be summarized in the following way:
a. Bloch’s equations in the rotating frame of reference are:

\[
\frac{du}{d(\omega_1 t)} + \beta u + \delta v = 0
\]

\[
\frac{dv}{d(\omega_1 t)} + \beta v - \delta u + M_z = 0
\]

\[
\frac{dM_z}{d(\omega_1 t)} + \alpha M_z - v = \alpha M_0
\]

(62)

where

\[
\alpha = \frac{1}{\omega_1 T_1}, \quad \beta = \frac{1}{\omega_1 T_2}, \quad \delta = \frac{\omega_0 - \omega}{\omega_1}
\]

\[\omega_1 = \gamma H_1 \] and \( u \) and \( v \) are, as conventionally used, the x and y components of the magnetization in the rotating frame. The field \( H_1 \) is applied in the x direction. \( M_0 \) is the static magnetization.

b. In the case of a large \( H_1 \) (or \( \omega_1 \)) and narrow \( \theta \) pulse \( (\theta = \gamma H_1 t_w) \), \( \beta \) and \( \delta \) are nearly zero. The Bloch equations can be integrated easily, giving:

\[
M_z(t_{w_1}) = M_0 \cos \theta_1
\]

\[
v(t_{w_1}) = -M_0 \sin \theta_1
\]

\[
u(t_{w_1}) = u(0) = 0
\]

(63)

at the end of a \( \theta \) pulse. These equations are described by saying that the vector \( M \) rotates as a fixed length vector.

c. In the case of solids \( T_2 \) is very small and \( \beta \) is not nearly zero. In the case of n-H_2, \( T_2 \approx 7.6 \) \( \mu \)sec at 4.2°K (see page 72). If \( \theta_1 = 180^\circ \) with \( t_w = 15 \) \( \mu \)sec, the value of \( \beta \) is of the order of one. In this case an integration of the Bloch’s equations gives:
\[ M_z(t_{w_1}) = M_0 e^{(-\beta/2)\theta_1} \cos \left[ (1 - \beta^2/4)^{1/2} \theta_1 \right] \]

\[ v(t_{w_1}) = -M_0 \left[ \frac{\beta}{2} e^{-\beta/2} \cos \left( (1 - \beta^2/4)^{1/2} \theta_1 \right) + \left( (1 - \beta^2/4)^{1/2} \right) e^{-\beta/2} \theta_1 \sin \left( (1 - \beta^2/4)^{1/2} \theta_1 \right) \right] \]

\[ u(t_{w_1}) = A e^{-\beta \theta_1} \]

and \( A = 0 \) (from initial conditions) at the end of the \( \theta_1 \) pulse.

For \( \theta_1 = 180^\circ \) and \( \beta = 1 \), the magnetization \( M_z \) is of the order of \( -\frac{M_0}{e} \) instead of \( -M_0 \) as it would be in case b. This is the advantage of measuring \( T_1 \) by the recovery process. It is not necessary to have an exact \( 180^\circ - 90^\circ \) pulse sequence.

The result obtained at 1.1°K where the hydrogen resonance line is split can be derived in the following way: Assume that the lineshape is a doublet consisting of two Lorentz shaped lines with the same width, different amplitudes (in the ratio 1:h) and separated by an amount \( \Delta \):

\[ g(\omega) = \frac{T_2}{(1+h)\pi} \left[ \frac{1}{1+T_2^2(\omega - \omega_0 - \Delta/2)^2} + \frac{h}{1+T_2^2(\omega - \omega_0 + \Delta/2)^2} \right] \]  

(65)

The free induction decay is the Fourier transform of \( g(\omega) \), i.e.,

\[ f(t) = \int_{-\infty}^{\infty} g(\omega) e^{i\omega t} d\omega \]

\[ = \exp \left( -t/T_2 \right) \left[ (1+h) \cos \frac{\Delta}{2} t + i(1-h) \sin \frac{\Delta}{2} t \right] \]

(66)

The observed signal is

\[ |f(t)| = \frac{1}{1+h} \exp \left( -t/T_2 \right) \left[ (1+h)^2 \cos^2 \frac{\Delta}{2} t + (1-h)^2 \sin^2 \frac{\Delta}{2} t \right]^{1/2} \]

(67)
In case the doublet is made of two identical parts \((h = 1)\):

\[
|f(t)| = \exp \left(-\frac{t}{T_2}\right) |\cos \frac{\Delta}{2} t|
\]

(68)

By measuring the period in Plate II-D, the value of \(\Delta\) can be obtained:

\(\Delta = 40.3\) gauss. A plot of the amplitudes of the relative maxima of Plate II-D gives \(T_2 \approx 14.5\) \(\mu\)sec, which corresponds to a Lorentzian line of \(\Delta = 3\) gauss peak to peak. The observed linewidth \(\Delta_0\) was 5.7 gauss at \(4.2^\circ\)K and 3.2 gauss when the splitting occurred (see Plate III).

A more realistic situation can be easily obtained in the following way:

It is known from broad line spectrometers that the splitting of \(H_2\) shows a small center line that should disappear at sufficiently low temperatures when all molecular rotation is quenched.\(^{30}\)

Therefore, instead of equation (65) we should use:

\[
g(\omega) = \frac{T_2}{2 + h} \left[ \frac{1}{1 + \frac{T_2^2 (\omega - \omega_0 - \frac{\Delta}{2})^2}{\omega - \omega_0 + \frac{\Delta}{2})^2}} \right] + \frac{h}{1 + \frac{T_2^2 (\omega - \omega_0)^2}{\omega - \omega_0 + \frac{\Delta}{2})^2}}
\]

where we assume all three components of the line have the same \(T_2\).

By analogy to equation (68), \(|f(t)|\) can be written immediately as:

\[
|f(t)| = |(h + \cos \frac{\Delta}{2} t)| \exp - \frac{t}{T_2}
\]

and this accounts for the fact that in Plate II-D the \(\cos \frac{\Delta}{2} t\) does not oscillate around a horizontal line.
B. Phase Separation

This work was originally started in the hope that information obtained from nuclear magnetic resonance experiments would provide additional data on the type of transition known as isotopic phase separation. In particular, it seemed probable that NMR experiments could readily distinguish a transition from the randomly mixed state (the high temperature equilibrium configuration) to the isotopically ordered state that involved a rearrangement of the isotopes into interpenetrating sublattices from one that involved only a clumping together into small domains. Kogan et al\(^9\) had reported observing such a phase separation at the relatively high temperature of 16.4°K, as shown in Figure 2. At such high temperatures the diffusion rates are large enough\(^{35}\) so that domains of macroscopic size can form in a relatively short time. Since the linewidth is dependent on the concentration of H\(_2\) molecules, one would expect to observe a transition from a simple line into a composite line with both a very broad and a very narrow component in the event a phase separation occurred. At high temperatures, T > 12°K, pulsed NMR had to be employed since the true linewidth was swamped by magnetic field inhomogeneities. At temperatures below 12°K the solid absorption line becomes very broad and steady-state (broad line) techniques are applicable. A set of resonance curves as shown in Figure 16 (T \(\approx\) 10°K) shows no evidence of a composite line characteristic of a phase separation.\(^{51}\) The curves have a rather large tail but about the same shape in all concentrations of H\(_2\). The only difference that exists between these curves (besides the shift in the position of the peak) is
that the lower concentration curves show a larger tail. This is obvious at 1.1°K where the curve E (10%) is almost resolved, but even at T ≈ 10°K the large tail can be observed (see, for instance, Figure 19). From the above data we concluded that the result of Kogan et al. is not confirmed because from their diagram (shown in Figure 2) no composite line should be expected for concentrations below 20% H₂ at any temperature below 16.4°K. There are several other aspects of our experiments that do not confirm their results. Nevertheless, all resonance lines are composite at 1.1°K, as shown in Figure 18, except pure H₂. The problem now is to interpret this result as due to phase separation in a region of temperature other than the one proposed by Kogan et al. or to interpret it as something else.

It was found that the transition from a single line, as observed above 4.2°K in Figure 22 (40%), to a composite lineshape (like the one shown in Figure 22 at 1.1°K) occurred very quickly, in a time less than two minutes, essentially in the time necessary to cool the sample from 4.2°K to 1.1°K with the Stokes pump all open. It was further found that prolonged maintenance of the temperature at 1.1°K for several hours did not result in any observable change in the composite line structure.

Since the experimental results of Kogan et al. could not be confirmed, the only remaining hope of finding phase separation in H₂ – D₂ rests on the theoretical possibilities arising from the positive excess Gibbs free energy, and the existence of an effective diffusion process. If the diffusion is thermally activated as found by M. Bloom, no appreciable phase separation will occur.
in a geological time, below 3°K. Again a chance exists if a diffusion process other than a thermally activated one occurs, as in the case of He^3.\textsuperscript{26}

C. Hindering of Rotation

In spite of all arguments against phase separation, the resonance line does become composite below 4.2°K for all concentrations as if phase separation occurs. An explanation could be also that hindering of the rotation takes place. The arguments in favor of this are the following. It is known that m-H\textsubscript{2} has almost free translational diffusion\textsuperscript{34} in the liquid and solid phases above 12°K. From 12°K down to 4°K the H\textsubscript{2} molecules have almost free rotation, and below 2.5°K the splitting of the line proves that the rotation is partially or totally frozen. The magnetic dipole interaction between the two protons in a given ortho molecule gives rise to a splitting due to the crystalline potential.\textsuperscript{30} The same type of freedom of motion should be expected for the hydrogen molecules when in mixtures with deuterium. As a matter of fact, more freedom could be expected since (in first approximation) deuterium simply permeates the space around the hydrogen molecules without any significant magnetic interaction. This hypothesis was verified when the λ-splitting of the hydrogen line was obtained for mixtures in the range from 95% to 100% just as if the ortho/para concentration were changed in pure H\textsubscript{2}, like in the experiment of Sugawara et al.\textsuperscript{31} Another important argument is the similarity of Sugawara's result (see Figure 4) for different ortho/para concentration of pure H\textsubscript{2} with the results shown in Figure 18 for different
H$_2$ - D$_2$ concentrations. If the composite lines of Figure 18 were to be explained as phase separation, pure hydrogen (ortho and para components) should also phase separate to explain the similarity with Sugawara's result.

If the ortho/para phase separation is assumed to be impossible, a crucial experiment to decide between phase separation and hindering of rotation of H$_2$ - D$_2$ mixtures could be made. It is sufficient to measure the specific heat of a mixture of normal deuterium with para-hydrogen (the para-H$_2$ molecules are spherically symmetric and have no rotation). If no anomaly is found, no phase separation exists. This experiment is out of the scope of this dissertation and is not reported here. It was performed once and the slight anomaly found was attributed to the hindering of rotation of the para-D$_2$ molecules in normal D$_2$. $^{49,52}$

No indication of the discontinuous change in heat capacity accompanying a phase separation was observed. The assumption of no ortho-para hydrogen phase separation is very likely to be true but so far cannot (at least logically) be ruled out. The correlation frequency and the apparent broadening of the second moment found by Gutowsky $^{53}$ and by Andrew and Jenks $^{54}$ could not be calculated. The temperature where the apparent second moment remains constant again is below 1°K and a He$^3$ cryostat or adiabatic demagnetization would be necessary. The words "apparent second moment" have been used because (as Anderson pointed out) the second moment is invariant with respect to motion and the apparent narrowing at higher temperatures is because weak side spectra are usually unobservable. The
behavior of the linewidth might be expected to resemble the behavior of the second moment and it is shown in Figure 25.

Mixtures of concentration below 50% have composite resonance lines at somewhat higher temperatures. At 4.2°K (see Figure 17) a broad and intense tail can be observed at 10% and 20%. For concentrations above 50% this temperature is below 4.2°K and is shown in Figure 24. This transition temperature is of the same order of magnitude as the transition temperature $T_C$ (consolute temperature) predicted by Prigogine. The same type of experimental curve could be plotted for pure $\text{H}_2$ from Sugawara's result (shown in Figure 4) if a large number of resonance lines were available between 4.2°K and 1.17°K. Therefore, the results of Figure 24 (above 50%) can be interpreted simply as a fortuitous coincidence with the predicted $T_C$ of Prigogine.

D. Saturation Behavior

One of the most interesting results of the study of hydrogen is its anomalous saturation behavior, first pointed out by Reif and Purcell.\cite{30} They found that the linewidth narrows when the rf field $H_1$ increases, and no explanation was given. Today several substances are known whose rf behavior does not follow BPP theory.\cite{40} The mixtures of hydrogen and deuterium have the same type of anomaly as pure hydrogen, as shown in Figure 26 (at 4.2°K). For low concentrations the linewidth is practically constant in the range of rf used. The largest value of $H_1$ used gives a saturation factor $S(S = \gamma H_1^2 T_1 T_2)$ of the order of 50 for pure hydrogen. Taking $T_2 \sim \frac{2}{\sqrt{3} \gamma \Delta H}$, the value of $\Delta H$ for a
mixture from equation (60) approximated to be \((\Delta H)_{\text{mix}} \approx (\Delta H)_{\text{pure}} \sqrt{x}\) and the value of \(T_1\) from equation (32), i.e., \(T_1 = 0.361 \frac{2}{\sqrt{3}} \sqrt{x}\) and substituting in the expression for the saturation factor \(S\), it is obtained that \(\frac{S_{\text{mix}}}{S_{\text{pure}}} \approx 1\). This means that at a given rf level the degree of saturation achieved in pure \(H_2\) is the same as in any composition of the mixture. This fact permits a direct comparison of the results in Figure 26.

The work of Reif and Purcell\(^{30}\) and Sugawara et al.\(^{31}\) were interpreted according to the Bloch equation and BPP theory. Redfield\(^{41}\) in a penetrating thermodynamic analysis has shown that BPP and Bloch equations cannot be used to interpret nuclear magnetic resonance results in solids at high rf power levels. Provotorov's\(^{42}\) theory is the only one that predicts narrowing of the linewidth with increasing rf power (at a constant temperature). A short summary of his theory is presented in Chapter IV. The parameter \(T'_1\) at 4.2°K was found to be \(\sim 0.4 T_1\) from the data in Figure 28 and the theoretical second moment for pure \(H_2\). A detailed derivation of this result is shown in the appendix. Both Provotorov's and BPP theories predict \(\chi''\) and \(\frac{d\chi''}{dH}\) to be proportional to \(1/H_1^2\) in the region of large saturation. As shown in Figure 27 the experimental points fit better a \(1/H_1\) curve for all concentrations in the range of rf used.
CHAPTER VIII

CONCLUSION

The behavior of $\text{H}_2 - \text{D}_2$ mixtures is quite similar to ortho-para mixtures of pure hydrogen. This means that an ortho-$\text{H}_2$ molecule surrounded by para-$\text{H}_2$ behaves as an ortho-$\text{H}_2$ surrounded by normal deuterium. This similarity holds so far as $\lambda$-splitting, lineshape and rf behavior is concerned.

The phase separation reported by Kogan et al. was searched for by visual experiments, pulsed techniques and a broad line spectrometer. A broad tail of about 15 gauss peak to peak and small amplitude can be seen at all concentrations in the range $4.2^\circ\text{K} - 10^\circ\text{K}$. Below $4.2^\circ\text{K}$ the amplitude of this tail increases rapidly with decreasing temperatures; it has about 12 gauss peak to peak and is more resolved for lower concentrations. These composite lines are more likely to be due to hindering of rotation rather than phase separation.

The rf behavior of the mixtures has the same anomaly as pure $\text{H}_2$. The linewidth decreases as rf increases. At very low concentration it remained about constant in the region of rf used (0.015 gauss to 0.15 gauss).

$T_1$ of pure hydrogen was measured at $4.2^\circ\text{K}$ by the recovery process of $180^\circ - 90^\circ$ pulse sequence. The values 0.39 sec and 0.48 sec were found in two different regions of the recovery curve. Beats were obtained in the free decay
after a 90° pulse at 4.2°K. They are of the same type as the Lowe-Norberg beats observed in calcium fluoride. At 1.1°K a series of beats due to the λ-splitting was found. The value 40.3 gauss for the side peaks of the λ-splitting was obtained in good agreement with other experiments.
APPENDIX

Relation Between $T_1$ and $T'_1$

$T'_1$ is introduced in Provotorov's theory through equations (55) and (56) where $H^0$ is the secular part of the dipole-dipole (d-d) interaction. We call it $H_d$, and Redfield calls it $H_{SS}$. The general expression for this d-d interaction is

$$H_d = \sum_{j>k} \left[ A_{jk} I_j I_k + B_{jk} \right]$$

Now we calculate $H_d^2$ which is made of several terms of the form $I_j \nu \mu I_{m} I_{n}$. Then we calculate the trace of each of these terms (this is done by Redfield on page 1807), obtaining:

$$\text{Tr} I_j \nu \mu I_{m} I_{n} = \frac{1}{9} I^2 (I+1)^2 (2I+1)^N \delta_{j,k} \delta_{m,n} \delta_{\nu,\mu}$$

(70)

and by substitution in the expression of $\text{Tr} H_d^2$, one obtains:

$$\text{Tr} H_d^2 = (1/9) I^2 (I+1)^2 (2I+1)^N \sum_{l>m} (3A_{lm}^2 + 2A_{lm} B_{lm} + B_{lm}^2)$$

(71)

The values of $A_{lm}$ and $B_{lm}$ for d-d interactions are as usual:

$$A_{lm} = \frac{1}{2} g^2 \beta^2 r_{lm}^3 (3 \cos^2 \theta_{lm} - 1)$$

(72)

$$B_{lm} = -\frac{3}{2} g^2 \beta^2 r_{lm}^3 (3 \cos^2 \theta_{lm} - 1)$$

where $\theta_{lm}$ is the angle of $r_{lm}$ with the z direction (direction of the dc field).
Substitution of (72) in (71) gives:
\[
\text{Tr } H_d^2 = (1/6)I^2(I+1)^2(2I+1)^N \sum_{l>m} (g\beta)^4 r_{lm}^6 (3 \cos^2 \theta_{lm} - 1)^2
\] (73)

The trace of \( I_z^2 \) is calculated by Slichter, page 53:
\[
\text{Tr } I_z^2 = (1/3)I(I+1)N(2I+1)^N
\] (74)

Substitution of (73) and (74) in (55) yields:
\[
\overline{H_0^2} = \frac{1}{2} I(I+1) 1/N (\gamma^2 \hbar^2)^2 \sum_{l>m} r_{lm}^{-6} (3 \cos^2 \theta_{lm} - 1)^2
\] (75)

where \( \gamma = g \beta \) and \( I = 1 \) for hydrogen (H\(_2\)).

The Van Vleck theory of moments gives the second moment \( M_2 \) as:
\[
M_2 = (3/4) \gamma^2 \hbar^2 I(I+1) 1/N \sum_{j>k} (1 - 3 \cos^2 \theta_{jk}) r_{jk}^{-6}
\] (76)

Therefore:
\[
\overline{H_0^2} = (2/3) \hbar^2 M_2
\] (77)

Substitution in equation (56) gives:
\[
\tau^2 = \left( \frac{3}{2M_2} \right) \frac{T_1'}{T_1}
\] (78)

The values of \( M_2 \) and \( \tau \) are obtained from experimental measurements in the following way: \( M_2 \) (at low rf level) is given by equation (33), empirically obtained by Dickson and Meyer\(^{37} \) and also in good agreement with our own observations, and \( \tau \) is obtained from the \( \lim \chi'' \) in equation (56), which is a Lorentzian function; therefore, \( \tau = (2/\sqrt{3}) \frac{1}{\Delta \omega} \). Here \( \Delta \omega \) is the peak to peak value of the linewidth, shown in Figure 28 as \( \Delta H \) in gauss. So, using equation
(33), both \( \tau \) and \( M_2 \) can be obtained from Figure 28, and the value of \( T'_1/T_1 \) is obtained from equation (77).

\[
\frac{T'_1}{T_1} \approx \frac{8}{81} \left( \frac{\Delta H^2_{\text{unsat.}}}{\Delta H^2_{\text{sat.}}} \right)
\]

\[
T'_1 \approx 0.4 T_1
\]

where \( (\Delta H)_{\text{unsat.}} \) and \( (\Delta H)_{\text{sat.}} \) are the values of \( \Delta H \) at low and high rf level, given in Figure 28.

By a simple argument one can ascertain the order of magnitude of \( T'_1 \). The Zeeman Hamiltonian is linear in the spin operators \( I_j \) and relaxes toward the lattice bath with a rate \( 1/T_1 \). The dipolar Hamiltonian is quadratic in the spin operators and hence should relax toward the lattice bath at a rate twice as fast as the Zeeman system if the spins flip independently (since a flip of either spin is sufficient to produce relaxation in the dipolar system) so \( T'_1 = T_1/2 \).

Provotorov's theory predicts narrowing of the linewidth with increasing rf fields. He shows how \( \chi' \) narrows with rf but he did not show explicitly how \( \chi'' \) narrows. If one proves that \( T'_1 = T_1/\delta \), then it is possible to reverse the argument used to derive equation (79) and show that \( (\Delta H)_{\text{sat.}} < (\Delta H)_{\text{unsat.}} \), i.e., narrowing of \( \chi'' \), for a sufficiently small value of \( \delta \).

The relation \( T'_1 = T_1/\delta \) can be proved using the same argument used by Anderson and Redfield\(^{56} \). They show that \( 2 \leq \delta \leq 3 \). The value \( \delta = 2 \) corresponds to a complete statistical independence of the d-d transitions and the value \( \delta = 3 \) corresponds to a complete correlation between these transitions.
The experimental value of $\delta$ from equation (79) is 2.5, and the saturated line is always narrower than the unsaturated for any value of $\delta$ in the range $2 \leq \delta \leq 3$. 
BIBLIOGRAPHY


30. F. Reif and E. M. Purcell, Phys. Rev. 91, 631 (1953).


34. B. V. Rollin and E. Watson, Conference de Physique des Basses Temperatures, Paris (1955); and Centre National de la Recherche Scientifique and UNESCO, Paris (1956), No. 76.


