

bound electron. Those for Ω_a , Ω_b , and Ω_c are zero, so that their subtraction would have no physical consequences. On the other hand,

$$(a|\Omega_d|a) = -i(a|\beta\alpha \cdot \nabla V|a)/2, \quad (77)$$

which is precisely the form of interaction of a magnetic moment with a static potential V . Thus, the lack of uniqueness of the subtraction prescription is just such as to make the magnetic moment correction indeterminate, while the correction to the potential is left uniquely determined. Now a purely magnetic measurement of the correction to the magnetic moment of the

electron has been made by Kusch and Foley,¹⁶ who obtain a value in good agreement with the value $\alpha/2\pi$ -Bohr magnetons theoretically computed by Schwinger.¹⁷ If we adopt this experimental and theoretical result, the $2^2S_{1/2} - 2^2P_{1/2}$ separation becomes uniquely determined to be just the value 1052 Mc/sec. obtained above by a direct subtraction (74) of the self-energies for the two states.

¹⁶ P. Kusch and H. M. Foley, *Phys. Rev.* **74**, 250 (1948), also J. E. Nafe and E. B. Nelson, *Phys. Rev.* **73**, 718 (1948).
¹⁷ J. Schwinger, *Phys. Rev.* **73**, 416 (1948) and Pocono Conference, 1948.

Study of Phase Transitions by Means of Nuclear Magnetic Resonance Phenomena*

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Although the nuclear magnetic resonance condition generally depends only on the gyromagnetic ratio of the resonating nuclei, the width and amplitude of the resonance depend critically on the substance containing the resonating nuclei. A basic factor affecting the line width is the characteristic flipping time for the substance, i.e., the average time it takes a molecule to change its orientation appreciably. This fact has been applied in a study of a group of molecular solids which exhibit two or more phases in order to investigate the mechanisms of these transitions. Of the two mechanisms proposed, rotational and order-disorder, the former was eliminated in favor of the latter for HCl, HBr, HI, H₂S, and H₂Se, while free molecular rotation is shown to be plausible in CH₄ and CH₃D.

I. INTRODUCTION

THE first successful detection of radiofrequency transitions between Zeeman levels of nuclei in liquids and solids was announced by Purcell, Torrey, and Pound¹ and by Bloch, Hansen, and Packard² in 1946. It became apparent early in these investigations that the characteristics of a nuclear magnetic resonance depend directly on the material in which the

resonating nuclei reside. This, coupled with the fact that the ratio of resonant frequency to magnetic field is a linear function of the nuclear g -factor, indicated three lines of research:

(a) The accurate measurement of nuclear g -factors.³

(b) An investigation of the interactions which affect the resonance characteristics, i.e., nuclear relaxation processes.⁴

(c) Study of internal properties of solids and liquids by means of nuclear magnetic resonance phenomena.⁵⁻⁹ It is one phase of the last of these

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¹ E. M. Purcell, H. C. Torrey, and R. V. Pound, *Phys. Rev.* **69**, 37 (1946).

² F. Bloch, W. W. Hansen, and M. Packard, *Phys. Rev.* **69**, 127 (1946). F. Bloch, W. W. Hansen, and M. Packard, *Phys. Rev.* **70**, 474 (1946).

³ F. Bitter, N. L. Alpert, D. E. Nagle, and H. L. Poss, *Phys. Rev.* **72**, 1271 (1947).

⁴ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948), hereafter to be referred to as B.P.P.

⁵ F. Bitter, N. L. Alpert, H. L. Poss, C. G. Lehr, and S. T. Lin, *Phys. Rev.* **71**, 738 (1947).

⁶ B. V. Rollin, *Nature* **158**, 669 (1946).

⁷ B. V. Rollin and J. Hatton, *Nature* **159**, 201 (1947).

lines of research with which this investigation is chiefly concerned.

If a substance containing magnetic nuclei of magnetic moment μ and angular momentum $I\hbar$ is placed in a z -directed magnetic field, H_0 , there will result a nuclear paramagnetism which may be found from Curie's law:

$$M_0 = N(g\mu_n)^2 I(I + DH_0) / 3kT, \quad (1)$$

where M_0 is the static magnetization, N the number of nuclei/cc, g the nuclear g -factor, μ_n the nuclear magneton, I the nuclear angular momentum in units of $\hbar/2\pi$, k the Boltzmann factor, and T the absolute temperature. Now if a radio-frequency field is introduced in the x - y plane with the Larmor frequency,

$$\nu_0 = \mu H_0 / I\hbar \quad \text{or} \quad \omega_0 = \gamma H_0, \quad (2)$$

where $\gamma = \mu/I\hbar$, a resonant absorption and dispersion will occur. For diamagnetic materials the ratio of ν_0 to H_0 generally depends only on the magnetic moment and angular momentum of the nuclei concerned, and the peak absorption will be found at the same resonance condition for the same nuclei, regardless of the material in which the nuclei reside. The width and magnitude of the nuclear magnetic resonance, however, are found to depend critically on the substance containing the resonating nuclei. More specifically, these properties are found to depend on two modes of interaction affecting the nuclei: (a) The interaction between the nuclei and the lattice containing them, expressed in terms of the spin-lattice or thermal relaxation time, T_1 . It is the resultant interchange of energy which enables the nuclear system to attain thermal equilibrium at a temperature T and to attempt to maintain this equilibrium upon exposure to resonance radiation. (b) The magnetic interaction between the nuclei, which is expressed in terms of a spin-spin relaxation time, T_2 . This effect manifests itself primarily in a broadening of the resonance line width. The experiments described below are chiefly concerned with this latter mode of interaction.

If a resonating nucleus is surrounded by magnetic nuclei there will be superimposed on H_0 a local magnetic field H_{10c} , which may be of the

order of several gauss. The resonant condition is then $\omega_0 = \gamma(H_0 + H_{10c})$. Since H_{10c} depends on the orientations and positions of all neighbors, the result is a dispersion of the magnetic fields at the various nuclei about the applied H_0 , the average field at the nuclei still being H_0 . From the resultant broadening in the energy levels, $\Delta E = \hbar\gamma H_{10c}$, we may define a time T_2 on the basis of the uncertainty principle of quantum mechanics: $T_2 = \hbar/\Delta E = 1/|\gamma|H_{10c}$. It should be noted that H_{10c} represents a deviation of the magnetic field from an average H_0 . Therefore, gradients in the magnetic field caused by magnetic field inhomogeneities serve also to broaden the line.***

Since the internuclear fields are expected to be of the order of a few gauss or more in magnitude, most solids fit well with this extremely elementary picture, giving resonance line widths of a few gauss or more. That this picture on the basis of a rigid lattice is inadequate becomes particularly obvious in the case of most liquids and gases and a few solids, where line widths of a small fraction of a gauss are found. The key to these narrower lines may be seen from the fact that no mode of spin-lattice relaxation is possible in the rigid lattice so far considered. A generally useful and satisfactory theory of both spin-lattice and spin-spin interactions has been developed by B.P.P.⁴ On the basis of general lattice motion they derive fairly accurate values for T_1 and explain details of line narrowing.

Qualitatively, the resonance line width is reduced by an averaging out of the internuclear fields resulting from the lattice motion. This is particularly obvious in the extreme case of a nucleus residing in a freely rotating molecule, since rotational periods are much smaller than times associated with the nuclear resonance. In most cases of interest all orientations of the molecule are equally probable. As a consequence the internuclear fields essentially average out to zero, so that an extremely narrow line results. Actually, in the case of water a line width of 10^{-4} gauss is predicted. In practice it is impossible to observe this "true" line width since it would require, at a working field of 7000 gauss, a homo-

⁸ B. V. Rollin, J. Hatton, A. H. Cooke, and R. J. Benzie, *Nature* **160**, 437 (1947).

⁹ G. E. Pake, *J. Chem. Phys.* **16**, 327 (1948).

*** There are other factors which may contribute to the line width but which do not enter into the cases under study. A more complete discussion of this matter may be found in reference 4.

generality of almost one part in 10^8 over the sample. Thus the line width in most liquids is determined entirely by the homogeneity of the magnet.

The theory referred to above approximates its description of the lattice motion by means of a single parameter τ_c . This so-called correlation time (or "flipping" time) is essentially the average time it takes for a molecule to change its position or orientation appreciably. This is very closely related, through a factor of the order of one, to the "characteristic relaxation time" introduced by Debye in his theory of polar molecules.¹⁰ The effect of τ_c on T_2 and on the line width may be seen as follows:

Let us denote by T_2'' the spin-spin relaxation time in the limiting case of the rigid lattice. Thus, for this case, T_2'' represents the average lifetime of a nucleus in a particular energy state (or orientation). Now if $\tau_c \gg T_2''$, the slow variation of the internuclear fields during the "lifetime" of a nuclear orientation will have a negligible effect on the spin-spin interaction. Therefore we have

$$\text{Case I: } \tau_c \gg T_2''. \quad T_2 = T_2'', \quad \Delta H = 1/\gamma T_2''. \quad (3a)$$

If, on the contrary, $\tau_c \ll T_2''$, considerable averaging out of the internuclear fields occurs during a normal nuclear level "lifetime." As a result the spin-spin interaction is greatly reduced, and the relaxation time increased accordingly. In this case it may be shown that, in general, the relaxation time varies inversely as the correlation time.

$$\text{Case II: } \tau_c \ll T_2''. \quad T_2 \propto (1/\tau_c), \quad \Delta H \propto \tau_c. \quad (3b)$$

Thus it becomes apparent that the line width is a sensitive function of the correlation time.

On the basis of a simplified calculation, by taking into account the effect of only the nearest neighbor of a resonating nucleus, B.P.P. find for T_2 the relation:

$$(1/T_2)^2 = K \tan^{-1}(2\tau_c/T_2), \quad (4)$$

where K is a constant which includes the internuclear distance and other constants which are independent of frequency and of temperature. This has the properties discussed above. Namely,

¹⁰ P. Debye, *Polar Molecules* (Dover Publications, New York, 1945), reprinted.

for $\tau_c \gg T_2$, $T_2 = (2/\pi K)^{1/2}$, which may be shown to be equal to T_2'' , while for $\tau_c \ll T_2$, we find $T_2 = 1/2K\tau_c$. The form of a plot of $\log T_2$ vs. $\log \tau_c$ is immediately apparent. This is made up of two predominant portions, a horizontal line for $\tau_c \gg T_2''$ and a line whose slope is -1 for $\tau_c \ll T_2''$. If one reasons that the correlation time loses its "control" of T_2 when it reaches a value equal to T_2 , one finds that the break between the horizontal and sloping part of this graph occurs near $\tau_c = T_2''/2^{1/2}$. Very little accuracy is lost if we approximate this plot by two straight lines, one horizontal and the other with slope -1 , intersecting at $\tau_c = T_2''/2^{1/2}$.

Another factor which affects T_2 is the spin-lattice relaxation time. It may be seen that if the motion of the lattice transporting the nuclei has frequency components near ν_0 , this motion is capable of inducing transitions between Zeeman levels. Although this picture is oversimplified, it indicates essentially the means of energy transfer between the lattice and the nuclei. T_1 is found to be $1/2W$, where W is the probability of an induced transition. Now if T_1 is comparable to T_2 , the former will also serve to limit the lifetime of a nucleus in a particular state. Thus T_1 may also contribute to the line width. However, under the conditions of the experiments, one of two situations generally exists. Either $T_1 \gg T_2$, which is usually the case for broad lines, or $T_1 \cong T_2$ for the sample, and both are in the range of 0.01 second to several seconds. In the former case T_1 has no effect on the line width, while in the latter case the line width is determined by the homogeneity of the magnetic field, and T_1 does not influence the experimentally observed line widths for small r-f fields.

II. PHASE TRANSITIONS IN SOLIDS

Many solids undergo drastic changes in their physical properties at critical temperatures. Such transitions may be placed in one of two categories. The so-called first-order transitions occur at one particular temperature and are accompanied by a latent heat, usually as a result of a change in crystal symmetry. In contrast, second-order transitions are identified by λ -points with an anomalously high specific heat over the transition temperature range, generally of the order of a few degrees Kelvin. One class of solids

showing second-order transitions is alloys. The order-disorder phenomenon responsible for the transitions in these substances is well understood. However, there is a large class of substances, including many molecular solids, which show second-order transitions whose mechanisms are not completely understood. These transitions may possibly be explained in terms of a change in molecular activity. It is this factor which points out the potentialities of studying this group of solids by the nuclear magnetic resonance experiment, since it has been shown that internal activity has a profound effect on the properties of the resonance. For the sake of completeness it should be noted that a few first-order transitions—e.g., in HCl—should also be of interest in any such investigation.

There are two conflicting theories to explain the transitions in question. One theory, put forward by Pauling¹¹ and Fowler,^{12,13} associates the transition temperature with a change from rotational oscillation of the molecules or ionic groups below the critical temperature to a phase in which most of the molecules are freely rotating. The existence of λ -point transitions may be derived by statistical mechanics by assuming the rotation to be a cooperative phenomenon. That is, one considers that the rotation of a molecule is not independent of the motions of its neighbors and that the potential against rotation is a function of the degree to which its neighbors are rotating.

The second theory, developed by Frenkel¹⁴ and Landau,¹⁵ assumes that the transition is from an ordered to a disordered state. In this theory there is assumed a preferred orientation, occupied by a majority of the molecules, below the transition, while above the transition the molecules occupy with equal probability one of two, or more, equilibrium orientations. It should be noted that both below and above the transition the molecules flip between equilibrium orientations. The distinguishing factor between the ordered and disordered phases is that the mole-

cules predominate in a preferred orientation in the ordered phase; however, in the disordered phase a preferred orientation ceases to exist.

It is quite possible that either of these mechanisms may be responsible in different cases.

Since the line width of the nuclear resonance depends on the average reorientation time of the molecule through τ_c , we see that it is potentially possible to gain information about these transitions and their associated mechanisms by means of a nuclear resonance in the substance in question. Let us now investigate the order of magnitude of the quantities involved, so as to determine what effect these mechanisms may be expected to have on the line width.

In general we should expect the line width in the rigid lattice to be three gauss or more. Since the gyromagnetic ratio γ is about 2.7×10^4 for protons, this indicates that T_2'' should be less than 12 microseconds. Now, as indicated in Section I, the line width is controlled by the molecular flipping time when τ_c is less than $T_2''/2^{\frac{1}{2}}$. Thus the line width is generally sensitive to τ_c for values of τ_c smaller than 8 microseconds. At 7000 gauss the limit of homogeneity of the magnet used during these experiments was roughly 0.2 gauss. Therefore the lowest values of τ_c which can be derived from line-width measurements would be in the range 0.05 to 0.5 microsecond.

We may obtain an idea of expected values of τ_c from Debye's *Polar Molecules*.¹⁶ For liquid normal propyl alcohol he lists values from 26×10^{-10} second at -60°C to 0.9×10^{-10} second at $+20^\circ\text{C}$ for the characteristic reorientation time defined in his theory. Also, we should expect the reorientation time for the case of a free rotation in a solid to be of the order of a rotational period: 10^{-13} second or less. Therefore, it would be expected that, for rotating molecules in a solid, characteristic times of at most 10^{-10} second would be found.

Ice may be considered as an example of a solid with non-rotating molecules. A fairly rapid motion occurs at temperatures just below the freezing point, but the activity decreases quite rapidly as the temperature is decreased. From experiments on the dielectric constant of ice at radio-frequencies Debye gives values of 2.7 micro-

¹¹ L. Pauling, *Phys. Rev.* **36**, 430 (1930).

¹² R. H. Fowler, *Proc. Roy. Soc. London A* **149**, 1 (1935).

¹³ R. H. Fowler, *Statistical Mechanics* (The Macmillan Company, New York, 1936), second edition, Ch. 21.

¹⁴ J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), Ch. 2.

¹⁵ L. Landau, *Physik. Zeits. Sowjetunion* **11**, 26, 545 (1937).

¹⁶ Reference 10, p. 108.

seconds at -5°C and 18 microseconds at -22°C for the reorientation time as defined in his development. Undoubtedly a considerable variation in these values would occur for different substances, but the above would lead us to expect values in the microsecond range. It should be noted that this range is precisely that in which the line width is effective in measuring τ_c .

The marked difference between the values of τ_c for rotation and non-rotation, a factor of at least 10^4 , should be carefully noted. In addition, it is important that in the case of non-rotation τ_c may possibly fall in a range in which it directly affects the observed line width, while for rotation τ_c is so small that the observed line width must, in all practical cases, be only as narrow as the homogeneity of the magnet permits.

The expected effect of phase transitions on line widths may now be discussed on the basis of the expected values of T_2'' and τ_c . For the case of a rotational transformation, the line should be broad, typical of most solids, below the transition; upon reaching the transition, where free rotation becomes predominant, one should expect a rapid decrease, over the range of the transition, to a narrow line limited in width by magnet inhomogeneity.

The picture in the case of an order-disorder transition is not so clear cut, since there may be *little or no change* in τ_c at such a transition. Even in this case there may be some sharp change in the line width at the transition temperature, since the critical temperature is frequently accompanied by a change in lattice constants or in crystal structure. The crystal structure generally becomes more symmetrical in the highest temperature phase. This would result in a change in T_2'' even if τ_c does not decrease to the range in which it affects T_2 . A discontinuous decrease of τ_c at the transition may, of course, contribute to a change in line width. In any case one might expect a decrease of τ_c with increasing temperature, which may or may not reveal itself in the line-width measurements. As Frenkel points out,¹⁴ τ_c should be a function of the type

$$\tau_c = \tau_{c0} \exp(U/kT), \quad (5)$$

where τ_{c0} is the period of the rotational oscilla-

tions which would occur under the influence of the local electric field and U is the activation energy required to reorient a small group of molecules. Of course U itself may be a complicated function of the temperature T .

To summarize, if a moderate change, or zero change, in line width occurs at the transition, this must be identified with the order-disorder mechanism. On the contrary, if a rapid change to a very narrow line occurs at the transition, the rotational transformation mechanism may be indicated. However, the order-disorder mechanism is not completely ruled out on the basis of this evidence alone.

A third mechanism which applies to a few cases, for example, rochelle salt, is the so-called displacive transition. In this case the unit cell of the crystal suffers a small distortion during which a new symmetry element appears or disappears. Although this type of transition has not yet been studied experimentally by the method proposed here, it is expected that this would show very little effect on the nuclear resonance line width.

Essentially complete lists of substances which exhibit phase transitions may be found in review articles by Eucken¹⁷ and by Smyth.¹⁸ As one would expect on the basis of the mechanisms introduced to explain the transitions, these transitions are found primarily in substances composed of light molecules or of internal groups which would have low moment of inertia.

Pauling¹¹ proves that for the hydrogen molecule and the methane molecule the eigenfunctions and energy levels, even in the lowest quantum state, closely approximate those for a freely rotating molecule. The case of hydrogen has recently been studied by Rollin and collaborators⁹ by the nuclear resonance method. Other substances which show transitions include: the hydrogen halides, except for the lightest member of the group, HF; the H_2X group, with the exception of the lightest member, H_2O ; the XH_3 group, also except for the lightest member, NH_3 ; a number of ammonium salts, including the ammonium halides; and a multitude of organic molecules.

¹⁷ A. Eucken, *Zeits. f. Elektrochemie* **45**, 126 (1939).

¹⁸ C. P. Smyth, *Chem. Rev.* **19**, 329 (1936).

III. APPARATUS AND CRYOGENY

The circuit used is essentially the one described by B.P.P. The water-cooled electromagnet used for most of these experiments was designed by F. Bitter and constructed in the Research Laboratory of Electronics shop. The magnet is fitted with detachable pole pieces eight inches in diameter and a gap of $2\frac{1}{4}$ inches. The pole faces are shimmed to minimize field gradients at the center of the gap. To satisfy the demands of current constancy—one part in 10^5 or better—the magnet was usually run from a bank of submarine storage batteries. The d.c. field is generally modulated at 60 or 30 cycles through the use of separately wound inner layers of the magnet coils.

A General-Radio 605-B signal generator was used in most of the experiments. In order to minimize unwanted frequency and amplitude modulation on the r-f carrier, the power supply of the r-f generator was replaced by a well-filtered and regulated d.c. power supply. Most of the experiments were carried out at 30 Mc in a magnetic field of about 7000 gauss. Narrow and intense resonances were most easily displayed on an oscilloscope, using a magnetic-field sweep several times the line width. For less intense resonances the sweep was reduced to a small fraction of a line width and final amplification was obtained by means of a 30-cycle, twin- T , narrow-band amplifier with a lock-in feature.¹⁹ The output of this instrument is proportional to the slope of the resonance curve. In this case the absorption component of the resonance is more generally used, and the width measured is the distance between the inflection points, i.e., between the peak deflections of the output meter. If one assumes a line shape resembling a universal resonance curve, as results from Bloch's development,²⁰ for example, the above definition of line width is $3\frac{1}{2}$ times the distance between half-value points, which is normally defined as the line width.†

The temperatures which must be obtained in

order to study practically all of the phase transitions of interest fall in the range from about 20°K to room temperature. Preliminary low temperature experiments were carried on in the $9\frac{1}{2}$ -inch gap between the unshimmed poles of the M.I.T. cyclotron magnet. These experiments were carried on in glass Dewars with appropriate liquid baths as the low temperature reservoir. In many cases the liquid had to be discarded just before making observations for one of two reasons: (a) Proton-containing liquids around the r-f coil gave appreciable signals. (b) A boiling effect, due to the lack of complete rigidity in the r-f coil, caused a large increase in background noise. Also, by removing the liquid and allowing the temperature to drift upward, it was possible to cover any temperature range desired. However, these methods were not generally suitable for quantitative measurements because: (a) The bridge balance was very sensitive to small changes in temperatures. (b) The continuous drift in temperature left the temperature and thermal equilibrium of the sample very much in doubt, particularly in regions of high specific heats in the vicinity of phase transitions.

The above work indicated the requirements on the cryostat used for most of the quantitative work. This was designed to fit in a glass Dewar specially made for use in the small electromagnet. This Dewar is narrow at the bottom in order to fit conveniently in the gap, and flares out at the top in order to provide a greater volume for a liquid reservoir.

The cryostat operates on the principle of a variable heat leak between a thick-walled copper pot containing the sample at the bottom and a reservoir containing a suitable liquid in the wide part of the Dewar. The heat leak is controlled by means of a heater placed just above the copper pot. The pot and the reservoir are connected by thin-walled brass tubing, which represents a compromise between too slow a heat leak on the one hand and a too rapid loss in liquid on the other. A copper tube was placed from the top of the reservoir to the top of the pot with a heater wound over almost its entire length. This was used to keep the entire gas column above the pot at a temperature at least as high as that of the pot, in order to prevent convection currents. The space between the copper tube and the reservoir

¹⁹ R. H. Dicke, *Rev. Sci. Inst.* **17**, 268 (1946).

²⁰ F. Bloch, *Phys. Rev.* **70**, 460 (1946).

† Bloch makes certain approximations which lead to the assumed line shape. This line shape is only an approximation, however. Since there is no completely adequate theory for line shape, any definition of line width is arbitrary to a certain degree.

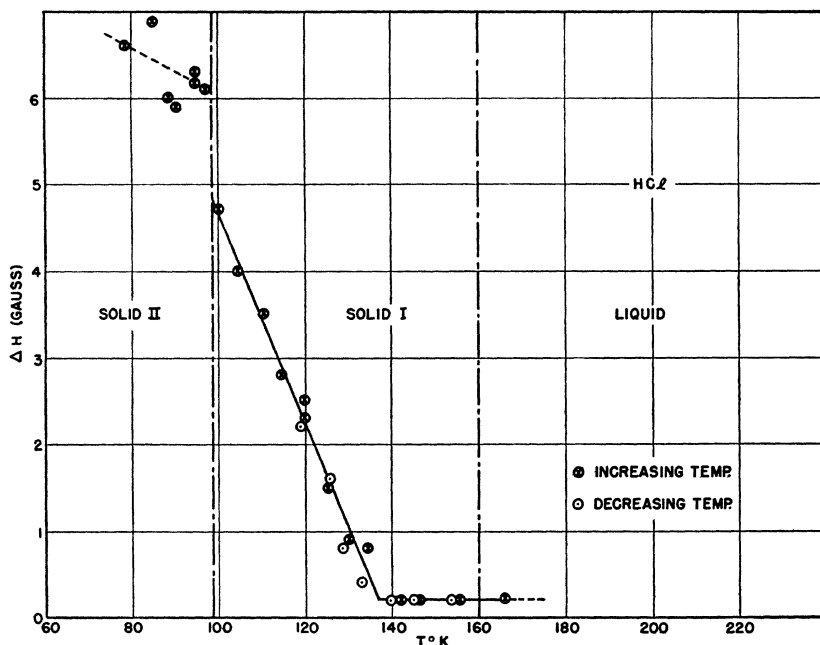


FIG. 1. Line width vs. temperature for hydrogen chloride.

was filled with an insulating material. The reservoir was made vacuum tight to permit pumping on the liquid and to enable convenient removal of explosive and noxious vapors. In addition, the construction of the cover was such that the space in the Dewar, but outside the reservoir, could be evacuated, so that the cryostat could be made adaptable for use with liquid hydrogen.

Resistance thermometers were used to determine temperature with one wound about midway along the copper pot and the other in the gas column several inches above the pot. Resistance was measured by means of a Leeds and Northrup Wheatstone Bridge (Type "S" testing set). This was found to be quite adequate for the purpose of the experiments above 80°K. Since the lower resistance thermometer reads the average temperature of the pot rather than the temperature of the sample, the time-dependent relationship between these was checked by placing a thermocouple in the position of the sample. As a result, a waiting period of the order of 20 minutes was adopted after changes in temperature of the order of 5 to 10K°. Generally, two or more readings of line width were taken over a time of 10 or more minutes after the waiting period, and data were not accepted until these could be repeated to within the estimated accuracy of the readings. To check this procedure, line-width

data were usually taken in the direction of increasing as well as decreasing temperature. Practically no cases were found of hysteresis resulting from a lack of thermal equilibrium.

Those samples which are gases at room temperature were condensed through a capillary opening into thin-walled glass ampules dipped in liquid nitrogen. After the sample was collected, the ampule was sealed by applying a small, hot flame to the capillary. The seal was then worked around into a hook so that the sample could be suspended from a string for ease in storing the samples and transferring them to the cryostat. The ampules were stored in liquid nitrogen. An outline of the chemical preparation of the samples is given in the appendix.

IV. RESULTS AND DISCUSSION

Those substances which have been studied in some detail include (a) normal and heavy methane, CH_4 and CH_3D ; (b) the hydrogen halides, HCl , HBr , and HI ; (c) the H_2X group, H_2S and H_2Se . In addition, some preliminary results will be reported for ammonium chloride and for natural and synthetic rubber.

4a. The Methanes

It was the exploratory work with normal methane which gave the first indication of the possible

application of this method to the study of phase transitions. No work has been done at hydrogen temperatures, the range of interest for these substances, since the construction of the cryostat. Therefore, the results for these solids were obtained entirely during the exploratory experiments.

Normal methane shows a single λ -point transition at 20.5K° , occurring over a range of 3K° . Its melting point is at 90.6°K . The methane crystal is cubic both above and below the λ -point, and the transition shows some hysteresis.^{††}

A line width of the order of 0.2 gauss was observed just above 77.4°K and 20.4°K . Since the lower temperature observation was believed to be above the λ -point, one experiment was carried on in liquid helium. Under these conditions a 10-gauss resonance was observed. Although no explicit temperature measurements were taken, the helium was known to have boiled away rapidly, since a drift in r-f balance conditions shortly after filling indicated a drifting temperature. There was no marked change in the appearance of the resonance for approximately 30 minutes. Then, within a period of less than one minute, during which the bridge was being re-balanced, the resonance became narrow, as had been observed above 20.4°K . We therefore conclude that there was a transition in the line width from about 10 gauss to roughly 0.2 gauss

in a range of order of less than 1K° . The corresponding transition in τ_c is therefore from greater than 2 microseconds to 0.03 microsecond *or less*. As was pointed out in Section II, this behavior is what would be expected in the case of a rotational transformation. However, the possibility that this is an order-disorder transition accompanied by a decrease in the flipping time to less than 0.03 microsecond is not excluded.

In the case of CH_3D two λ -points are found, at 15.5°K with a range of 2° , and at 22.6°K with a range of 3° . The crystal structure of this solid has not been investigated, to the knowledge of the author. The melting point of deuterated methane is also at 90.6°K .

A line-width behavior very similar to that observed in normal methane was found at the higher temperature λ -point. No investigation was carried on below 20.4°K . In this case a resonance of the order of 3 gauss in width was observed very near 20.4°K . This line narrowed to less than 0.3 gauss in a very small temperature range slightly above 20.4°K , which was believed to be the transition temperature. This change in line width represents a change in τ_c from greater than 5 microseconds below the transition to less than 0.3 microsecond above the transition.

As is the conclusion for CH_4 , the behavior of the nuclear resonance line width in CH_3D in the vicinity of its upper λ -point is what one would

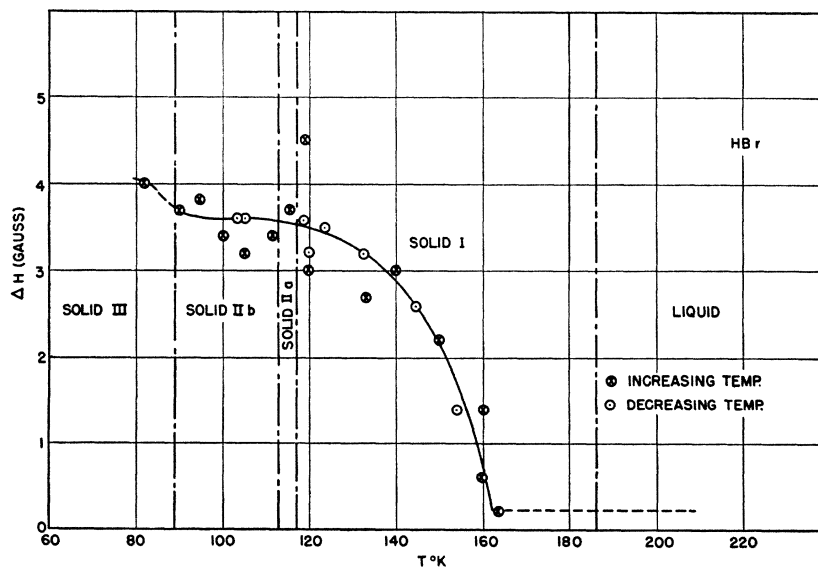


FIG. 2. Line width *vs.* temperature for hydrogen bromide.

^{††} Data concerning transition temperatures, etc., are from references 17 and 18.

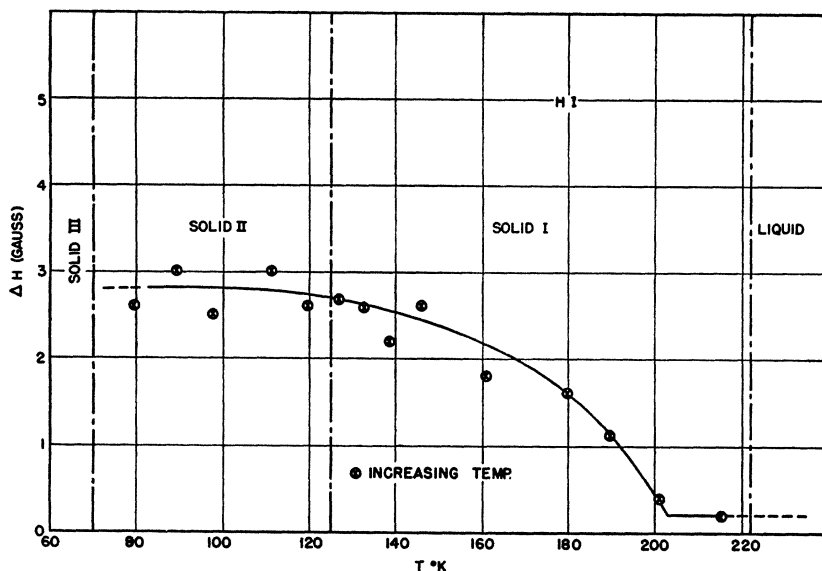


FIG. 3. Line width vs. temperature for hydrogen iodide.

expect for a rotational transformation. However, the possibility of its being an order-disorder transition is not absolutely eliminated. Although observations were not carried down to the lower λ -point, by process of elimination one would expect this to be an order-disorder transition.

4b. The Hydrogen Halides

HCl shows a first-order transition at 98.36°K which is accompanied by a change in crystal structure from cubic in the higher temperature modification to a less symmetrical structure at lower temperatures. HCl melts at 158.9°K.

The resultant curve of line width *versus* temperature, shown in Fig. 1, divides into three sections. In the comparatively short temperature range investigated below the transition the line width appears to be decreasing slowly with increasing temperature. This line width is probably a measure of the rigid-lattice line width, and the temperature variation may then be attributed to slight changes in the lattice constants with temperature. It would be difficult to prove this assumption until an accurate rigid-lattice line width can be computed for the lower temperature modification.

An apparently sharp drop in line width at the transition temperature constitutes the boundary between the first and second portions of the graph. In the temperature range from 98.4°K to about 135°K the graph indicates almost a per-

fectly linear decrease in line width with the temperature. In this case we are almost certainly in the range where ΔH is proportional to τ_c , which implies a linear decrease in τ_c from about 3 microseconds at 100°K to about 0.08 microsecond at 135°K. It is likely that the sharp drop at the transition is due at least in part to a change in the rigid-lattice line width accompanying the change in crystal structure. There is also some possibility that this may be associated with a small discontinuity in the characteristic flipping time.

Beyond 135°K the observed line width is determined entirely by the homogeneity of the magnetic field. This limiting line width is roughly 0.2 gauss at a resonant field of 7000 gauss. No change in the amplitude of the resonance, as observed on the oscilloscope, was noted upon melting the sample. There is little to be gained by speculating as to the variation of τ_c above 135°K, although it should be noted that the extreme possibility of free molecular rotation setting in below the melting point is not ruled out by these data. However, this does not imply a rotational transformation, for which case free molecular rotation sets in at the transition. Therefore, there is no doubt that this line-width variation fits in with what would be expected for the order-disorder transition mechanism. The possibility of a rotational transformation is completely eliminated.

Hydrogen bromide has λ -points at 89°K, with

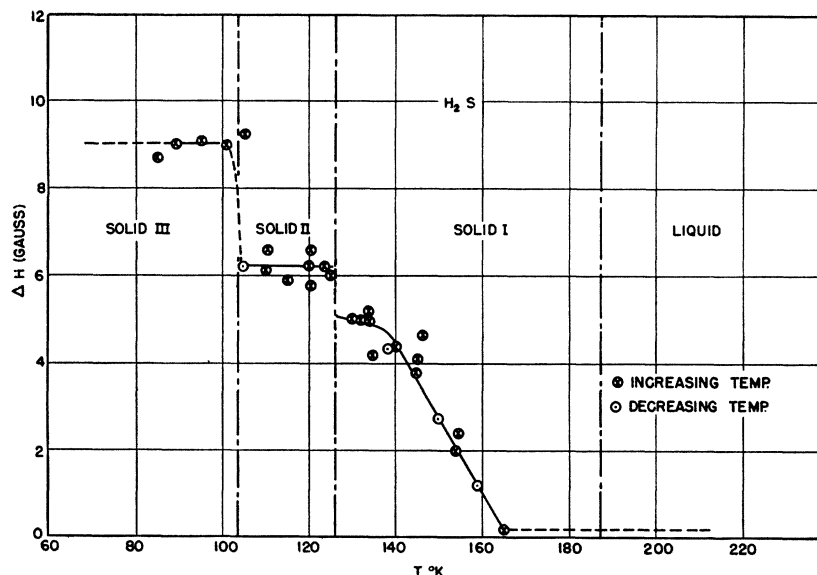


FIG. 4. Line width *vs.* temperature for hydrogen sulfide.

a 3° range, and at 113° and 117°K , with a 2.5° and 1.5° range, respectively. A change from a less symmetrical structure to a cubic structure occurs at the lowest transition. Hysteresis is found at all three transitions. HBr melts at 186.2°K .

Referring to the line width *versus* temperature graph in Fig. 2, we see that there may be a slight change in line width at the lowest transition. However, in the temperature range between 90° and about 140°K , the line-width curve is characterized by a very slow decrease with increasing temperature. It is believed that in this range we are measuring the rigid-lattice line width. It would therefore appear that τ_c has become sufficiently small to take control of the line width in the vicinity of 140°K . Above this temperature the line width responds similarly to what was found in the higher temperature modification of HCl. Between 140° and about 160°K this line width drops very rapidly from about 3 gauss to the observable limit of about 0.2 gauss, the drop representing, on the basis of our interpretation, a decrease in τ_c from roughly 5 microseconds to about 0.3 microsecond. Again there is a range of somewhat over 20K° in the solid state in which the observed line width depends only on the homogeneity of the magnetic field. As in the case of HCl, the possibility of a rotational transformation at any of the λ -points is clearly eliminated, while the data satisfy the implications of the order-disorder mechanism.

The remaining member of the hydrogen halide series, hydrogen iodide, has two λ -transitions at 70° and 125°K , each with a range of 5° . HI is tetragonal (face-centered) above 70°K , while no data seem to be available for the lowest temperature modification.

The line width *versus* temperature data, shown in Fig. 3, are almost identical in character to those found for HBr. In this case the investigation has not been carried to the lowest temperature modification. For HI the line width is almost constant from 80°K to about 150°K , and drops rapidly from about 2.5 gauss to the observable limit of about 0.2 gauss between 150° and about 200°K . This represents an assumed decrease in τ_c from about 6 microseconds to roughly 0.5 microsecond. Again there is a temperature range of somewhat over 20K° in the solid state in which the observed line width is determined entirely by the homogeneity of the magnetic field. As is the case for HCl and HBr, the data clearly deny the Pauling-Fowler interpretation of the λ -points in favor of the Frenkel-Landau interpretation.

4c. Hydrogen Sulfide and Hydrogen Selenide

The lighter substance of the two, H_2S , shows phase transitions at 103.6°K and at 126.2°K . The former is a λ -transition with a range of 0.9K° and some hysteresis, while the latter is apparently a first-order transition, sharp and showing

no hysteresis. The intermediate-temperature modification is known to be cubic. H_2S melts at 187.6°K .

The graph of the line width *versus* temperature data for H_2S , as shown in Fig. 4, may be interpreted in much the same way as the results for the hydrogen halides. In the lowest temperature modification the line width is apparently constant and is probably the rigid-lattice line width for this phase. A sharp drop in line width occurs in the vicinity of 103.6°K , the lower transition temperature, and the line width is constant in the range of the intermediate-temperature modification, leading us again to interpret this as the rigid-lattice line width for this phase. At the upper transition temperature another small discontinuity in line width apparently occurs followed by a sharp break in the slope at about 135°K . If we interpret this as the temperature at which τ_c becomes effective in narrowing the line, this indicates an approximately linear variation in τ_c from 3 microseconds to 0.1 microsecond between 135° and 165°K . Again there is a range of about 20K° in the solid state in which the observed line width is limited only by the homogeneity of the magnetic field. As is the case with the hydrogen halides, the above behavior eliminates the possibility of a rotational transforma-

tion and indicates the order-disorder mechanism as the source of the transitions.

Hydrogen selenide shows two phase transitions in the solid state. The one at 82.3°K is a λ -point with a range of 7° and showing some hysteresis, while the upper transition at 172.5°K is sharp with no hysteresis, and may be a first-order transition, similar to H_2S . Hydrogen selenide is known to be cubic in its two higher temperature modifications. The melting point is at 207.4°K .

The nuclear resonance data for protons in H_2Se , shown in Fig. 5, have somewhat different characteristics from those described for the previous cases. There is some decrease in line width at the lower transition. However, the drastic increase in line width between 110° and about 140°K , and the subsequent decrease between 140° and 172°K , have no precedence. If one assumes that the line width is proportional to τ_c in this range, then the indicated variation in τ_c is very startling. It was noted in Section II that τ_c should be proportional to $\exp(U/kT)$, where U is the activation energy required to reorient a small group of molecules. Thus the variation in the case of H_2Se indicates that the barrier against reorientation would have to increase drastically between 110° and 140°K , so as to more than compensate for the inverse temperature depend-

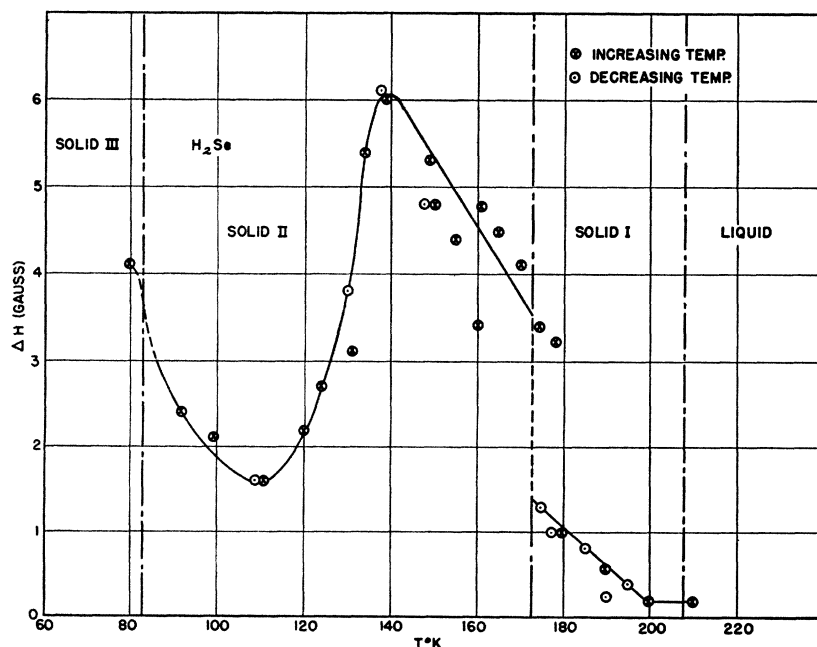


FIG. 5. Line width *vs.* temperature for hydrogen selenide.

ence in the exponential. It is difficult to see how this could happen.

Although there is a considerable dispersion in the data in the vicinity of the upper transition, there seems to be a discontinuous decrease in the line width at this temperature to the comparatively narrow width of about 1.4 gauss, followed by a decrease to the observable limit of 0.2 gauss at 200°K, in this case only about 8K° below the melting point. It is apparent, in spite of the strange behavior noted above, that the rotational mechanism is clearly eliminated by the data in favor of the order-disorder mechanism.

One factor which may have contributed to the strange results in the case of H₂Se is the possibility of the presence of some HCl as impurity.

4d. Preliminary Results for Ammonium Chloride and for Rubber-Like Materials

In both cases data were taken only during the exploratory experiments.

In the case of NH₄Cl, which has a λ -point at 242.8°K, a line width of about 5.5 gauss was found at room temperature and somewhere in the vicinity of the λ -point. At nitrogen temperature a line width of 18 gauss was observed. As in the other cases, this definitely indicates that this is an order-disorder type of transition,²¹ and not a rotational transformation, as has frequently been assumed.¹⁸

In natural, unvulcanized rubber a narrow line was observed, limited only by the homogeneity in the magnetic field. Therefore, the possibility of extremely short flipping times for the methyl side groups or for the hydrogen bonds, for example, is quite plausible. However, there is an apparent decrease in the number participating in this motion as the temperature is decreased, since the amplitude of the resonance decreases drastically while there is no change in the other characteristics of the resonance. A small, narrow pip is still visible at dry-ice temperature, about -78°C. Vulcanization had no effect at room temperature, while carbon loading did seem to broaden the resonance slightly. As was expected, a sample of GR-S synthetic rubber gave only a broad resonance.

4e. Summary of the Results

We have indicated and applied a method capable of distinguishing the mechanism of those λ -points, as well as a few first-order transformations, for which the transitions may be attributed to a change in molecular reorientation time. In the experimental studies it was shown in most cases that the transitions cannot possibly be associated with the onset of molecular rotation but satisfy, instead, the conditions of an order-disorder transformation. Those substances which fall into this classification are HCl, HBr, HI, H₂S, H₂Se, and NH₄Cl. In a few cases the results indicate the plausibility of a rotational transformation, although the order-disorder mechanism is not absolutely eliminated for these transitions. These exceptional solids are CH₄ and CH₃D at the upper transition, as well as natural rubber, for which internal rotation is shown to be reasonable but is not proved unquestionably.

The experimental data for the methanes, in particular, should be made more quantitative under better conditions of temperature control. In addition, measurements of the spin-lattice relaxation time T_1 may possibly eliminate the ambiguity in these rare cases. This follows from the fact that T_1 is also a function of the characteristic flipping time,⁴ with the advantage that no limitations will be imposed in the direction of short flipping times by the homogeneity of the magnetic field. However, the measurement of T_1 is much more difficult than the measurement of line width, or T_2 , which has been shown to be adequate in most cases.

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²¹ A. W. Lawson, Phys. Rev. **57**, 417 (1940).

staff, who prepared chemically many of the solids studied.

APPENDIX

Following is a brief outline of the methods by which the commercially unavailable samples were produced. In all cases at least one stage of fractionation was carried on before condensation into the ampules.

a. Hydrogen Chloride

Hydrogen chloride was prepared by dropping concentrated sulfuric acid on a mixture of hydrochloric acid and sodium chloride. The gas was dried by passing it through four tubes of P_2O_5 . It was collected in a 100-ml flask in a liquid nitrogen trap.

b. Hydrogen Bromide

Forty-eight percent hydrobromic acid was dropped slowly onto a mixture of freshly ignited sand and phosphoric pentoxide. The resulting gas was passed through two tubes of red phosphorus to remove free bromine, and through three tubes of P_2O_5 to remove water vapor. The gas was first collected in a 100-ml flask (drawn down in the neck) submerged in a liquid nitrogen bath.

c. Hydrogen Iodide

Hydrogen iodide was prepared by the substitution reaction $NaI + H_3PO_4 \rightarrow HI \uparrow + NaH_2PO_4$. Moderate heat was applied. The apparatus was completely covered with aluminum foil to prevent decomposition of the hydrogen iodide by light. Free iodine was removed by freezing out in a $\frac{3}{4}$ -inch Pyrex coil in a $-30^\circ C$ trap. The temperature of the trap was maintained by regulating a dry air flow through a glass-wool-packed U-tube immersed in liquid nitrogen. This temperature was easily kept to within $\pm 1^\circ C$. Further traces of iodine were removed by passing the gas through two tubes of red phosphorus. Moisture was removed by passing the gas through three tubes of P_2O_5 . The gas was collected in two U-tubes in liquid nitrogen baths. The HI first condensed into the U-tubes as a pure white solid.

It was observed then that after a few seconds' exposure to light a progressive discoloration of the solid HI took place, probably due to decomposition of the HI. Although considerable effort was made to prevent exposure to light during the fractionation, some decomposition did take place. The finished frozen gas therefore shows some discoloration, presumably due to free I_2 .

d. Hydrogen Selenide

Hydrogen selenide was made by dropping dilute HCl slowly onto freshly made aluminum selenide: $Al_2Se_3 + (3+x)H_2O \rightarrow 3H_2Se + Al_2O_3 \cdot xH_2O$. The aluminum selenide was prepared by mixing 50 grams of finely divided precipitated selenium with 30 grams of aluminum powder that had been washed with acetone and ether: $2Al + 3Se \rightarrow Al_2Se_3$. Five grams of the mixture were placed in a fire-clay crucible and ignited with glowing magnesium ribbon. Every few seconds three grams of the mixture were added to the glowing mass in the crucible. The aluminum selenide was stored in a vacuum desiccator until used. Dilute hydrochloric acid was slowly dropped from the dropping funnel onto the freshly made aluminum selenide. The evolved hydrogen selenide passed through a drying train of two tubes of $CaCl_2$ and three tubes of phosphorus pentoxide. It was collected in a 100-ml flask in a liquid nitrogen bath. Metaphosphoric acid was used to lubricate the ground-glass joints in the glass system.

e. Deuterated Methane

The methyl deuteride was prepared by the Grignard reaction: $CH_3I + Mg \rightarrow CH_3MgI$; $CH_3MgI + D_2O \rightarrow CH_3D \uparrow + MgI(OD)$, carried on in dibutyl ether as solvent. The dibutyl ether and methyl iodide were first carefully dried and redistilled. The heavy water was dropped slowly on to the methyl magnesium iodide. The gas resulting from the reaction passed through concentrated sulfuric acid to remove the dibutyl ether, and then through three tubes of P_2O_5 for drying. In this case the gas was condensed directly into the ampules.