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NUCLEAR SPIN-LATTICE RELAXATION  
AND MOLECULAR MOTION IN BENZENE  
AND SOME BENZENE DERIVATIVES

by

ROGER FIGGINS

Thesis submitted for the degree of  
Doctor of Philosophy  
in the  
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ABSTRACT

Proton spin-lattice relaxation times,  $T_1$ , have been measured in liquid benzene, liquid 1,3,5 trideuterobenzene and liquid bromobenzene, over a wide temperature range. The  $T_1$ 's of these liquids for a series of solutions in their respective perdeuterated analogues are also reported. The intermolecular and intramolecular contributions to  $T_1$  are separated by the technique of extrapolation to zero concentration.

An experimental technique for separating the intramolecular dipolar and spin-rotation contributions to  $T_1$  is discussed for the cases of benzene and 1,3,5 trideuterobenzene. The results of this separation are examined critically in the light of independent measurements of similar parameters. Reliable values for the reorientational correlation time,  $\tau_d$ , are obtained.

An attempt to separate out a possible intermolecular spin-rotation interaction is discussed.

Approximations for the intramolecular dipolar interaction for a many spin molecule are discussed. A simple indication of departure from non-exponential decay is considered and compared with more rigorous theory.

## CONTENTS

		Page
CHAPTER I	SPIN SYSTEMS	
I.1	Introduction.	1
I.2	Populations. $T_1$ and $T_2$ .	3
I.3	Relaxation interactions.	7
I.4	The chemical shift.	8
I.5	An ensemble of non-interacting spins in a steady field.	10
	References.	14
CHAPTER II	MEASUREMENT OF RELAXATION TIMES	
II.1	Adiabatic fast passage.	15
II.2	The spectrometer.	19
II.3	Sample preparation.	27
	References.	30
CHAPTER III	THE DENSITY MATRIX AND ITS TIME DEPENDENCE	
III.1	Introduction.	31
III.2	Properties of the density matrix.	35
III.3	The interaction representation.	37
III.4	The correlation function.	38
III.5	The time dependence of the density matrix.	40
	References.	44

CHAPTER IV	CONTRIBUTIONS TO SPIN-LATTICE RELAXATION.	
IV.1	The anisotropic chemical shift	45
IV.2	Indirect spin-spin coupling	46
IV.3	Electric quadrupole interactions.	47
IV.4	Paramagnetic impurities.	48
IV.5	Dipole-dipole interactions.	49
IV.6	The spin-rotation interaction.	59
	References.	65
CHAPTER V	EXPERIMENTAL RESULTS AND DISCUSSION	
V.1	Introduction.	66
V.2	Benzene.	69
V.3	1,3,5 trideuterobenzene.	78
V.4	Bromobenzene.	83
V.5	Intermolecular spin-rotation interactions.	85
	References.	89
CHAPTER VI	NON-EXPONENTIAL DECAY	110
	References.	113
	SUMMARY AND CONCLUSIONS.	115
	ACKNOWLEDGEMENTS.	121

CHAPTER I

SPIN SYSTEMS

I.1 Introduction

Atomic nuclei which possess both angular momentum and magnetic moment exhibit resonant absorption of radiofrequency electromagnetic radiation when placed in a magnetic field.

A nucleus may consist of particles coupled together, so that, for any particular state, the nucleus possesses a magnetic moment  $\underline{\mu}$  and angular momentum  $\underline{J}$ . These two vectors may be taken as parallel and proportional, so that,

$$\underline{\mu} = \gamma \underline{J}$$

where  $\gamma$  is the gyromagnetic ratio of the nucleus. The energy state of a nucleus cannot be changed during experiments of nuclear magnetic resonance, so  $\underline{\mu}$  is a constant.

We may define a dimensionless angular momentum operator, the nuclear spin,  $I$ , by

$$\underline{J} = \hbar \underline{I} .$$

$\underline{I}^2$  then has eigenvalues  $I(I+1)$ . Any component of  $\underline{I}$  (e.g.  $I_z$ ) commutes with  $\underline{I}^2$  so that we may specify simultaneous eigenvalues of both  $\underline{I}^2$  and  $I_z$ . The eigenvalue of  $I_z$ ,  $m$ , may have any of the  $2I+1$  values  $I, I-1, \dots, -I$ .

If we place a macroscopic magnetic moment  $\underline{\mu}$ , with angular momentum  $\underline{J}$ , in a magnetic field  $\underline{H}_0$ , it experiences a torque  $\underline{\mu} \wedge \underline{H}_0$ . The classical equation of motion of the dipole is (Newton's second law)

$$\frac{d\mathbf{J}}{dt} = \boldsymbol{\mu} \wedge \underline{H}_0$$

or 
$$\frac{d\boldsymbol{\mu}}{dt} = \gamma \boldsymbol{\mu} \wedge \underline{H}_0. \quad (1.1)$$

Changes in  $\boldsymbol{\mu}$  are perpendicular to both  $\boldsymbol{\mu}$  and  $\underline{H}_0$ . Hence the dipole precesses about the direction  $\underline{H}_0$ . The interaction energy is given by  $E = -\boldsymbol{\mu} \cdot \underline{H}_0$ .

The equation of motion in a frame of reference rotating at some frequency,  $\omega$ , may be shown to be [1]

$$\left(\frac{d\boldsymbol{\mu}}{dt}\right)_{\omega} = \gamma \boldsymbol{\mu} \wedge \left[\underline{H}_0 + \frac{\omega}{\gamma}\right].$$

That is, the equation of motion is unchanged, so long as we write for  $H_0$  an effective field

$$H_z = H_0 + \frac{\omega}{\gamma}.$$

We now add a magnetic field  $H_1$ , rotating in phase with  $\boldsymbol{\mu}$ . The resultant magnetic field in the rotating frame is

$$H_{\text{eff}} = \left[ \left(H_0 + \frac{\omega}{\gamma}\right)^2 + H_1^2 \right]^{1/2}$$

and it is about this field that  $\boldsymbol{\mu}$  will precess.  $\boldsymbol{\mu}$  and the source of  $H_1$  now repeatedly exchange energy as  $-\boldsymbol{\mu} \cdot H_0$  is continuously changing. The greatest exchange of energy occurs when

$$H_0 + \frac{\omega}{\gamma} = 0$$

and  $\boldsymbol{\mu}$  precesses about  $H_1$ .

Thus we observe a resonance phenomenon in our model if we choose

$$\underline{\omega} = \underline{\omega}_0 = -\gamma H_0.$$

That is, when the rotating field  $H_1$  has the so called Larmor frequency of the dipole concerned. In practice,  $H_1$  may be applied as a sinusoidal

alternating field. This may be decomposed into two fields rotating in opposite directions. The effect of the component rotating in the direction opposite to  $\underline{\mu}$  is negligible if  $H_1 \ll H_0$ , as will be the case from now on [2].

Quantum mechanically we must write for the interaction of a single nucleus with the field  $H_0$ , the Hamiltonian

$$H = -\underline{\mu} \cdot \underline{H}_0 .$$

If we chose  $\underline{H}_0$  to be along the z axis.

$$H = -\gamma \hbar H_0 I_z$$

so that the eigenvalues of this Hamiltonian are

$$E = -\gamma \hbar H_0 m, \text{ where } m = I, I-1, \dots, -I.$$

Generally, we have a set of equally spaced energy levels between which we may expect to induce and detect transitions.

These transitions are induced by means of an applied alternating magnetic field  $H_1$ . We may show that only transitions for which  $\Delta m = \pm 1$  are permitted. So the quantum of energy needed to cause a transition is given by

$$\hbar \omega = \gamma \hbar H_0 .$$

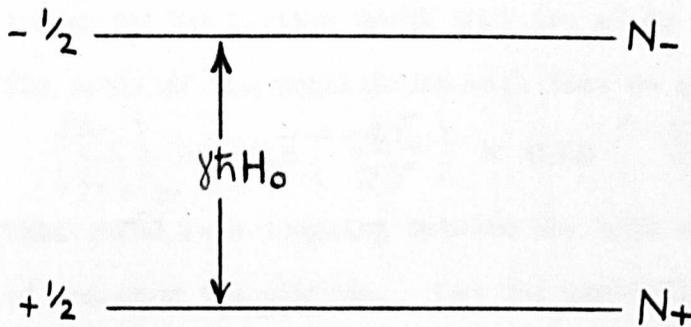
$$\text{or } \omega = \gamma H_0 .$$

This is the required angular frequency of  $H_1$ , as shown earlier. For magnetic fields of 3,000 to 10,000 gauss, nuclear resonance frequencies are typically 10 Mc/s.

## I.2 Populations $T_1$ and $T_2$

Consider a macroscopic sample containing spins one half, in which

we observe a resonance, figure(1.1)



Figure(1.1)

Let the numbers of nuclei in the  $m$  states  $+\frac{1}{2}$ ,  $-\frac{1}{2}$  be  $N_+$  and  $N_-$  respectively.  $N$ , the total number of spins, is a constant, but  $N_-$  and  $N_+$  change under the influence of the alternating field. If the probabilities per unit time of inducing a transition up or down are given by  $W_{\uparrow}$  and  $W_{\downarrow}$  respectively, the variation of  $N_+$  is given by

$$\frac{dN_+}{dt} = N_- W_{\downarrow} - N_+ W_{\uparrow} .$$

However, from time dependent perturbation theory, we may show [ 1 ] ,

$$W_{\uparrow} = W_{\downarrow} = W .$$

The problem now arises that if we apply no alternating magnetic field, i.e.  $W=0$  , the populations of the levels cannot change. This is contrary to experience as we know an unmagnetized sample will become magnetized when placed in a steady field. This corresponds to  $N_+$  being larger than  $N_-$  . The process of magnetization thus requires a certain number of transitions from the upper to the lower energy state, i.e. the nuclei give up energy. We must postulate a system, in general called the "lattice" to accept this energy. For example, this might be the Kinetic energies of the molecules containing the nuclei.

From the thermodynamic point of view, heat flows from the spin system to the lattice until they are at an equilibrium temperature,  $T$ .

The ratio of the populations will then be given by the Boltzmann factor

$$\left(\frac{N_-}{N_+}\right)_0 = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(-\frac{\gamma \hbar H_0}{kT}\right).$$

Thus there is a coupling between the spin system and the lattice capable of inducing transitions. Let the probabilities' per unit time of transitions up or down be  $W'_\downarrow$  and  $W'_\uparrow$  respectively. The rate equation is now

$$\frac{dN_+}{dt} = N_- W'_\downarrow - N_+ W'_\uparrow \quad (1.2)$$

but now the transition probabilities cannot be placed equal. However, we know in the steady state condition, i.e. when equilibrium magnetization has been reached,  $\frac{dN_+}{dt} = 0$ , so that

$$\left(\frac{N_-}{N_+}\right)_0 = \frac{W'_\uparrow}{W'_\downarrow} = \exp\left(-\frac{\gamma \hbar H_0}{kT}\right).$$

The difference from the previous case, of course, is that here the energy conditions of both the lattice and the spins must allow a transition.

If we put

$$N = N_+ + N_-$$

$$n = N_+ - N_-$$

then equation(1.2) becomes

$$\frac{dn}{dt} = N(W'_\downarrow - W'_\uparrow) - n(W'_\downarrow + W'_\uparrow)$$

$$\text{or } \frac{dn}{dt} = \frac{n_0 - n}{T_1} \quad (1.3)$$

where  $n_0 = N \left[ \frac{W'_\downarrow - W'_\uparrow}{W'_\downarrow + W'_\uparrow} \right]$  and  $\frac{1}{T_1} = (W'_\downarrow + W'_\uparrow)$ .

Solving for  $n$  gives

$$n = n_0 \left[ 1 - \exp\left(-\frac{t}{T_1}\right) \right]$$

so the population difference increases exponentially with a characteristic time,  $T_1$ , called the spin-lattice relaxation time.

From equation (1.2), the total rate equation is

$$\frac{dn}{dt} = -2Wn + \frac{n_0 - n}{T_1},$$

so in the steady state, 
$$n = \frac{n_0}{1 + 2WT_1}.$$

The rate of absorption of energy, for populations little disturbed from their equilibrium values, is

$$\begin{aligned} \frac{dE}{dt} &= n\hbar\omega W \\ &= n_0\hbar\omega \frac{W}{1 + 2WT_1}. \end{aligned}$$

$W$  is proportional to  $|H_1|^2$ , so we can increase the power absorbed by the nuclei by increasing  $W$ , so long as  $2WT_1 \ll 1$ . When this condition is violated the absorbed power levels off, in spite of increasing  $H_1$ . This is "saturation".

The large nuclear concentrations and the small distances between nuclear spins in bulk matter result in relatively strong spin interactions. The result is a broadening of the resonance line, as each nucleus sees the steady field plus the weak fields due to its neighbours. That is, there is a distribution of resonance frequencies. In a solid the resonance line is broadened to the extent of several gauss, and the shape of these lines can often be described by a Gaussian distribution. For example, the proton resonance line width in polyethylene is about 15 gauss.

In liquids rapid molecular motion tends to average out fields due to other nuclei and the resonance lines are narrow; in practice usually determined by the homogeneity of  $H_0$  across the sample.

The coupling between spins allows energy transfer from one spin to

another, leading to thermal equilibrium inside the spin system itself in a time which is shorter than  $T_1$ . This is the spin-spin relaxation time and is denoted by  $T_2$ .

### 1.3 Relaxation Interactions

Let us now consider some possible relaxation processes. To maintain absorption in the stationary state there must be some mechanism restoring equilibrium (the Boltzmann distribution). If the induced nuclear magnetism is displaced from equilibrium, we must find an interaction which determines  $T_1$ .

The spontaneous emission which usually limits the lifetime of an atom in an electronically excited state to  $10^{-8}$  seconds, is negligibly small in the radio frequency region. The coefficient of spontaneous emission,  $A$ , of radiation from a dipole is given by

$$A = \frac{8\pi h \nu^3 B}{c^3}$$

where  $\nu$  is the frequency concerned and  $B$  the coefficient of absorption. For protons in a field of 10 kilogauss one finds by substitution,  $A \approx 10^{-25}$  seconds<sup>-1</sup>, which corresponds to a lifetime of  $10^{19}$  years.

In addition to spontaneous emission we must consider the transitions induced by the thermal radiation field. Here we find  $T_1 \approx 10^3$  years, (noting that the wavelength is large compared with the dimensions of the "black body", i.e. the resonant circuit [3]).

Electric forces, which act during atomic or electronic collisions and to which are attributed many of the macroscopic properties of matter, do not perturb the nuclear spins. Only an electric field gradient can interact with a nuclear quadrupole moment as will be discussed later.

So we must return to magnetic interactions associated with the nuclear magnetic moment.

So far the only magnetic field we have considered acting on the nucleus is the externally applied field, ( $H_0 + H_1$ ). However, every nucleus must experience a field due to possible neighbouring nuclear magnetic dipoles. Taking into account this dipole-dipole interaction means adding to the Zeeman term in the Hamiltonian for the spins, a term,

$$\mathcal{H}_D = \sum_i \gamma_i \hbar I_i \sum_j \left[ \frac{\gamma_j \hbar I_j}{r_{ij}^3} - \frac{3\gamma_j \hbar r_{ij} (\underline{r}_{ij} \cdot I_j)}{r_{ij}^5} \right] \quad (1.4)$$

$\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$  is the vector joining the  $i$ th and  $j$ th spins.

The dipole-dipole interaction of nuclei at fixed positions leads only to a broadening of the nuclear energy levels, and hence of the absorption line. For an interaction to be capable of inducing transitions it must be time dependent. The only possible time dependent quantity in equation(1.4) is  $\underline{r}_{ij}$ . This is not unexpected; we know of the rapid motion of molecules in liquids and gases from other sources.

Any time dependent magnetic field at the site of a nucleus may induce transitions, if it contains the appropriate frequencies in its Fourier spectrum. More detailed analyses of these interactions follow in chapter IV.

#### I.4 The Chemical Shift

We have tacitly assumed that the resonance frequency of a nucleus is simply a function of its gyromagnetic ratio and the applied field. However, generally, the frequency is also dependent on the molecular

environment of the nucleus. This is because the molecular electrons "screen" the nuclei by a very small amount from the applied field. Thus resonant nuclei in different parts of the same molecule may experience slightly different resultant steady fields, so a resonant frequency spectrum is obtained.

The magnetic coupling of the electrons to the nucleus arises from the magnetic fields originating either from the motion of the electric charges or from the magnetic moment associated with the electron spin. The former gives rise to the so called chemical shifts; the latter to Knight shifts in metals and to a coupling between nuclear spins. In a diamagnetic or paramagnetic substance the average field a nucleus experiences owing to the electrons vanishes when  $H_0$  vanishes. Hence we may write the resonance frequency as

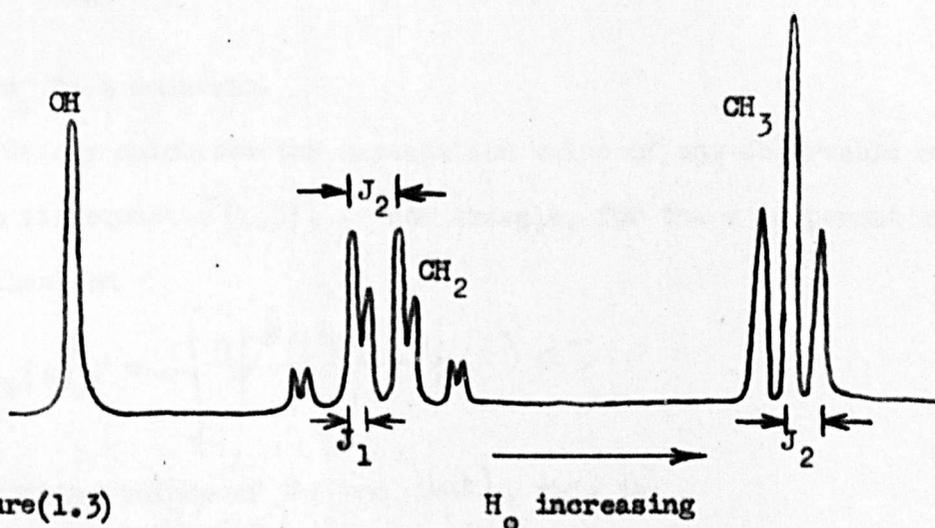
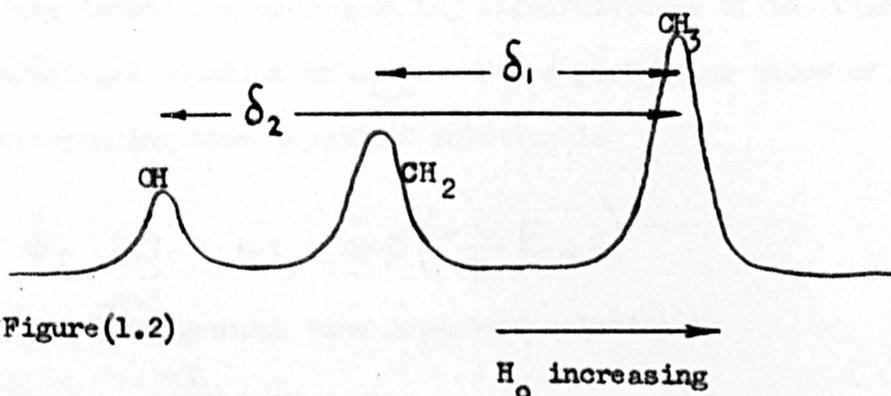
$$\omega = \gamma [H_0 + \Delta H]$$

where  $\Delta H$  is the change in the field due to the electrons. We may define a field independent chemical shift  $\delta$ , by

$$\Delta H = -\delta H_0$$

for protons the entire range of  $\delta$  covers about 1 part in  $10^5$ ; for fluorine nuclei, about 6 parts in  $10^4$ .

A common example of the chemical shift is the proton spectrum of ethanol. A low resolution spectrum is shown in figure (1.2). The peaks are due to absorption by the hydroxyl, methylene, and methyl groups respectively.  $\delta_1$  and  $\delta_2$  are 2.48 and 4.20 parts per million. With increased resolution, the spectrum appears as figure (1.3).



The splittings occur because of interactions between spins of the form

$$\mathcal{H} = \hbar \underline{\mu}_1 \cdot \underline{J} \cdot \underline{\mu}_2$$

where  $\underline{J}$  is the indirect spin-spin coupling constant, in general a tensor. The effect of a time dependent "J coupling" will be discussed in Chapter IV.

### I.5 An ensemble of non-interacting spins in a steady field

We have shown that for a spin in a steady field  $H_0$ , the energies  $E_m$  are

$$E_m = -\gamma \hbar H_0 m.$$

We may denote the corresponding eigenfunctions of the time independent Schrodinger equation by  $u_{I,m}$ . For a particular value of  $m$ , the corresponding time dependent solution is

$$\psi_{I,m}(t) = u_{I,m} \exp\left(-\frac{i}{\hbar} E_m t\right)$$

and the most general time dependent solution is

$$\psi(t) = \sum_{m=-I}^{+I} c_m u_{I,m} \exp\left(-\frac{i}{\hbar} E t\right) \quad (1.5)$$

where  $c_m$  is a constant.

We may calculate the expectation value of any observable of the system via equation (1.5). For example, for the  $x$  component of the magnetization

$$\langle \mu_x(t) \rangle = \int \psi^*(t) \mu_x \psi(t) d\tau.$$

Substituting values of  $\mu_x$  and  $\psi(t)$ , this is,

$$\langle \mu_x(t) \rangle = \sum_{m,m'} g \hbar c_{m'}^* c_m (m' | I_x | m) \exp\left[\frac{i}{\hbar} (E_{m'} - E_m) t\right] \quad (1.6)$$

where  $(m' | I_x | m) \equiv \int u_{I,m'}^* I_x u_{I,m} d\tau$

is a time independent matrix element. Expressions like equation (1.6) would hold for any operator, and, in general, are time dependent with terms oscillating harmonically. The possible frequencies are

$$\frac{E_{m'} - E_m}{\hbar}.$$

Since the matrix elements  $(m' | I_x | m)$  are zero unless  $m' = m \pm 1$ ,

the terms in equation (1.6) have an angular frequency of  $\pm \gamma H_0$ . Thus

$\langle \mu_x(t) \rangle$  oscillates in time at the classical precession frequency.

Now consider equation (1.6) for spin  $\frac{1}{2}$ . We have,

$$\langle \mu_x(t) \rangle = \gamma \hbar \left[ c_{\frac{1}{2}}^* c_{-\frac{1}{2}} \left( \frac{1}{2} \mid I_x \mid -\frac{1}{2} \right) \exp(-i\gamma H_0 t) \right. \\ \left. + c_{-\frac{1}{2}}^* c_{\frac{1}{2}} \left( -\frac{1}{2} \mid I_x \mid \frac{1}{2} \right) \exp(i\gamma H_0 t) \right]$$

$$= 2\gamma \hbar \operatorname{Re} \left[ c_{\frac{1}{2}}^* c_{-\frac{1}{2}} \left( \frac{1}{2} \mid I_x \mid -\frac{1}{2} \right) \exp(-i\omega_0 t) \right]$$

where we take the real part of the square bracket. But

$$\left( \frac{1}{2} \mid I_x \mid -\frac{1}{2} \right) = \frac{1}{2}$$

and if we write the coefficients as

$$c_{\frac{1}{2}} = a \exp(i\alpha)$$

$$c_{-\frac{1}{2}} = b \exp(i\beta).$$

$$\langle \mu_x(t) \rangle = \gamma \hbar ab \operatorname{Re} \left[ \exp(-i\alpha + i\beta - i\omega_0 t) \right]$$

$$\text{or, } \langle \mu_x(t) \rangle = \gamma \hbar ab \cos [\alpha - \beta + \omega_0 t].$$

Similarly we may show

$$\langle \mu_y(t) \rangle = -\gamma \hbar ab \sin [\alpha - \beta + \omega_0 t]$$

$$\text{and } \langle \mu_z(t) \rangle = \gamma \hbar \left( \frac{a^2 - b^2}{2} \right).$$

$$\text{If we write } \langle \underline{\mu} \rangle = \underline{i} \langle \mu_x \rangle + \underline{j} \langle \mu_y \rangle + \underline{k} \langle \mu_z \rangle$$

then  $\langle \underline{\mu} \rangle$  behaves as a vector precessing about the  $\underline{H}_0$  direction.

At time  $t$ , the orientation may be specified quite arbitrarily by specifying  $a$ ,  $b$  and  $(\alpha - \beta)$ . Of course, this means that spins are not found only parallel or antiparallel to  $H_0$ . Here we may describe an expectation value for the magnetization which may take up any direction with respect to the steady field.

Each spin in our ensemble of non-interacting spins will be described by a wave function; but, in general, it will not be one of the eigenstates, ( $m = \pm \frac{1}{2}$ ) but a linear combination of these states. A particular spin has a particular set of values of  $a$ ,  $b$ ,  $\alpha$  and  $\beta$ . At  $t=0$ , for example, there will be a distribution of values of  $(\alpha - \beta)$ , the orientation of the spin in the  $x$ ,  $y$  plane. However, in equilibrium we know that the transverse component of magnetization is zero. That is, there is a random distribution of  $(\alpha - \beta)$ . We also know that there is a small induced polarization, so, on average,  $a > b$ .

In equation (1.6) we may relabel the complex constants, putting

$$C_{mm'} = C_{m'm}^*$$

In our particular example,

$$C_{+\frac{1}{2}+\frac{1}{2}} = a^2$$

$$C_{-\frac{1}{2}-\frac{1}{2}} = b^2$$

$$C_{+\frac{1}{2}-\frac{1}{2}} = ab \exp[i(\alpha - \beta)]$$

$$C_{-\frac{1}{2}+\frac{1}{2}} = ab \exp[i(\beta - \alpha)].$$

The  $C_{m'm}$  may be considered to be the elements of a complex matrix  $C$ .  
Of interest is the fact that the diagonal elements are proportional to the populations of the various states, while the off-diagonal elements are related to the components of magnetic moment perpendicular to the steady field.

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CHAPTER II

MEASUREMENT OF RELAXATION TIMES

II.1 Adiabatic Fast Passage

The technique of A.F.P. (adiabatic fast passage) was first successfully used for the detection of nuclear resonance signals by Bloch [1] in 1946. It has subsequently been used by many workers to measure  $T_1$  [2,3,4,5].

From the equation of motion (1.1), writing  $\underline{M}$  for  $\underline{\mu}$ , we have,

$$\frac{d}{dt}(M^2) = 2\underline{M} \cdot \frac{d\underline{M}}{dt} \propto \underline{M} \cdot \underline{M} \wedge \underline{H}_0 = 0$$

i.e. the magnitude of the magnetization,  $|\underline{M}|$ , is a constant. In a frame rotating with instantaneous angular velocity  $\underline{\Omega}$ , the time dependence of  $\underline{M}$  becomes

$$\frac{\partial \underline{M}}{\partial t} = \gamma \underline{M} \wedge \left( \underline{H} + \frac{\underline{\Omega}}{\gamma} \right). \quad (2.1)$$

If we select a frame such that the field  $\underline{H}$  is continuously aligned along the z axis,  $H_x = H_y = 0$ , and, expanding equation (2.1),

$$\frac{\partial M_z}{\partial t} = M_x \Omega_y - M_y \Omega_x$$

After any time  $t$ , the change in  $M_z$  is

$$\Delta M_z = M_z(t) - M_z(0) = \int_0^t [M_x \Omega_y - M_y \Omega_x] dt. \quad (2.2)$$

If the time variation of  $\underline{\Omega}$  is sufficiently slow, i.e. if

$$\Omega \ll \gamma H$$

then  $\frac{\partial M_z}{\partial t} \approx \gamma H M_y$  and  $\frac{\partial M_y}{\partial t} \approx -\gamma H M_x$

so that  $|\Delta M_z| \approx \left| \frac{M \Omega}{\gamma H} \right| \ll M.$

Thus if the rotation of  $\underline{H}$  is sufficiently slow, the angle of the magnetization with the instantaneous direction of  $\underline{H}$  is constant. This is the adiabatic theorem.

If we hold the main field,  $H_z$ , well off its resonant value,  $H_0$ , the situation in the frame rotating about  $H_z$  at  $\omega_0 (= \gamma H_0)$  is shown in figure (2.1).

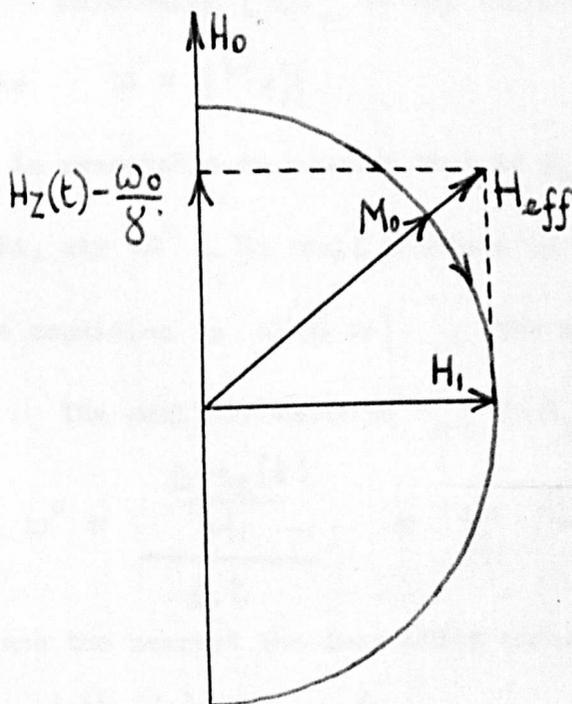


Figure (2.1)

If  $H_z(t) - \frac{\omega_0}{\gamma} \gg H_1$ ,  $\tan \theta = \frac{H_1}{H_z(t) - \frac{\omega_0}{\gamma}} \approx 0$

and the resultant effective field,  $H_{eff}$ , will be parallel to  $H_0$ . A resultant equilibrium nuclear magnetization would be aligned in this

direction. If  $H_z(t)$  is changed from  $H_z(t)$  to  $-H_z(t)$  uniformly,  $H_{\text{eff}}$  sweeps from  $\theta = 0^\circ$  to  $\theta = 180^\circ$ . If this rotation at all instants satisfies the adiabatic condition, then the magnetization,  $\underline{M}_0$ , will follow  $H_{\text{eff}}$  and itself be turned through  $180^\circ$ . This can also be effected by a  $180^\circ$  pulse, although here we have the advantage of being able to measure the induced signal as  $\underline{M}_0$  passes through the x,y plane. Also we see that for linear field sweeps, the angular velocity of  $H_{\text{eff}}$  is not constant, showing the necessity of the integral in equation (2.2).

Physically [6,2] we may imagine  $\underline{M}_0$  precessing about  $H_{\text{eff}}$  at a rate  $\omega' = \gamma H_{\text{eff}}$ .

It is reasonable to suppose that if  $H_{\text{eff}}$  rotates much more slowly than this, say  $\omega''$ ,  $\underline{M}_0$  will continue to precess and not be "lost", i.e. the condition is  $\omega' \gg \omega''$ ; the adiabatic theorem.

The smallest value of  $H_{\text{eff}}$  is  $H_1$  and the largest value of  $\omega''$  is

$$\omega'' = \frac{\frac{\Delta H_z(t)}{H_1}}{\Delta t} = \frac{1}{H_1} \frac{dH_z(t)}{dt}$$

Hence the nearest the inequality comes to being violated is

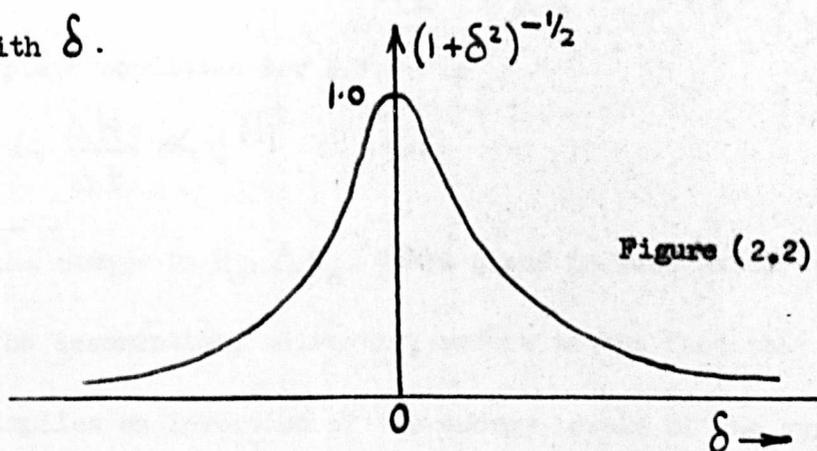
$$\frac{dH_z(t)}{dt} \ll \gamma H_1^2$$

At any instant the transverse component of M, along the direction  $H_1$

is given by  $M_x = M(1 + \delta^2)^{-1/2}$

where  $\delta = \frac{H_z(t) - \frac{\omega_0}{\gamma}}{H_1}$ .

Thus  $M_x$  varies as  $(1 + \delta^2)^{-1/2}$ , and figure (2.2) shows how this function varies with  $\delta$ .



As

$$(1 + \delta^2)^{-1/2} = \frac{1}{\frac{H_1^2 + [H_z(t) - \frac{\omega}{\gamma}]^2}{H_1}}$$

the line width in figure (2.2) goes to zero as  $H_1$  goes to zero.

Similarly the line width becomes large as  $H_1$  becomes large.

Neglecting other contributions to line broadening, such as an inhomogeneous  $H_0$ , we see that  $H_1$  is a convenient measure of the line width.

At the passage through resonance there will be a transverse magnetization equal to the initial value  $M_0$ , so long as no relaxation has taken place during the half passage. The condition for this is that the resonance line is swept through in a time much faster than the transverse relaxation time, which is  $T_2$ .

The time spent in resonance is

$$\frac{H_1}{\frac{dH_z(t)}{dt}}$$

Hence another requirement is  $\frac{H_1}{T_2} \ll \frac{dH_z(t)}{dt}$ .

The complete condition for A.F.P. is

$$\frac{H_1}{T_2} \ll \frac{\Delta H_0}{\Delta t} \ll \gamma H_1^2$$

where the change in  $H_0$ ,  $\Delta H_0$ , takes place in time  $\Delta t$ .

The description, adiabatic, refers to the fact that a reversal of  $M_0$  implies an inversion of the energy levels of the system without change in the populations. If we pass through resonance from below, i.e. initially  $H_z(t) < H_0$ , then  $H_{\text{eff}}$  will be  $180^\circ$  out of phase with  $H_1$ . The resulting displayed signal, obtained by comparing the induction signal and  $H_1$ , will be inverted.

## II.2. The Spectrometer

A Varian DP60 high resolution/wide line nuclear magnetic resonance spectrometer provides the main field,  $H_0$ , of about 13 kilogauss, and the radio frequency field at 56.4 Mc/s. The magnet power supply is stabilized by applying a difference voltage to the grids of eight 304 TL power triodes arranged in parallel. The magnet coils are cooled by circulation of water around a closed circuit, past a heat exchanger cooled by tap water. A pressure switch ensures that the H.T. line of the power supply is broken should the pressure of the closed system drop below a predetermined level. It has been found that only nylon

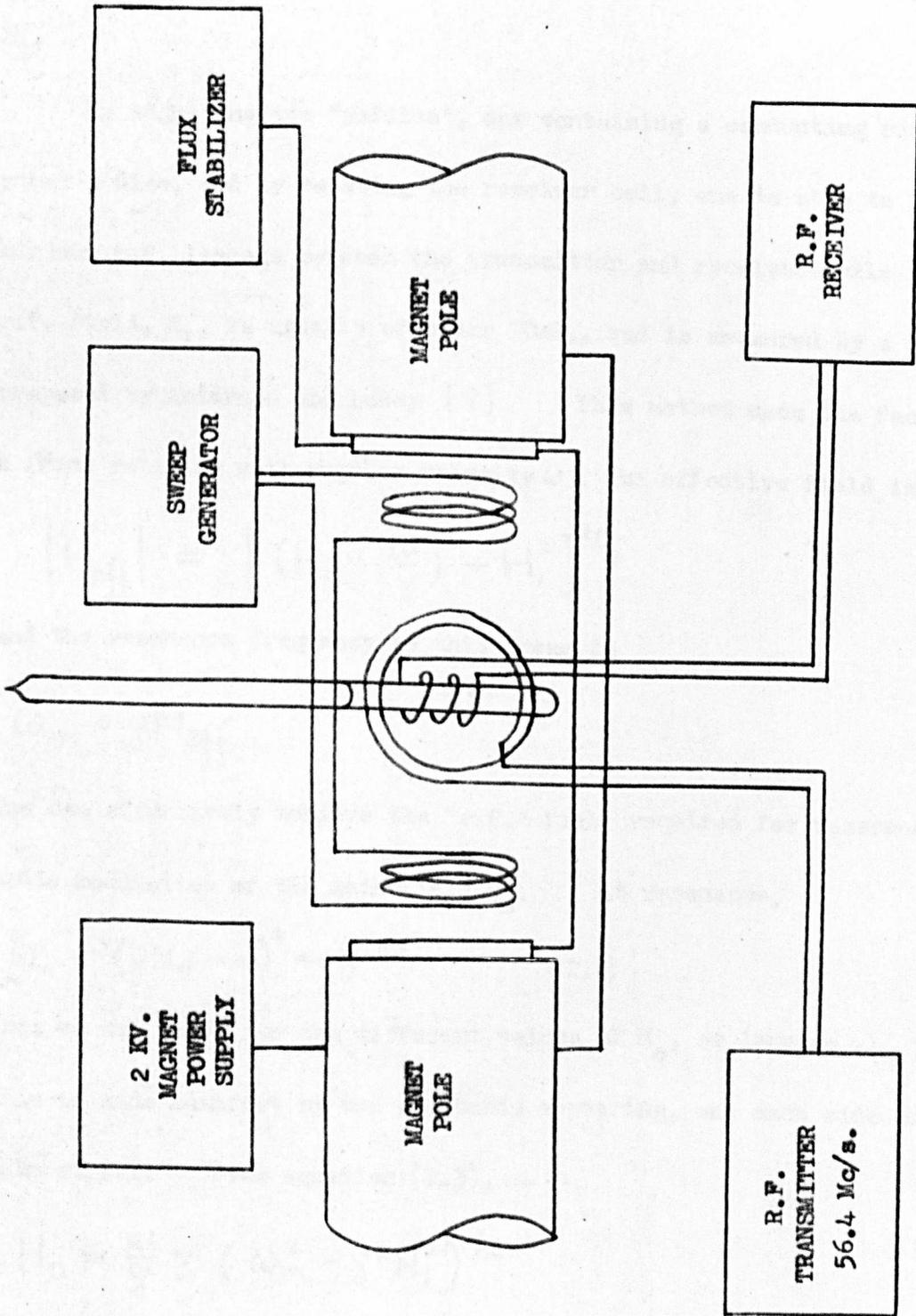
reinforced polyethylene tubing is sufficiently strong to withstand the pressure of the closed system.

A second, field sensitive, stabilizer is also employed. Here a current, induced in pick-up coils by changes in the actual field of the magnet is amplified and passed through a second set of coils in such a way as to oppose the original change. Thus magnetic field variations from sources external to the magnet system, such as stray magnetic fields, moving ferromagnetic objects as well as variations from noise internal to the system are corrected for. This "super" stabilizer may be switched on about one hour after the main field. Drift due to changing temperature is then small, and can be corrected for by the stabilizer.

A useful facility exists for injecting an artificial constant voltage signal into the field sensitive stabilizer. Hence the resonance signal may be moved back and forth across the oscilloscope trace.

The components of the spectrometer needed to measure  $T_1$  are shown in the schematic diagram, figure (2.3).

The sample probe contains, essentially, (a) a radio frequency transmitter coil, wound as a single wire Helmholtz pair onto the surface of an insulating cylinder, (b) a three turn receiver coil wound on to the sample dewar and orthogonal with the first coil, (c) a radio



Figure(2.3). Block diagram of Spectrometer.

frequency amplifier, and, (d) a pair of Helmholtz coils for sweeping  $H_0$ .

By adjusting two "paddles", one containing a conducting ring, the other a disc, and by rotating the receiver coil, one is able to reach minimum r.f. leakage between the transmitter and receiver coils. The r.f. field,  $H_1$ , is usually of order 10mG., and is measured by a method proposed by Anderson and LeRey [7]. This method uses the fact that in a frame rotating with angular velocity  $\omega$ , the effective field is

$$|H_{eff}| = \left[ \left( H_0 - \frac{\omega}{\gamma} \right)^2 + H_1^2 \right]^{1/2}$$

and the resonance frequency in this frame is

$$\omega_m = \gamma H_{eff}.$$

One can effectively achieve the "r.f." field required for resonance, by audio modulation of the main field  $H_0$ . At resonance,

$$\omega_m = (\gamma H_0 - \omega)^2 + \gamma^2 H_1^2. \quad (2.3)$$

Thus we may solve for two different values of  $H_0$ , so long as  $\omega_m > \gamma H_1$ .

This is made manifest by two sidebands appearing, one each side of the main signal. From equation (2.3),

$$H_0 = \frac{\omega}{\gamma} \pm (\omega_m^2 - \gamma^2 H_1^2)^{1/2}$$

so the separation sidebands,  $d$ , is

$$d = 2(\omega_m^2 - \gamma^2 H_1^2)^{1/2}.$$

If one measures  $d$  at several frequencies,  $\omega_m$ , and plots  $d^2$  against  $\omega_m^2$ , a straight line is produced with intercept  $\gamma^2 H_1^2$  at  $d^2 = 0$ .

An exact value of  $H_1$  is not required in the measurement of  $T_1$ .

$T_1$  is measured as follows. On waiting a sufficient time after switching on  $H_0$ , an equilibrium magnetization,  $M_0$ , will be established. A fast passage with a sweep  $\Delta H_0 = 1.5$  gauss produces a narrow absorption signal of height  $S_0$ . Assuming a linear amplifier,  $S_0$  will be proportional to  $M_0$  so long as  $H_z(t)$  was sufficiently different from  $H_0$  for there to have been no transverse component of magnetization before passage through resonance. This is ensured in practice by waiting at one end of the sweep, and passing through resonance near the other end of the sweep.

A general magnetization  $M'$  ( $\leq M_0$ ) will be inverted by a fast passage and will produce a signal  $S'$ . It will immediately begin to grow back into the direction  $H_0$ , exponentially with characteristic time  $T_1$ . If we perform this fast passage at time  $t = 0$ , the time dependence of the magnetization will be as in figure (2.4).

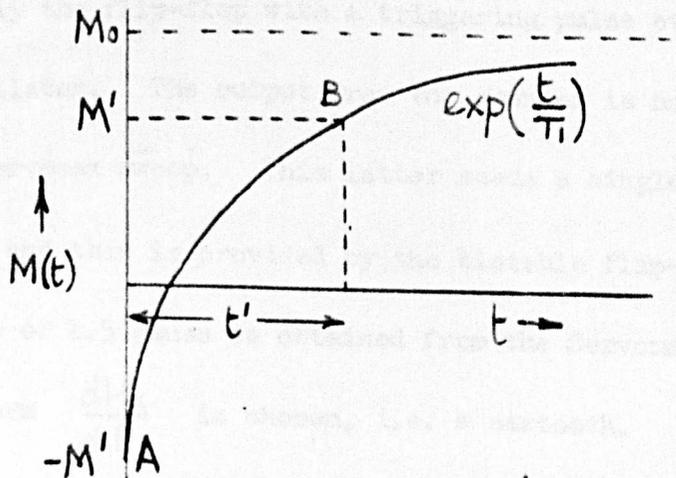


Figure (2.4).

After time  $t'$ , chosen so that at  $t = t'$ ,  $M(t) = M'$ , a second fast passage will produce a second signal, equal to  $S'$ , but inverted with respect to it.

The time dependence of the magnetization shown in figure (2.4) is given by

$$M = (M_0 + M') \left[ 1 - \exp\left(-\frac{t}{T_1}\right) \right] - M'$$

After time  $t'$ ,  $M = M'$ , and, on solving for  $T_1$ , we find,

$$T_1 = \frac{t'}{\ln \frac{M_0 - M'}{M_0 + M'}} = \frac{t'}{\ln \frac{S_0 - S}{S_0 + S}} \quad (2.4)$$

In fact any initial magnetization on being subjected to single rapid passages at intervals of time  $t'$  will eventually follow the path A to B in figure (2.4). This may be seen by drawing the time dependence of an initial value of  $M(t)$ , different from  $M'$ , throughout many intervals  $t'$ .

The experimental arrangement for producing and automatically timing the field sweep,  $\Delta H_0$ , is shown in figure (2.5). The audio oscillator has a continuously variable output frequency of 10c/s to 33Kc/s. The counter is arranged to supply the flip-flop with a triggering pulse every thousand cycles of the oscillator. The output from the counter is not sufficient to trigger the Servomex sweep. This latter needs a single voltage step of  $\pm 50$  volts, and this is provided by the bistable flip-flop. With amplification, a sweep of 1.5 gauss is obtained from the Servomex and a wave form giving uniform  $\frac{dH_z}{dt}$  is chosen, i.e. a sawtooth.

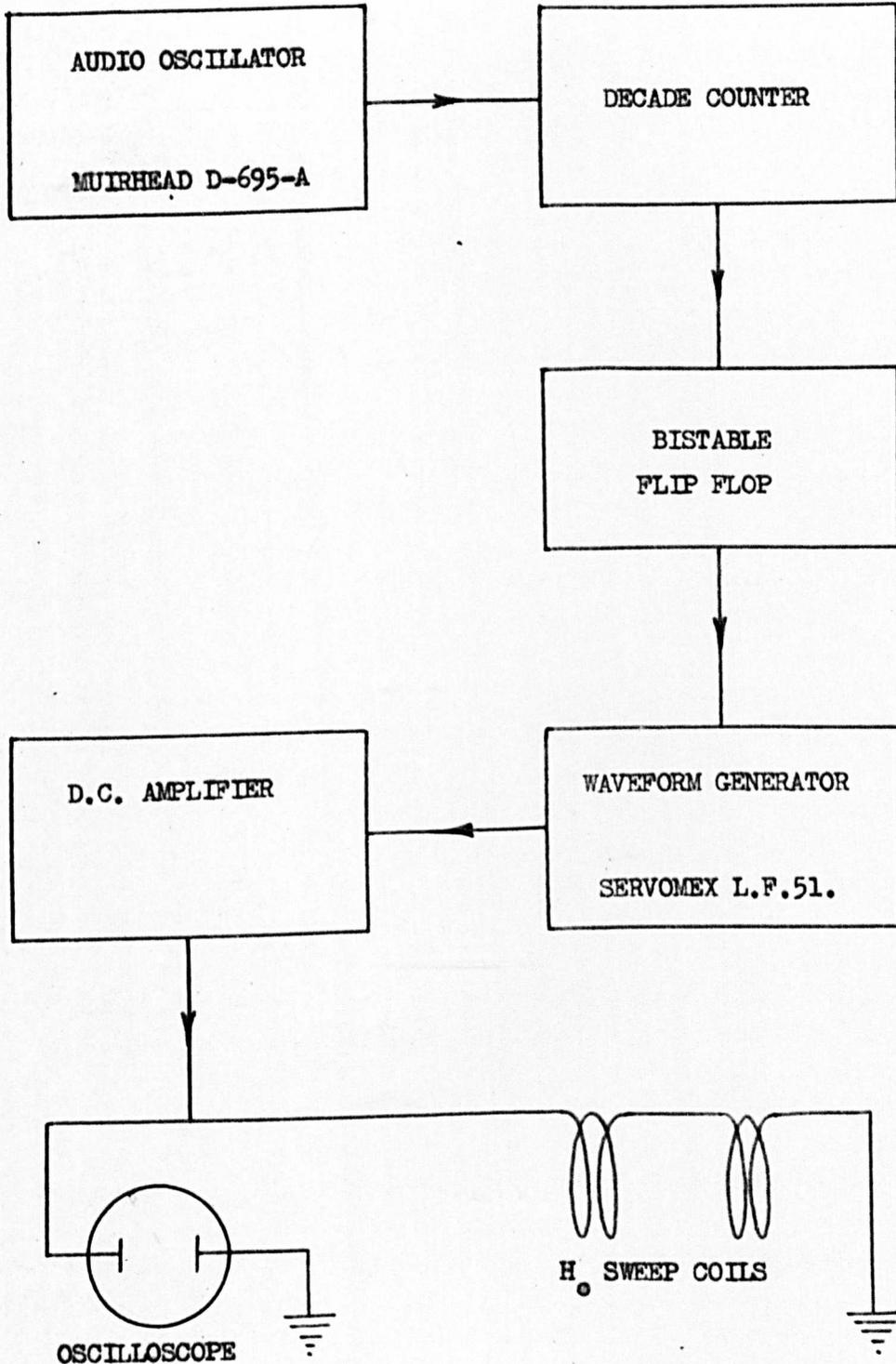


Figure (2.5). Production of field sweep  $\Delta H_0$ .

The procedure for measuring  $T_1$  is then as follows. A long waiting time, say about  $6T_1$ , is introduced between complete cycles of the waveform generator. Resonance is offset from the centre of the sweep as explained previously.  $S_0$  is measured.

With resonance at the centre of the sweep field, fast passages are made for half cycles of the waveform generator, separated by waiting times  $t'$ .  $t'$  is usually chosen to be equal to  $T_1$ . From equation (2.4) we see that for best accuracy, neither  $S_0 - S'$  nor  $S'$  itself should be small. Thus it is convenient to have  $S' \approx \frac{1}{2}S_0$ , i.e.  $t' \approx T_1$ . After some time, the signal on each sweep will have a constant magnitude  $S'$ . Substituting in equation (2.4) gives  $T_1$ .

Sample temperatures, above room temperature, are achieved by passing heated air through the probe at constant pressure. An upper limit of about  $230^\circ\text{C}$  was chosen. This represents the maximum current produced by the probe heater power supply, and is a convenient limit, as the probe, glassware and dewars are designed to reach  $200^\circ\text{C}$ . Low temperatures are reached by passing cold nitrogen gas over the sample. This gas is produced by boiling off the liquid, and the rate determined by the current passing through a heater, placed in the liquid nitrogen. Under the worst conditions, i.e. at high temperatures, the sample temperature could be held to  $\pm 2^\circ\text{C}$ . The temperature of the heat

exchange gas was measured after it had passed over the sample. The difference between this temperature and the temperature of the sample, measured in another experiment, was never greater than  $0.5^{\circ}\text{C}$ . The temperature gradient over the sample was negligible.

### II.3 Sample preparation

The benzene was of 'AnalaR' grade and the bromobenzene of spectroscopic quality. The perdeuterobenzene, 1,3,5 trideuterobenzene and perdeuterobromobenzene were obtained from commercial sources, and the stated atomic purities were better than 99.5%, 99% and 98% respectively. All liquids were used without further purification. They were contained in sample tubes of Pyrex glass of overall length 5 cm, outside diameter 6 mm, and wall thickness 1.5 mm. The actual liquid sample was a cylinder 1 cm long and 3 mm in diameter. This volume was separated from the rest of the tube by a small constriction, as has been shown to be necessary [8]. This is to prevent vapour molecules from diffusing back into the body of the liquid. These vapour molecules may not have been exposed to the r.f. field, so their nuclei may have a different polarization from those in the liquid. The vapour also has a different  $T_1$ .

The critical filling fraction of a sample tube is about  $\frac{1}{3}$ .

Critical filling ensures that liquid exists right up to the critical

point, and does not completely fill the tube or evaporate before this temperature is reached. A simple piece of apparatus was constructed to observe the filling characteristics of each sample up to the critical point. The sample is placed in a transparent glass dewar and hot air blown over it. A copper-constantan thermocouple, placed on the sample, measures its temperatures. The liquid meniscus is observed while the temperature is increased. The temperature at which the meniscus just disappears is the critical point. In this way the chance of a sample exploding when fitted into the glassware in the probe is minimized.

Molar fractions,  $x$ , of liquid mixtures were measured by weighing the constituent liquids as they were added to the sample tubes. An accuracy of 1%, for  $x$  is claimed. Losses by evaporation were negligible as the samples were frozen between weighing and degassing. The total weight of the sample tube and its contents before and after degassing was virtually constant. Dissolved atmospheric oxygen was removed by the technique of "freeze pump-thaw". Oxygen molecules carry an unpaired electron whose gyromagnetic ratio is about three orders of magnitude greater than that for a proton. It will be shown in chapter IV that for a given set of nuclei undergoing intermolecular dipolar interactions with non-resonant spins,

$$T_1 \propto \gamma_s^2$$

where  $\gamma_s$  is the gyromagnetic ratio of the non-resonant spins. Thus the relaxing effect of the oxygen impurity is strong.

A completely greasefree vacuum line was constructed. Greaseless taps were used (Springhams). Dissolved vacuum grease had appeared as an impurity in some earlier samples; its presence revealed by an apparent lowering of  $T_1$  at high temperatures. The sample tube is attached to the vacuum line by a clean polypropylene sleeve. The liquid is frozen and the space above it evacuated and isolated. On thawing, the liquid evolves bubbles of dissolved air. The cycle is repeated several times until there is no increase in pressure due to gas leaving the liquid. The partial pressure of a gas dissolved in a liquid is proportional to the partial pressure of that gas on the liquid surface. That is, a dynamic exchange equilibrium is set up. Exposure to a pressure of say  $7.6 \times 10^{-4}$  mm of mercury reduces the number of dissolved air molecules by a factor of  $10^6$ . For the case of mixtures it is essential to freeze the sample for a considerable time to ensure all vapour is condensed. Otherwise slight fractional distillation might occur, although the relevant freezing points are close. Another reason for preparing the sample the required size before degassing was one of economy. All samples were frozen and finally sealed off under a pressure not greater than  $5 \times 10^{-3}$  mm of mercury, so all measurements refer to liquids under their own normal vapour pressure.



CHAPTER III

THE DENSITY MATRIX AND ITS TIME DEPENDENCE

III.1 Introduction

We have seen that for an ensemble of spin one half systems, each spin has a wave function of the form

$$\psi = c_{1/2} u_1 + c_{-1/2} u_2$$

where  $u_1$  and  $u_2$  are the eigenstates of the operator  $I_z$  with eigenvalues  $\frac{1}{2}$  and  $-\frac{1}{2}$  respectively.  $|c_{1/2}|^2$  is the probability of occupation of state  $u_1$ .

In equilibrium, for N systems,

$$\begin{aligned} M_z = N \langle \mu_z \rangle &= N \gamma \hbar \langle I_z \rangle = N \gamma \hbar \int \psi^* I_z \psi \\ &= N \gamma \hbar (|c_{1/2}|^2 - |c_{-1/2}|^2). \end{aligned} \quad (3.1)$$

We shall show later, that

$$\begin{aligned} M_+ = M_x + iM_y &= N \gamma \hbar c_{1/2}^* c_{-1/2} \\ \text{and } M_- = M_x - iM_y &= N \gamma \hbar c_{1/2} c_{-1/2}^* \end{aligned} \quad \left. \vphantom{\begin{aligned} M_+ = M_x + iM_y \\ \text{and } M_- = M_x - iM_y \end{aligned}} \right\} (3.2)$$

Thus unless each coefficient  $c_{1/2}$  or  $c_{-1/2}$  equals zero, which is only the case for complete polarization, the equilibrium magnetization of the sample should have a component at right angles to  $H_0$ . This is not observed experimentally. Thus we must assume  $c_{1/2}$  and  $c_{-1/2}$  are different for each spin, and that the average,

$$\overline{c_{1/2}^* c_{-1/2}} = \frac{1}{N} \sum_i c_{1/2}^{i*} c_{-1/2}^i = 0.$$

We may also write the averages,

$$|c_{1/2}|^2 = p_+ \quad \text{and} \quad |c_{-1/2}|^2 = p_-,$$

as the relative populations of the two levels.

We may generalize equation(1.6) for any spin operator  $Q$ . Over

the  $N$  spin systems the average value of  $Q$  will be

$$\langle Q \rangle = \frac{1}{N} \sum_{k=1}^N \sum_{n,m} c_m^{k*} c_n^k \int \psi^* Q \psi$$

or, using a bar to indicate an average,

$$\langle \bar{Q} \rangle = \sum_{n,m} \overline{c_m^* c_n} (m|Q|n). \quad (3.3)$$

To compute an observable we need to specify either all the  $c_n$ 's or the

products  $c_n c_m^*$ ; the latter will be the more convenient. We may

arrange the coefficients  $\overline{c_n c_m^*}$  to form a matrix, a representation

of an operator  $\rho$ , the density matrix for the ensemble of spin

systems,

$$\text{i.e.} \quad (n|\rho|m) = \overline{c_n c_m^*}.$$

Equation (3.3) becomes,

$$\begin{aligned} \langle \bar{Q} \rangle &= \sum_{n,m} (n|\rho|m) (m|Q|n) \\ &= \sum_n (n|\rho Q|n) \\ &= \text{Trace}(\rho Q) = \text{Trace}(Q\rho). \end{aligned}$$

We notice  $(n|\rho|m) = \overline{c_n c_m^*}$

and  $(m|\rho|n) = \overline{c_m c_n^*}$

$\therefore (n|\rho|m) = (m|\rho|n)$

or,  $\int u_n^* \rho u_m d\tau = \left[ \int u_m^* \rho u_n d\tau \right]^* = \int (\rho u_n)^* u_m d\tau$

which is the condition for  $\rho$  to be Hermitian. Also,

$$\text{Tr}(\rho) = \text{Tr}(\rho \hat{1})$$

where  $\hat{1}$  is the unit matrix, therefore,

$$\text{Tr}(\rho) = 1.$$

The wave function,  $\psi_k = \sum_n c_n u_n$ , describing the  $k$ th system will change with time and if the  $u_n$ 's are constant, the coefficients  $c_n$  are time dependent. If the Hamiltonian of the system is  $\mathcal{H}$ , the corresponding Schrödinger equation is,

$$-\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = \mathcal{H} \psi$$

or  $-\frac{\hbar}{i} \sum_n \frac{dc_n}{dt} u_n = \sum_n c_n \mathcal{H} u_n.$

We can pick out the equation for one particular  $c_k$  by multiplying by  $u_k^*$  and integrating. We find,

$$-\frac{\hbar}{i} \frac{dc_k}{dt} = \sum_n c_n (k|\mathcal{H}|n).$$

Therefore,  $\frac{d}{dt} (k|\rho|m) = \frac{d}{dt} (\overline{c_k c_m^*})$

$$= \overline{c_k \frac{dc_m}{dt}} + \frac{dc_k}{dt} \overline{c_m^*}$$

$$= \frac{i}{\hbar} \sum_n \left[ \overline{c_k c_n^*} (n | \mathcal{H} | m) - (k | \mathcal{H} | n) \overline{c_n c_m^*} \right]$$

$$= \frac{i}{\hbar} (k | \rho \mathcal{H} - \mathcal{H} \rho | m).$$

In operator form, this may be written as

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}]. \quad (3.4)$$

This is similar to the equation of motion of an observable except for a change of sign.

Should  $\mathcal{H}$  be independent of time, a solution of equation (3.4) is,

$$\rho(t) = \exp\left(-\frac{i}{\hbar} \mathcal{H} t\right) \rho(0) \exp\left(\frac{i}{\hbar} \mathcal{H} t\right).$$

If the  $u_n$  are the eigenfunctions of  $\mathcal{H}$ , then the  $k, m$  element of the time dependent density matrix  $\rho(t)$  is,

$$(k | \rho(t) | m) = \int u_k^* \exp\left(-\frac{i}{\hbar} \mathcal{H} t\right) \rho(0) \exp\left(\frac{i}{\hbar} \mathcal{H} t\right) u_m d\tau$$

$$= \int \left[ \exp\left(-\frac{i}{\hbar} \mathcal{H} t\right) u_k \right]^* \rho(0) \exp\left(\frac{i}{\hbar} \mathcal{H} t\right) u_m d\tau.$$

As  $\mathcal{H} u_n = E_n u_n$

$$(k | \rho(t) | m) = \exp\left[\frac{i}{\hbar} (E_m - E_k) t\right] (k | \rho(0) | m).$$

If the spin system is in thermal equilibrium at temperature  $T$ , the populations of the eigenstates are given by the Boltzmann factor, so

that the diagonal elements of  $\rho$  are given by

$$\overline{c_m c_n^*} = \frac{\exp\left(\frac{-E_m}{kT}\right)}{Z}$$

where the partition function,  $Z = \sum_n \exp\left(-\frac{E_n}{RT}\right)$ ,

must be included to ensure  $\text{Tr} \rho = 1$ .

If we write

$$c_n = |c_n| \exp(i\alpha_n),$$

$$\overline{c_m c_n^*} = |c_m| |c_n| \exp[i(\alpha_m - \alpha_n)].$$

If the phases  $\alpha_n$  are independent of the amplitudes  $|c_n|$ , then the right hand side will average to zero for all terms for which  $m \neq n$ .

Hence the off diagonal elements of  $\rho$  vanish as we expect for thermal equilibrium.

### III.2 Properties of the density matrix

Let us now consider the calculation of  $Q$  from the density matrix, when the representative set of  $Q$  is changed. Suppose we transform to a new representation given by

$$Q' = U^{-1} Q U$$

$$\text{and let } \psi^k = \sum_q d_q^k \sigma_q$$

$$\text{where } \sigma_q = \sum_n u_n U_{nq}.$$

$$\text{But } U_{nq}^* = (U^{-1})_{qn}$$

$$\therefore c_n^k = \sum_q d_q^k U_{nq}$$

$$\text{and } d_q^k = \sum_n c_n^k U_{nq}^*.$$

The density matrix in the new representation is given by

$$\begin{aligned} \rho'_{ij} &= N^{-1} \sum_k d_j^{k*} d_i^k \\ &= N^{-1} \sum_k \sum_{n,m} c_n^{k*} U_{nj} c_m^k U_{mi} \end{aligned}$$

$$= \sum_{n,m} (U^{-1})_{im} \rho_{mn} U_{nj}.$$

Thus  $\rho' = U^{-1} \rho U,$

and  $Q' = \text{Tr}(\rho' Q') = \text{Tr}(U^{-1} \rho U U^{-1} Q U)$   
 $= \text{Tr}(U^{-1} \rho Q U).$

When a trace is taken, the order is irrelevant,

$$\therefore Q' = \text{Tr}(\rho Q).$$

Hence the calculation of  $Q'$  is independent of its representation  $\sigma_q$ .

For a spin one half system placed in a field, we have seen the wavefunction may be written

$$\psi(t) = c_{1/2} u_{1/2} \exp\left(-\frac{i}{\hbar} E_{1/2} t\right) + c_{-1/2} u_{-1/2} \exp\left(-\frac{i}{\hbar} E_{-1/2} t\right)$$

$$= c_{1/2} u_{1/2} \exp\left(-\frac{i\omega_0 t}{2}\right) + c_{-1/2} u_{-1/2} \exp\left(\frac{i\omega_0 t}{2}\right).$$

Hence  $\rho_{11} = c_{1/2} c_{1/2}^*$

$$\rho_{12} = c_{1/2} c_{-1/2}^* \exp(-i\omega_0 t)$$

and  $\rho_{21} = c_{-1/2} c_{1/2}^* \exp(i\omega_0 t)$

so that the explicit form of the density matrix is

$$\rho = \begin{pmatrix} aa^* & ab^* \exp(-i\omega_0 t) \\ a^* b \exp(i\omega_0 t) & bb^* \end{pmatrix}$$

where we have defined  $c_{1/2} = a \exp(i\alpha)$  etc., but have neglected the constant phase factors.

The operator for each component of spin  $\frac{1}{2}$  may be represented by a Pauli operator, e.g.

$$I_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad I_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

So ensemble averages of  $I_z$ ,  $I_x$ , and  $I_y$  may be specified by

$$\bar{I}_z = \text{Tr}(\rho I_z) = \frac{1}{2}(aa^* - bb^*)$$

$$\bar{I}_x = \text{Tr}(\rho I_x) = \frac{1}{2}[ab^* \exp(-i\omega_0 t) + a^* b \exp(i\omega_0 t)]$$

$$\bar{I}_y = \text{Tr}(\rho I_y) = \frac{1}{2}[ab^* \exp(-i\omega_0 t) - a^* b \exp(i\omega_0 t)].$$

which justify the remarks made in equation(3.2) .

### III.3 The interaction representation

If the Hamiltonian for our spin system consists of a time independent term,  $\mathcal{H}_0$ , and a time dependent term  $\mathcal{H}_1(t)$ , the equation of the density matrix becomes

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}_0 + \mathcal{H}_1(t)] \quad (3.5)$$

Let us define a quantity  $\rho'$ , by

$$\rho = \exp\left(\frac{-i}{\hbar} \mathcal{H}_0 t\right) \rho' \exp\left(\frac{i}{\hbar} \mathcal{H}_0 t\right) \quad (3.6)$$

Substituting (3.6) into (3.5) we have a differential equation for  $\rho'$ ,

$$\frac{-i}{\hbar} [\mathcal{H}_0, \rho] + \exp\left(\frac{-i}{\hbar} \mathcal{H}_0 t\right) \frac{d\rho'}{dt} \exp\left(\frac{i}{\hbar} \mathcal{H}_0 t\right) = \frac{i}{\hbar} [\rho, \mathcal{H}_0 + \mathcal{H}_1]$$

If we define  $\mathcal{H}'_1 = \exp\left(\frac{i}{\hbar} \mathcal{H}_0 t\right) \mathcal{H}_1 \exp\left(-\frac{i}{\hbar} \mathcal{H}_0 t\right)$

we find,

$$\frac{d\rho'}{dt} = \frac{i}{\hbar} [\rho', \mathcal{H}'_1(t)].$$

Hence we have in effect removed the term  $\mathcal{H}_0$ . The transformation to the new  $\mathcal{H}'_1$  is canonical and is called the interaction representation.

### III.4 The correlation function

Consider a time dependent function  $y(t)$ .  $y(t)$  is a random function if its value at any time  $t$  is a random variable, occurring with probability  $p(y,t)$ . The average value of  $y(t)$  at time  $t$  is,

$$\overline{y(t)} = \int y p(y,t) dy.$$

If  $f(y)$  is a function of  $y$ ,  $f(y)$  is also a random function of  $t$ , and

$$\overline{f(t)} = \int p(y,t) f(y) dy.$$

Values of  $y(t)$  corresponding to different times are not in general independent variables, but show a correlation. We shall consider only that correlation for two different times,  $t_1$  and  $t_2$ . We define the correlation function,  $G(t_1, t_2)$ , of the random function  $f(y)$  by,

$$G(t_1, t_2) = \overline{f(t_1) f^*(t_2)}$$

relative to the times  $t_1, t_2$ .

Stationary random functions are independent of time, that is, independent of the origin in time. We shall deal only with this class of random function, so that  $G(t_1, t_2)$  depends on  $t_1$  and  $t_2$  only through the difference  $t_2 - t_1 = \tau$ .

We may write,

$$\begin{aligned} G(\tau) &= \overline{f(t) f^*(t + \tau)} \\ &= \overline{f(t) f^*(t - \tau)} \end{aligned}$$

if the behaviour of the function is symmetrical in the past and future,

$$\text{i.e. } G(\tau) = G(-\tau).$$

If  $f(t)$  and  $f(t + \tau)$  were uncorrelated, we could average each separately, then, if  $\overline{f(t)} = 0$ ,

$$G(\tau) = \overline{f(t) f^*(t+\tau)} = 0.$$

For  $\tau = 0$ ,  $G(0) = \overline{|f(t)|^2} \geq 0$

In typical physical systems,  $f(t)$  will be some perturbation varying with time due to some physical movement. For example, we shall be interested in molecular motion in liquids. For times less than some critical time  $\tau_c$ , the "correlation time", the motion may be considered correlated, so that

$$f(t) \approx f(t + \tau_c).$$

$G(\tau)$  is very small for  $|\tau| \gg \tau_c$ . The shape of the function will be as in figure (3.1).

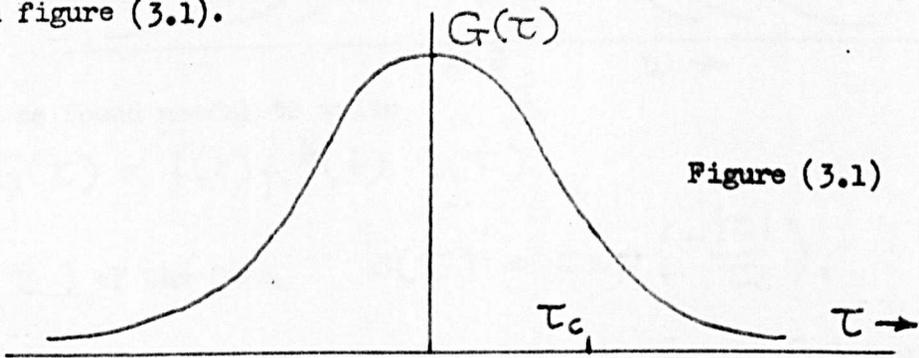


Figure (3.1)

For future reference, let us define a Fourier transform of  $G(\tau)$ ,

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(-i\omega\tau) d\tau.$$

The inverse relationship is

$$G(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} J(\omega) \exp(i\omega\tau) d\omega.$$

$J(\omega)$  may be thought of as the spectral density of  $G(\tau)$ , and will contain frequencies up to the order  $1/\tau_c$ , as shown in figure (3.2).

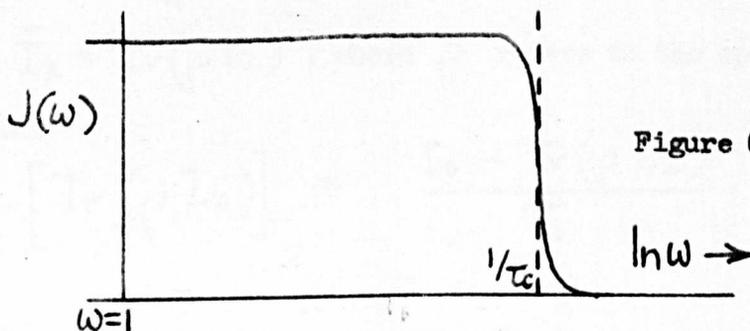
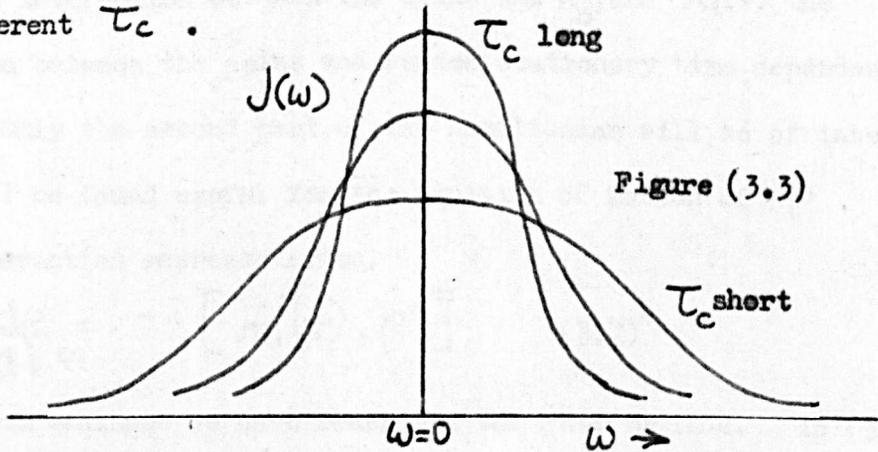


Figure (3.2)

As  $G(0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} J(\omega) d\omega$

is independent of  $\tau_c$ , we see that the area under the spectral density curve remains fixed as  $\tau_c$  varies. Figure (3.3) shows the curves for three different  $\tau_c$ .



It will be found useful to write

$$G(\tau) = f(t) f^*(t) c(\tau)$$

with  $c(\tau)$  of the form,  $c(\tau) = \exp\left(-\frac{|\tau|}{\tau_c}\right)$ ,

a correlation function which is often used for many physical processes. This may break down for small  $\tau$ , as an exponential correlation function produces a cusp at the origin, i.e. a sharp change of slope.

### III.5 The time dependence of the density matrix

By analogy with equation (1.3) the rate of change of the magnetization in the z direction is related to  $T_1$  by

$$\frac{d\bar{I}_z}{dt} = \frac{I_0 - \bar{I}_z}{T_1}$$

But as  $\bar{I}_z = \text{Tr}(\rho I_z)$ , where  $\rho$  refers to the spin system under discussion,

$$\frac{d}{dt} [\text{Tr}(\rho I_z)] = \frac{I_0 - \text{Tr}(\rho I_z)}{T_1}$$

This would suggest that a useful starting point in the derivation of an equation for  $T_1$  is the equation of motion of  $\rho$ .

Consider a Hamiltonian  $[\mathcal{H}_0 + \mathcal{H}_1(t)]$  acting on the spin system.  $\mathcal{H}_0$  is the interaction between the spins and  $H_0$ , and  $\mathcal{H}_1(t)$  the interaction between the spins and random stationary time dependent magnetic fields. Only the second part of the Hamiltonian will be of interest here and it will be found useful for the equation of motion of  $\rho$  to be in the interaction representation.

$$\text{i.e. } \frac{d\rho'}{dt} = -i [\mathcal{H}'_1(t), \rho'] \quad (3.7)$$

where for convenience we have redefined the Hamiltonians. In (3.7)

$$\rho' = \exp(i\mathcal{H}_0 t) \rho \exp(-i\mathcal{H}_0 t)$$

$$\text{and } \mathcal{H}'_1(t) = \exp(i\mathcal{H}_0 t) \mathcal{H}_1(t) \exp(-i\mathcal{H}_0 t).$$

Integrate equation (3.7) from  $t=0$ , then

$$\rho'(t) = \rho'(0) - i \int_0^t [\mathcal{H}'_1(t'), \rho'(t')] dt' \quad (3.8)$$

$\rho'(t')$  is unknown, but we may find an approximate solution by replacing it by  $\rho'(0)$ , its value at  $t=0$ . Hence we may make a closer

approximation by an iteration procedure, obtaining a better value of

$\rho'(t')$  to put in the integrand of (3.8). Thus

$$\rho'(t) = \rho'(0) - i \int_0^t [\mathcal{H}'_1(t'), \{ \rho'(0) - i \int_0^{t'} [\mathcal{H}'_1(t''), \rho'(0)] dt'' \}] dt'$$

+ higher terms

$$= \rho'(0) - i \int_0^t [\mathcal{H}'_1(t'), \rho'(0)] dt' - \int_0^t \int_0^{t'} [\mathcal{H}'_1(t'), [\mathcal{H}'_1(t''), \rho'(0)]] dt' dt''$$

+ higher terms (3.9)

Equation(3.9) is entirely equivalent to ordinary time dependent perturbation theory taken to second order, but we are interested in the behaviour of terms  $a_n a_m^*$  rather than  $a_n$  and  $a_m$  separately. Because of the statistical nature of  $\mathcal{H}_1(t)$  we may introduce the new variable,  $\tau = t - t'$ , then, differentiating equation (3.9) , we write the approximation,

$$\frac{d\rho'}{dt} = -i[\mathcal{H}_1(t), \rho'(0)] - \int_0^t d\tau [\mathcal{H}_1(t), [\mathcal{H}_1(t-\tau), \rho'(0)]] \quad (3.10)$$

We now define a correlation time,  $\tau_c$ , for the random Hamiltonian  $\mathcal{H}_1(t)$ , which is a time such that for  $\tau_c < \tau$ ,

$$\overline{\mathcal{H}_1(t) \mathcal{H}_1(t+\tau)} > 0$$

and for  $\tau_c > \tau$ ,  $\overline{\mathcal{H}_1(t) \mathcal{H}_1(t+\tau)} = 0$ .

From equation(3.10) if  $\mathcal{H}_1(t)$  is a random operator, so is  $\rho'$ , and the observable behaviour of our ensemble of spins will be found by taking an ensemble average on each side of equation.(3.10) . For times,  $t$ , longer than  $\tau_c$ ,  $\mathcal{H}_1(t)$ ,  $\mathcal{H}_1(t+\tau)$  or  $\rho'(0)$  are uncorrelated. In particular  $\mathcal{H}_1(t)$  and  $\rho'(0)$  may be averaged separately, i.e.

$$\overline{[\mathcal{H}_1(t), \rho'(0)]} = [\overline{\mathcal{H}_1(t)}, \overline{\rho'(0)}] = 0.$$

Since we are dealing with stationary perturbations the ensemble average of  $\mathcal{H}_1(t)$  is equivalent to a time average, in general we will suppose the time average to vanish, because of the random nature of  $\mathcal{H}_1(t)$ .

We make three further assumptions.

(a) We may replace  $\rho'(0)$  by  $\rho'(t)$  on the right hand side of equation(3.10) . Over long times, and with short correlation times,

$\rho'(t)$  is very little different from  $\rho'(0)$  [3].

(b) We may extend the upper limit of the integral to infinity.

This is reasonable as contributions to the integral

$$\int_0^t \overline{\mathcal{H}'_1(t) \mathcal{H}'_1(t-\tau)} d\tau$$

for values of  $\tau > \tau_c$  are negligible.

(c) We may neglect higher order terms in the approximation for  $\rho'(t)$ .

This is valid for short  $\tau_c$ , as higher order terms fall off as  $\tau_c$  [3].

Hence, 
$$\frac{d\rho'}{dt} = - \int_0^\infty d\tau \left[ \overline{\mathcal{H}'_1(t) \mathcal{H}'_1(t-\tau)}, \rho'(t) \right] \quad (3.11)$$

where  $\rho'$  is now the average density matrix. That the ensemble average of  $\mathcal{H}'_1(t)$  vanishes amounts to assuming that  $\mathcal{H}'_1(t)$  does not produce a frequency shift [1,2].

In general, equation (3.11) may be expressed in more useful form if we write  $\mathcal{H}'_1(t)$  as

$$\mathcal{H}'_1(t) = \sum_q F^{(q)}(t) A^{(q)}$$

where the  $A^{(q)}$  are spin operators and the  $F^{(q)}$  random functions of time.

The Hermitian properties of the Hamiltonian are maintained by making the

convention 
$$F^{(-q)} = F^{(q)*}$$

and 
$$A^{(-q)} = A^{(q)\dagger}.$$

The operators  $A^{(q)}$  are transformed to the interaction representation by

$$A'^{(q)} = \exp(i\mathcal{H}_0 t) A^{(q)} \exp(-i\mathcal{H}_0 t) = \sum_p A_p^{(q)} \exp(i\omega_p^{(q)} t).$$

Substituting in equation (3.11) and noting that specifically time dependent terms average to unity, we have

$$\frac{d\rho'}{dt} = - \sum_{q,p} [A_p^{(-q)}, [A_p^{(q)}, \rho'(t)]] \int_0^\infty C_q(\tau) \exp(-i\omega_p^{(q)}\tau) d\tau$$

where  $C_q(\tau) = \overline{F^{(q)}(t) F^{(q)}(t+\tau)}$ .

At frequency  $\omega_p^{(q)}$  the spectral density of  $F^{(q)}$  is ,

$$J_q(\omega_p^{(q)}) = \int_{-\infty}^{\infty} C_q(\tau) \exp(-i\omega_p^{(q)}\tau) d\tau.$$

Finally the so called master equation is

$$\frac{d\rho'}{dt} = -\frac{1}{2} \sum_{q,p} J_q(\omega_p^{(q)}) [A_p^{(-q)}, [A_p^{(q)}, \rho']].$$

For a particular type of perturbation the J's and A's have to be calculated in detail. In the next chapter we shall consider all sources of time dependent fields which could cause nuclear relaxation.

### CHAPTER III. REFERENCES

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CHAPTER IVCONTRIBUTIONS TO SPIN-LATTICE RELAXATION.IV.1. The anisotropic chemical shift interaction

It has been mentioned that there exists a coupling between the main field  $H_0$  and a spin  $I$ , of form

$$-\gamma \hbar H_0 \cdot \underline{A} \cdot \underline{I}.$$

$\underline{A}$  is the chemical shift tensor whose components have definite values in the frame of the molecule. The trace of this tensor,

$$A_{11} + A_{22} + A_{33} = 3\delta_0$$

is seen as a small frequency shift, given by,

$$\Delta\omega = \delta_0 \omega_0$$

where  $\omega_0$  is the Larmor frequency.

The off-diagonal elements of  $\underline{A}$  are dependent on the molecular orientation and can cause relaxation whenever there is molecular motion.

It may be shown [1] that the relaxation times  $T_1$  and  $T_2$  due to this interaction are proportional to  $H_0^2$ , so the field dependence of the relaxation times should enable this contribution to be recognised.

A physical picture of the interaction may be introduced as follows.

The magnetic field at the site of a nucleus is given by

$$H_n = (1 - \sigma) H_0$$

where  $\sigma$  represents the shielding. If this quantity is anisotropic it

has different values for different orientations of the molecule with respect to  $H_0$ . So  $H_n$  is time dependent through molecular reorientation.

#### IV.2 Indirect spin-spin coupling. (J coupling).

The first evidence of this interaction came with the discovery of field independent splittings in high resolution spectra, as in the case of ethyl alcohol given in section (I.4). This coupling is via the electron spins.

The Hamiltonian is of the form

$$\mathcal{H}_J = \hbar \underline{I}_i \cdot J \cdot \underline{I}_j .$$

The isotropic part of the coupling tensor,  $J$ , may be measured from high resolution spectra. If  $J$  is time dependent, through for example, exchange processes or isomeric changes, its anisotropic part can cause relaxation.

In this case the correlation time of the interaction would depend on the exchange rate. However, for most substances  $J$  is small, and as the relaxation rate due to this contribution depends on  $J^2$  [1], it may be neglected in the presence of stronger interactions. Moreover, in the liquids studied experimentally in this work, there is no evidence of exchange. Another possible relaxing effect occurs if the nuclei under investigation are  $J$  coupled to another group which has a very short relaxation time.

### IV.3 Electric Quadrupole interactions.

So far we have considered only the magnetic interactions of the nucleus with its surroundings. However, we must consider the possibility of electric fields reorienting the nucleus. That such an effect is possible is easily seen by considering a nucleus with a non spherically symmetric charge distribution. For example, the nucleus might be slightly prolate. The electrostatic energy of the nucleus then depends on the nuclear orientation with respect to the neighbouring charges, both nuclear and electronic. If the positions of the neighbouring charges are time dependent, through, for example, molecular motion, the energy changes of the nucleus may well equal those needed for transitions between its magnetic energy levels. So relaxation will occur, and we have the apparent anomaly of an electric interaction causing magnetic transitions. Alternatively, we may consider the nuclear electric quadrupole moment interacting with an electric field gradient.

The quadrupole interaction is observed only for those nuclei with  $I > \frac{1}{2}$ . Nuclei with  $I \leq \frac{1}{2}$  have no electric quadrupole moment.

The contribution to the relaxation time of a spin 1 nucleus, from the quadrupole coupling is [1] ,

$$\frac{1}{T_{1Q}} = \frac{3}{8} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{e^2 q Q}{\hbar}\right)^2 \tau_Q \quad (4.1)$$

where  $\eta$  is an asymmetry parameter,  $Q$  the nuclear quadrupole moment and  $q$

the electric field gradient at the nuclear site. This electric field gradient is fixed in the molecule and  $\tau_Q$  is the correlation time associated with the reorientational motion of a vector along this gradient.

Usually for liquids, for spins greater than one half, the quadrupole interaction is dominant and others may be neglected. For example, as the total charge on a molecule is zero, the intermolecular electric field gradients are likely to be small. For polar liquids this may not be true, but the intermolecular contribution is still usually small.

That intramolecular quadrupolar interactions dominate magnetic interactions may be shown as follows. Calculated relaxation times for magnetic interactions only are much longer than those actually measured. For example, for relaxation of deuterons in perdeuterobenzene by magnetic interactions only, one calculates  $T_1 \approx 3 \times 10^4$  seconds. Experimentally  $T_1 \approx 5$  seconds. Also, the deuteron relaxation time in perdeuterobenzene is unchanged by dilution in benzene [2]. Thus, not only are magnetic interactions insignificant, intermolecular quadrupole interactions are shown to be negligible also.

#### IV.4 Interactions with paramagnetic impurities. Wall relaxation.

The magnetic dipole moment of a paramagnetic ion, or any particle containing an unpaired electron spin, such as an oxygen molecule, is about three orders of magnitude greater than a nuclear moment. Dipolar

interactions are thus considerably stronger. A trace of paramagnetic impurity can dominate relaxation processes. In general, the diffusion coefficient of an impurity will be different from that of the host molecule. The more rapidly the impurity diffuses, the more nuclear spins will it encounter and the greater will be its relaxing effect.

The most common impurity of this type, for the liquids to be discussed, is dissolved atmospheric oxygen. Proton and fluorine nuclear relaxation times are reduced from order 20 seconds to order 3 seconds when the samples are exposed to the atmosphere.

It has been suggested that the percentage of the molecules in a sample tube making collisions with the walls of the tube per unit time, may be large enough to affect  $T_1$ . The cause could be a change in correlation time, i.e. the rate of motion, or interactions with the walls. D.W.G. Smith, of this laboratory, has measured proton  $T_1$ 's for simple liquids held in large sample tubes also containing many thin walled glass capillary tubes. The increase in area of glass in contact with the liquid did not affect  $T_1$ .

#### IV.5 Dipole-dipole interactions

The nuclear magnetic dipolar interaction mentioned previously is time dependent through two distinct types of motion. The intramolecular

dipolar interaction depends only on the reorientational motion of the vector joining two nuclei in the same molecule. The intermolecular dipolar interaction depends on the length and direction of the vector joining nuclei in different molecules. To a small degree changes in this vector will be due to reorientational motion.

This interaction will now be considered in greater detail.

The Hamiltonian for the dipolar interaction between spin I and spin S

$$\text{is } \hbar \mathcal{H}_d = \hbar^2 \gamma_I \gamma_S \left[ \frac{\underline{I} \cdot \underline{S}}{r^3} - \frac{3(\underline{r} \cdot \underline{I})(\underline{r} \cdot \underline{S})}{r^5} \right].$$

We write the spins in terms of their components,  $I_x$ ,  $I_y$  and  $I_z$ , and put

$$I_+ = I_x + iI_y$$

$$I_- = I_x - iI_y,$$

the raising and lowering operators respectively. Also we express the Cartesian coordinates given by  $\underline{r}$ , in terms of the spherical coordinates,

$r, \theta, \varphi$ . We may now write the Hamiltonian in the well known form

$$[7], \quad \hbar \mathcal{H}_d = \frac{\gamma_I \gamma_S \hbar^2}{r^3} [A + B + C + D + E + F]$$

where,

$$A = I_z S_z (1 - 3 \cos^2 \theta)$$

$$B = -\frac{1}{4} [I_+ S_- + I_- S_+] (1 - 3 \cos^2 \theta)$$

$$C = -\frac{3}{2} [I_+ S_z + I_z S_+] \sin \theta \cos \theta \exp(-i\varphi)$$

$$D = -\frac{3}{2} [I_- S_z + I_z S_-] \sin \theta \cos \theta \exp(i\varphi)$$

$$E = -\frac{3}{4} I_+ S_+ \sin^2 \theta \exp(-2i\varphi)$$

$$F = -\frac{3}{4} I_- S_- \sin^2 \theta \exp(2i\varphi).$$

We have made contact with equation (3.12) as the dipolar Hamiltonian

can now be written, 
$$\hbar \mathcal{H}_d = \sum_q F^{(q)} A^{(q)}$$

where 
$$F^{(0)} = \frac{1 - 3 \cos^2 \theta}{r^3}$$

$$F^{(1)} = \frac{\sin \theta \cos \theta \exp(-i\varphi)}{r^3}$$

$$F^{(2)} = \frac{\sin^2 \theta \exp(-2i\varphi)}{r^3}$$

and 
$$A^{(0)} = a \left[ -\frac{2}{3} I_z S_z + \frac{1}{6} (I_+ S_- + I_- S_+) \right]$$

$$A^{(1)} = a [ I_z S_+ + I_+ S_z ]$$

$$A^{(2)} = \frac{1}{2} a I_+ S_+$$

where 
$$a = -\frac{3}{2} \gamma_I \gamma_S \hbar.$$

We assume isotropic random motion for the orientation of the vector  $\underline{r}$ , so

the correlation function becomes

$$F^{(q)}(t) F^{(q)*}(t+\tau) = G^{(q)}(\tau)$$

and 
$$J^{(q)}(\omega) = \int_{-\infty}^{\infty} G^{(q)}(\tau) \exp(-i\omega\tau) d\tau.$$

Now replace  $\rho'$  by  $\rho' - \rho'_0$  in equation (3.13).  $\rho'_0$  is the

equilibrium density matrix. The total magnetization in the z direction

is  $(I_z + S_z)$ . We operate on  $(I_z + S_z)$  by both sides of equation (3.13)

and take the trace, thus,

$$\frac{d}{dt} \overline{[I_z + S_z]} = -\frac{1}{2} \sum_q J_q(\omega_I) \left[ A^{-q}, [A^q, I_z + S_z - (I_z + S_z)_0] \right].$$

We must expand the commutator, noting that the contributions from the terms with  $q = 0$  are zero, as

$$[A^0, I_z + S_z] = 0.$$

Eventually we find for like spins [1],

$$\frac{d}{dt} \overline{[I_z + S_z]} = -\frac{3}{2} \gamma^4 \hbar^2 I(I+1) [J_1(\omega_I) + J_2(2\omega_I)] \overline{[I_z + S_z - (I_z + S_z)_0]}.$$

But we know the equation of  $T_1$  is

$$\frac{d}{dt} \overline{[I_z + S_z]} = \frac{I_z + S_z - (I_z + S_z)_0}{T_1}$$

therefore, by comparison,

$$\frac{1}{T_1} = \frac{3}{2} \gamma^4 \hbar^2 I(I+1) [J_1(\omega_I) + J_2(2\omega_I)] \quad (4.2.)$$

for the dipole-dipole interaction of two like spins. The generalization

to interactions with several pairs of like spins, provided their motion

is not correlated, is given by,

$$\frac{1}{T_1} = \frac{3}{2} \gamma^4 \hbar^2 I(I+1) \sum_k [J_1^{(k)}(\omega_I) + J_2^{(k)}(2\omega_I)].$$

In a similar way we may calculate  $T_2$ , using  $(I_x + S_x)$  in place of  $(I_z + S_z)$

and find [1], for like spins,

$$\frac{1}{T_1} = \gamma^4 \hbar^2 I(I+1) \left[ \frac{3}{8} J_0(0) + \frac{15}{4} J_1(\omega_I) + \frac{3}{8} J_2(2\omega_I) \right].$$

If the same short correlation time is assumed for all the random quantities concerned, we can show [1],

$$J_0 : J_1 : J_2 = \overline{|F^{(0)}|^2} : \overline{|F^{(1)}|^2} : \overline{|F^{(2)}|^2} = 6 : 1 : 4 .$$

On calculating  $T_2$  for interactions between unlike spins in a similar manner, we find [1], for all other things being equal,

$$\frac{1/T_2 \text{ like}}{1/T_2 \text{ unlike}} = \frac{3}{2} \quad \text{extreme narrowing only.}$$

i.e. nonresonant spins are  $1\frac{1}{2}$  times less efficient for causing relaxation than resonant spins. In particular for proton-proton and proton-deuteron interactions,

$$\frac{T_{1 \text{ H-D}}}{T_{1 \text{ H-H}}} = \frac{3}{2} \left( \frac{8D}{8H} \right)^2 \frac{I_H(I_H+1)}{I_D(I_D+1)} \approx 24 \quad (4.3)$$

where the symbols have obvious meanings.

We need now to express the spectral densities  $J(\omega)$  in terms of the macroscopic parameters of the motion of the liquid molecules. That is, in introducing liquid theory, we need to find a model to approximate molecular behaviour. We assume the intramolecular distance  $r$  is fixed, which will be the case for the rigid molecules considered experimentally later. Molecular vibrations are the main means of changing internuclear distances, but they are not effective for nuclear relaxation as the relative change in distance is too small and the correlation time of the motion is too short.

We will first consider interactions between two like spins in the same molecule. This is the intramolecular dipolar interaction, and the time dependence is introduced solely through the rotation of the molecule. A basic assumption is that the motion of the molecules is Brownian, that is, the motion of spheres of radius  $a$  diffusing in a medium of viscosity  $\eta$ .

The probability,  $f(\theta, \varphi) = f(\Omega)$ , of finding a fixed axis of the sphere in the solid angle  $\sin\theta d\theta d\varphi$  is given by the ordinary diffusion equation,

$$-\frac{\partial}{\partial t} f(\Omega) = D \Delta f(\Omega) \quad (4.4)$$

where the diffusion constant,  $D = \frac{kT}{\beta}$ . The damping term  $\beta$  for rotation of a macroscopic sphere in a viscous medium was calculated by Stokes as  $\beta = 8\pi\eta a$ .

A solution of equation (4.4) may be written as a series of spherical harmonics,  $Y_{l,m}$ , i.e.,

$$f = \sum_{l,m} c_{l,m} Y_{l,m}(\Omega).$$

If at  $t = 0$ , the sphere is in the position  $\Omega_0$ ,

$$f = \delta(\Omega - \Omega_0)$$

and we find an expression for the coefficients

$$c_{l,m} = Y_{l,m}^*(\Omega_0) \exp\left(-\frac{t}{\tau_l}\right)$$

where  $\tau_l = \frac{D}{a^2} l(l+1)$ .

We need now the correlation function,

$$G(\tau) = F^*(\Omega) F(\Omega_0).$$

This may be shown to be [1],

$$G(\tau) = \frac{1}{4\pi} \iint F^*(\Omega) F(\Omega_0) f(\Omega) d\Omega d\Omega_0. \quad (4.5)$$

The random functions  $F^{(1)}$  and  $F^{(2)}$  are given in terms of the normalized spherical harmonics by

$$F^{(1)}(\Omega) = r^{-3} \sqrt{\frac{8\pi}{15}} Y_{2,1}(\Omega),$$

$$F^{(2)}(\Omega) = r^{-3} \sqrt{\frac{32\pi}{15}} Y_{2,2}(\Omega).$$

From equation (4.5),

$$G^{(1)}(\tau) = \frac{2}{15} r^{-6} \exp\left(\frac{-|\tau|}{\tau_d}\right)$$

and  $G^{(2)}(\tau) = \frac{8}{15} r^{-6} \exp\left(\frac{-|\tau|}{\tau_d}\right).$

So,

$$J_1(\omega) = \frac{1}{r^6} \frac{4}{15} \frac{\tau_d}{1+\omega^2\tau_d^2} \quad \text{and} \quad J_2(\omega) = \frac{1}{r^6} \frac{16}{15} \frac{\tau_d}{1+\omega^2\tau_d^2}.$$

From equation (4.2) we have, finally, for the relaxation time for two spins undergoing random isotropic Brownian reorientation with a dipolar interaction,

$$\frac{1}{T_1 \text{ intra}} = \frac{2}{5} \frac{8^4 h^2}{r^6} I(I+1) \left[ \frac{\tau_d}{1+\omega^2\tau_d^2} + \frac{4\tau_d}{1+\omega^2\tau_d^2} \right].$$

For rapid molecular motion, as is encountered in the liquids to be

considered later,  $\omega^2 \tau_d^2 \ll 1$ , so,

$$\frac{1}{T_1 \text{ intra}} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_d$$

for spins  $\frac{1}{2}$ . For a molecule containing several protons we may write

$$\frac{1}{T_1 \text{ intra}} = \frac{3}{2} \gamma^4 \hbar^2 \sum_j r_{ij}^{-6} \tau_d \quad (4.6)$$

for the  $i$ th nucleus.  $r_{ij}$  is the distance between the  $i$ th and  $j$ th nucleus.

This is equivalent to assuming the interactions additive, i.e. no correlation. However, Fenzke [3] has calculated  $T_1 \text{ intra}$  for a six spin system and finds that equation (4.6) is a good approximation.

The time dependence of the dipolar interaction between nuclei in different molecules may be produced by the relative translation of the two molecules and again Brownian motion is assumed to be responsible for the Fourier spectrum. We will now consider this problem.

We need to calculate  $F(t) F^*(t+\tau)$  for spins in a spherical shell between  $r$  and  $r+dr$  around the relaxing spin. The mean square displacement in any direction of a macroscopic particle in time  $t$  is given by [4],

$$\overline{r^2} = 6Dt.$$

If we assume the equation holds for microscopic particles, i.e. molecules, we may use it to define a time,  $\tau'$ , taken for a molecule to diffuse a distance  $d$ , the molecular diameter.

$$\tau' = \frac{d^2}{6D}. \quad (4.7)$$

$\tau'$  is a convenient measure of the rate of molecular translation and is called the translational correlation time. Of course, the choice of distance,  $d$ , is arbitrary, but convenient in that we may imagine molecular positions to be correlated so long as changes in position are less than the molecular size.

Again we suppose the diffusion equation to be adequate in describing molecular motion. We follow a derivation by Torrey [5].

The solution of the equation,

$$\frac{\partial}{\partial t} f(r, t) = D \Delta f$$

where  $f(r, 0) = \delta(r - r_0)$  is

$$f(r, r_0, t) = (8\pi Dt)^{-3/2} \exp\left[ -\frac{(r - r_0)^2}{8Dt} \right]. \quad (4.8)$$

Equation (4.8) is the probability that two molecules a distance  $r_0$  apart at time  $t=0$ , will be a distance  $r$  apart at  $t=t$ .

The correlation function for each of the three functions  $F^{(0)}$ ,  $F^{(1)}$  or  $F^{(2)}$  is [1],

$$G(\tau) = \alpha_m N \iint \frac{Y_{2,m}^*(\Omega_0)}{r_0^3} \frac{Y_{2,m}(\Omega)}{r^3} f(r, r_0, t) dr_0^3 dr^3 \quad (4.9)$$

where  $\alpha_1 = \frac{8\pi}{15}$  ;  $\alpha_2 = \frac{32\pi}{15}$  ;  $\alpha_3 = \frac{48\pi}{15}$ .

In equation (4.9)  $r$  and  $r_0$  may not go below a lower limit  $d$ , the distance of closest approach for molecules. By expanding the integrand into Bessel functions, we may show [1],

$$J(\omega) = \frac{N}{aD} \int_0^{\infty} \frac{[J_{3/2}(u)]^2}{u^3} \frac{du}{1 + \frac{\omega^2 \tau_t^2}{u^4}} \quad (4.10)$$

where, for mathematical convenience, we have defined  $\tau_t = \frac{a^2}{2D}$ .

Hence we have another, equally valid, expression for the translational correlation time.

For simplicity we make the assumption, realized in the liquids to be discussed later, that molecular motion is rapid, i.e.

$$\tau \ll 1/\omega_0.$$

Equation (4.10) is classical, and we may show [1] that,

$$J(\omega) = J(0) = \frac{2}{15} \frac{N}{aD}$$

$$\text{and } J_1 = \frac{8\pi}{15} J \quad ; \quad J_2 = \frac{32\pi}{15} J$$

so from equation (4.2), for the intermolecular dipolar interaction between like spins,

$$\frac{1}{T_{1 \text{ inter}}} = \frac{4\pi N \gamma^4 \hbar^2 I(I+1)}{15 a D} \quad (4.11)$$

Hubbard [6] has made a correction for the effect of rotation on the intermolecular interaction. He allows for the nuclei not being at the centre of a spherical molecule. A smaller distance of closest approach is also possible. He finds, for spins  $\frac{1}{2}$ ,

$$\frac{1}{T_{1 \text{ inter}}} = \frac{12}{5} \pi \hbar^2 \gamma^4 \frac{N}{aD} \left[ 1 + 0.233 \left(\frac{b}{a}\right)^2 + 0.15 \left(\frac{b}{a}\right)^4 + \dots \right] \quad (4.12)$$

where  $b$  is the distance of the nuclei from the centre of the molecule.

In terms of  $\tau_t = \frac{a^2}{2D}$ , this is,

$$\frac{1}{T_{1 \text{ inter}}} = \frac{24\pi}{5} k^2 \gamma^4 \frac{N}{a^3} \left[ 1 + 0.233 \left(\frac{b}{a}\right)^2 + 0.15 \left(\frac{b}{a}\right)^2 + \dots \right] \tau_t. \quad (4.13)$$

#### IV.6 Relaxation by the spin-rotation interaction.

This interaction is between nuclear magnetic moments and magnetic fields produced at the positions of the nuclei by rotation of the molecule. Molecules are distributions of electric charge and their rotations cause time dependent magnetic fields due to the time dependence of their angular velocities.

The interaction was first considered for relaxation in hydrogen gas [7]. The effect of the molecular collisions is greater on the rotational angular momentum,  $\underline{J}$ , than on the spins.  $\underline{J}$  is sensitive to the strong electric forces acting during a collision. Spins of one half, at least, are sensitive only to the much weaker magnetic fields. Recently it was realized that this interaction is important also for liquids, particularly near the critical point [8].

Consider a molecule, with moment of inertia  $I_0$  about a given axis, rotating about that axis with angular velocity  $\omega$ . The magnetic field produced by rotation at the site of the  $i$ th nucleus will be proportional to  $\omega$ . Let this field be  $H_r(t)$ . It will be time dependent through the time dependence of  $\omega$ .

The interaction Hamiltonian for the nucleus is,

$$\hbar \mathcal{H}_{sr} = -\underline{\mu}_i \cdot \underline{H}_r(t) = -\hbar \gamma \underline{I} \cdot \underline{H}_r(t) \quad (4.14)$$

$$\begin{aligned} \text{or } \mathcal{H}_{sr} &= -\gamma [I_x H_{rx} + I_y H_{ry} + I_z H_{rz}] \\ &= -\gamma \left[ \frac{1}{2} I_+ H_{r-} + \frac{1}{2} I_- H_{r+} + I_z H_{rz} \right]. \end{aligned}$$

Writing  $\mathcal{H}_{sr}$  in the expansion used before,

$$\mathcal{H}_{sr} = \sum_q A^{(q)} F^{(q)}(t)$$

and making the following identities,

$$\left. \begin{aligned} A^{(0)} &= I_z & F^{(0)} &= -\gamma H_{rz} \\ A^{(1)} &= I_+ & F^{(1)} &= -\frac{1}{2}\gamma H_{r-} \\ A &= I_- & F &= -\frac{1}{2}\gamma H_{r+} \end{aligned} \right\} \quad (4.15)$$

Operating on  $I_z$  by equation (3.13) and taking the trace, gives,

$$\frac{dI_z}{dt} = -\frac{1}{2} \sum_q J_q(\omega^{(q)}) \text{Tr} \left\{ [A^{(-q)}, [A^{(q)}, I_z]] (\rho' - \rho'_0) \right\} \quad (4.16)$$

where  $\omega^{(0)} = 0$ ;  $\omega^{(1)} = \omega$  and  $\omega^{(-1)} = -\omega$ .

$$\omega = \gamma H_0.$$

Substituting equation (4.15) into equation (4.16) gives

$$\begin{aligned} \frac{dI_z}{dt} &= -J_1(\omega) \text{Tr} \left\{ [I, [I_+, I_z]] (\rho' - \rho'_0) \right\} \\ &= 2J_1(\omega) (I_{z0} - \bar{I}_z) \end{aligned}$$

$$\text{where } J_1(\omega) = \frac{\gamma^2}{4} \int_{-\infty}^{\infty} \overline{H_{r+}(t) H_{r-}(t+\tau)} \exp(-i\omega\tau) d\tau$$

where the bar denotes the time average. But,

$$\overline{H_{r+} H_{r-}} = \frac{2}{3} \overline{H_r^2}$$

and if we assume the correlation function for  $H_r(t)$  is exponential with

time constant  $\tau_{sr}$ , i.e.,

$$H_r^*(t) H_r(t+\tau) = |H_r|^2 \exp\left(\frac{-|\tau|}{\tau_{sr}}\right)$$

we have  $J_1(\omega) = \frac{\gamma^2 \overline{H_r^2}}{3} \tau_{sr}$ .

$T_1$  is given by the equation,  $\frac{d\bar{I}_z}{dt} = \frac{I_{z0} - \bar{I}_z}{T_1}$ .

So from equation (4.14) we have,

$$\frac{1}{T_{1sr}} = \frac{2}{3} \gamma^2 \overline{H_r^2} \tau_{sr}. \quad (4.18)$$

We wish now to make contact with the usual form of the interaction, between a nuclear spin  $I$ , and the molecular angular momentum,  $J$ .

i.e.  $\mathcal{H}_{sr} = - \underline{I} \cdot \underline{c} \cdot \underline{J}$  (4.19)

where  $\underline{c}$  is the spin-rotation constant, in general a tensor quantity.

By comparing equations (4.14) and (4.19), we find,

$$\overline{H_r^2} = \frac{(\underline{c} \cdot \underline{J})^2}{\gamma^2}. \quad (4.20)$$

Both  $\underline{c}$  and  $\underline{J}$  have their frame of reference fixed in the molecule, and,

$$(\underline{c} \cdot \underline{J})^2 = c_{xx}^2 J_{xx}^2 + c_{yy}^2 J_{yy}^2 + c_{zz}^2 J_{zz}^2$$

For a sphere,  $\overline{J_{xx}^2} = \overline{J_{yy}^2} = \overline{J_{zz}^2} = \frac{1}{3} \overline{J^2}$ .

Also we write  $I_0 \omega = \hbar J$ .

although the assumption of quantized rotation must be regarded as an approximation.

Assuming equipartition of energy among three degrees of freedom,

$$\frac{1}{2} I_0 \omega^2 = \frac{3}{2} kT$$

Also  $c$  may be written in terms of its diagonal elements,

$$c^2 = c_{xx}^2 + c_{yy}^2 + c_{zz}^2.$$

Finally, from equation, (4.18) ,

$$\frac{1}{T_{1\text{ sr}}} = \frac{2}{3} \frac{I_0 kT}{\hbar^2} (c_{xx}^2 + c_{yy}^2 + c_{zz}^2) \tau_{\text{sr}}.$$

From equation (4.20) ,

$$\overline{H_r^2} = \frac{\overline{\omega^2} I_0^2}{3\hbar^2 \gamma^2} (c_{xx}^2 + c_{yy}^2 + c_{zz}^2)$$

so the mean square fluctuating field  $H_r^2$  depends on a quantity  $\frac{I_0^2 c^2}{\gamma^2}$

and not  $c^2$  alone. This is confirmed for the cases of protons in  $H_2$  and

HD and for deuterons in HD and  $D_2$ . We expect  $H_r^2/\omega^2$  to be the same in

all four cases and that  $\frac{I_0^2 c^2}{\gamma^2}$  is also constant. In fact  $c^2$  has

been measured for these cases [9] and  $\frac{I_0^2 c^2}{\gamma^2}$  , in the appropriate

units, equals 13,000, 12,900, 13,500 and 13,700 respectively.

Hubbard [10] has made a more rigorous calculation, beginning only

with the interaction

$$H_{\text{sr}} = -\underline{I} \cdot \underline{c} \cdot \underline{J}.$$

He finds, for a spherical molecule,

$$\frac{1}{T_{1\text{ sr}}} = \frac{2}{3} \frac{I_0 kT}{\hbar^2} (2c_{\perp}^2 + c_{\parallel}^2) \tau_{\text{sr}} \quad (4.21)$$

where  $c_{\perp} = c_{xx} = c_{yy}$  ;  $c_{\parallel} = c_{zz}$  .

A necessary condition for equation (4.21) to hold is that,  $\tau_{\text{sr}} \ll \tau_d$

It seems quite plausible that a molecule in a liquid should undergo many collisions and hence many changes in its angular velocity, before it can reorient by an appreciable amount. For a gas  $\tau_{sr}$  is an average time between collisions, and  $\tau_d$  is likely to be the same order of magnitude.

Brown, Gutowsky and Shimomura [11] have derived a model for the spin-rotation interaction in liquid  $\text{CH}_2\text{FCl}_2$ . Here the molecule is postulated to make a sudden jump from one orientation to a new uncorrelated orientation at a random moment. Thus the spin-rotation field at the nucleus is "pulsed". The pulses are separated by an average time  $\tau_d$ . Let the length of the pulse be  $\Delta$  and let us write,  $\frac{\Delta}{\tau_d} = q$ . For a gas,  $q$  is of order unity. For a liquid,  $q$  is a measure of the "quenching" of molecular rotation in a liquid.

Let us consider a molecule in a liquid rotating with angular velocity  $\omega_1$ , about a fixed axis. After time  $\tau_{sr}$  suppose it has turned through an angle  $\theta_1$ , then,

$$\theta_1 = \omega_1 \tau_{sr}$$

After another average time  $\tau_{sr}$ , with angular velocity  $\omega_2$  it will trace out an angle,

$$\theta_2 = \omega_2 \tau_{sr}$$

Hence we may write, after some time  $t$ ,

$$\sum_i \theta_i^2 = \left[ \sum_i \omega_i^2 \right] \tau_{sr}^2.$$

In time  $t$ , there will on average be  $n$  changes in  $\omega$ , where  $n = \frac{t}{\tau_{sr}}$ .

Hence the mean total square angle of rotation is

$$\begin{aligned} \sum_i \theta_i^2 = \bar{\theta}^2 &= \frac{\sum_i \omega_i^2}{n} n (\tau_{sr})^2 \\ &= \bar{\omega}^2 t \tau_{sr}. \end{aligned}$$

When the orientation of the molecule has changed appreciably, say by

one radian,  $t = \tau_d$

$$\text{and } \tau_d \tau_{sr} = \frac{1}{\bar{\omega}^2},$$

$$\text{but, } \frac{1}{2} I_0 \bar{\omega}^2 = \frac{1}{2} kT$$

by equipartition, if only one axis is allowed.

Thus,

$$\tau_d \tau_{sr} = \frac{I_0}{kT}.$$

If rotation is allowed about any axis,  $\bar{\theta}^2$  is increased by a factor

two or three. Also  $\frac{1}{2} I_0 \bar{\omega}^2 = \frac{3}{2} kT$

$$\text{so that } \tau_d \tau_{sr} = \frac{I_0}{n kT}, \quad \text{where } 6 < n < 9 \quad (4.22)$$

A derivation such as this is not at all rigorous, but the result agrees with a more precise calculation made by Hubbard, [10]. He states  $n = 6$ .

From equation (4.22) we see that  $\tau_{sr}$  has an opposite temperature dependence to  $\tau_d$ . Correspondingly  $T_{1\ sr}$  has an opposite temperature dependence to  $T_{1\ intra\ dipolar}$  as has been found experimentally in many liquids [8, 12, 13, 14, 15].

CHAPTER IV. REFERENCES

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CHAPTER V.RESULTSV.1 Introduction

Measurements of the proton spin-lattice relaxation time,  $T_1$ , in liquid benzene, liquid 1, 3, 5 trideuterobenzene and liquid bromobenzene are reported. (Figures 5.1, 5.2 and 5.3). Also shown are proton  $T_1$ 's for various solutions of known concentration of these liquids in their perdeuterated analogues.  $x$  is the molar fraction of the protonated molecule. We discuss the results of a search for a possible intermolecular spin-rotation effect.

Benzene was chosen because it has been the subject of many N.M.R. investigations [1, 2, 3, 7, 12] It is a relatively simple "classical" liquid, with well known properties. 1, 3, 5 trideuterobenzene is virtually identical to benzene in its common physical and chemical properties, but its nuclear magnetism is changed radically, and in a simple manner. Bromobenzene has a similar arrangement of protons to benzene, but we expect the motion of its larger molecules to be different.

For benzene and 1, 3, 5 trideuterobenzene and their solutions, measurements were made from the lowest possible supercooled temperature to just below the critical temperature. Measurements on bromobenzene and its solutions were made from the supercooled liquid to about 60°C. The reasons for the low upper limit will be discussed later. All

relaxation times are plotted on a logarithmic scale against  $10^3/T$  where  $T$  is the absolute temperature. This tends to produce a straight line plot for dipolar interactions, the most common relaxing mechanism, especially at lower temperatures. An explanation may be given as follows. We normally write  $T_{1 \text{ inter}}$  in terms of a translational diffusion coefficient  $D$ . Stokes has derived an expression for  $D$  in terms of the liquid viscosity  $\eta$ , i.e.

$$D = \frac{kT}{6\pi a\eta} \quad (5.1)$$

If this expression holds for microscopic particles,

$$T_{1 \text{ inter}} \propto \frac{T}{\eta}.$$

The determination of the reorientational correlation time,  $\tau_d$ , is closely related to the problem encountered in the theory of Debye of dielectric dispersion in polar liquids. He finds [4] a correlation

time, 
$$\tau_D = \frac{4\pi\eta a^3}{kT}$$

Here the function whose correlation time is required is  $\cos\theta$ .

The angular factors of the spacial functions  $F^{(0)}$ ,  $F^{(1)}$ ,  $F^{(2)}$ ,

encountered in nuclear relaxation belong to the spherical harmonic  $Y_2(\theta, \varphi)$ ,

whereas  $\cos\theta$  belongs to  $Y_1(\theta, \varphi)$ . The correlation time of  $Y_l(\theta, \varphi)$

for a sphere in a viscous liquid is [5],

$$\frac{8\pi\eta a^3}{l(l+1)kT}.$$

Hence we have the relationships,

$$\tau_d = \frac{\tau_D}{3} \quad \text{and} \quad \tau_d = \frac{4\pi\eta a^3}{3kT}. \quad (5.2)$$

Thus  $T_{1 \text{ intra}} \propto \tau_d \propto \frac{T}{\eta}$ .

The viscosity may often have an exponential temperature dependence expressed empirically as,

$$\eta = \eta_0 \exp\left(\frac{\Delta E}{kT}\right)$$

where  $\Delta E$  is the so called activation energy, and is independent of temperature. Activation energy may be supposed to represent a potential barrier to some sort of motion, in this case, diffusive motion. So,

$$\ln T_1 \propto \frac{-\Delta E}{kT} + (\ln T - \ln \eta_0).$$

It may be shown that variation of  $(\ln T - \ln \eta_0)$  will be slow compared with  $\frac{\Delta E}{kT}$ . Thus,

$$\ln T_1 \propto -\frac{1}{T}.$$

As the protonated liquids are successively diluted, the average inter proton distance is increased and the corresponding proton dipolar interaction decreased. For benzene and 1, 3, 5 trideuterobenzene it is noticed that for strongly diluted samples at higher temperatures, a more obvious turn over or maximum in  $T_1$  is obtained. Short  $T_1$ 's are often the result of impurities, but this must be discounted here due to the care taken in sample preparation.  $T_1$ 's may also be artificially shortened by exchange between the liquid and vapour phases. The vapour,

above the liquid surface, is mostly out of the r.f. field. Also its relaxation time is short. It is hoped that exchange has been minimized by using sample tubes which have a very narrow constriction between the liquid and vapour [6]. Proton-deuteron exchange, important in other systems [7], is not likely here. Proton relaxation times at room temperature are unchanged by prolonged heating near the critical point.

The maxima could be due to an unexpected behaviour of the dipolar interaction. However the temperature dependence of viscosity for benzene shows no such irregularity. It is assumed that viscosity of 1, 3,5 trideuterobenzene behaves in the same way.

This leaves the explanation that as we progressively reduce the inter dipolar interaction another interaction becomes relatively more important. This new interaction must have an opposite temperature dependence to the dipolar interaction, and is surely the spin-rotation interaction [8,9].

## V.2 Benzene

The results for benzene and solutions of benzene in perdeuterobenzene are shown in figure (5.1). For the pure liquid there is a slight deviation from the straight line at higher temperatures, as has been noticed previously [6]. As  $x$  is reduced the point at which the deviation becomes obvious occurs at lower temperatures. For none of the samples is a

distinct maximum seen.

Figure (5.4) shows a typical plot of  $1/T_1$  experimental against molar fraction,  $x$ , at  $20^\circ\text{C}$ .

The relaxation time in a mixture is,

$$\frac{1}{T_1 x} = \frac{1}{T_1 \text{ intra}} + \frac{x}{T_1 \text{ inter H-H}} + \frac{1-x}{T_1 \text{ inter H-D}} \quad (5.3)$$

where  $T_1 \text{ intra}$  is the relaxation time due to all intramolecular interactions.  $T_1 \text{ inter H-H}$  is the intermolecular relaxation time for pure benzene.  $T_1 \text{ inter H-D}$  is the relaxation time of protons in a benzene molecule entirely surrounded by perdeuterobenzene molecules. Being able to add the transition probabilities,  $1/T_1$ , in equation (5.3) presupposes that the corresponding interactions are uncorrelated.

$T_1 \text{ inter H-H}$  and  $T_1 \text{ inter H-D}$  are certainly not independent; they have the same correlation time. Also, intermolecular interactions are contributed to, in small part, by rotations.

By drawing graphs of type figure (5.4) at different temperatures, extrapolating to zero  $x$ , and noting

$$\frac{T_1 \text{ inter H - D}}{T_1 \text{ inter H - H}} = 24,$$

we may calculate the variations of  $T_1 \text{ inter}$  and  $T_1 \text{ intra}$  with temperature. This is shown in figure (5.5). The correctness of these graphs depends on the assumption that the type and rate of molecular motion of benzene molecules is unaltered by deuteration or on dilution in perdeuterobenzene.

This is very plausible as the parameters of the liquids which are dependent on molecular motion are very similar. It has been shown that the deuteron relaxation time at constant temperature for solutions of perdeuterobenzene in benzene is independent of molar fraction [10]. Thus  $\tau_d$  is independent of molar fraction. It is reasonable to assume the same for  $\tau_t$ .

The increase in viscosity of benzene on deuteration is about 6% at 25°C [11], and this has been taken into account in calculating the results shown in figure (5.5). The effect is strongest at lower temperatures but barely affects  $T_1$  inter. This change of viscosity has been measured at only three temperatures and figure (5.6) shows an estimate of how  $\left[ \frac{\eta_{C_6D_6}}{\eta_{C_6H_6}} - 1 \right]$  changes with temperature. These are likely to be different from the true curves by a very small amount.

The temperature dependences of  $T_1$  inter and  $T_1$  intra, figure (5.5), are widely different.  $T_1$  inter rises nearly linearly with an activation energy of 3.0 kcal.Mole<sup>-1</sup>.  $T_1$  intra rises less sharply with an activation energy of 1.2 kcal.Mole<sup>-1</sup>. These figures agree with previous measurements made over a small range in temperature, [12]. However at higher temperatures  $T_1$  intra exhibits a possible shallow maximum. Certainly the deviation from the straight line is considerable. At about 190°C. the two contributions to  $T_1$  are equal.

The errors shown in figure (5.5) are calculated as follows.

The best line is drawn for  $1/T_1$  v.  $x$  by the method of least squares.

The mean deviation is calculated and these limits used to define lines with extreme slopes. The difference between intercepts is  $2e$  where  $e$  is the error in  $1/T_1$  at  $x=0$ .

From equation (4.11), putting  $D = \frac{kT}{6\pi a \eta}$ , for spins  $\frac{1}{2}$

$$\frac{1}{T_1 \text{ inter}} = \frac{36}{5k} \pi^2 h^2 \gamma^2 \left( \frac{\eta N}{T} \right) \quad (5.4)$$

and in figure (5.7) we show the effect of removing the temperature dependence of the three quantities on the right hand side, and normalizing to  $25^\circ\text{C}$ . The effect of the viscosity is by far the greatest.

$T_1 \text{ inter}(\eta, T, N)$ , that is with constant  $\eta$ ,  $T$  and  $N$ , varies less than  $T_1 \text{ inter}$  but falls with increasing temperature.  $T_1 \text{ inter}(\eta, N)$  is constant almost to the critical point. Also shown is  $T_1 \text{ inter}(D, N)$  over the range for which  $D$  is available [13]. Another way of looking at this is to note that the activation energies of self diffusion and viscosity are 3.1 and 3.2 kcal.Mole<sup>-1</sup> respectively. It is perhaps not surprising to find close agreement with  $T_1 \text{ inter}$  (activation energy 3.0 kcal.Mole<sup>-1</sup>) as all these processes depend on translational motion. This suggests  $T_1 \text{ inter}$  is predominantly due to translational motion.

In the Hubbard equation for  $T_1 \text{ inter}$ , (equation 4.22) we use for  $d$  the value obtained from the close packing of spheres and the known density at the melting point. This gives  $d = 5.88\text{\AA}$ . Also  $a = d/2$

and  $b = 2.47\text{\AA}$ . We calculate,  $T_1 \text{ inter} = 35 \text{ sec.}$  at  $25^\circ\text{C}$ . This is in reasonable agreement with the experimental value of 27 sec. considering the far from spherical shape of the molecule and the approximations used to calculate  $d$ .

In integrating equation (4.9) we have assumed a uniform radial distribution function for the molecules. That is, the integrand in equation (4.9) should be multiplied by a term  $g(r)$ , which we define

$$\begin{aligned} \text{as } g(r) &= 0 & r < d \\ g(r) &= 1 & r \geq d. \end{aligned}$$

In general the radial distribution function,  $g(r)$ , is not simple [15]. Ideally one would like to evaluate equation (4.9) using the experimental values of  $g(r)$ , but no experimental values are available for benzene. However, one may calculate  $g(r)$  with some confidence [16]. The use of a more realistic radial distribution function results in the lowering of the calculated  $T_1$  by about 15% [16,17]. Thus with this correction we calculate  $T_1 = 30 \text{ sec.}$

From equation (4.13) the translational correlation time,  $\tau_t$ , is  $100 \times 10^{-12} \text{ sec.}$ , but this is very sensitive to the value of the doubtful quantity  $d$ .

Since protons in benzene are near the periphery of the molecule it might be appropriate to consider each interaction with nuclei in other molecules as independent. The distance of closest approach

would now be that appropriate to a hydrogen atom in a molecule, i.e. the van der Waals distance,  $d \approx 2.4\text{\AA}$ . The appropriate formula for  $T_1$  inter is now [14],

$$\frac{1}{T_1 \text{ inter}} = \frac{2\pi}{5} N_s \frac{8^4 h^2}{dD}$$

where  $N_s$  is the number of spins per unit volume. This gives

$T_1 \text{ inter} = 18 \text{ sec. at } 2.5^\circ\text{C.}$ , which is in as good agreement with

experiment as that deduced from equation (4.13). The corresponding

correlation time,  $\tau_t'$ , is  $13 \times 10^{-12}$  sec. The motion concerned is

modulation of the neighbouring proton distance rather than the inter-

molecular distance and so is faster than  $\tau_t$ .

Comparison between experimental and theoretical values of  $T_1 \text{ inter}$  is not possible up to the critical temperature, as the value of  $D$  is not known over the whole temperature range.

We assume our derivation of equation (4.16) is valid over the whole temperature range. The deviation of  $T_1 \text{ intra}$  from a straight line to a possible flat maximum then suggests that the reorientational correlation time,  $\tau_d$ , decreases, becomes constant and increases with temperature. This is physically not plausible as we expect molecular motion to quicken considerably over the large temperature range concerned. Incidentally, it has been pointed out that arguments of this sort break down for ethane [18]. In the drastic change from solid ethane to the liquid,  $T_1$  remains

constant. However, this molecule is not rigid and internal rotations may change considerably on melting.  $T_1$  for benzene changes discontinuously through the melting point. We may suppose then that the maximum in  $T_1$  intra is due to the spin-rotation interaction, as discussed previously [6,8].

We write,

$$\frac{1}{T_1 \text{ intra}} = \frac{1}{T_1 \text{ intra d}} + \frac{1}{T_1 \text{ sr}} \quad (5.5)$$

where  $T_1$  intra d is the dipolar part of the intra molecular relaxation time.

For spherical molecules the spin-rotation contribution to  $T_1$  is given by

$$\frac{1}{T_1 \text{ sr}} = \frac{2}{3} \frac{I_0 k T}{\hbar^2} (2C_L^2 + C_{\parallel}^2) \tau_{\text{sr}}. \quad (5.6)$$

We also use the Hubbard relationship

$$\tau_d \tau_{\text{sr}} = \frac{I_0}{6kT}. \quad (5.7)$$

Then from equations (5.5), (5.6), (5.7) and (4.6),

$$\frac{1}{T_1 \text{ sr}} \times \frac{1}{T_1 \text{ intra d}} = \frac{\hbar^2}{6} \gamma^4 I_0^2 \left( \sum r_{ij}^{-6} \right) (2C_L^2 + C_{\parallel}^2) = B \quad (5.8)$$

which is a constant, independent of temperature, for a given molecule.

From equation (5.8) a necessary condition is that the slopes of  $T_1$  sr and  $T_1$  intra d, against the temperature, are equal and opposite. Also, at the maximum of  $T_1$  intra,

$$T_1 \text{ sr} = T_1 \text{ intra d} = 2 T_1 \text{ intra} \quad (5.9)$$

from which B is obtained. Equation (5.9) is not wholly independent of (5.8) but depends on the two slopes being equal and opposite over the region of the maximum. We may solve equations (5.8) and (5.9) for  $T_{1 \text{ intra d}}$  and  $T_{1 \text{ sr}}$ , shown in figure (5.8). Both  $T_{1 \text{ intra d}}$  and  $T_{1 \text{ sr}}$  have straight line plots not demanded by the equations. The activation energy of  $T_{1 \text{ intra d}}$  is now 1.84 kcal.Mole<sup>-1</sup>, in excellent agreement with the deuterium  $T_1$  activation energy of 1.86 kcal.Mole<sup>-1</sup> in heavy benzene [19,20]. The activation energy for Rayleigh light scattering (that is, from electrons bound in the molecule and which depends on molecular reorientation through the reorientation of the optical polarizability tensor) is 1.35 kcal.Mole<sup>-1</sup> [21].

For deuterium quadrupolar relaxation the spin-lattice relaxation time is given by,

$$\frac{1}{T_{1Q}} = \frac{3}{8} \left( \frac{e^2 q Q}{h} \right)^2 \tau_Q$$

where Q is the electric field gradient at the site of the nucleus concerned.  $\tau_Q$  is a correlation time corresponding to reorientation of a vector parallel to this gradient.

For isotropic reorientation,

$$\tau_Q = \tau_d.$$

From the deuterium relaxation time in perdeuterobenzene [20] we may

calculate the quadrupole coupling constant,  $\frac{e^2 q Q}{h^2} = 200 \text{ kc/s.}$

This quantity has also been measured, independently, from the splitting of the broad line N.M.R. spectrum in solid perdeuterobenzene, as 193 kc/s [22]. It is not likely that the coupling constant changes on freezing.

$Q$  is an intramolecular parameter and will depend on molecular size and configuration. Thus we have good agreement and  $\tau_d$ , calculated from

$T_1$  intra d is confirmed over a large temperature range.

In figure(5.9) is shown the variation of the various correlation times with temperature. Also shown is an independent measurement of  $\tau_d$  found from Raman broadening effects [23]. At 25°C.,  $\tau_d < \tau_t$ . This is consistent with the relative magnitudes of the activation energies. One is tempted to use the symmetry of the molecule to explain these differences in correlation time and activation energy and to imagine easy reorientation about the hexad axis. At higher temperatures,  $\tau_{sr}$  approaches  $\tau_d$  as has been noticed for other liquids [6]. The Hubbard relation is rigorously true only for  $\tau_{sr} \ll \tau_d$ . Let us assume for lack of further information that it remains true even if  $\tau_{sr} \approx \tau_d$ . With the value of  $\tau_{sr}$  calculated from  $\tau_d$  via equation (5.7), we may find a value for  $(2C_{\perp}^2 + C_{\parallel}^2)$  from equation (5.6).

We find  $(2C_{\perp}^2 + C_{\parallel}^2) = (3.8 \text{ kc/s})^2$ .

This is a large value; although benzene is a moderately large molecule.

$c$  can be measured for only a few molecules as the splitting of the spectrum in a molecular beam experiment has to be completely resolved. The

interaction, however, does cause line broadening from which the quantity  $(2C_{\perp} + C_{\parallel})$  may be found. In general this does not give a good estimate of  $(2C_{\perp}^2 + C_{\parallel}^2)$ , since  $C_{\perp}$  and  $C_{\parallel}$  may be of different sign. Ramsey [24] estimates  $(2C_{\perp}^2 + C_{\parallel}^2) < 1$  for benzene. This discrepancy may well be a manifestation of the fact that we are using equation (5.6) for a non-spherical molecule. It has been found for other non-spherical molecules that the factor 6 in equation (5.7) should be replaced by a factor of order unity [7, 25]. A large value of the spin-rotation constant may suggest that the factor 6 is too large for benzene.

### V.3. 1, 3, 5 trideuterobenzene

The experimental proton relaxation times for 1, 3, 5 trideuterobenzene ( $C_6H_3D_3$ ) and for solutions of trideuterobenzene in perdeuterobenzene are shown in figure (5.2). Here the maxima in  $T_1$  are well defined and also move towards lower temperatures in increasing dilution. That protons are not intramolecular nearest neighbours is reflected in the long  $T_1$ 's.

For a sample of protonated molar fraction  $x$ , the measured  $\frac{1}{T_1}$ ,

$$\frac{1}{T_1} = \frac{1}{T_1 \text{ intra}} + \frac{x}{T_1 \text{ inter H} \rightarrow \text{3H+3D}} + \frac{1-x}{T_1 \text{ inter H} \rightarrow \text{6D}} \quad (5.10)$$

and a typical plot, at 20°C. of  $1/T_1$  v.  $x$  is shown in figure (5.10).

$T_{1 \text{ inter H-3H+3D}}$  is the intermolecular contribution in pure  $C_6H_3D_3$  and

$T_{1 \text{ inter H-6D}}$  is the intermolecular interaction for a  $C_6H_3D_3$  molecule entirely surrounded by molecules of  $C_6D_6$ .

Equation (5.10) may be rewritten,

$$\frac{1}{T_{1x}} = \frac{1}{T_{1 \text{ intra}}} + \frac{x}{T_{1 \text{ inter H-3H}}} + \frac{x}{T_{1 \text{ inter H-3D}}} + \frac{1-x}{T_{1 \text{ inter H-6D}}}$$

where  $T_{1 \text{ inter H-3H}}$  is the relaxation time for interactions between protons.  $T_{1 \text{ inter H-3D}}$  is due to the interaction between protons and deuterons in  $C_6H_3D_3$  molecules. But,

$$T_{1 \text{ inter H-6D}} = \frac{1}{2} T_{1 \text{ inter H-3D}}$$

as a group of three deuterons in a molecule will have the same intermolecular interaction with a proton whether they be on a  $C_6D_6$  molecule or a  $C_6H_3D_3$  molecule. Thus,

$$\frac{1}{T_{1x}} = \frac{1}{T_{1 \text{ intra}}} + \frac{x}{T_{1 \text{ inter H-3H}}} + \frac{2-x}{T_{1 \text{ inter H-3D}}}$$

We solve for  $T_{1 \text{ intra}}$  and  $T_{1 \text{ inter}}$ , noting that,

$$\frac{T_{1 \text{ inter H-3D}}}{T_{1 \text{ inter H-3H}}} = 24$$

and present their temperature dependence and errors, calculated as previously discussed, in figure (5.11).

As before, the variations of the two contributions are widely different.  $T_{1 \text{ inter}}$  rises sharply with an activation energy of 3.0 kcal.Mole<sup>-1</sup>.  $T_{1 \text{ intra}}$  is virtually constant within experimental

error, but may exhibit a very shallow maximum.

Using the argument given previously, we do not expect  $\tau_d$  to remain constant over this extreme temperature range, as implied by the  $T_{1 \text{ intra}}$  curve. The best line through the experimental points exhibits a maximum of 400 sec. at about  $70^\circ\text{C}$ . Calculating a value of B as before we may decompose this curve into the two components  $T_{1 \text{ intra d}}$  and  $T_{1 \text{ sr}}$ , as shown in figure (5.12). Again each line is straight, within experimental error, not demanded by the equations.  $T_{1 \text{ intra d}}$  rises with activation energy  $1.9 \text{ kcal.Mole}^{-1}$ . At  $25^\circ\text{C}$ .,  $T_{1 \text{ intra d}} = 500 \text{ sec}$ .  $T_{1 \text{ sr}}$  is larger than that found for benzene. The increase ranges from 20% at room temperature to 8% near the critical temperature.

At  $25^\circ\text{C}$ . we may calculate a value for  $T_{1 \text{ intra d}}$  for  $\text{C}_6\text{H}_3\text{D}_3$  using a value of  $\tau_d$  obtained from  $T_{1 \text{ intra d}}$  for  $\text{C}_6\text{H}_6$  at the same temperature. It is likely that molecular reorientation is only slightly changed on trideuteration. We must add the proton-deuteron, proton-proton intramolecular interactions, assuming that internuclear distances remain unchanged on deuteration. The proton-deuteron interaction is marginally the stronger.

We calculate at  $25^\circ\text{C}$ .,  $T_{1 \text{ intra d}}' = 1140 \text{ sec}$ . That is, more than a factor two greater than the measured value.

Setting aside questions of errors in  $T_{1 \text{ intra d}}$  let us consider possible causes of relaxation other than the expected proton-deuteron,

proton-proton interactions. The calculated relaxation time is so long that a small interaction, normally neglected, may be important. Worthy of consideration is the dipolar interaction between protons and carbon 13 nuclei which have  $\gamma = 0.67 \times 10^4 \text{ gauss}^{-1} \text{ sec.}^{-1}$  and  $I = \frac{1}{2}$ . The natural abundance of  $C^{13}$  is only 1.1% but the short length of the H-C bond ( $1.08 \text{ \AA}$ ) makes the intramolecular contribution significant. Thus 1.1% of the protons in a sample of  $C_6H_3D_3$  will, in addition to interactions with other protons and deuterons, experience relaxation due to the nearest neighbour  $C^{13}$  nucleus. This small minority of protons will have short  $T_1$ 's and the remaining 98.9% will have longer  $T_1$ 's. If one could measure the intramolecular contribution directly, one would expect to see non-exponential decay.

In a sample of 100  $C_6H_3D_3$  molecules, the magnetization of slowly relaxing protons varies as

$$M'_Z = 98.9 \left[ 1 - \frac{t}{T_1'} + \frac{t^2}{2T_1'^2} - \dots \right].$$

For the rapidly relaxing protons,

$$M''_Z = 1.1 \left[ 1 - \frac{t}{T_1''} + \frac{t^2}{2T_1''^2} - \dots \right].$$

So the actual decay seen is,

$$M_Z = 100 \left[ 1 - t \left( \frac{98.9}{T_1'} + \frac{1.1}{T_1''} \right) + \dots \right].$$

and the apparent relaxation time is given, to the first approximation, by,

$$\frac{1}{T_1} = \frac{98.9}{T_1'} + \frac{1.1}{T_1''}$$

For  $C_6H_3D_3$  we now calculate,  $T_1 \text{ intra d} = 1000 \text{ sec.}$

Let us consider relaxation caused by intermolecular dipolar interactions with protonated impurities in  $C_6H_3D_3$  and  $C_6D_6$ . In the former case the interaction is extrapolated to zero, at  $x = 0$ . In the latter, our  $C_6D_6$  was better than 99% pure; whether this is atomic or molar purity is immaterial to the intermolecular interaction. It is interesting to consider the effect of a 0.05% impurity of  $C_6H_6$  in  $C_6D_6$ . (The smallest amount detectable by mass spectroscopic means is 0.1% [26]). This alters the derived  $T_1 \text{ intra}$  line as shown in figure(5.13) increasing  $T_1 \text{ intra}$  most strongly at lower temperatures. The derived  $T_1 \text{ intra d}$  now has activation energy  $1.7 \text{ kcal.Mole}^{-1}$  but equals 620 sec. at room temperature.

Intermolecular interactions with  $C^{13}$  nuclei are negligible due to the increased distance of closest approach.

If  $C_6H_3D_3$  contains as impurity a benzene derivative with adjacent protons, then its apparent  $T_1 \text{ intra}$  will be shortened. Part of its signal will be provided by rapidly relaxing protons. An analysis by the manufacturers gave 99.5% chemical purity, for  $C_6H_3D_3$ , by vapour phase chromatography. Mass spectroscopy gave 95.8%  $d_3$ , 3.0%  $d_4$ , 1.2%  $d_2$ . Isomers cannot be detected by mass spectroscopy so it is reasonable to expect a significant percentage of protons to have protons as nearest neighbours. However, the effect on the calculated  $T_1 \text{ intra d}$  will still

be no more than about 10%. The final difference between experiment and theory for  $T_1$  intra d cannot be explained.

#### V.4 Bromobenzene.

The experimental proton  $T_1$ 's for bromobenzene and for solutions of bromobenzene in perdeuterobromobenzene are shown in figure (5.3). The lower temperature limit is the supercooled liquid freezing point. The upper temperature limit marks the onset of anomalous lowering of the  $T_1$  values. The results are wholly consistent with a permanent chemical change occurring with prolonged heating. In some cases a brown deposit on the walls of the sample tube was noticed. After heat damage, relaxation times are shortened over the whole temperature range. A similar effect has been noticed for deuterium  $T_1$ 's in  $C_6D_5Br$  [27]. The temperature range for the sample  $x = 0.19$  is limited due to the poor signal to noise ratio, (about 6:1).

The experimental lines show no tendency to curve. One may expect a possible spin-rotation interaction to be small for a heavy molecule far from its critical temperature (397°C.).

For molar fraction  $x$ , the measured relaxation time,  $T_{1x}$ , is given by,

$$\frac{1}{T_{1x}} = \frac{1}{T_{intra}} + \frac{x}{T_{inter H-H}} + \frac{1-x}{T_{inter H-D}} + \frac{1}{T_{inter H-Br}}$$

where the symbols have obvious meanings. A typical plot of  $1/T_1$  against  $x$  is shown in figure (5.14). The isotope  $\text{Br}^{79}$  has

$\gamma = 0.67 \times 10^4 \text{ gauss}^{-1} \text{ sec.}^{-1}$  and is 50.57% abundant.  $\text{Br}^{81}$  has

$\gamma = 0.12 \times 10^4 \text{ gauss}^{-1} \text{ sec.}^{-1}$  and is 49.43% abundant. Using an average

value for  $\gamma^2$ , one can show,

$$T_1 \text{ inter H-Br} \approx 5T_1 \text{ inter H-D}$$

and so  $T_1 \text{ inter H-Br}$  may be neglected. The small contribution from bromine in the intramolecular interaction may also be neglected. In figure (5.15) is shown the temperature dependence of  $T_1 \text{ intra}$  and  $T_1 \text{ inter}$ . No correction is made for increase in viscosity on deuteration. No viscosity measurements are available for  $\text{C}_6\text{D}_5\text{Br}$ . The percentage increase in mass and moment of inertia on deuteration for this molecule is much smaller than for the previous two cases, and it is likely that the viscosity effect can be safely neglected.  $T_1 \text{ intra}$  and  $T_1 \text{ inter}$  both rise linearly with activation energy  $2.7 \text{ kcal.Mole}^{-1}$ . The deuteron  $T_1$  in  $\text{C}_6\text{D}_5\text{Br}$  has been measured over the same temperature range [20], and within experimental error an identical activation energy has been found. That  $T_1 \text{ inter}$  and  $T_1 \text{ intra}$  have the same temperature dependence is in direct contrast with the previous two cases. An explanation based on the asymmetry of the molecule is plausible but verification depends on more measurements on asymmetric molecules.

Figure (5.15) also shows the effect on  $T_1 \text{ inter}$  of holding; density

constant,  $T_1 \text{ inter}^{(N)}$ ; density and viscosity constant,  $T_1 \text{ inter}^{(N, \eta)}$ ; and density, viscosity and temperature constant,  $T_1 \text{ inter}^{(N, \eta, T)}$ .

All these "corrections" are normalized to  $-56^\circ\text{C}$ .

Averaging over the intramolecular proton-proton distances, we

calculate, 
$$\frac{1}{T_1 \text{ intra}} = 6.3 \times 10^9 \tau_d.$$

So that  $\tau_d$  varies from  $24 \times 10^{-12}$  sec. at  $-56^\circ\text{C}$ . to  $4.4 \times 10^{-12}$  sec. at  $60^\circ\text{C}$ ., as shown on figure (5.16) together with  $\tau_c$  calculated from equation (4.13). Also shown is the dielectric relaxation time  $\tau_D$ , reduced by a factor 3, for bromobenzene, extrapolated to zero concentration in carbon tetrachloride [28]. Unfortunately, this solute-solvent system is likely to give a value for  $\tau_D$  different from that in the pure liquid.

#### V.5 The Intermolecular Spin-Rotation Interaction.

We cannot calculate  $\tau_{sr}$  for benzene from equation (5.6),

i.e. independent of  $\tau_d$ , as the spin-rotation constant for this molecule has not been measured, although Ramsey [24] claims it to be less than  $(1 \text{ kc/s})^2$ . Thus we cannot examine experimentally the numerical factor

in Hubbard's expression, 
$$\tau_d \tau_{sr} = \frac{I_0}{6RT} \quad (5.11)$$

as has been done for example for HCl [25].

At the maximum of  $T_1 \text{ intra}$ , we have

$$T_1 \text{ intra d} = T_1 \text{ sr} = 2T_1 \text{ intra}^{(\text{max.})},$$

which gives the value for  $T_{1\text{ sr}}$  least dependent on the Hubbard relationship, although the assumption of equal and opposite slopes for  $T_{1\text{ sr}}$  and  $T_{1\text{ intra d}}$ , over the range of the maximum, is still necessary. Using the values of  $T_{1\text{ sr}}$  calculated in this way for water and ammonia, it has been found that the numerical factors for these molecules are 0.5 and 1.4 respectively [9].

Using a value of  $\tau_{\text{sr}}$  from equation (5.11), we calculate a value of  $(3.8 \text{ kc/s})^2$  for the spin rotation constant for benzene. If this figure is too large, it suggests that a larger numerical factor should be used in the Hubbard relationship. For example if

$$\tau_{\text{d}} \tau_{\text{sr}} = \frac{I_0}{kT} \quad (5.12)$$

we find  $(2C_{\perp}^2 + C_{\parallel}^2) \approx (1.5 \text{ kc/s})^2$ , which may be a more reasonable value. It is difficult to attach any great importance to the correctness of equation (5.12), because if it were true,  $\tau_{\text{sr}} > \tau_{\text{d}}$ , which violates Hubbard's basic assumption.

A second possibility is that if the Hubbard relationship is correct and if our value for  $(2C_{\perp}^2 + C_{\parallel}^2)$  is too large we may have overlooked a contribution to the relaxing mechanism. For mobile liquids, i.e. those for which  $\omega_0 \tau_c \ll 1$ ,

$$\frac{1}{T_{1\text{ experimental}}} = \text{interaction} \times \text{correlation time.}$$

For a given experimental  $T_1$  our calculated correlation time is too large

if the interaction is too small. The interaction of interest will have correlation time  $\tau_{sr}$ . One such interaction is the intermolecular spin-rotation interaction. This is due to time dependent magnetic fields at a nuclear site produced by the rotational motion of neighbouring molecules. It has been considered for HCl and is probably negligible in this case [ 25 ] . We seek to show the existence of this interaction experimentally. For protons in benzene the intramolecular spin-rotation interaction is relatively small even at high temperatures, so we expect the corresponding intermolecular interaction to be small also. However, for fluorine relaxation in perfluorobenzene, spin-rotation plays an important role even at room temperature [ 6,8 ]. This liquid exhibits a well defined maximum. At lower temperatures the relaxation is dominated by the dipolar, and at higher temperatures by the spin-rotation interaction. If this latter is wholly intramolecular, reducing the intermolecular interaction by dilution in the usual way will result in increased  $T_1$ 's only at the lower temperatures.

The most suitable available solvent liquids were benzene and perdeuterobenzene. Several solutions of perfluorobenzene in these liquids were made. However, it was found that the mixtures have freezing points well above either of the two constituents, revealing a strong interaction between the constituent molecules. This effect has been noticed previously [ 30 ] and is probably due to strong hydrogen

bonding. For some liquids, e.g. perfluorobenzene and mesitylene, this bonding is so strong that a solid "complex" may be crystallized out of the mixture. It has been pointed out that there is no spectroscopic evidence, e.g. optical absorption, for the existence of this "complex" in the liquid mixture [ 31 ]. This is certainly true for high resolution N.M.R. One finds that the proton spectra for pure benzene and a benzene perfluorobenzene mixture are identical [ 32 ].

Fluorine relaxation times, up to the critical temperature, for perfluorobenzene and for solutions in benzene and perdeuterobenzene are shown in figure (5.17). Results for perfluorobenzene are identical with those obtained previously [ 8 ]. For the solution of  $C_6F_6$  in  $C_6H_6$ , with fluorinated molar fraction,  $x_F = 0.5$ , the fluorine  $T_1$  follows the pure liquid  $T_1$  up to about  $120^\circ C$ . At higher temperatures it is appreciably longer. This is approximately the reverse of the temperature dependence expected if the spin-rotation interaction is wholly intramolecular.

For the solution,  $x_F = 0.22$ , the fluorine  $T_1$  is longer over the whole temperature range. For the case  $x_F = 0.26$ , for perfluorobenzene in perdeuterobenzene,  $T_1$  is shorter at lower temperatures than the same benzene solution; another anomaly.

Obviously the effect of the molecular "complex" interaction is considerable and one cannot expect to solve the initial problem. However, these results may be explained crudely by considering a model for the

complex molecule. The maximum melting point of the mixtures ( $23.7^{\circ}\text{C}.$ ) occurs with molar ratio 1:1. This clearly demonstrates the existence of a 1:1 molecular complex. If we assume only one molecule of each type is involved, then the most likely configuration is that with least potential energy. This will be for a "sandwich" with fluorine and hydrogen atoms as close as possible. For the molar ratio 1:1, the maximum number of complex molecules is likely and the greatest effect will be measured. One would expect the correlation times for these large molecules to be long, so that  $T_1$  is shortened. (This could also be the result of increased nuclear interaction within the complex). This is observed for  $x_F = 0.5$ . For the solution with  $x_F = 0.22$ , the ratio of numbers of complex to benzene molecules is 3:8 and one would expect the effective correlation times to be shorter than for the case  $x_F = 0.5$ .

The corresponding proton  $T_1$ 's are shown in figure (5.18). The same general explanation may be given for these measurements.

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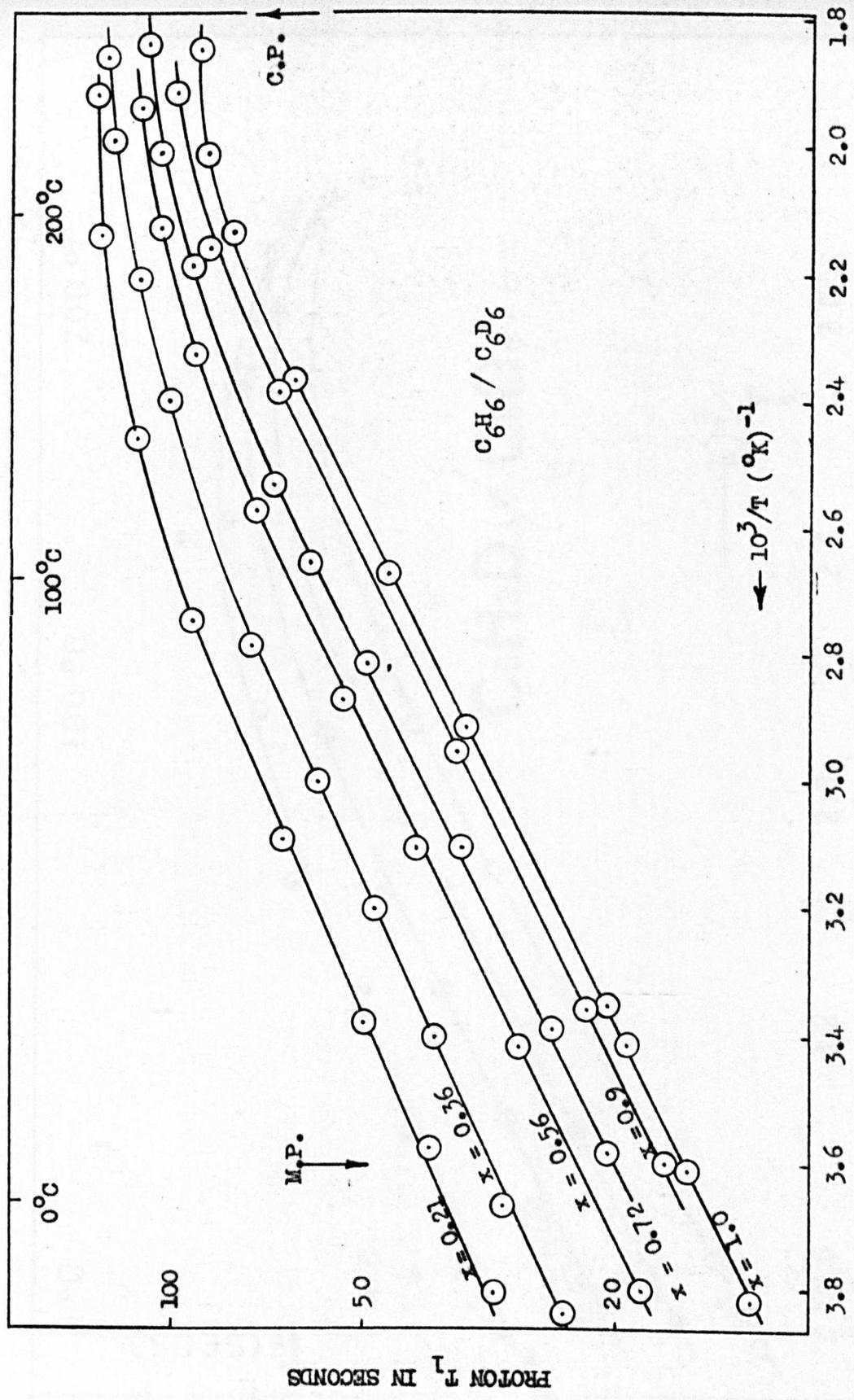


Figure (5.1)

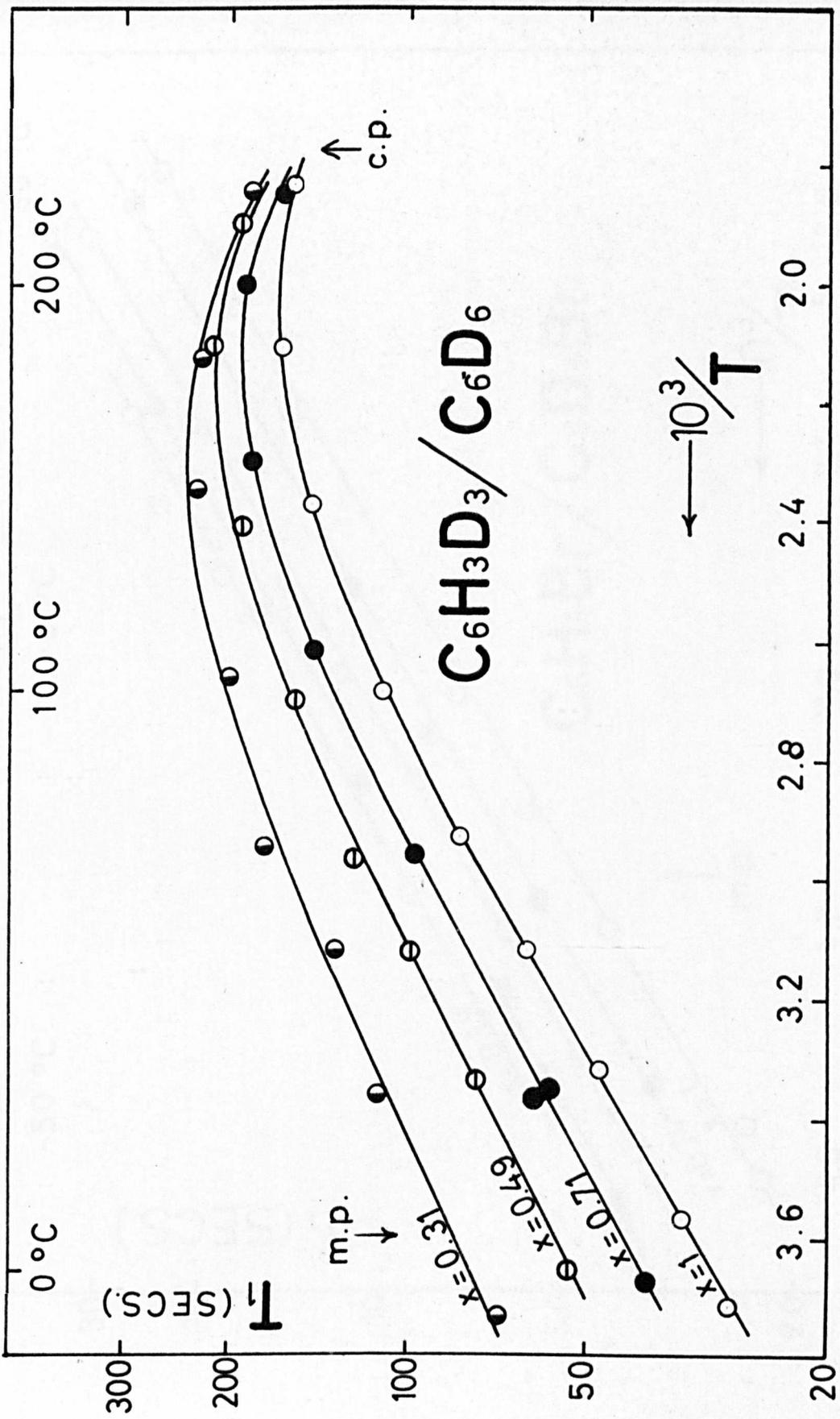


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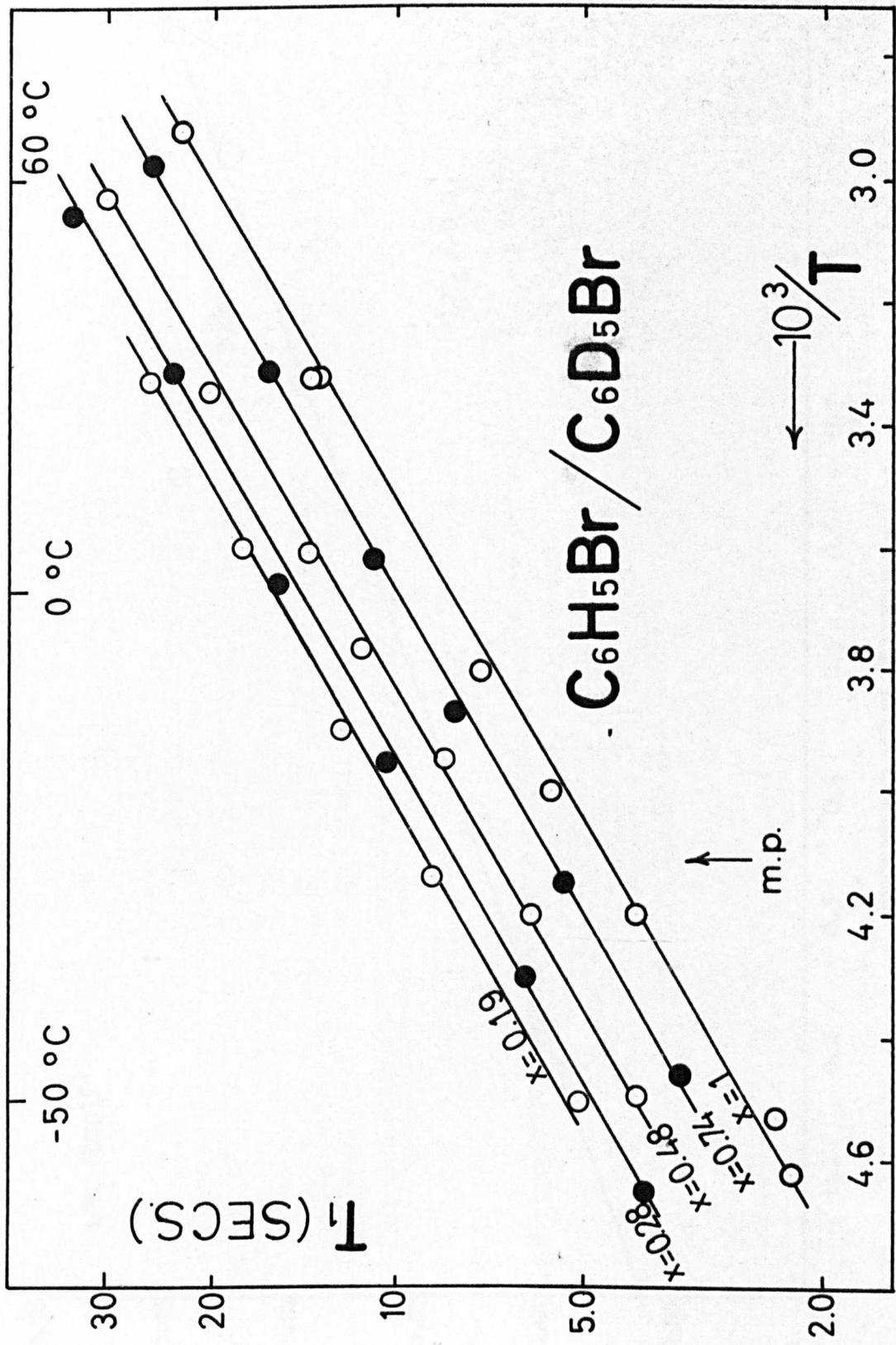


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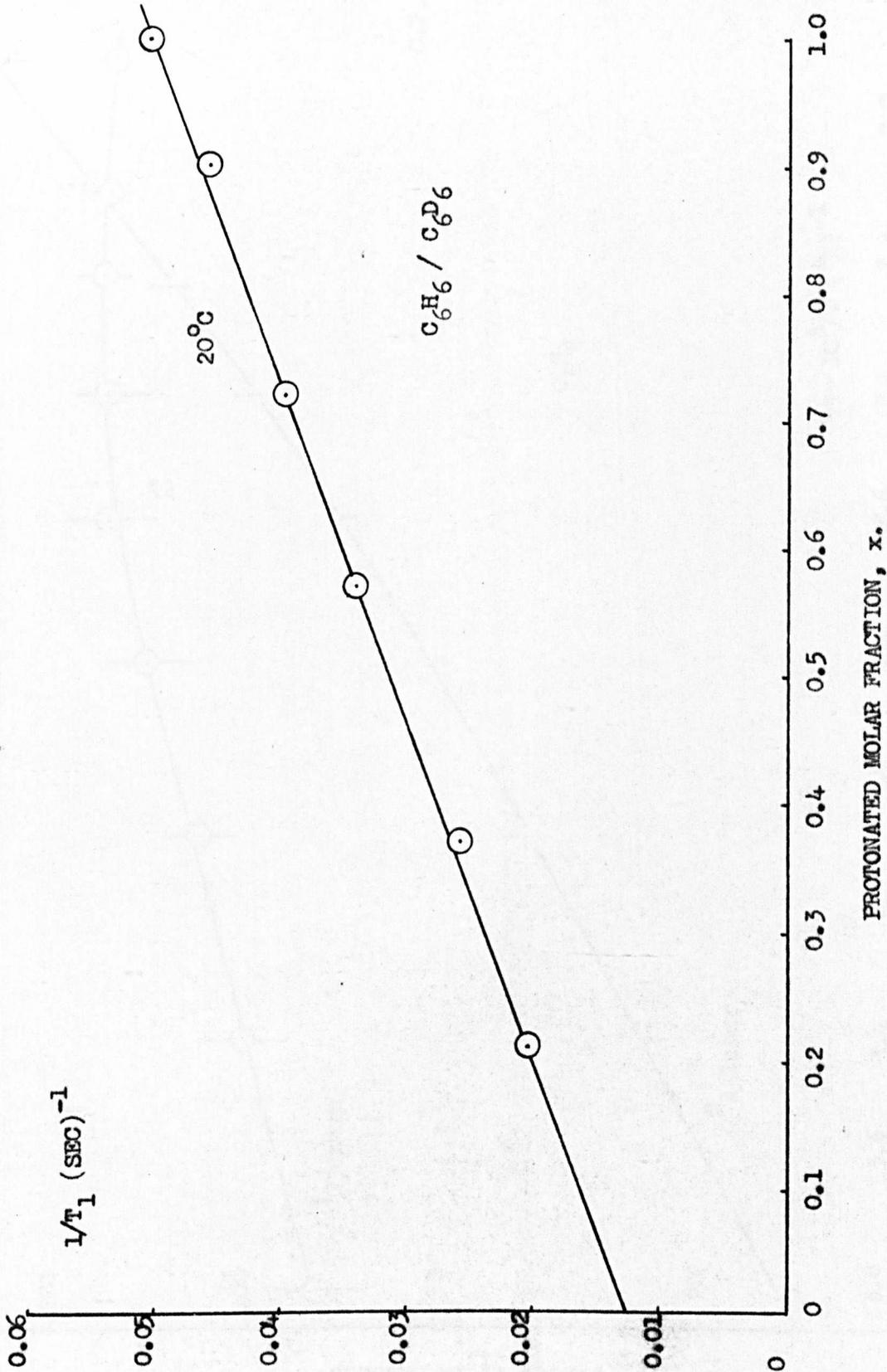


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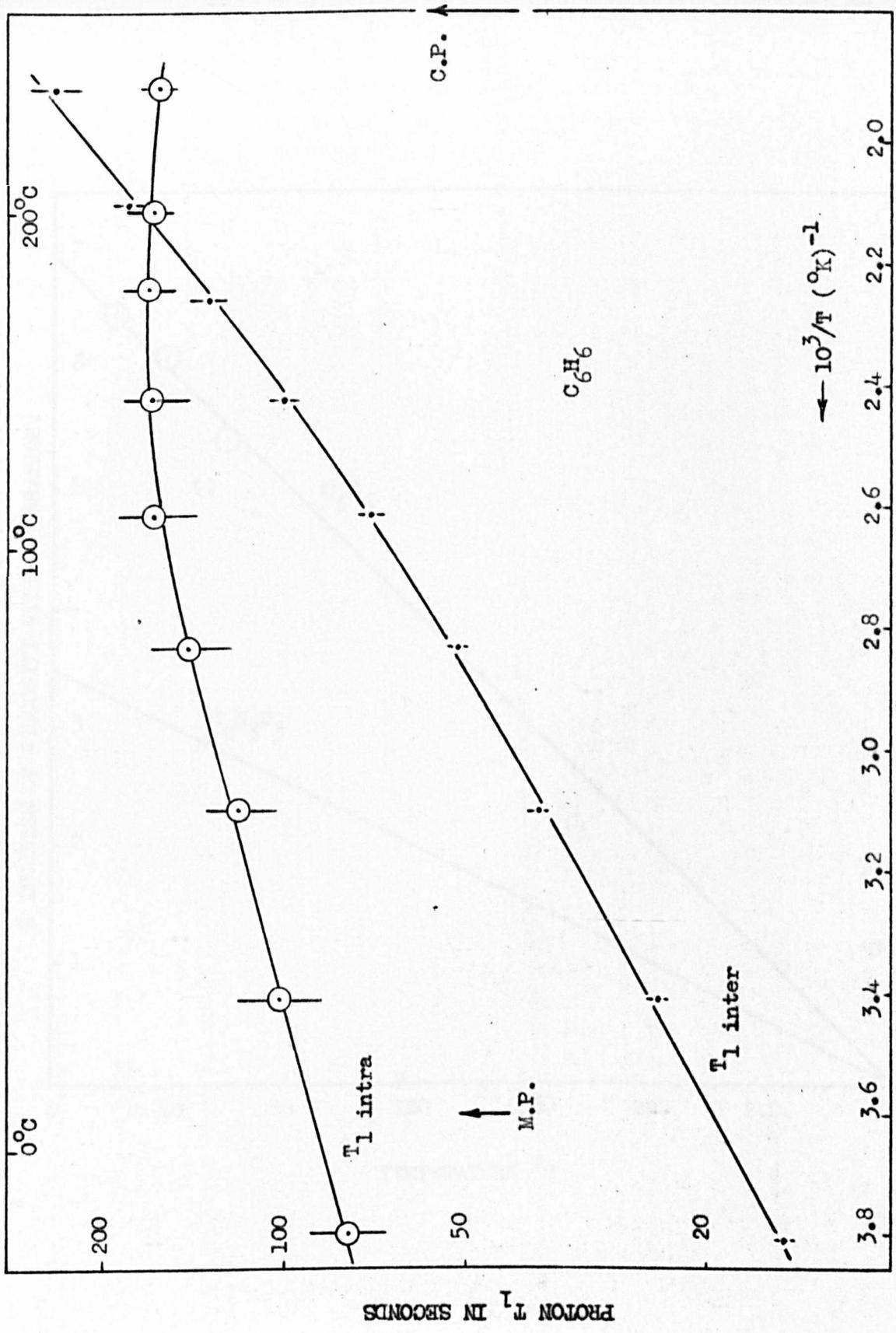


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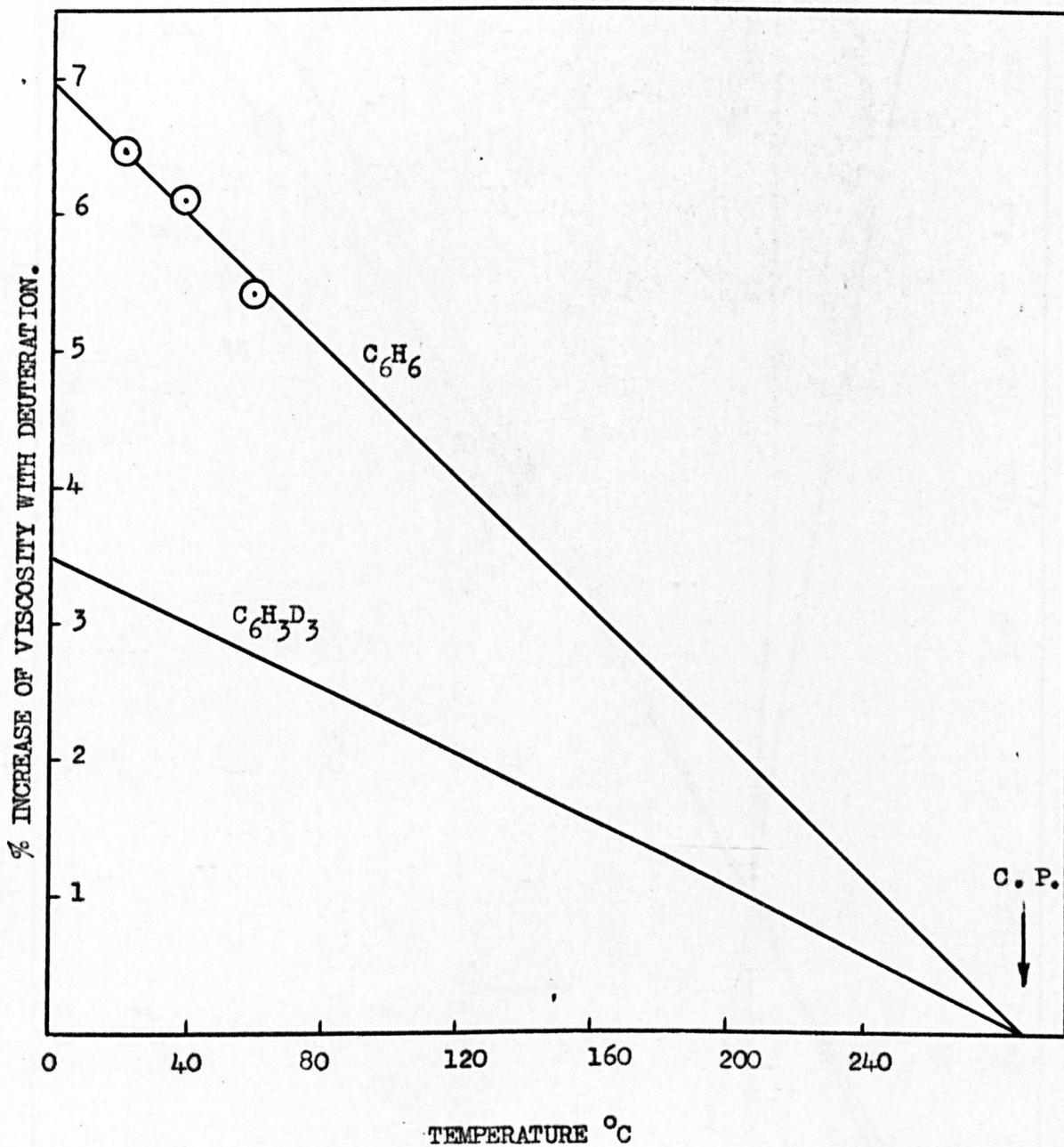


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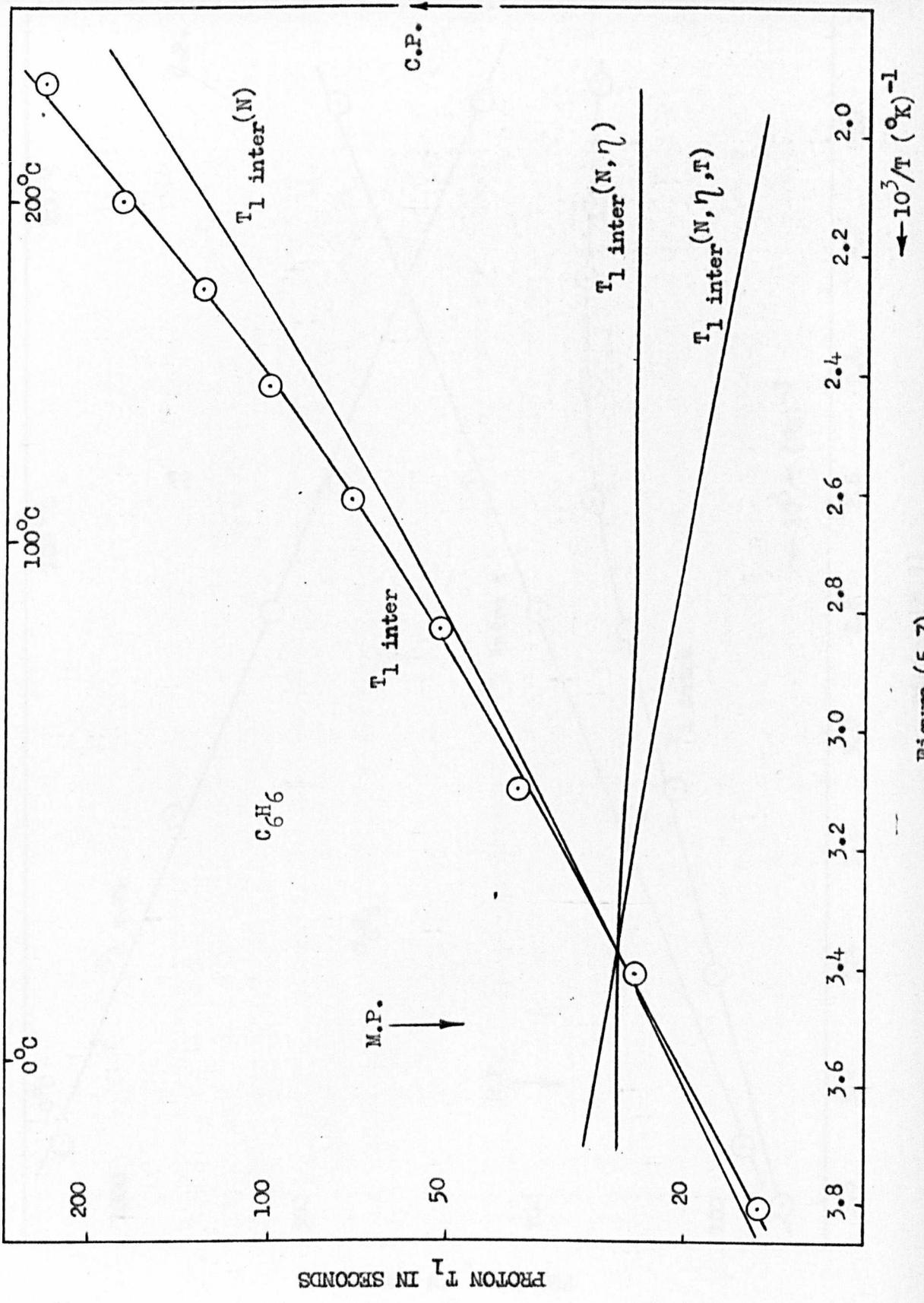


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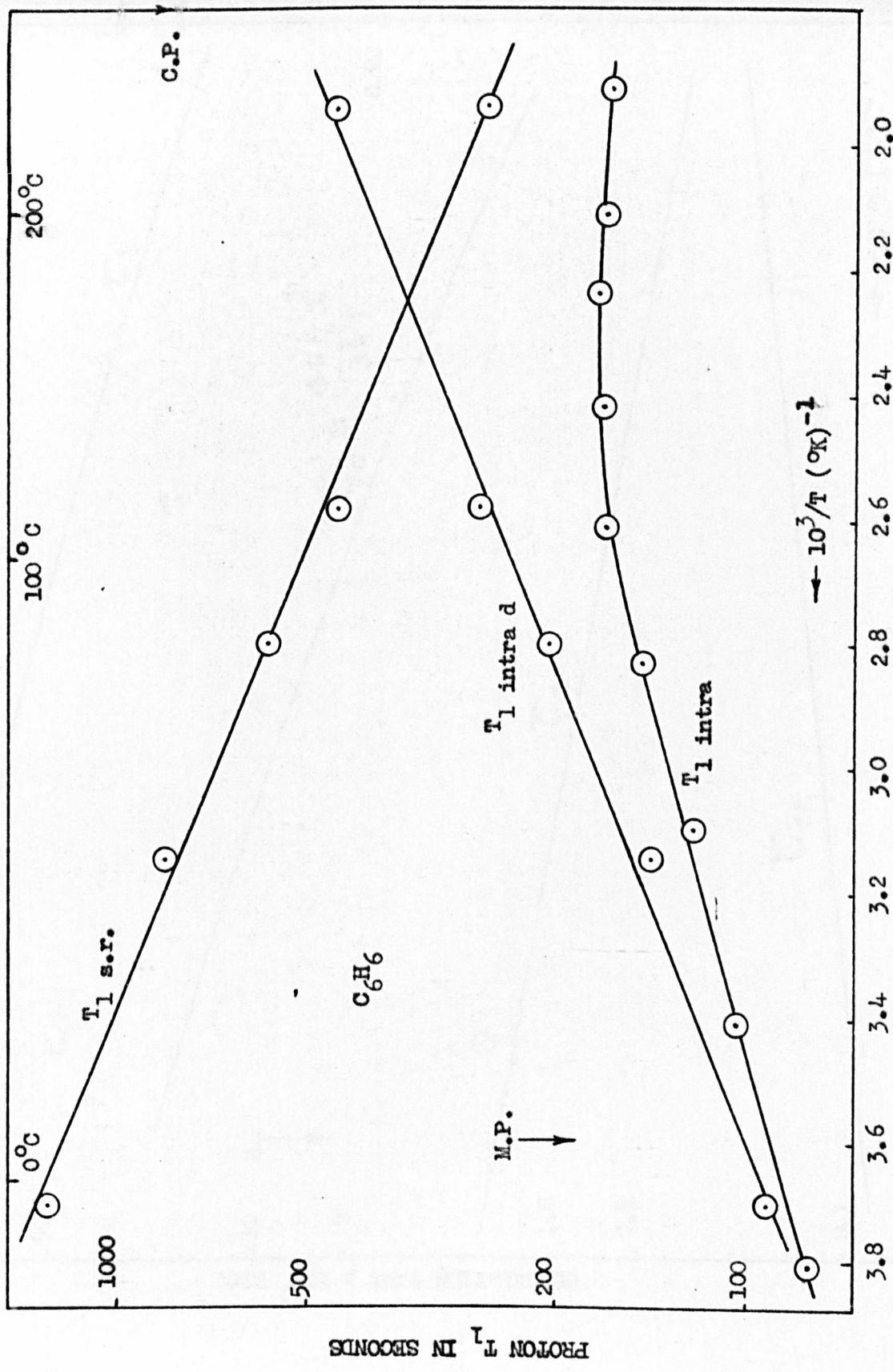


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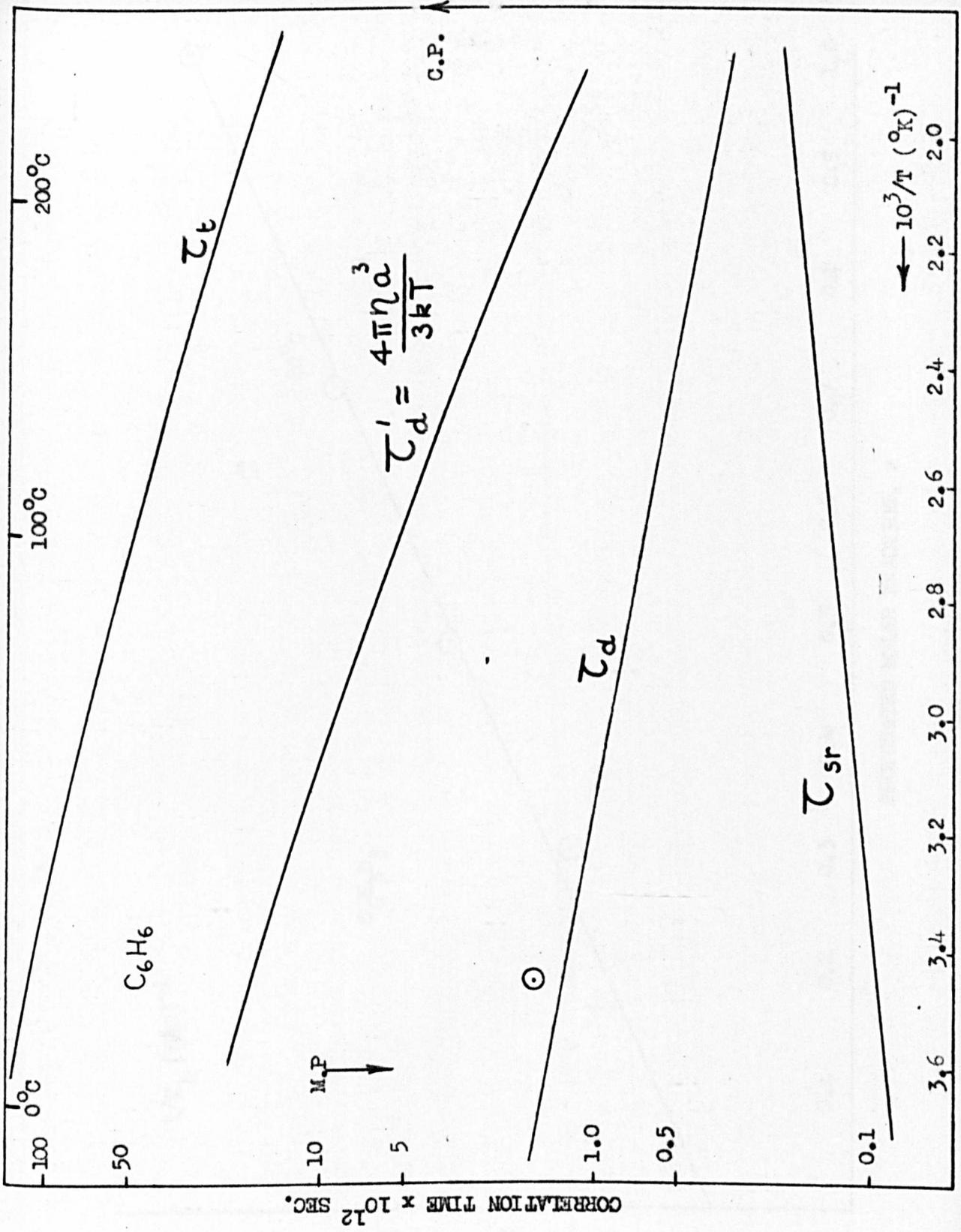


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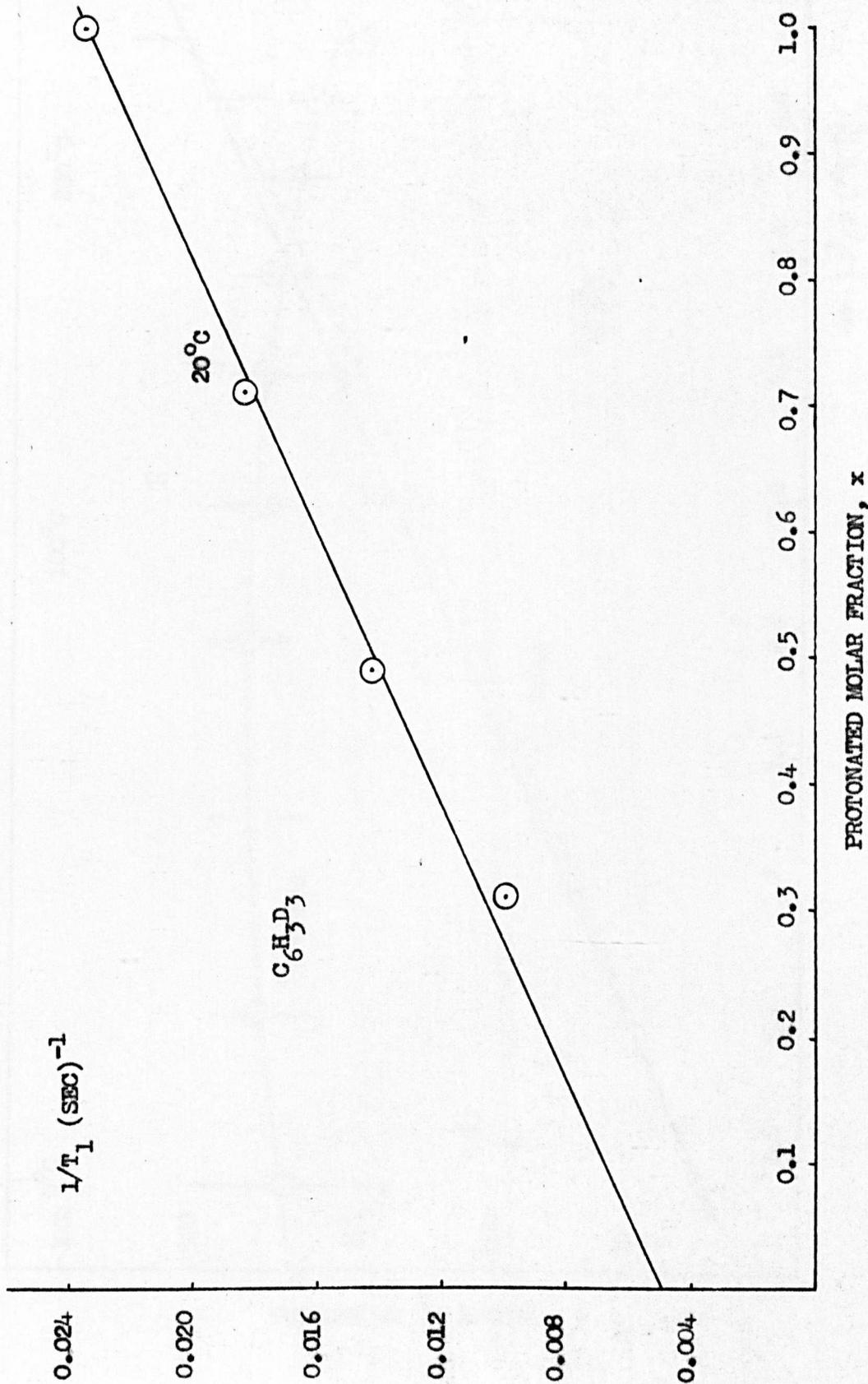


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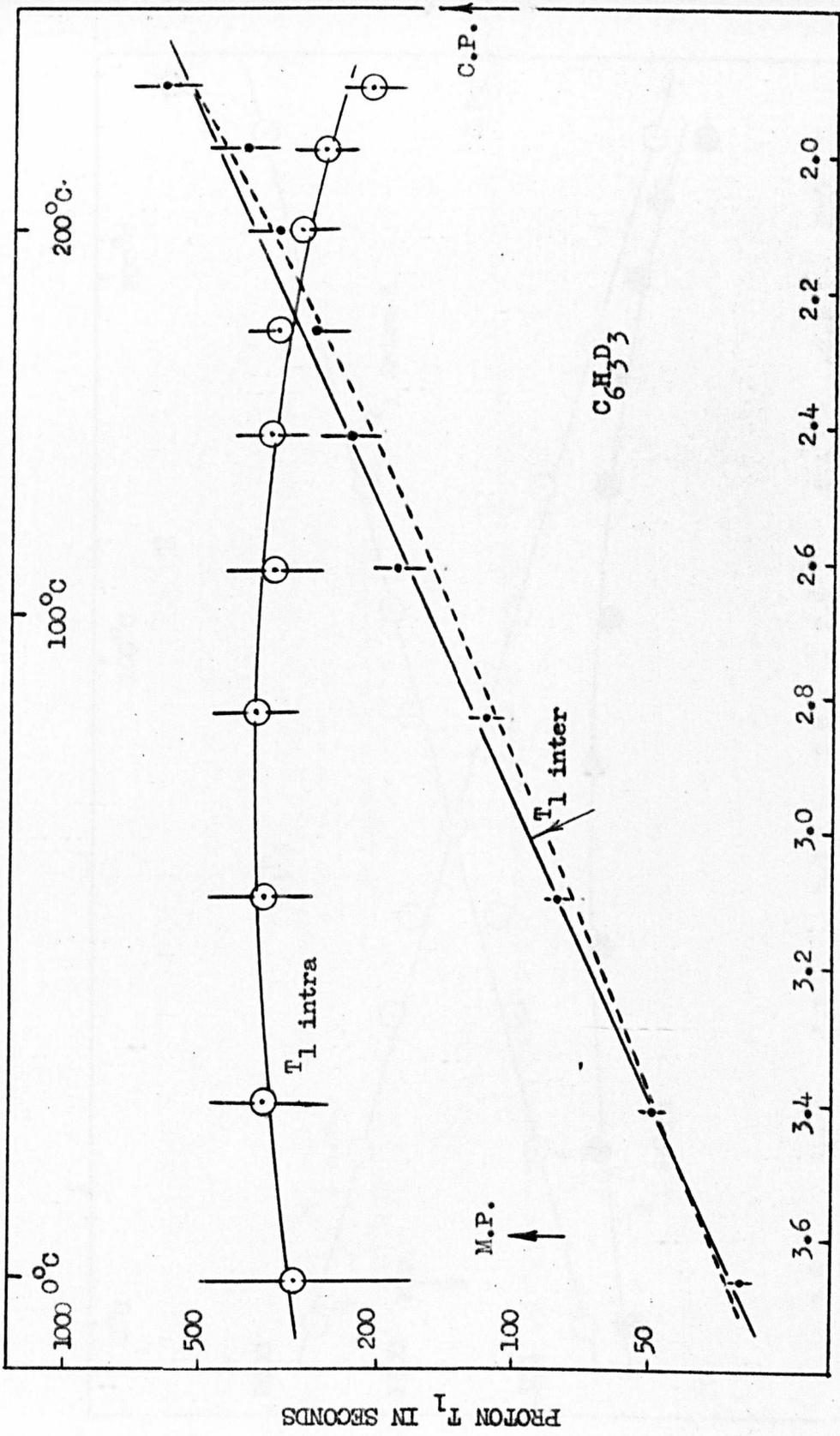


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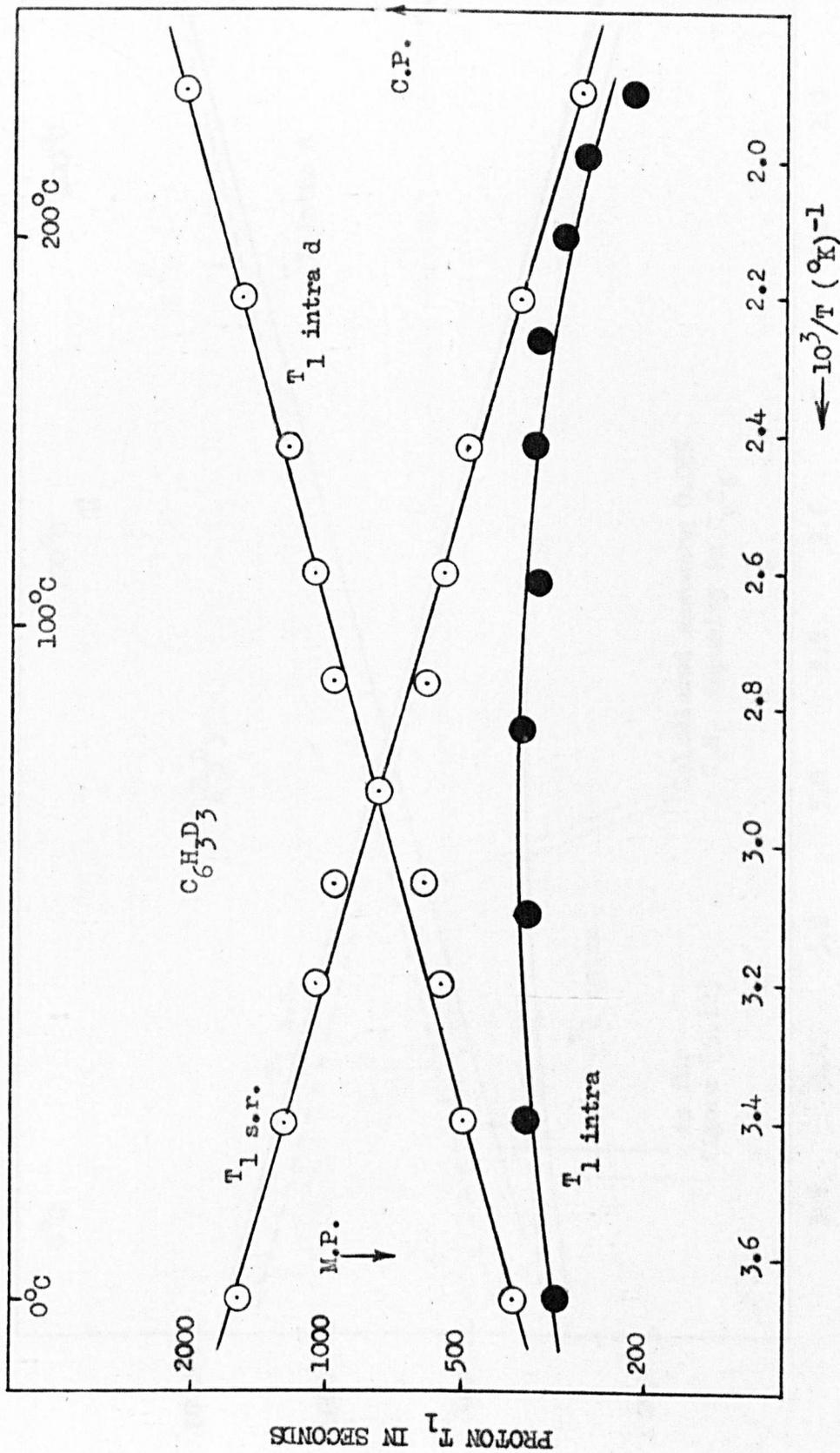


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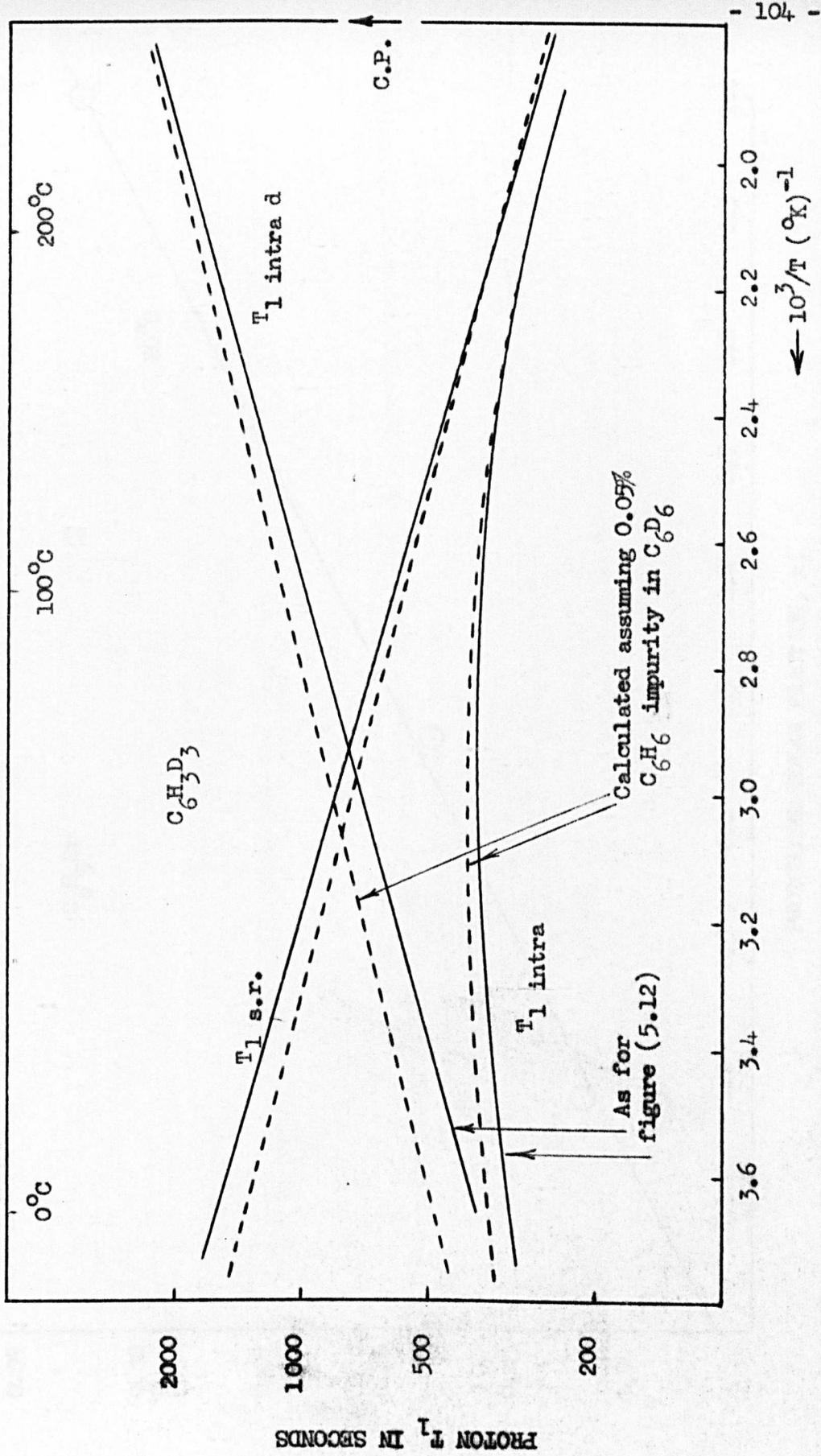


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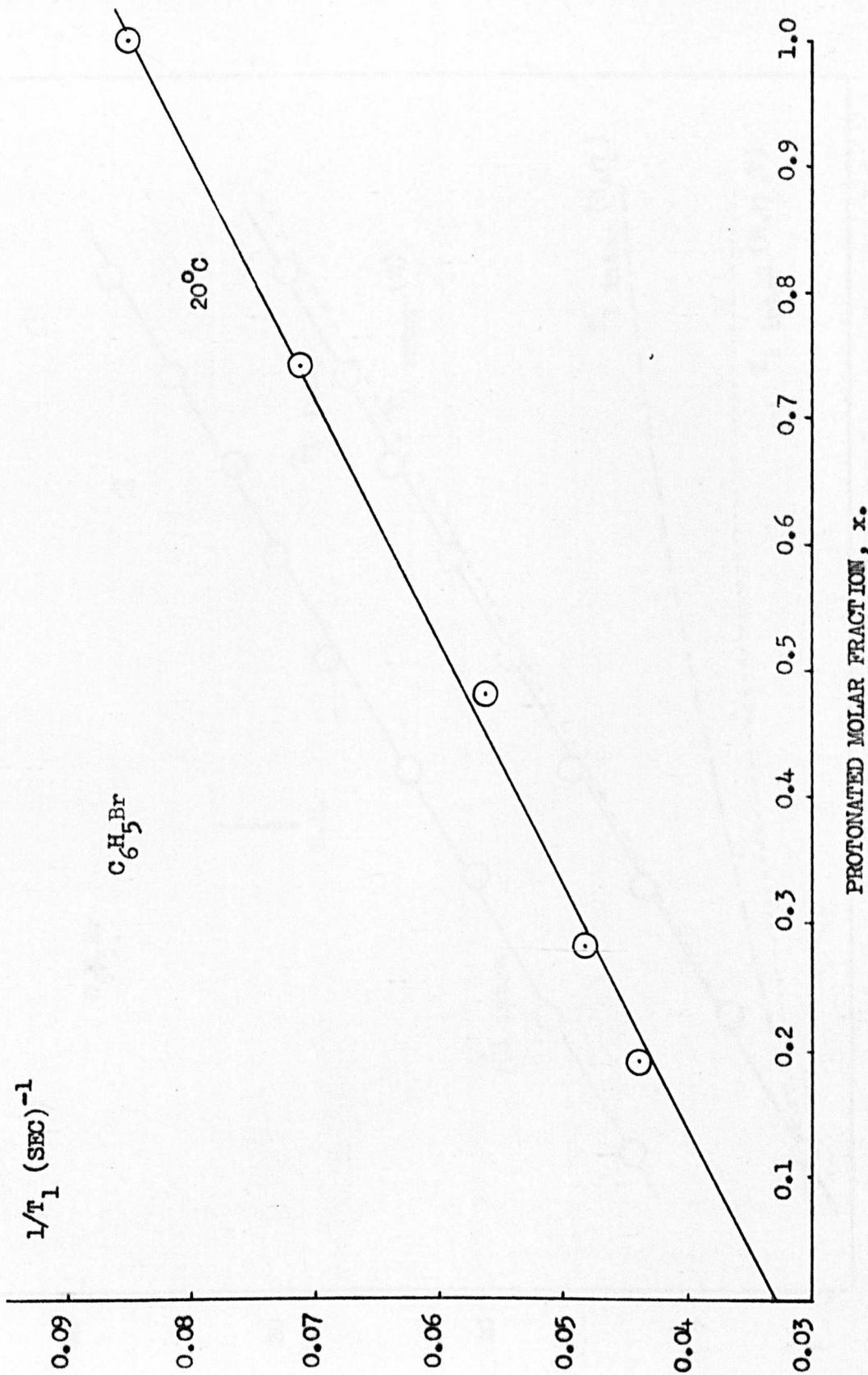


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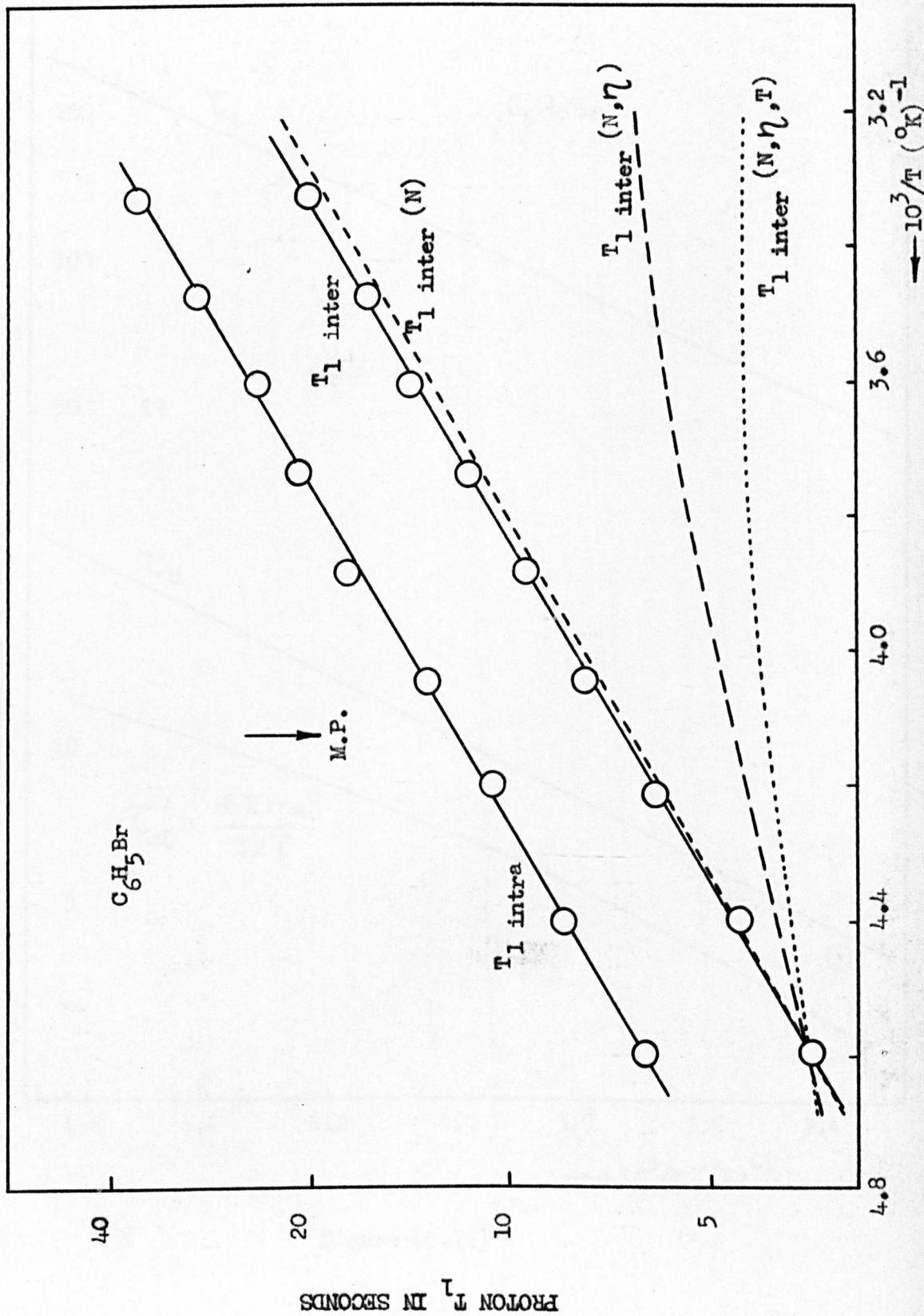


Figure (5.15)

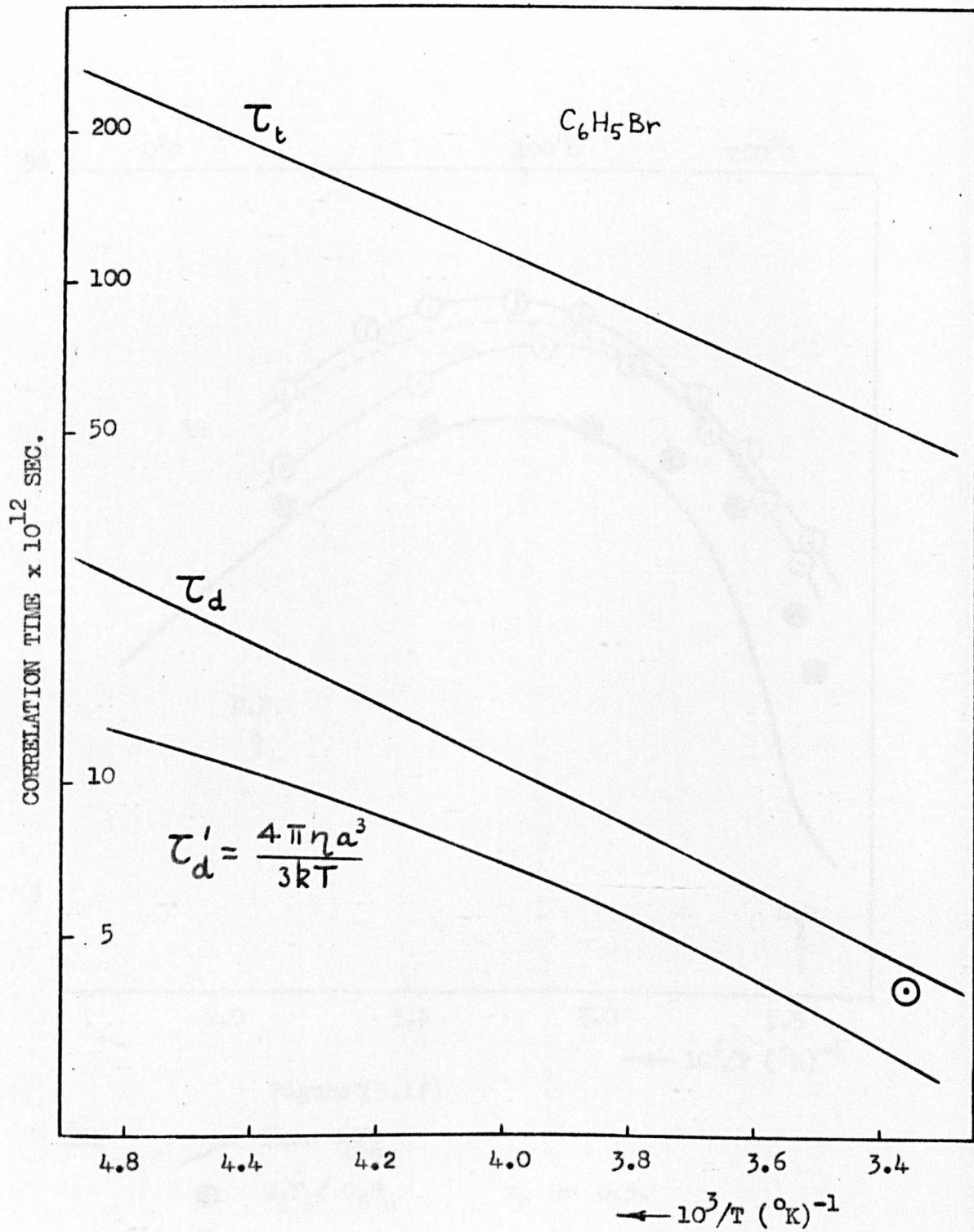


Figure (5.16)

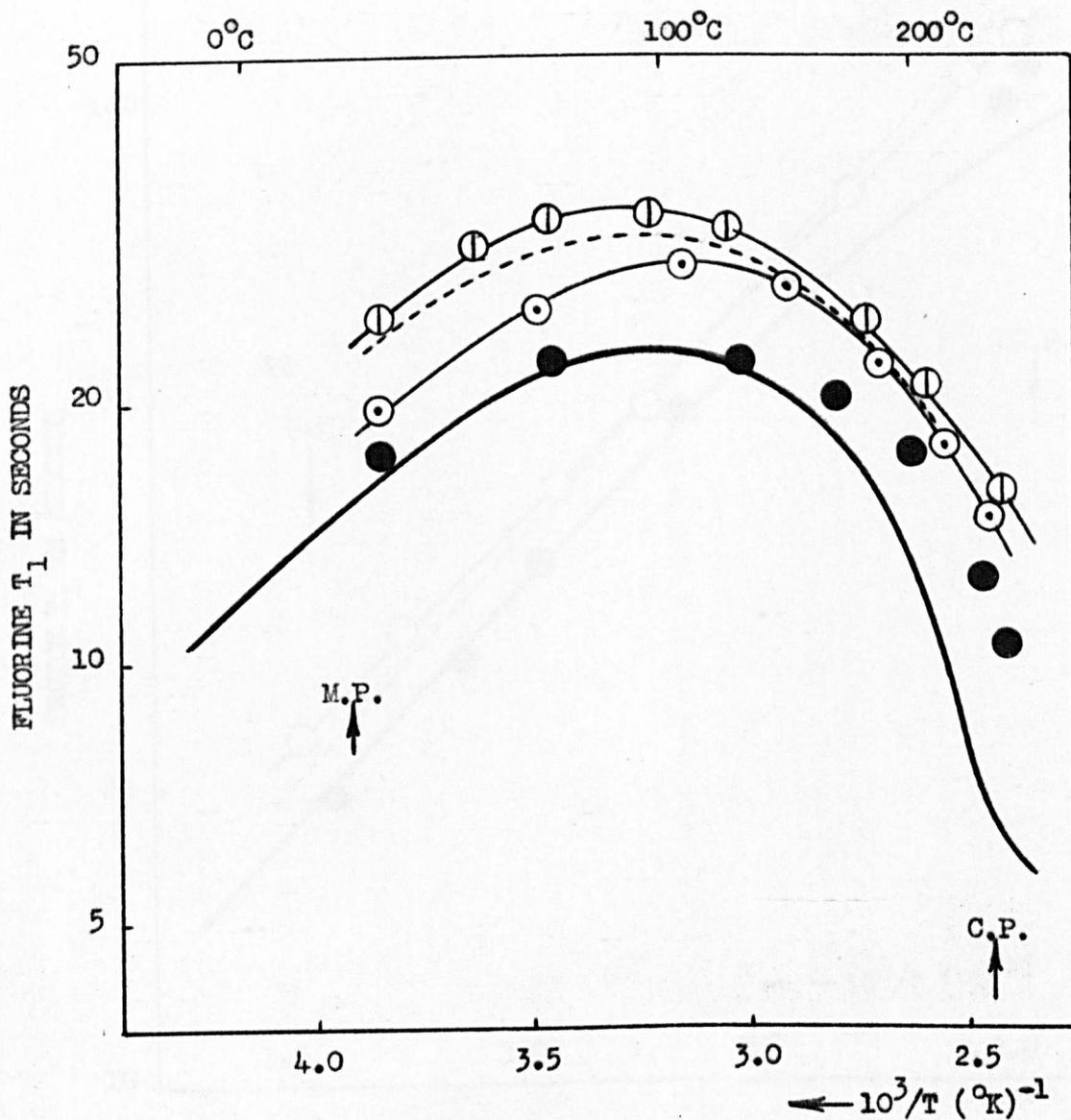


Figure (5.17)

Key

- Pure  $\text{C}_6\text{F}_6$
- $\text{C}_6\text{F}_6 / \text{C}_6\text{H}_6$        $x_{\text{F}} = 0.5.$
- ⊙  $\text{C}_6\text{F}_6 / \text{C}_6\text{H}_6$        $x_{\text{F}} = 0.22.$
- ⊗  $\text{C}_6\text{F}_6 / \text{C}_6\text{D}_6$        $x_{\text{F}} = 0.26.$
- - -  $\text{C}_6\text{F}_6 / \text{C}_6\text{D}_6$        $x_{\text{F}} = 0.51.$

(Experimental points omitted for clarity).

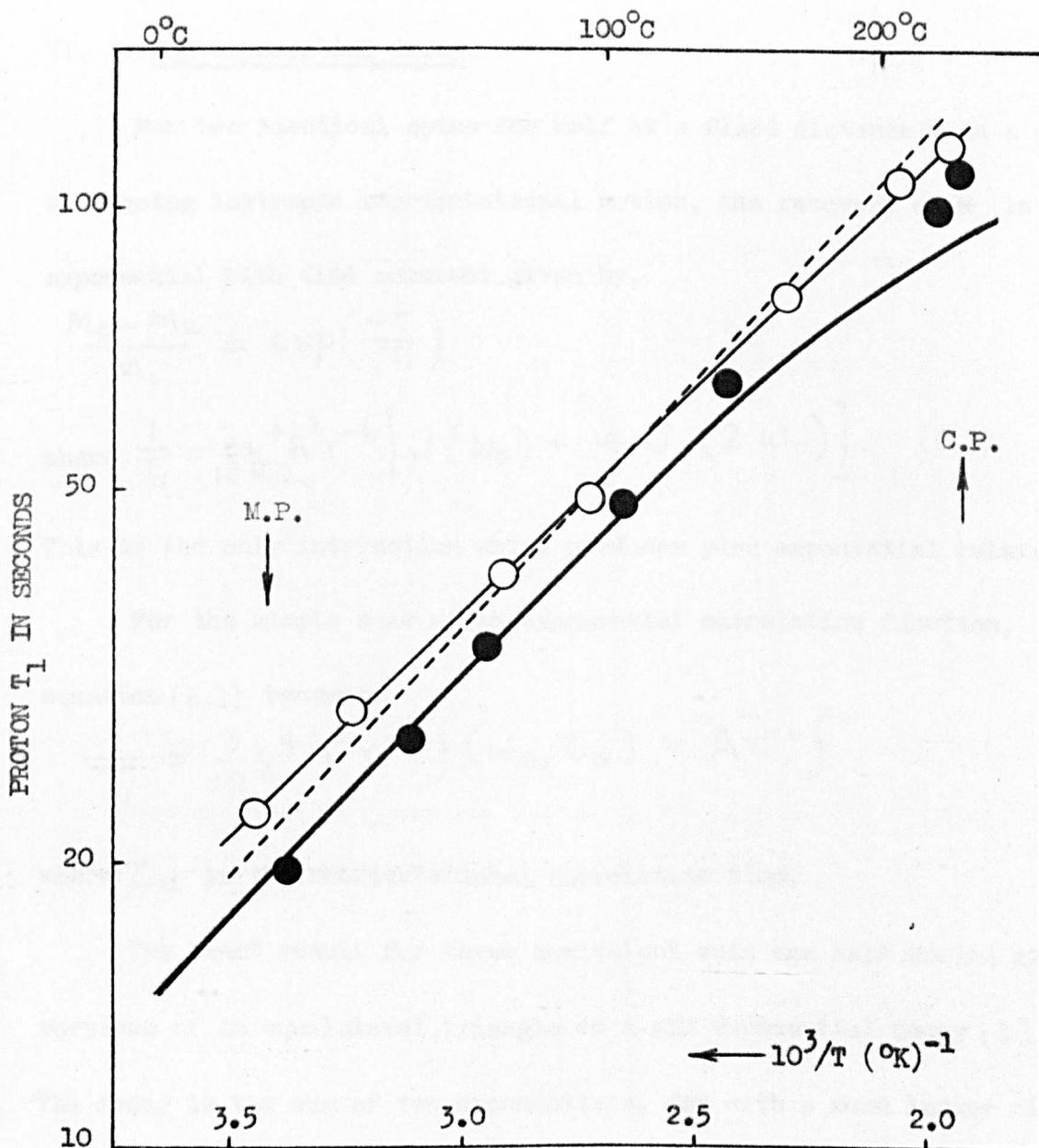


Figure (5.18)

Key

- Pure  $\text{C}_6\text{H}_6$
- $\text{C}_6\text{H}_6 / \text{C}_6\text{F}_6$   $x_{\text{H}} = 0.5$ .
- $\text{C}_6\text{H}_6 / \text{C}_6\text{F}_6$   $x_{\text{H}} = 0.78$ .
- - -  $\text{C}_6\text{H}_6 / \text{C}_6\text{F}_6$   $x_{\text{H}} = 0.31$ .

(Experimental points omitted for clarity).

CHAPTER VI

VI. 1. Non exponential decay.

For two identical spins one half at a fixed distance  $r$  in a molecule undergoing isotropic reorientational motion, the recovery of  $M_z$  is exponential with time constant given by,

$$\frac{M_0 - M_z}{M_0} = \exp\left(\frac{-t}{T_1}\right)$$

$$\text{where } \frac{1}{T_1} = \frac{3}{10} \gamma^4 \hbar^2 r^{-6} \left[ J(\omega_0) + 4 J(2\omega_0) \right]. \quad (6.1)$$

This is the only interaction which produces pure exponential relaxation.

For the simple case of an exponential correlation function, equation (6.1) becomes,

$$\frac{1}{T_1} = \frac{3}{10} \gamma^4 \hbar^2 r^{-6} f(\omega_0, \tau_d) = A r^{-6} f$$

where  $\tau_d$  is the reorientational correlation time.

The exact result for three equivalent spin one half nuclei at the vertices of an equilateral triangle is a non exponential decay [1]. The decay is the sum of two exponentials, one with a much longer time constant than the other. For four spins placed at the vertices of a tetrahedron, the exact result also gives a non exponential decay, the sum of three exponentials. The approximation to one exponential is very close. These results depend slightly on  $\omega_0 \tau_d$ , but it would be very difficult to detect the departure from exponentiality experimentally.

For a general system of N spins in a molecule, without considering an explicit form for the relaxation, we may write,

$$\frac{dM_z(t)}{dt} = f(M_z, t).$$

The Taylor expansion is,

$$\begin{aligned} M_z(t) &= M_z(0) + t \dot{M}_z(0) + \frac{t^2}{2!} \ddot{M}_z(0) + \dots \\ &= M_z(0) \left[ 1 + t \frac{\dot{M}_z(0)}{M_z(0)} + \frac{t^2}{2!} \frac{\ddot{M}_z(0)}{M_z(0)} + \dots \right]. \end{aligned}$$

$$\left. \begin{aligned} \text{We write } \frac{-\dot{M}_z(0)}{M_z(0)} &= \frac{1}{T_1} \\ \text{and } \frac{\ddot{M}_z(0)}{M_z(0)} &= \frac{1}{T_1'^2} \end{aligned} \right\} (6.2)$$

Then if  $(T_1)^2 = T_1'^2$ , at least up to terms in  $t^2$ , the decay of  $M_z$  is exponential.

The expectation value of the magnetization in the z direction is,

$$\langle M_z \rangle = \text{Tr} [ \rho(t) \underline{M}_z ]$$

where  $\rho(t)$  is the density matrix of the system. Similarly we have

$$\left. \begin{aligned} M_z(0) &= \text{Tr} [ \rho(0) \underline{M}_z ] \\ \dot{M}_z(0) &= \text{Tr} [ \dot{\rho}(0) \underline{M}_z ] \\ \text{and } \ddot{M}_z(0) &= \text{Tr} [ \ddot{\rho}(0) \underline{M}_z ]. \end{aligned} \right\} (6.3)$$

Thus in principle, from the time dependence of the density matrix, it is possible to calculate  $T_1$  and  $T_1'$  from equation (6.2). Recently Fenzke [2] has given an approximate solution for the problem of up to six spins at fixed distances. He calculates  $T_1$  and  $T_1'^2$  via equation (6.3) and

defines a quantity,

$$C = \frac{1/T_1'^2 - (1/T_1)^2}{(1/T_1)^2} \quad (6.4)$$

as a measure of the departure from true exponential decay for  $M_z$ , for the molecule considered. Hubbard's are the only exact results on which equation (6.4) may be tested.

However, we shall show that Fenzke's results may be approximated to by assuming that the total dipolar interaction is equal to the sum of constituent pair interactions. This implies that all pair interactions are independent. We know, of course, that the time dependence of these interactions are correlated, in fact they share the same correlation function.

Thus any pair interaction,  $ij$ , gives a contribution to the decay of nucleus  $i$  of,  $A f r_{ij}^{-6}$ .

So for  $i$ , the total interaction is

$$\frac{1}{T_1 i} = A f \sum_j r_{ij}^{-6}$$

and the decay of  $M_z$  is approximated by  $\exp(-t/T_1)$ , as all decays of like nuclei in the same molecule by intramolecular dipolar interactions are observed to be exponential experimentally.

Consider a spin,  $i$ , interacting with two other spins  $j$  and  $k$ .

Let  $r_{ij} > r_{ik}$ .

For the  $ij$  interaction, the magnetization,  $M_z$ , of  $i$  will vary as

$$M_{Z ij} = M_0 \left[ 1 - \frac{t}{T_1} + \frac{t^2}{2T_1^2} - \dots \right].$$

For the ik interaction,

$$M_{Z ik} = M_0 \left[ 1 - \frac{t}{T_1'} + \frac{t^2}{2T_1'^2} - \dots \right]$$

and  $T_1' < T_1$ .

The observed decay will be,

$$M_Z = M_0 \left[ 1 - \frac{t}{2} \left( \frac{1}{T_1} + \frac{1}{T_1'} \right) + \frac{t^2}{4} \left( \frac{1}{T_1^2} + \frac{1}{T_1'^2} \right) - \dots \right].$$

So we may define our approximate C, for this case, by,

$$C' = \frac{\frac{1}{2} \left( \frac{1}{T_1^2} + \frac{1}{T_1'^2} \right) - \left( \frac{1}{T_1} + \frac{1}{T_1'} \right)^2}{\left( \frac{1}{T_1} + \frac{1}{T_1'} \right)^2}.$$

If nuclei are equivalent with respect to internuclear distances, i.e.

$r_{ij} = r_{ik}$  etc.,  $C' = 0$ . This would be the case for the 3 and 4 spin systems discussed previously. The exact value of C (Fenzke's value) is very small for these cases.

In table 6.1 are shown comparisons of C and C' for proton spin systems in various species of deuterated benzene. Only proton-proton intramolecular interactions are considered. C' follows C remarkably well.

#### CHAPTER VI. REFERENCES

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Benzene Molecule Type (Positions of protons around the ring)	$1/T_1$ <del>xxx</del>	$C'$	$C$ (for $\omega_0 \tau_d = 1$ )
1,2,3,4,5,6	2.09	0	0.028
1,2,3,4,5	1.67	0.081	0.101
1,2,3,4	1.54	0.097	0.124
1,2,3,5	1.06	0.411	0.437
1,2,4,5	1.05	0	0.017
1,2,3	1.38	0.11	0.128
1,2,4	0.70	0.429	0.457
1,3,5	0.07	0	0.007 <del>xxxx</del>
1,2	1.0 <del>*</del>	0	0
1,3	0.04	0	0
1,4	0.02	0	0

Table (6.1)

\*  $1/T_1$  is normalized to this value.

~~xxx~~ All  $T_1$  values agree with Fenzke.

~~xxxx~~ Hubbard's value for  $\omega_0 \tau_d \ll 1$  is 0.0031. This agrees with Fenzke for  $\omega_0 \tau_d \ll 1$ .

SUMMARY AND CONCLUSION

We have seen that the technique of separating the intermolecular and intramolecular contributions to nuclear spin-lattice relaxation in liquids by measurements on solutions in neutral liquids is successful. The success depends on there being a suitable "identical" neutral liquid available and the proton-deuteron substitution seems the only one likely to be of use for some time. The technique has the advantage that it removes all intermolecular interactions without ambiguity and all intramolecular interactions remain. Thus the spin-rotation interaction can be seen. An alternative technique could be, for example, to measure the deuteron  $T_1$  of a perdeuterated liquid, and, from the appropriate quadrupole coupling constant, calculate  $\tau_d$ . Thus  $T_1$  intra d for the equivalent protonated molecule could be found. Subtraction from the measured proton  $T_1$  would then give  $T_1$  inter. However, this technique gives only dipolar intramolecular interactions, and depends on knowing the quadrupole coupling constant which is known for relatively few molecules.

Benzene

We may have confidence in the correctness of the separation of the contributions to proton relaxation in benzene for the following reasons.

- (a) The activation energy of  $T_1$  intra d agrees with the activation energy for the deuteron  $T_1$  in perdeuterobenzene. We have

advanced reasons for believing that these two parameters depend on the same rate process.

(b) The reorientational correlation time,  $\tau_d$ , calculated from  $T_{1 \text{ intra } d}$  gives a good value for the quadrupole coupling constant for perdeuterobenzene.

(c)  $T_{1 \text{ inter}}$  has approximately the temperature dependence one would expect from equation (5.4). We expect  $T_{1 \text{ inter}}(N, \eta, T)$  to be independent of temperature. In fact  $T_{1 \text{ inter}}(N, \eta, T)$  decreases by only a factor 2 over the entire liquid range.  $T_{1 \text{ inter}}$  changes by a factor of about 30.

$T_{1 \text{ inter}}(D, N)$  agrees with  $T_{1 \text{ inter}}(N, \eta, T)$  but has greater experimental error. This suggests that equation (5.1) is a good approximation for D in terms of  $\eta$  and T, but that  $\eta$  can be measured more accurately than D.

The only check on the correctness of the derived  $T_{1 \text{ sr}}$  values is to substitute into equation (4.21). Here we need both the spin-rotation constant and the spin-rotation correlation time. This latter can only be found, via the Hubbard relationship, equation (5.7), from  $\tau_d$ . Thus our check is not independent. Alternatively we may calculate a value for the spin-rotation constant from equation (4.21). The discrepancy between this value,  $(3.8 \text{ kc/s})^2$ , and that of Ramsey,

$(1 \text{ kc/s})^2$ , is large, and is not fully understood.

1,3,5 trideuterobenzene. For 1,3,5 trideuterobenzene we make the following remarks.

(a) The activation energy for  $T_{1 \text{ intra d}}$  agrees with that for benzene within experimental error.

(b) Within experimental error the actual values of  $T_{1 \text{ sr}}$  agree with those for benzene as expected.

(c) The values of  $T_{1 \text{ intra d}}$  calculated using  $\tau_d$  of benzene are larger than the experimental values by a factor 2.

(d) The reorientational correlation time is the same for benzene and 1,3,5 trideuterobenzene as, at room temperature, the deuteron  $T_1$ 's for these liquids are equal [1]. It is reasonable to assume that the quadrupole coupling constant is the same for deuterons in either molecule.

(e) In figure (5.11) the pecked line shows the temperature dependence of  $2 T_{1 \text{ inter}}$  for benzene. The agreement with  $T_{1 \text{ inter}}$  for 1,3,5 trideuterobenzene is close. The effect of the intermolecular proton-deuteron interaction in 1,3,5 trideuterobenzene is small.

(b) and (e) give some confidence in the correctness of the separation.

(a) suggests that we have overlooked an interaction with correlation time

$\tau_d$  : no explanation can be given.

Bromobenzene Previous reports of the temperature dependence of  $T_1$  for bromobenzene show a marked lowering of  $T_1$  above about  $20^\circ\text{C}$  [2,3]. This same effect has been noticed for our experiments, although here, this lowering is permanent. No detailed explanation can be given. The experimental results shown in figure (5.3) are reproducible. The following observations give confidence that the experimental separation of  $T_1$  intra d and  $T_1$  inter is correct.

(a) At  $25^\circ\text{C}$  the dielectric correlation time for bromobenzene is  $12 \times 10^{-12}$  sec. [4]. We calculate from  $T_1$  intra d at the same temperature,  $\tau_d = 4.5 \times 10^{-12}$  sec. Thus there is good agreement between  $\tau_{D/3}$  and  $\tau_d$  as expected.

(b) The activation energy for dipolar rotation (averaged over a temperature range of  $1^\circ\text{C}$  to  $55^\circ\text{C}$ ) for bromobenzene is  $2.65 \text{ Kcal.mole}^{-1}$ . [5]. This agrees well with the activation energy for  $T_1$  intra d which is  $2.7 \text{ Kcal.mole}^{-1}$ .

(c) The dependence of  $T_1$  inter on density, viscosity and temperature is approximately as expected from equation (5.4). As for benzene, the contribution from viscosity provides the greatest temperature dependence. We expect  $T_1$  inter ( $N, \eta, T$ ) to be independent of temperature. In fact, over the temperature range  $-56^\circ\text{C}$  to  $+40^\circ\text{C}$ ,  $T_1$  inter ( $N, \eta, T$ ) increases by a factor of about 1.2 while  $T_1$  inter increases by a factor of about 6.

Benzene, Perfluorobenzene mixtures. The experimental results for these mixtures are difficult to interpret unless detailed knowledge of the motion and structure of the "complex" molecules is available. Also of interest are the  $T_1$  values below room temperature. However it was not possible to supercool these mixtures. It is reasonable to claim that the existence of the complex in the liquid phase has been demonstrated.

Agreement between  $\tau_d$  and  $\tau'_d \left( = \frac{4\pi\eta a^3}{3kT} \right)$  is within an order of magnitude for both benzene and bromobenzene over the temperature ranges of experimental results. One is tempted to make "corrections" to the expression  $\tau'_d = \frac{4\pi\eta a^3}{3kT}$  in an attempt to reach better agreement.

Gierer and Wirtz [6] have shown, in a simple but physically plausible argument, that for molecular rotation in pure liquids one should use a "microviscosity",  $\eta_m$ , rather than the macroscopic shear viscosity  $\eta$ . They show  $\eta_m = 0.16\eta$ . Hence, using  $\eta_m$ , we would have better agreement between  $\tau_d$  and  $\tau'_d$  for benzene, but worse agreement for bromobenzene. Thus it would seem quite unprofitable to make "corrections" to quantities whose derivations may contain many approximations, and which may be evaluated by substituting quantities with large errors, such as  $a^3$ . Such "corrections" must wait until a more comprehensive list of values of  $\tau_d$  is available.

Similarly close comparisons between  $\tau_d$  and  $\tau_t$  are likely to be unfruitful as physical pictures of these parameters are difficult to draw from their definitions. For example, it may be very misleading to assign a definite angle of jump to  $\tau_d$  or a definite distance of flight for  $\tau_t$ .

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