

## Nuclear Spin-Lattice Relaxation in Hydrogen Gas\*

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The proton spin-lattice relaxation time,  $T_1$ , for hydrogen gas has been measured, using pulse techniques, as a function of gas density,  $\rho$ , temperature, and orthohydrogen concentration. The maximum density investigated was of order 900 amagats and the temperature range extended from 20 to 400°K. The radial dependence of the anisotropic part of the intermolecular potential due to the interaction of two hydrogen molecules has been deduced from a comparison of the temperature dependence of  $T_1/\rho$  in the dilute gas above 80°K with some calculations based on the theory of Oppenheim and Bloom. It is, approximately, an inverse thirteenth power of the intermolecular separation for the ortho-para interaction and an inverse sixth power for the ortho-ortho interaction. The results above 80°K are found to be sensitive to quantum-mechanical diffraction effects, in the manner suggested by Lipsicas and Bloom, and the temperature independence of  $T_1/\rho$  for dilute normal hydrogen gas above 80°K is shown to result from the different radial dependence of the ortho-ortho and ortho-para interactions. The results for  $T_1$  in the very dense gas appear to be consistent with the idea of a liquid-like assembly of molecules with predominantly short-range intermolecular interactions. Calculations are not available at the present time for comparison with any of the results below about 80°K, which are expected to be strongly influenced by quantum-mechanical effects. Some qualitative discussion is given of the dilute and dense gas results in this temperature range. At very low orthohydrogen concentrations, an unusual density dependence of  $T_1$  is observed in the temperature range 34–42°K. It appears that this effect is connected with the critical temperature phenomena, but it is not understood at present.

### INTRODUCTION

PREVIOUS measurements<sup>1–3</sup> of the proton spin-lattice relaxation time,  $T_1$ , in pure hydrogen gas have shown that the mechanism for the exchange of energy between the proton spin system and the heat reservoir, or “lattice,” represented by the translational degrees of freedom of the molecules is that predicted by Schwinger.<sup>4</sup> The random changes in the angular momentum substates,  $m_J$ , of the molecules, due to intermolecular collisions, modulate the intramolecular magnetic fields experienced by the nuclei, and the Fourier component of this modulation at the Larmor frequency of the nuclei can induce transitions necessary for relaxation. The proton spin system considered here is solely that of the orthohydrogen molecules, since a parahydrogen molecule has no net nuclear spin and ortho-para transitions are forbidden.

Using the values of the intramolecular magnetic fields deduced from molecular beam measurements, Schwinger was able to relate  $T_1$  to the mean lifetime,  $\tau_1$ , of the orthomolecules in the three magnetic substates of the  $J=1$  rotational state, assuming that all the molecules are in the lowest rotational state (low-temperature assumption). At the gas densities,  $\rho$ , used in our experiments,  $\tau_1$  is considerably shorter than the

nuclear Larmor period, and, for this case, Schwinger obtained

$$1/T_1 = 2.7 \times 10^{12} \tau_1. \quad (1)$$

At low densities (“dilute gas”), where only binary collisions are important (but with  $\tau_1$  still short compared to the nuclear Larmor period), one may rewrite  $\tau_1$  in terms of a cross section,  $\sigma$ , for collisions which cause transitions between the magnetic substates

$$\tau_1 = 1/\rho \langle \sigma v \rangle_{av}, \quad (2)$$

where  $v$  is the relative velocity of a pair of molecules and  $\langle \sigma v \rangle_{av}$  represents an average over the velocity distribution at the temperature of the gas. Thus, for the dilute gas at constant temperature,  $T_1$  is directly proportional to the gas density.

Since it is only the relatively weak *anisotropic* part of the intermolecular potential which is responsible for changes in the angular momentum substates of the molecules,  $T_1$  measurements may serve to probe that part of the intermolecular interaction which is too weak to have much effect on most of the other transport properties of hydrogen gas.

However, Schwinger’s calculation makes no attempt to relate  $T_1$  directly to the intermolecular interactions and a more detailed theory, such as that of Oppenheim and Bloom,<sup>5</sup> has to be used in order to extract from the experimental data quantitative values for the interaction parameters.

The Oppenheim-Bloom theory considers the interaction of a pair of molecules separated by a distance  $r$ , under the assumptions that (1) The isotropic part of the interaction Hamiltonian is the same for ortho-ortho and ortho-para pairs, while the anisotropic term is dif-

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<sup>1</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

<sup>2</sup> M. Bloom, *Physica* **23**, 237 (1957).

<sup>3</sup> M. Lipsicas and M. Bloom, *Can. J. Phys.* **39**, 881 (1961). This paper is referred to as LB.

<sup>4</sup> N. Bloembergen, in *Nuclear Magnetic Relaxation* (W. A. Benjamin, Inc., New York, 1961).

<sup>5</sup> I. Oppenheim and M. Bloom, *Can. J. Phys.* **39**, 845 (1961).

ferent. (2) The anisotropic interaction is too small to have any effect on the dynamical motion of the molecules. (3) All the orthohydrogen molecules are in the  $J=1$  state.

An effective Hamiltonian,  $H_R^{\text{eff}}$ , is used for the anisotropic interaction

$$H_R^{\text{eff}} = E_a \sum_{i,k} \sum_m Y_{lq}(\theta_{ik}, \phi_{ik}) K_m^i / x_{ik}^p, \quad (3)$$

where  $x=r/a$  is the separation of a pair of molecules in units of  $a$  (the Lennard-Jones parameter),  $\theta_{ik}, \phi_{ik}$  are the polar and azimuthal angles of the vector joining molecule  $i$  to molecule  $k$ ,  $Y_{lq}(\theta, \phi)$  is a spherical harmonic, and  $p$  and  $l$  are treated as parameters to be determined from experiment.  $E_a$  is the strength of the anisotropic interaction at  $r=a$  and the  $K_m^i$  are functions of  $J$  operators.

The resulting expression for  $T_1$  is

$$T_1 = \frac{3.7 \times 10^{-13} \rho a^4}{\hbar^2} \left( \frac{M}{kT} \right)^{1/2} E_a^2 C \int_0^\infty F(y) dy, \quad (4)$$

where

$$F(y) = \left[ \int_0^\infty \frac{[g(x)]^{1/2} J_{l+\frac{1}{2}}(xy)}{x^{p-3/2}} dx \right]^2, \quad (5)$$

$\rho$  is the gas density in amagats;  $M$  is the mass of the hydrogen molecule;  $C$  is a number arising from matrix elements of the  $K_m$  operators;  $J_{l+\frac{1}{2}}(xy)$  is the Bessel function of order  $l+\frac{1}{2}$ ; and  $g(x)$  is the radial distribution function of the gas molecules.

The reader will find a more detailed discussion of the use of the Hamiltonian,<sup>3,5,6</sup> Eq. (3), and the form of the radial distribution function. The relation between Eq. (4) and Schwinger's result, Eq. (1), has been discussed by LB [their Eq. (23)].

For the dilute gas, where only pairs of molecules interact, we may write

$$g(x) = \exp[-V(x)/kT], \quad (6)$$

where  $V(x)$  is the isotropic part of the intermolecular potential.

For the dense gas, where three-body and higher order collisions also take place, one can extend the Oppenheim-Bloom theory by applying density corrections to (6). These corrections result in a density dependence of  $T_1$  of form

$$T_1 = A\rho + B\rho^2 + C\rho^3 + \dots \quad (7)$$

For the limiting case of the liquid, Oppenheim and Bloom derive a relation for  $T_1$  in terms of the coefficient of self-diffusion,  $D$ ,

$$T_1 \propto \frac{\rho}{\hbar^2 D} \int_0^\infty \frac{F(y)}{y} dy. \quad (8)$$

<sup>6</sup> M. Bloom, in *Proceedings of the Seventh International Conference on Low-Temperature Physics*, edited by C. M. Graham and A. C. Hollis Hallet (University of Toronto Press, Toronto, 1961), p. 61.

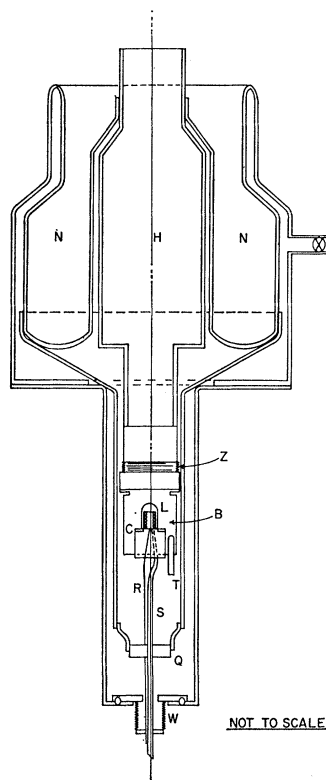


Fig. 1. Schematic diagram of metal cryostat (not to scale) N nitrogen space, H hydrogen space, Z heater coil, B beryllium-copper bomb, L NMR coil, C soft copper pressure gasket, R rf lead, S stainless steel high-pressure tubing, Q nitrogen-cooled terminal block, W monel bellows, T platinum resistance thermometer.

In the present work we have made measurements of  $T_1$  over the temperature range 20 to 400°K, up to maximum densities of order 900 amagats, for both normal hydrogen and mixtures of orthohydrogen and parahydrogen gas. We have been able to correlate some of our results with detailed numerical calculations based on the Oppenheim-Bloom theory, particularly for the dilute gas. We are able to suggest a possible interpretation of much of our other results and draw some interesting conclusions on the nature of the anisotropic interactions in hydrogen.

#### EXPERIMENTAL PROCEDURE AND APPARATUS

In all our measurements, we have used a 30.2 Mc/sec pulsed nuclear magnetic resonance (NMR) spectrometer and a 12-in. pole face diameter, 2-in. gap, Harvey-Wells electromagnet. The spectrometer has a continuously running crystal oscillator and a Blume-type<sup>7</sup> gated amplifier system. We have used a two-pulse  $\pi$ ,  $\pi/2$  sequence for all our measurements of  $T_1$ , measuring the amplitude of the  $\pi/2$  pulse as a function of the separation in time,  $\tau$ , between the two pulses.

At the hydrogen boiling point (approximately 20°K) a glass capillary tube was used to house the sample, the resonance coil being wound on the outside of the tube. In all other measurements, the gas sample was kept under pressure in a beryllium-copper pressure vessel designed for a maximum working pressure of 1000 atm.

<sup>7</sup> R. Blume, *Rev. Sci. Instr.* **32**, 554 (1961).

The inside chamber of the vessel was lined with a Teflon liner, inside which was a tight-wound, twelve-turn coil, one end of which was brought out and connected to a shielded rf cable. The main pressure closure was provided by a threaded plug bearing down on a soft copper gasket. The high-frequency lead, 0.032-in. diam enamelled copper wire was brought out through a Teflon bushing in the closure plug, the Teflon being squeezed against the copper wire by means of a pressure screw. At temperatures above about 350°K this type of seal was found to suffer from electrical insulation breakdown, mainly due to embrittlement of the enamel insulation under pressure. We have had some success in prolonging the lifetime of our seals under these conditions by using Anaconda type ML coated wire.

Our high-pressure system consists of a 20 cc capacity, 1000 atm High Pressure Equipment Company screw-type pressure generator connected to the high-pressure vessel through  $\frac{1}{8}$ -in. o.d.,  $\frac{1}{16}$ -in. i.d., stainless steel tubing and miniature valves. Matheson ultrahigh-purity hydrogen-gas cylinders were used in all our work. All gas pressures were measured by means of Heisse 12-in.-diam Bourdon-type gauges, and temperatures were measured by means of a National Bureau of Standards calibrated Hartmann and Braun platinum resistance thermometer.

All the low-temperature measurements, other than at 20°K, were made using a metal cryostat, Fig. 1. The lowest temperature attained by the gas sample in this cryostat, with liquid hydrogen at atmospheric pressure as the coolant, was 25.5°K. Temperatures down to about 22°K were achieved by pumping on the coolant and higher temperatures were achieved by use of the heater, Z, placed between the coolant and the high pressure vessel. It was found possible to achieve temperature stability of order 10 mdeg or better over periods of 15 min.

The amplitude of the NMR signal, using a single  $\pi/2$  pulse, was used to measure the orthohydrogen con-

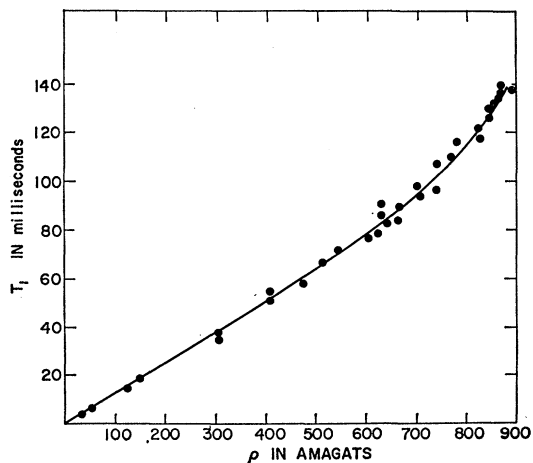


FIG. 2. Density dependence of  $T_1$  in normal hydrogen at 77.5°K.

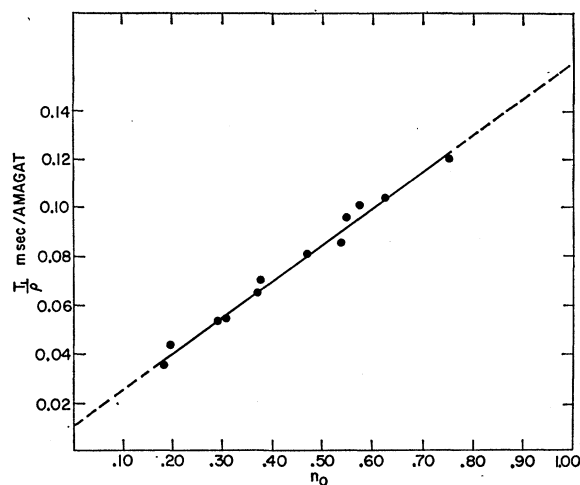


FIG. 3. Dependence of  $T_1/\rho$  at 77.5°K on orthohydrogen concentration.

centration of our samples, calibration being provided by a similar measurement on a sample of normal hydrogen. Since compressibility tables for hydrogen were not available for pressures greater than about 350 atm, density measurements in the high-pressure region were made using the amplitude of the NMR signal,<sup>8</sup> in a manner similar to the determination of the orthohydrogen concentration.

We estimate the accuracy of our  $T_1$  measurements to be  $\pm 4\%$  or better, except at the highest temperatures where our accuracy was only  $\pm 7\%$ .

We estimate the maximum error in our absolute temperature measurements to be of order 0.5°K below 35°K, and of order 0.7% at all other temperatures. Our absolute pressure measurements are correct to 0.5 psi below 500 psi and to 2 psi above this pressure.

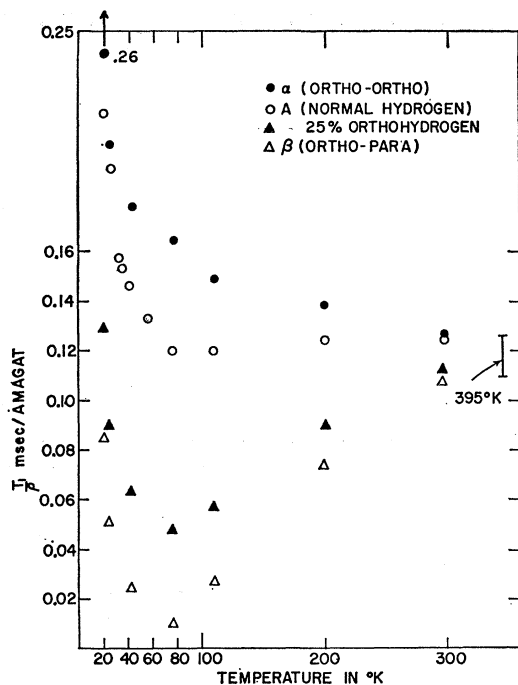
## EXPERIMENTAL RESULTS AND DISCUSSION

### A. The Dilute Gas

In Fig. 2 we show the density dependence of  $T_1$  for normal hydrogen gas at a fixed temperature of 77.5°K. The low-density, dilute-gas, region shows the linear dependence,  $T_1 = A\rho$ , expected on the basis of Eqs. (1) and (2). Preliminary calculations<sup>9</sup> have shown that the coefficient  $B$  in Eq. (7) is quite small and is thus not detectable in our measurements, the linear dependence of  $T_1$  on  $\rho$  continuing up to about 400 amagats. The slope,  $T_1/\rho$ , of the linear region is a function of both the orthohydrogen concentration and the temperature of the gas. In Fig. 3 we show the dependence of  $T_1/\rho$  at 77.5°K on the fraction  $n_0$  of orthohydrogen for mixtures of orthohydrogen and parahydrogen gas. At all temperatures between 20 and 400°K we find, within ex-

<sup>8</sup> M. Lipsicas, M. Bloom, and B. H. Muller, J. Chem. Phys. **34**, 1813 (1961).

<sup>9</sup> I. Oppenheim (private communication).

FIG. 4. Temperature dependence of  $T_1/\rho$  for the dilute gas.

perimental error,

$$T_1/\rho = \alpha n_o + \beta n_p, \quad (9)$$

where  $n_o$  and  $n_p$  are the relative fractions of ortho-hydrogen and parahydrogen, respectively, ( $n_o + n_p = 1$ ), and  $\alpha$  and  $\beta$  are temperature-dependent. Any theory which assumes that the anisotropic intermolecular interaction can be represented as the sum of pair interactions between ortho-ortho and ortho-para pairs will predict a relation of form (9). At all temperatures below 350°K we find  $\alpha > \beta$ , which expresses the fact that the anisotropic interaction for ortho-ortho pairs is stronger than for ortho-para pairs, largely because of the quadrupole-quadrupole term in the ortho-ortho interaction.

In Fig. 4 we plot the temperature dependence of  $T_1/\rho$  for the dilute normal gas, for the ortho-ortho interaction ( $\alpha$ ), for the ortho-para interaction ( $\beta$ ) and for 25% orthohydrogen. We note, in particular, that the temperature dependence of  $\alpha$  is quite different from that of  $\beta$ .

For a hard-sphere model, where  $V(x) = \infty$  for  $x \leq 1$  and  $V(x) = 0$  for  $x > 1$ , the integrand in Eq. 4 is temperature-independent, so that  $T_1/\rho$  would have a  $T^{-1/2}$  temperature dependence. For a more realistic intermolecular potential, the integration over  $[g(x)]^{1/2}$  contributes an added temperature dependence to the  $T^{-1/2}$  term. Wade and Oppenheim<sup>9</sup> have made some numerical calculations of the integral in Eq. (4) for a Lennard-Jones intermolecular potential over a limited range of  $l$  and  $p$  values in the temperature range 75 to 400°K. The temperature dependence of the integral is found to be very insensitive to the value of  $l$ .

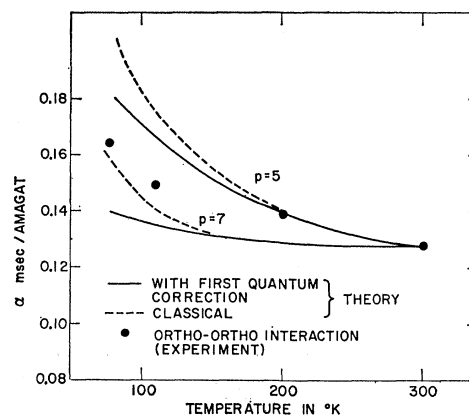
TABLE I. Comparison of theory and experiment for the ortho-para interaction.

Temperature (°K)	Calculated $T_1/\rho$ for $l=2$		$\beta$ experimental (msec/amagat)
	$p=11$	$p=13$	
185	0.0845	0.0695	0.065

In Fig. 5 we compare the curves of  $T^{-1/2} \int_0^\infty F(y) dy$  for  $l=2$ , calculated by Wade and Oppenheim, with the extrapolated experimental values of  $T_1/\rho$  for the ortho-ortho interaction ( $\alpha$ ). The curves have been normalized to the experimental values at 300°K. We note that (1) The ortho-ortho interaction corresponds to approximately  $p=6$ . (2) Application of the first quantum correction to the radial distribution function reduces the temperature dependence of  $\int_0^\infty F(y) dy$ . The physical interpretation of this quantum effect is that in a collision in the quantum region, the larger average effective size of the molecules prevents them from approaching each other as closely on the average as in the classical case.

In Table 1 we compare the extrapolated experimental values of  $T_1/\rho$  for the ortho-para interaction,  $\beta$ , with some calculations of Wade and Oppenheim at 370 and 185°K, using the classical radial-distribution function, and normalizing the calculations to experiment at 370°K.

The ortho-para interaction, then, corresponds to approximately  $p=13$  in this temperature range. We see that the ortho-ortho interaction is a relatively long-range interaction as compared to the ortho-para interaction. At temperatures of order 100°K, the short-range ortho-para interaction is not as effective as the ortho-ortho interaction because the average closest distance of approach,  $\delta$ , of the molecules is still large, but as the temperature is raised,  $\delta$  decreases until at high temperatures ( $\gtrsim 300^\circ\text{K}$ ) the short-range interactions predominate and there is little to distinguish the ortho-ortho and ortho-para interactions. Also, at temperatures

FIG. 5. Temperature dependence of  $\alpha$  above 80°K.

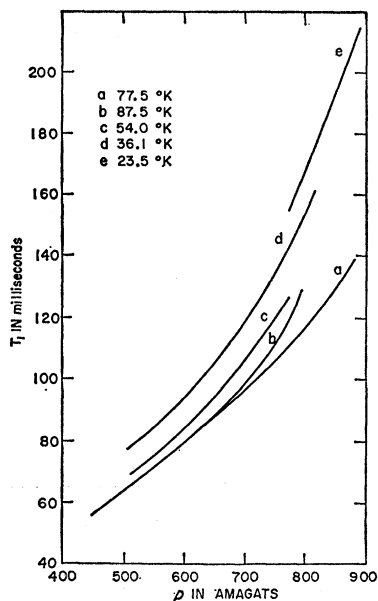


FIG. 6. Density dependence of  $T_1$  in dense normal hydrogen.

above about 300°K, an appreciable fraction of the molecules are in higher  $J$  states (at 400°K, in normal hydrogen, 10%  $J=0$ , 55%  $J=1$ , 15%  $J=2$ , 20%  $J=3$ ) which in itself removes much of the difference in range between the ortho-ortho and ortho-para interactions.

The temperature independence of  $T_1/\rho$  for normal hydrogen in the temperature range 100 to 400°K is thus quite fortuitous, a result of the particular mixture of the longer range ortho-ortho interaction and the shorter range ortho-para interaction.

In the quantum region, one must also take account of the change in the momentum distribution of the molecules which arises from the noncommutation property of the position and momentum operators, i.e., the momentum distribution function of the quantum gas depends on the spatial configuration of the molecules. In the Oppenheim-Bloom theory of the quantum gas an "effective" temperature  $T_e$  ( $T_e \geq T$ ) is, therefore, used where

$$\frac{3}{2}kT_e = \langle p^2/2m \rangle. \quad (10)$$

In Eq. (10),  $p$  and  $m$  refer, respectively, to the momentum and mass of a gas molecule, and the average is over an ensemble in which a pair of molecules are separated by a fixed distance,  $R$ .

Below about 80°K,  $\beta = T_1/\rho$  for the ortho-para interaction increases very rapidly with decreasing temperature, at a rate considerably faster than either  $T^{-1/2}$  or  $T_e^{-1/2}$ . On the other hand,  $\alpha = T_1/\rho$  for the ortho-ortho interaction, in this temperature range, exhibits a rate of increase which is less than  $T^{-1/2}$  down to about 30°K. This suggests that the longer range ortho-ortho interaction is still sensitive to the change in  $\delta$  resulting from quantum mechanics down to about 30°K. Below this temperature, the rate of change of  $\alpha$  with temperature is substantially the same as that for  $\beta$ , so that  $\delta$  here is

presumably so large that even the ortho-ortho interaction is insensitive to changes in  $\delta$ . We are unable, at this time, to account for the difference between  $T^{-1/2}$  and the observed rate of rise of  $\beta$  with decreasing temperature.

### B. The Very Dense Gas

In Fig. 6, we show the density dependence of  $T_1$  in the very dense normal hydrogen gas ( $\rho > 400$  amagats) at a number of temperatures, and include, for comparison, the density dependence of  $T_1$  in the liquid under pressure at 23.5°K. At a gas density of 400 amagats, the molecular mean free path is of order 2 Å, and we are essentially dealing with a liquid-like system. This is clearly illustrated by the fact that the density dependence of  $T_1$  at 23.5°K is merely an extrapolation to lower temperatures of the dependence in the very dense gas.

In Fig. 7, we plot  $T_1/\rho$  as a function of  $\rho$ , for  $\rho > 400$  amagats at a number of temperatures. It appears that, for  $400 < \rho < 700$  amagats, we may express the density dependence of  $T_1$  in the form

$$T_1 \text{ (in msec)} = Q(T)\rho^2 + 0.125\rho, \quad (11)$$

where  $T$  denotes the true temperature.

In Fig. 8 we show the temperature dependence of  $Q$ . The most striking feature of Fig. 8 is the very rapid increase in  $Q$  as the temperature decreases below 77.5°K. We also note that, whereas in the dilute normal gas  $T_1/\rho$  is substantially independent of temperature between 77.5 and 88.5°K,  $Q$  shows a 35% increase over this temperature range. We believe this difference between the dilute and very dense normal gases arises from the change in  $\delta$  with density; it is to be expected that  $\delta$  decreases with increasing density at fixed temperature. A decrease in  $\delta$  will increase the contribution

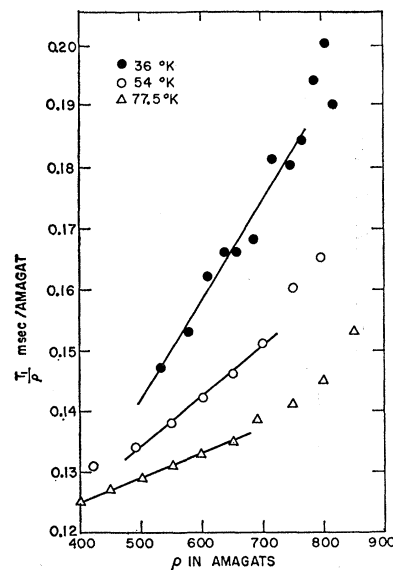


FIG. 7. Density dependence of  $T_1/\rho$  in dense normal hydrogen gas.

of the ortho-para interaction and will thus increase the  $T_1/\rho^2$  term,  $Q$ , for the very dense gas more rapidly with increasing temperature than  $T_1/\rho$  for the dilute gas.

The density corrections used to obtain Eq. (7) are clearly inadequate for the very dense gas, and we are led to compare our results with the Oppenheim-Bloom theory for the liquid, Eq. (8). Fortunately, the NMR technique allows us to measure the diffusion coefficient,  $D$ , of our dense gas samples, independently of the  $T_1$  measurements. In Fig. 9 we plot  $DT_1$  for a number of densities,  $\rho$ , as a function of temperature, using our preliminary results for  $D(\rho)$ . We hope to compare this plot with calculations of the temperature dependence of  $\int_0^\infty [F(y)/y]dy$  when these become available. This comparison is of particular interest, since it may also enable an estimate to be made of the relative importance of two factors, which, as has been noted by Oppenheim and Bloom, have not been taken into account in deriving Eq. (8):

(1) In the quantum region, when the mean de Broglie wavelength of the molecules becomes comparable with  $\delta$ , account must be taken of the quantum statistics, the hydrogen molecule system obeying Bose-Einstein statistics rather than the Maxwell-Boltzmann statistics assumed in the Oppenheim-Bloom theory.

(2) The simple diffusion equation may not apply<sup>6</sup> for the very short-range interactions which appear to be involved. It is interesting to note that we have found, both at 77.5 and at 36°K, that  $Q$  is practically independent of the ortho-hydrogen concentration between about 40 and 75% orthohydrogen. This would again

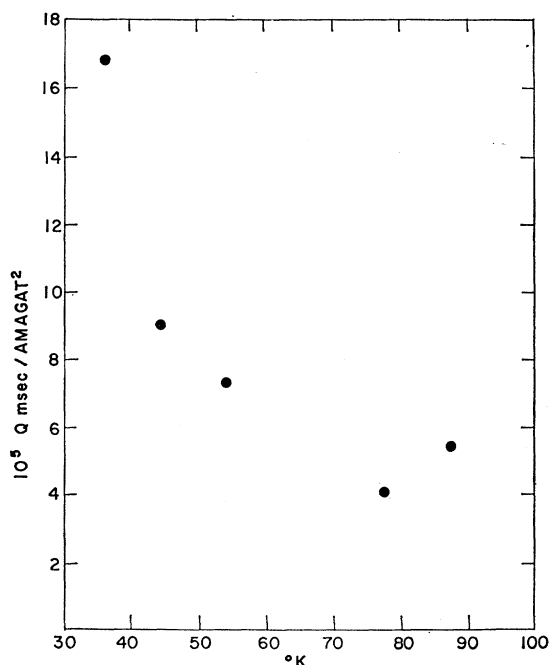


FIG. 8. Temperature dependence of  $Q$  in normal hydrogen gas.

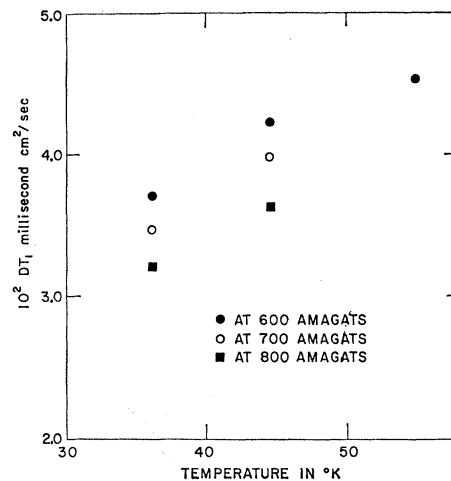


FIG. 9. Temperature dependence of  $DT_1$  for normal hydrogen gas.

seem to confirm that it is largely the short-range interactions which are effective in the very dense gas.

### C. Some Measurements Near the Critical Point

Measurements made near the critical temperature of normal hydrogen (33.2°K), using hydrogen gas samples of between 4 and 16% orthohydrogen concentration, showed a more complicated density dependence of  $T_1$  than that discussed hitherto. These effects were found to diminish very rapidly with increasing orthohydrogen concentration. In Fig. 10 we show the density dependence of  $T_1$  for two different orthohydrogen concentrations, 4 and 16%, at 34°K, and in Fig. 11 at 36°K for 7.5, 9, and 11% orthohydrogen. In all cases,

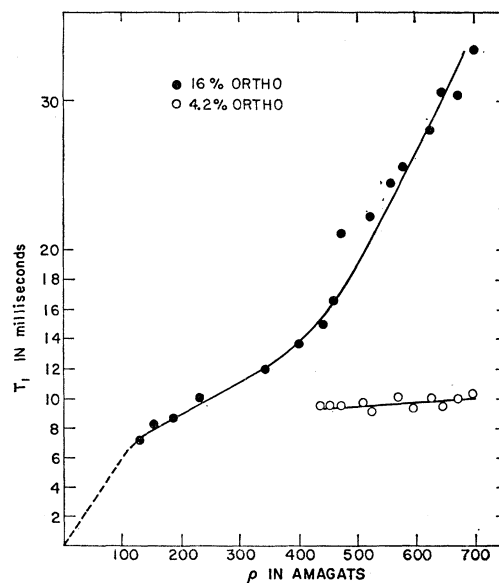


FIG. 10. Density dependence of  $T_1$  at 34°K for low orthohydrogen concentrations.

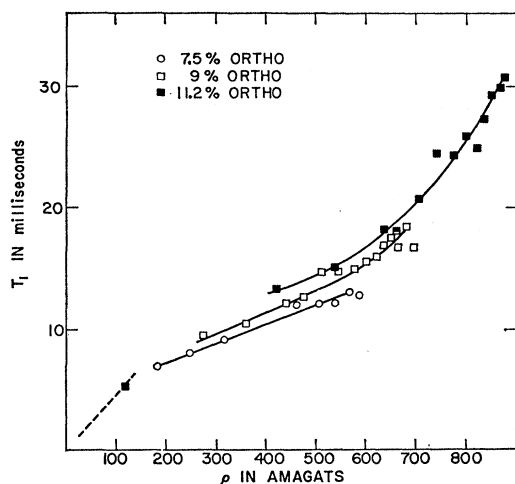


FIG. 11. Density dependence of  $T_1$  at 36°K for low orthohydrogen concentrations.

the initial slope  $T_1/\rho$  for  $\rho < 100$  amagats agrees with the values interpolated from Fig. 4. This confirms that the dilute gas obeys Eq. (9). However, in the region between about 150 and 400 amagats there is an unusual change in  $T_1/\rho$ . This effect is most marked at 34°K, but it is still discernible at 42°K. It would appear as though the orthomolecules in this density region interact with a greater proportion of paramolecules than at lower, or higher, densities. Now, the density region considered here is precisely that in which the compressibility of the gas undergoes large changes, at temperatures close to the critical point. This suggests that these results are related, at least in part, to the critical point phenomena. Furthermore, no such change in  $T_1/\rho$  is observed, in the temperature range 30–40°K, for mixtures of normal hydrogen and helium containing approximately 10% orthohydrogen, 3% parahydrogen and 87% helium. Since helium molecules play a similar role to parahydrogen molecules with respect to the anisotropic interaction with orthohydrogen molecules (both helium and parahydrogen are in the  $J=0$  state), the absence of any effect in the helium-orthohydrogen interaction is presumably due to the fact that the critical temperature of the hydrogen-helium mixture is very different from that of the ortho-para hydrogen mixture. Further work is in progress, including some measurements at the critical point.

## CONCLUSIONS AND FURTHER DISCUSSIONS

The measurements of  $T_1$  in the dilute gas, at temperatures above about 100°K, show a very marked difference between the range of the ortho-ortho and ortho-para interactions. The ortho-ortho interaction is contributed to mainly by the  $1/r^6$  dispersion term and the  $1/r^5$  quadrupole-quadrupole term, whilst the ortho-para interaction is dominated by the  $1/r^{13}$  valence term. A similar difference in the effective range of interaction has been observed by Williams<sup>10</sup> and by Johnson and Waugh,<sup>11</sup> in  $T_1$  measurements on mixtures of hydrogen with other gases, the range of interaction being found to depend on the symmetry of the foreign gas molecule (e.g., H<sub>2</sub>-N<sub>2</sub> long range, H<sub>2</sub>-He short range). Our results also substantiate the argument, presented in LB (p. 905), that the quantum-mechanical diffraction effect can decrease the cross section of reorientational collisions by virtue of the fact that the molecules do not approach each other as closely, on the average, as in the classical gas. Below about 80°K, however, higher order quantum corrections have to be applied and we are, at present, unable to compare our results in this temperature range with detailed calculations. It is hoped, eventually, to compare the measured values of  $T_1$  directly with the absolute values of  $T_1/E_a^2$  predicted by Eq. (4). One should then be able to give precise values for  $l$  and  $p$ , and also estimate the interaction energy  $E_a$ .

Our  $T_1$  measurements in the very dense gas appear to be consistent with the idea of a liquid-like assembly of molecules with predominantly short range interactions. It is hoped, when numerical calculations have been completed, to use our results in order to estimate the relative importance of (1) quantum statistics and (2) diffusion by "long jumps" in the very dense gas at low temperatures.

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<sup>10</sup> D. L. Williams, Can. J. Phys. 40, 1027 (1962).

<sup>11</sup> C. S. Johnson and J. H. Waugh, J. Chem. Phys. 36, 2266 (1962).