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STUDIES RELATING TO THE
STRUCTURE OF ALUMINUM HYDRIDE

BERKELEY, CALIFORNIA

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Robert F. Nickerson
(Thesis)

December 16, 1957

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ABSTRACT

The object of the work described in this paper was to determine the molecular structure of AlH_3 , using the techniques of "nuclear spin resonance." Attempts to prepare ether-free AlH_3 that were unsuccessful are described. Also it was not possible to observe the deuterium signal in AlD_3 . It was possible, by the use of the proton signal of the ether in AlD_3 , to obtain the nuclear spin resonance absorption curve for AlH_3 by subtracting out the contributions of the ether protons to the resonance signal. A model is proposed to explain the features of the nuclear spin resonance absorption curve. The existence of LiAl_2H_7 , which has been postulated elsewhere, is assumed in order to explain the data obtained from high-resolution nuclear spin resonance experiments.

FOREWORD

This paper describes the work done to determine the molecular structure of AlH_3 . The presentation of this research can be conveniently divided into three sections, as follows:

1. A description of the attempts to prepare ether-free AlH_3 ;
2. The nuclear spin resonance studies of solid AlH_3 ;
3. The high-resolution nuclear spin resonance studies of the reaction

INTRODUCTION

For a number of years, the diatomic molecule Al-H was known only to the spectroscopists in that they attributed certain band spectra to the molecule AlH. Many reports describing these spectroscopic studies have appeared in the literature. The first chemical preparation of AlH₃ is reported by Stecher and Wiberg in which they prepared hydride compounds of aluminum by reacting the vapor of trimethyl aluminum with an excess of hydrogen in an electric discharge at elevated temperatures.¹ They were able to isolate from their reaction mixture only a polymeric compound of the general formula (AlH₃)_x. The method yielded an impure product with many by-products.

In 1947 a paper published by Finholt, Bond, and Schlesinger reported the preparation of AlH₃ using a metathetical reaction between LiAlH₄ and AlCl₃.² This method also produced a polymeric compound having the formula (AlH₃)_x. However, the yields were good, about 90% and up, and produced a comparatively pure compound. The AlH₃ was solvated by a considerable amount of ether, though, and any attempts the investigators made to remove it by heating and evacuation resulted in decomposition of the hydride.*

Since the first preparation of this new compound some investigators have speculated on its molecular structure. The difficulty is that, as in the diborane problem, there is an insufficient number of electrons to form the number of chemical bonds necessary for the construction of any model for the polymer.

Wiberg first proposed a linear structure in which the aluminum atoms are connected by single hydrogen bridges.¹ (See Fig. 1.) In 1947, a paper by H. C. Longuet-Higgins³ appeared in which he proposed a structure comprising a two-dimensional lattice with a type of bonding based on the Pitzer "protonated double bond"⁴ that had

* All references to ether made in this paper will be to diethyl ether.

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Fig. 1. Section of an AlH_3 linear polymer.

been successful in accounting for the electron-deficient bonding occurring in the boron hydrides. He extended this concept to AlH_3 by proposing that the unit >Al-H can polymerize as >B-H does, but whereas the polymerization of the latter stops when the boron atom has its four valency-shell orbitals occupied, the polymerization of the former continues until six of its valency orbitals are occupied. This is an extension of the idea of a "covalency maximum" to this and other anomalous compounds. Thus, according to this concept, the monomeric AlH_3 could then polymerize in two dimensions by the continued formation of bridge linkages as shown in Fig. 2. If it is assumed that (a) the hydrogen atoms form bridges in pairs between aluminum atoms, every aluminum atom being joined octahedrally to six hydrogen atoms, and (b) all Al-H bonds in the giant molecule are crystallographically equivalent, then it follows that the aluminum atoms must be arranged in two-dimensional layers, with the aluminum atoms in each layer at the vertices of a hexagonal tessellation. One such layer is illustrated in Fig. 2. However, if Pitzer's view of the "protonated double bond" is accepted, it seems likely that the hydrogen atoms in the group may be arranged, not at the vertices of an octahedron, but at the vertices of a trigonal prism with the aluminum atom at the center. Thus where the octahedral structure would utilize sp^3d^2 hybrid bonds, the trigonal prism would be made up from Al-X σ orbitals constructed from a linear combination of 3s, 3p_x , 3p_y orbitals (z axis perpendicular to the plane of heavy atoms); of the remaining orbitals, 3p_z , 3d_{xy} , 3d_{xz} can be linearly combined to give three π orbitals directed toward the three X atoms and having nodal planes $z = 0$. The protons would be situated near the antinodes of these π bonds, that is, at the vertices of a trigonal prism (Fig. 3). This configuration leads to the same arrangement of heavy atoms in $(\text{AlH}_3)_n$ as the octahedral configuration.

In 1953 Wiberg proposed a two-dimensional structure of the same type without going into detail on what type of bonding occurs. . 5

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Fig. 2. . Projection of one layer of the two-dimensional AlH_3 polymer.

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Fig. 3. The arrangement of the aluminum atoms of $(\text{AlH}_3)_n$ if the "protonated double bond" concept is correct.

In 1957 Rundle further extended the concept of electron-deficient bonding.⁶ He expounded the principle of bond delocalization. This type of bonding was possible if an atom, usually metallic, with more low-energy orbitals than valence electrons combined with atoms or groups containing no unshared electron pairs. Under these circumstances it appears that delocalization of bonding occurs so as to use all the low-energy orbitals of the metallic atom. Examples of such metallic atoms are boron, with three valence electrons and four sp^3 orbitals, and platinum IV, with four valence electrons and six sp^3d^2 orbitals.

To validate these concepts, it is necessary to know the structures of such compounds. A few of the boron hydrides have been worked out, but other members of this family of compounds characterized by electron-deficient bonds should be known. For this reason it was decided to determine the molecular structure of AlH_3 since its synthesis, as given in the literature, appeared to be relatively simple and the reactions involved well characterized.

THE EXPERIMENTAL PROBLEM

The methods available for determining the structure of AlH_3 are not numerous. X-ray diffraction, the most common means of determining crystal and molecular structures of chemical compounds, has been tried but it has not been possible for the investigators to obtain sufficient information to determine the structure of AlH_3 ; AlH_3 , being a solid, cannot be studied with electron diffraction. Two other tools are available. They are infrared-spectrum analysis and nuclear spin resonance.* NSR seemed the more promising approach to this problem and therefore it was utilized for this investigation.

The use of NSR for obtaining structure information, in essence, involves the use of nuclei as probes that are sensitive to their environment and hence to the position of other nuclei surrounding them; the position, in turn, is determined by the molecular structure. (The reasons and theory for this are treated in a later section.) In working with proton spin resonance, it is necessary that only one chemical type of proton be present, namely those belonging to AlH_3 . As related above, the method of synthesizing AlH_3 as described by Finholt et al. produces a compound containing large amounts of ether of solvation. Since the protons in ether complicate the spectra of such a preparation and probably make it virtually impossible to obtain any useful structural information, there are three ways out of this difficulty. They are

- (a) preparing ether-free AlH_3 ,
- (b) using a deuterated ether as the solvent,
- (c) studying AlD_3 .

Method (a) is the preferred choice as (b) would require either an exceedingly expensive chemical or involve a lengthy and laborious

*The more famous name is nuclear magnetic resonance, but many authorities prefer the use of nuclear spin resonance since it is more descriptive of the physical phenomenon. The term will henceforth be abbreviated NSR.

synthesis; (c) would be more convenient than (b) but the magnitude of the spin resonance signal available from deuterons is much less than that from protons.

A note to the J. Am. Chem. Soc. in 1955 described a method for preparing nonsolvated aluminum hydride.^{7, 8} The appearance of this note was the main reason for choosing method (a) rather than either of the alternatives.

I. SYNTHESIS OF ETHER-FREE ALUMINUM HYDRIDE

The method for synthesizing aluminum hydride as described by Finholt et al. involves mixing ether solutions of AlCl_3 and LiAlH_4 in a closed, dry system in amounts according to the stoichiometric ratio as given by the equation²

The LiCl precipitates and may be separated by passage of the reaction mixture through a filter. The clear filtrate, upon standing, produces a white precipitate, which is the AlH_3 . The ether may then be removed by vacuum distillation. Such a preparation contains large amounts of ether in amounts up to 30 mole %. The authors reported, however, that they were able to lower this figure to about 17 mole % by heating the compound to 80°C and continuously evacuating over a period of several days. Any attempts to use higher temperatures resulted in decomposition of the AlH_3 .

AlH_3 containing any appreciable amount of ether could not be used for nuclear spin resonance experiments because of the large background signal that would be contributed by the ether protons. The note by Rice describes a variation of the procedure indicated above that produces an AlH_3 preparation free of ether.^{7, 8} This variation of technique consists of running the filtered reaction mixture, which is free of LiCl , into a rapidly stirred inert solvent which may be pentane, petroleum ether, or some similar liquid. By such action, the authors state, the AlH_3 is forced to precipitate, because of its insolubility in the inert solvent, before the hydride has a chance to form a complex with the ether. The resulting precipitate is then separated from the solvents by vacuum distillation. The dry precipitate is evacuated at room temperature for approximately 12 hours to remove the last traces of the solvents.

The synthesis involved the following procedures (see Fig. 4). Ether solvent was dried over sodium and refluxed for several hours

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Fig. 4. Apparatus for the synthesis of AlH_3 .

⊗ stopcock, ⊕ ball joint, A. reflux still for drying ether with LiAlH_4 , B. mixing flask for dissolving LiAlH_4 in ether, C. settling and storage flask, D. reaction flask, E. evacuation vessel - made of 4-inch flanged pyrex pipe, 1. to argon supply, 2. container for transferring LiAlH_4 , 3. filters, 4. drying tube, 5. to ether still, 6. container for transferring AlCl_3 , 7. copper wire, 8. to cold trap and vacuum pump, 9. magnet stirrer, 10. buret.

with LiAlH_4 . The glass components of the apparatus were oven-dried and when they were assembled, argon was swept through the system at a slow rate for several hours to remove any traces of moisture. These precautions were always observed for each new assembly to prevent the presence of moisture. All transfers of the chemicals involved were done in a dry box.

LiAlH_4 was refluxed with dry ether overnight in Flask B. The mixture was allowed to settle for several hours and the supernatant liquid was then forced through Filter 3; the filtrate was stored in C. To determine its concentration, a small measured amount was withdrawn from the buret 10, for analysis. Then (computed from the LiAlH_4 solution concentration and the weight of AlCl_3 in 6) the correct volume of LiAlH_4 solution was mixed with the AlCl_3 in D which had been previously dissolved in dry ether. Upon mixing a vigorous reaction immediately took place but subsided quickly. Stirring was continued for 15 seconds, then the LiCl formed was allowed to settle. After a minute, the reaction mixture was forced slowly through Filter 3, down the copper wire, 7, into E, while the petroleum ether was stirred. After the addition was complete, the ether and petroleum ether were removed by vacuum distillation. When all the solvents had been removed, evacuation was continued overnight while the solid was stirred to break up the precipitate.

The hydrogen content of this product was then determined by the measurement of the volume of gas evolved upon hydrolysis of a given weight of product. *

To determine the presence of ether in the product, an amount of AlH_3 was thermally decomposed and the resulting gases were analyzed

* NaOH was found to produce a cleaner hydrolysis reaction than an acid solution. The latter did not readily dissolve the aluminum produced by the thermal decomposition of the hydride due to the large amount of heat liberated by the hydrolysis reaction.

on a mass spectrograph. * This product gave an analysis of 4.4% H, which corresponds to 43% AlH_3 . However, within a day the product turned black, indicating decomposition. This is believed to be caused by the presence of AlCl_3 in the product.⁸

Because of the instability, this means of preparation was considered to be unsatisfactory and a method to guard against an excess of either AlCl_3 or LiAlH_4 was considered necessary. The setup shown in Fig. 5 was used, which provided a means to separate the AlH_3 precipitate from the bulk of the solvent by filtration. The procedure followed for this preparation was substantially the same as that given above except for the following changes:

- a. Filter cups b and b' were used in place of fritted glass filters because of their greater filtering efficiency for fine precipitates.
- b. Excess LiAlH_4 was used which was to be removed by continuous treatment with dry ether using a modified Soxhlet extractor; a', G. However, a synthesis carried out in the apparatus shown in Fig. 5 produced a product that darkened considerably after a day. Since this indicated decomposition, this preparation had to be discarded.

At this time a simple experiment was tried. A solution of AlCl_3 in ether was poured into some petroleum ether. The AlCl_3 did not precipitate out. This indicated that the LiAlH_4 and AlCl_3 solutions may be added in as close to stoichiometric amounts as possible. Then when the hydride had been precipitated by the petroleum ether, any small excess of LiAlH_4 would not interfere. However, if AlCl_3 was present in slight excess, it remained in solution and stayed in the filtrate when the AlH_3 was filtered out. Thus there would be a distinct advantage to filtering out the AlH_3 rather than distilling off the solvents and leaving the AlCl_3 behind

* This means of analysis became standard practice during the course of this investigation.

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Fig. 5. Apparatus for the synthesis of ether-free AlH_3 .
 ○ ball joint, ⌘ stopcock, C. storage flask for LiAlH_4 solution,
 D. reaction vessel, E. pentane storage, F. filtrate collector,
 G. ether storage for treatment of filtrate by continuous extraction,
 1. to LiAlH_4 solution vessel (see vessels A and B of Fig. 4),
 2. to argon supply, 3. to ether-drying still, 4. to pentane-drying
 still, 5. to drying tube, 6. glass rod, a. filter cup con-
 tainer made from 2-inch pyrex flanged pipe, b. filter cup,
 c. AlCl_3 container, d. magnetic stirrer.

(which causes the hydride to be unstable), as was done in the technique originally described.^{7, 8}

A preparation using this technique was carried out using the setup shown in Fig. 6. The procedure in this was very similar to those given above. The reaction mixture of LiAlH_4 and AlCl_3 was filtered free of LiCl in a, b, the AlH_3 suspension in c was then filtered in a' b' and the filtrate was collected in D. After the precipitate had been drained, it was evacuated overnight for thorough drying.

The following day vessel a', containing the dry precipitate, was closed off and transferred to a dry box where the AlH_3 was removed, pulverized, and transferred to a round-bottomed flask. This flask, attached with a stopcock, was removed from the dry box and attached to a vacuum line and the AlH_3 was placed under a high vacuum at 50°C for several days to assure complete removal of any remaining solvents.*

Upon analysis, this hydride preparation had the following composition:

Aluminum	Average 46.0%	Theor. 89.9%
Hydrogen	Average 4.94%	Theor. 10.1%
Hydrogen/Aluminum = 2.88.		

In order to ascertain if this preparation contained any ether, a sample was thermally decomposed and the resulting gases collected and subjected to analysis by a mass spectrograph. The results of this analysis were:

* During this treatment, the hydride proved to be quite stable, showing no signs of decomposition (which would be manifested by darkening). This indicated that the preparation was free of AlCl_3 . The filtrate in vessel D proved to contain some AlCl_3 , which became evident when it was added to water.

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Fig. 6. Apparatus used for the synthesis of ether-free AlH_3 .
 ○ ball joint, ○ stopcock, A. storage vessel for LiAlH_4 solution, B. vessel for dissolving AlCl_3 and mixing with LiAlH_4 solution (A, B connected with tygon tubing), C. pentane vessel, D. filtrate collector, a. filter cup container made from 2-inch pyrex flanged pipe, b. filter cup, 1. to cold trap and vacuum pump, 2. to argon supply, 3. to ether-drying still, 4. to pentane-drying still, 5. to drying tube, 6. magnet stirrer, 7. glass rod, 8. serum-bottle stopper.

80% H_2
18.5% ether
1.5% xylene*

Upon calculation these results yielded a hydride of the composition $AlH_3 \cdot 0.35 Et_2O$. Such a molecular formula gave the following composition of the solid:

Hydrogen 5.4% ,
Aluminum 48% ,
Ether 46% ,

which agreed favorably with the hydrogen, aluminum analysis. Clearly, a hydride having an ether content of this magnitude could not be suitable for an NSR investigation.

It was decided at this point that there were certain conditions necessary for the preparation of the ether-free AlH_3 other than those specified in the literature. The most probable variables would be the temperature at which the reaction takes place and the time lag between reaction and precipitation. For this reason, it was decided that it would be necessary to carry out a systematic investigation of what effect there would be on the ether content of AlH_3 , if the temperature and time lag were varied. Figures 7 and 8 illustrate the setups used for this series of preparations. Table I summarizes the observations and results of these synthesis. In each case, the general procedure was similar to those given before.

*Xylene was a constituent of every gas sample subjected to analysis by the mass spectrograph, despite attempts to determine its source and eliminate it.

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Fig. 7. Apparatus for the preparation of ether-free AlH_3 .
 ○ ball joint, ⊗ stopcock, A. solution storage and reaction vessel, B. pentane storage, C. filtrate collector, a. filter cup container, b. filter cup, c. serum-bottle stopper, d. magnet stirrer, e. tygon tubing, f. glass rod, g. sintered glass filters (Ace D), 1. to argon supply, 2. to pentane-drying still, 3. to drying tube, 4. to cold trap and vacuum pump.

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Fig. 8. Apparatus for the preparation of ether-free AlH_3 .
 ○ ball joint, ⊗ stopcock, A. solution storage and reaction vessel, B. pentane storage, C. filtrate collector, a. filter cup container, b. filter cup, c. serum-bottle stopper, d. magnet stirrer, e. tygon tubing, f. glass rod, g. sintered glass filters (Ace D), 1. to argon supply, 2. to pentane-drying still, 3. to drying tube, 4. to cold trap and vacuum pump.

Table I

No.	Conditions and Procedure	Fig. Ref.	Observations	Results-Anal.	Remarks
1	LiAlH ₄ and AlCl ₃ solutions frozen, before mixing, with liq. N ₂ ; mixture filtered after complete thawing.	8	No immediate change upon thawing. Apparent precipitate formed proved to be ether crystals.	no hydride formed.	The solutions froze sufficiently rapidly to prevent precipitation of the solutes. Filtration apparently took place before the mixture could warm to a temperature at which the reaction could take place.
2	LiAlH ₄ and AlCl ₃ solutions frozen, before mixing, with liq. N ₂ . Thawing and warming allowed until definite reaction had taken place.	9	No immediate change after thawing. Mixture turned cloudy after a few minutes; cloudiness increased with time.	H: 3.15% av. Theor. 10.1%. - - - gases evolved upon thermal decomposition: ether 10%.	Filter cup of Fig. 8 replaced by sintered glass filter to allow more rapid filtration to keep the transit time of the reaction mixture to a minimum.

No.	Conditions and Procedure	Fig. Ref.	Observations	Results-Anal.	Remarks
3	LiAlH ₄ and AlCl ₃ solutions precooled separately with dry ice-acetone bath. Mixture filtered 5 minutes after mixing.	9	No immediate effect Precipitate slowly formed after a minute.	H: 3.32% av. - - - gas from thermal decomp. ether: 13%	
4	LiAlH ₄ and AlCl ₃ solutions precooled to 0° C. Mixture was allowed to stand for a minute after mixing.	9	Reaction took place instantly.	H: 2.42% av. - - - gas from thermal al decomp. ether: 8.9% ethane: 8.4% H ₂ : 76.1%.	Ethane may be attributed to the ether which had the C-O bond broken during the thermal decomposition of the hydride. Thus: Total ether: = 8.9 + $\frac{1}{2} \times 8.4 = 13.1$ Total H ₂ = 76.1 + $\frac{1}{2} \times 8.4 = 80.3$
5	LiAlH ₄ and AlCl ₃ solutions mixed at room temperature then filtered quickly after a few seconds.	9		H: 2.39% av. - - - Therm- al decomp. ether: 7.9% ethane: 7.4% H ₂ : 79%.	Total H ₂ = 79.0 + $\frac{1}{2} \times 7.4 = 82.7$ Total ether = 7.9 + $\frac{1}{2} \times 7.4 = 11.6$

Results and Discussion

The results of the synthesis are summarized in Table II.

Table II

Sample No.	%H Content	Moles ether Moles AlH_3	Temp. of evacuation	Remarks
a *	†	0.44	20°C (approx)	
b *	†	0.35	20°C (approx)	
c *	†	0.22	80°C	
1	5.4	0.35	50°C	Slow mixing of reactants at room temperature
2	3.15	0.17	50°C	Solution precooled to -197°C
3	3.32	0.23	50°C	Solution precooled to -78°C
4	2.42	0.24	50°C	Solution precooled to 0°C
5	2.39	0.21	50°C	Mixed at room temp. - no time lag

*Data from Ref. 2

†Not given

In each of these preparations, the dry solid was a white, light, and fluffy powder. These solids were of low bulk density and were all pyrophoric. It was also noticed that the precipitate formed in the reaction, for the most part, was not retained by the fritted glass filters. This was true for both the Ace C and D types. An E filter was not tried because of the slowness of the filtration. As a consequence a large proportion of the LiCl formed was mixed with the AlH_3 . This explains why the hydrogen content of the preparations was so far below

the theoretical value. Also the ether made up an appreciable fraction of the total weight of these samples. The filter-cup method of filtering was found to be effective but also quite slow.

The table points up a common denominator between the various samples: the almost constant ether content of these hydride preparations. Even the AlH_3 prepared by the original method of Finholt et al. gave as a lower limit an ether content that was the same as that obtained in these preparations. This constant ether content suggests that the amount of ether complexed by the hydride is a stoichiometric relation process. A strong possibility is that the reaction forming the hydride,

which involves the use of an ether solution of AlCl_3 , is the cause. Since ether forms a strong complex with AlCl_3 , the formation of the Al-H bonds may not be capable of breaking this complex.⁹ Hence the ether remains with the aluminum and is incorporated into the hydride. Thus the reaction would be

The mole ratio of ether to AlH_3 indicated by this equation--0.25--is in fact close to that which is found.

If the unwanted ether is accounted for by such a relationship, then it may be possible to remedy the difficulty by using a reactant other than AlCl_3 . Such a reactant should be a chloride that reacts smoothly with LiAlH_4 to produce a hydride that is volatile, so as to not contaminate the AlH_3 , not react with the AlH_3 , and be safe to handle. An investigation of the various possibilities shows that SiCl_4 does fulfill all these requirements.

In order to test the hypothesis concerning an AlCl_3 etherate, AlH_3 was prepared in the setup shown in Fig. 8 according to the reaction

This reaction produced a precipitate which, while suspended in the pentane, had a rusty brown color. When the precipitate was filtered from the pentane, it had an amber color. The precipitate, when drained and evacuated overnight, did not undergo any apparent physical change. The following day the precipitate was pulverized, put under a high vacuum, and heated to 50°C. After a few hours, the compound became grayish and a slow continuous evolution of gas was noted. A sample of this gas was analyzed with a mass spectrometer which showed that it contained largely hydrogen with less than 1% ether. After two days of evacuation, the evolution of gas was negligible, but the compound was a dark gray color. When it was hydrolyzed to determine the hydrogen content, the volume of hydrogen produced was very small (and could be attributed entirely to Al). Hence it was quite apparent that any AlH_3 that had been formed had completely decomposed.

There are two possible explanations for this instability: (a) that the AlH_3 produced was ether-free but that it needed the 1/5 to 1/4 mole of ether, which was found in all previous preparations, for stability, (b) that the silane produced either reacted with, combined with, or was adsorbed by the AlH_3 and that its presence was the cause of instability.

It is suggested that, if a stable ether-free AlH_3 is possible, this type of synthesis would be the best approach (since the sample prepared using SiCl_4 contained a very small amount of ether). However, it would be a matter of determining the best conditions and trying various chlorine compounds. Such attempts, however, would not necessarily be successful. For this reason it was deemed advisable to make use of the compound AlD_3 for obtaining information on the molecular structure. The presence of ether in this compound would be inconvenient but not fatal to the investigation.

II. NUCLEAR SPIN RESONANCE STUDIES OF AlH_3

Theory: Structure of the Absorption Curve

In addition to its well-known properties of mass, charge, and spin, the atomic nucleus possesses, in general, a magnetic moment similar to that of the electron but with a strength on the order of only $1/1000$ that of the electron. Therefore, like an electron, the nucleus has degenerate Zeeman energy levels. Unlike the electron, a nucleus may have $I > \frac{1}{2}$ so that there may be more than two energy levels, all equally spaced. The application of a magnetic field H_0 to a nucleus of spin I then produces $2I + 1$ levels with an energy spacing between them of $g \beta H_0$, where β is the nuclear magneton, 5.049×10^{-24} erg/gauss, and $g \beta I$ is the nuclear magnetic moment. If $g \beta H_0$ is large compared with all other interactions, as is the case here, a system composed of a large number of such nuclei can be described in terms of these $2I + 1$ Zeeman levels and their populations. Transitions from one to another of these levels may be induced by the application of a weak oscillatory magnetic field, at the frequency of resonance $\nu = g \beta H_0/h$ and perpendicular to H_0 . * For protons, as an example, with $H_0 = 10,000$ gauss, ν is 42.6 Mc/sec. In thermal equilibrium, the population of each energy level of the spin system corresponds to a Boltzmann distribution and there is a net absorption of energy from the radio-frequency field. It is this effect which is measured in the experiments to be cited here.

In addition to the strength or amplitude of this absorption, the shape of the absorption curve must also be considered, for the shape depends markedly on the relative positions of the absorbing nuclei. This is the result of two factors: (a) two similar nuclei may simultaneously induce transitions in each other owing to the interaction of their own magnetic fields, (b) the magnetic moment of one nucleus produces a static magnetic field at other nuclei in its vicinity. The

* Several books and many reviews treating NSR are now available. 10-18

first factor limits the lifetime of a nuclear spin state and causes a dispersion of the energy levels according to the uncertainty principle. The second factor causes the magnetic field at any nucleus to be the sum of the permanent field H_0 and all the local fields from all the nuclei in the vicinity.

In certain molecules two or three nuclei may be relatively isolated from all other like nuclei (such as protons in $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ or in CH_3CCl_3), in which case the absorption line exhibits fine structure. The actual shape then yields considerable information about the internuclear distances and orientation.¹⁹⁻²¹ More commonly, the number of near neighbors is sufficiently great that the line shape exhibits no fine structure. In this case recourse may be had to the second moment of the line shape, which may be expressed as

$$\langle \Delta H_2 \rangle^2 = \frac{\int_{-\infty}^{\infty} (H-H_0)^2 f(H) dH}{\int_{-\infty}^{\infty} f(H) dH}, \quad (4)$$

where H_0 is the magnetic field strength at the center of the absorption line and $f(H)$ describes the line shape. The second moment has been related by Van Vleck to the molecular configuration of the sample.²² For a powdered sample containing one or more magnetically active species, the expression can be written as

$$\langle \Delta H_2 \rangle^2 = \frac{6}{5} \cdot \frac{I(I+1)}{N} g^2 \beta^2 \sum_{j < k} r_{jk}^{-6} + \frac{4}{15} \frac{\beta^2}{N} \sum_{j, f} I_f (I_f+1) g_f^2 r_{jf}^{-6}. \quad (5)$$

Here N is the number of nuclei at resonance in the molecule or subgroup to which the spin-spin interactions are considered to be confined. Thus a value of the second moment may be computed for any assumed model of the molecule being investigated. This value

may then be compared with values obtained by the graphical integration from the experimental curves. In practice, as will be seen, experimental technique determines the first derivative of the absorption curve.*

Unfortunately the use of NSR for the problem of determining the molecular structure of AlD_3 is not without difficulties. Unknown in this problem, besides the molecular structure, is the Al-D bond distance. For this reason there are two parameters that must be handled in making second-moment calculations for prospective models by use of Eq. (5). Also unknown are the dipolar contributions of nuclei that are not included in the second-moment calculations because they are contained in separate neighboring molecules. Nevertheless, since they are in the vicinity, they can add their own contributions to the line width. Ordinarily it would not be possible to draw any conclusions about a model, lacking information about Al-D bond distances and approximations of contributions to the line width from intermolecular contributions, but the technique of double resonance enables one to circumvent these difficulties.

The technique of double resonance is the same as that described above except for one added feature. While the absorption curve is being traced out, by use of a radio-frequency oscillating magnetic field at the resonance frequency of one kind of magnetically active nuclei (in this case deuterons), a second radio-frequency field is applied at the resonance frequency of one of the other types of magnetically active nuclei (in this case aluminum), and at a very much greater power level. This second high-power saturating radio-frequency magnetic field has the effect of adding energy to the aluminum nuclei

*The necessary graphical integrations for this work were carried out on a Nordsick type differential analyzer which, with the control panel properly set up, enables one to obtain the second moments directly.²³

at a rate that is in excess of the rate at which they can exchange energy with the lattice. Because of this, the aluminum spin system becomes heated up and the nuclei change their energy levels at a high rate and hence their orientation with respect to the main field H_0 . In the process their static magnetic contribution to the main field at the sites of deuterons is time-averaged to zero. Thus in such an experiment on AlD_3 , the shape of the absorption curve can be attributed only to the deuterons. By comparing the second moments of experimental curves obtained from single resonance experiments (where the aluminum nuclei make their contributions) to the second moments of curves obtained from double resonance experiments (i. e., with no aluminum nuclei contributions), it is possible to draw conclusions about the position of aluminum nuclei with respect to the deuterons by comparing these experimental values with calculations made on the assumption of chemically reasonable models.

Calculation of Theoretical Second Moments

A. Longuet-Higgins Model Involving sp^3d^2 Hybrid Three-Center Bonds

If it is assumed that true sp^3d^2 bonding occurs in AlD_3 , then it can be seen that all bond angles are known and that second-moment calculations may be made involving only one unknown parameter, the Al-D bond distance. By studying Fig. 9 it may be seen that for any given polymeric layer, there are two layers of deuterium atoms and one layer of aluminum atoms. If one deuteron is labeled and the effects of its neighbors on it are calculated, it will be a representative of all other deuterons. Then by use of the Van Vleck formula given by Eq. (5), a quantity representing the theoretical second moment of the absorption curve may be calculated. The second moment itself cannot be calculated without an accurate value for the Al-D bond distance, but it will be given in terms of this bond distance.

In the use of Eq. (5), the parameter that must be determined is the distance of each nucleus from the reference deuteron. These

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Fig. 9. Projection of one layer of the two-dimensional AlH_3 polymer.

calculations will be done, using Fig. 9 in three steps: (a) calculating the contribution of the deuterons in the same layer as the reference nucleus labeled with numbers, (b) contributions of deuterons in the lower layer labeled with lower-case letters, (c) contributions of the aluminum nuclei labeled with capitol letters. The reference deuteron is at the origin, O. The number and distance of various nuclei from the reference point may be calculated by simple rules of geometry and trigonometry.

Given the Van Vleck equation

$$\langle \Delta H_2 \rangle^2 = \frac{6}{5} \frac{I(I+1)}{N_s} g^2 \beta^2 \sum_{j>k} r_{jk}^{-6} + \frac{4}{15} \frac{\beta^2}{N_s} \sum_{j,f} I_f (I_f + 1) g_f^2 r_{jf}^{-6}, \quad (5)$$

Then for the deuteron, we have

$$I = 1,$$

$$g\beta = 0.857 \times 5.049 \times 10^{-24} = 4.33 \times 10^{-24}$$

$$N_s = 1;$$

for the aluminum nuclei, we have

$$I = 5/2,$$

$$g_f \beta = 3.638 \times 5.049 \times 10^{-24} / 2.5 = 7.35 \times 10^{-24},$$

$$N_s = 1$$

By substitution, we can obtain

$$\langle \Delta H_2 \rangle^2 = \frac{6}{5} \frac{1(1+1)}{1} (4.33 \times 10^{-24})^2 \times (10^{-8} \sum_{j>k} r'_{jk})^{-6} + \frac{4}{15} \frac{5}{2} \frac{5+1}{2} (7.35 \times 10^{-24})^2 (10^{-8} \sum_f r'_{jf})^{-6}, \quad (5')$$

$$\langle \Delta H_2 \rangle^2 = 45.0 \sum_k (r'_{jk})^{-6} + 126.0 \sum_f (r'_{jf})^{-6},$$

when r' is in angstrom units.

Determination of $\sum_k r_{jk}^{-6}$ in terms of AlD bond distance: R_0 .

For the following calculations, R_0 will represent the AlD bond distance and R_{0n} where $n = 1, 2, 3$, etc. will represent the distance between the reference deuteron and the indicated deuteron.

1. Upper layer of deuterons

Type	Number	Distance/ R_0
1	6	$R_{01} = \sqrt{1^2 + 1^2} = \sqrt{2}$
2	6	$R_{02} = \sqrt{2} \sin 120^\circ / \sin 30^\circ = \sqrt{6}$
3	6	$R_{03} = 2 R_{01} = 2 \sqrt{2}$
4	12	$R_{04} = \sqrt{[(2\sqrt{2})^2 + (\sqrt{2})^2 - 2(\sqrt{2})(\sqrt{2}) \cos 120^\circ]} = \sqrt{14}$
5	6	$R_{05} = 3\sqrt{2}$
6	6	$R_{06} = 2 R_{02} = 2\sqrt{6}$
7	12	$R_{07} = \sqrt{[(2 R_{02})^2 + R_{01}^2]} = \sqrt{26}$

$$\begin{aligned}
 \sum_k \left(\frac{R'_j}{R_0} \right)^{-6}_{jk} &= 6 (\sqrt{2})^{-6} + 6 (\sqrt{6})^{-6} + 6 (2\sqrt{2})^{-6} + 12 (\sqrt{14})^{-6} = \\
 &= \frac{6}{2^3} + \frac{6}{6^3} + \frac{6}{2^9} + \frac{12}{14^3} \\
 &= 0.750 + 0.028 + 0.012 + 0.005 \\
 &= 0.795.
 \end{aligned}$$

2. Lower layer of deuterons

Type	Number	Distance as measured in same plane
a	3	$d_{0a} = R_0 \sin 30^\circ / \sin 120^\circ = \sqrt{6}/3$
b	3	$d_{0b} = 2R_0 \sin 30^\circ / \sin 120^\circ = 2\sqrt{6}/3$
c	6	$d_{0c} = R_{04} \sin 30^\circ / \sin 120^\circ = \sqrt{42}/3$

Type	Number	Distance as measured in same plane
d	6	$d_{0d} = R_{07} \sin 30^\circ / \sin 120^\circ = \sqrt{78}/3$
e	3	$d_{0e} = 4R_{01} \sin 30^\circ / \sin 120^\circ = 4\sqrt{6}/3$
f	6	$d_{0f} = (d_{0a}^2 + 2R_{01}^2 - 4d_{0a} R_{01} \cos 150^\circ)^{\frac{1}{2}} = \sqrt{114}/3$

Perpendicular distance between layers: h

$$h^2 = R_{01}^2 - d_{0a}^2 = 4/3$$

$$R_{0k} = (4/3 + d_{0k}^2)^{\frac{1}{2}}$$

Type	Number	Distance
a	3	$R_{0a} = (4/3 + d_{0a}^2)^{\frac{1}{2}} = \sqrt{2}$
b	3	$R_{0b} = (4/3 + d_{0b}^2)^{\frac{1}{2}} = 2$
c	6	$R_{0c} = (4/3 + d_{0c}^2)^{\frac{1}{2}} = \sqrt{6}$
d	6	$R_{0d} = (4/3 + d_{0d}^2)^{\frac{1}{2}} = \sqrt{10}$
e	3	$R_{0e} = (4/3 + d_{0e}^2)^{\frac{1}{2}} = \sqrt{12}$
f	6	$R_{0f} = (4/3 + d_{0f}^2)^{\frac{1}{2}} = \sqrt{14}$

From the above information one obtains

$$\begin{aligned}
 \sum_k \left(\frac{R_{0k}}{R_{0j}} \right)^{-6} &= 3(\sqrt{2})^{-6} + 3(2)^{-6} + 6(\sqrt{6})^{-6} + 6(\sqrt{10})^{-6} + \\
 &\quad + 3(\sqrt{12})^{-6} + 6(\sqrt{14})^{-6} \\
 &= 0.375 + 0.047 + 0.028 + 0.007 + 0.001 \\
 &= 0.458.
 \end{aligned}$$

3. Aluminum nuclei

Let p = perpendicular distance between plane of aluminum nuclei
and the plane of the reference deuteron,

d_{jf} = perpendicular distance between the reference deuteron
and a given aluminum nucleus,

then we have

$$R_{jf} = (p^2 + d_{jf}^2)^{\frac{1}{2}},$$

where

$$p^2 = h^2/4 = 1/3.$$

Type	Number	d_{jf}	$(R/R_0)_{jf}$
A	2	$\sqrt{2/3}$	1
B	2	$\sqrt{8/3}$	$\sqrt{3}$
C	4	$\sqrt{14/3}$	$\sqrt{5}$
D	4	$\sqrt{26/3}$	$\sqrt{9}$
E	2	$\sqrt{32/3}$	$\sqrt{11}$
F	4	$\sqrt{38/3}$	$\sqrt{13}$
G	2	$\sqrt{50/3}$	$\sqrt{17}$

The results are:

$$\begin{aligned} \sum_f \left(\frac{R'_{of}}{R_0} \right)^{-6} &= 2(1)^{-6} + 2(\sqrt{3})^{-6} + 4(\sqrt{5})^{-6} + 4(\sqrt{9})^{-6} + 2(\sqrt{11})^{-6} \\ &= 2.000 + 0.074 + 0.032 + 0.005 + 0.002 \\ &= 2.113. \end{aligned}$$

Upon substitution of the three summations into Eq. (5') one obtains

$$\begin{aligned} \langle \Delta H_2 \rangle^2 &= [45.0 (0.795 + 0.458) + 126.0 (2.113)] R_0^{-6} \\ &= 322 R_0^{-6} \text{ gauss}^2. \end{aligned} \quad (5'')$$

As indicated above, an accurate value for R_0 was not known. This obstacle may be overcome by utilizing a ratio. The theoretical second moment of the absorption curve can be calculated including and excluding the factors involving the aluminum nuclei. To include in the calculation the factor representing the effect of the aluminum nuclei corresponds to the regular NSR experiment. To exclude from the calculation the factor representing the aluminum nuclei corresponds to NSR experiments using double resonance. It is then possible to obtain a ratio of theoretical second moments as given by Eq. (6):

$$\frac{\langle \Delta H_2 \rangle_{\text{tot.}}^2}{\langle \Delta H_2 \rangle_{\text{D only}}^2} = \frac{322 R_0^{-6}}{56.4 R_0^{-6}} = 5.72, \quad (6)$$

where

$\langle \Delta H_2 \rangle_{\text{tot}}^2$ is the calculated second moment including the factors representing the aluminum nuclei,

$\langle \Delta H_2 \rangle_{\text{D only}}^2$ is the calculated second moment involving the deuterons only.

This ratio may then be compared with the ratio obtained from the second moments of the experimental curves from normal NSR and from double-resonance NSR experiments. Also accomplished, by comparison of these ratios rather than of absolute values, is the elimination of the line-broadening effects of intermolecular nuclei.

If the structure for which these second-moment calculations were made is not octahedral, but the protons form the hydrogen bridges as protonated double bonds, the over-all structure is unchanged but the D-to-D and Al-to-D bond distances are slightly different because the D-Al-D angles vary from the 90° of the sp^3d^2 structure. However for these experiments, the two types of structures are sufficiently close as to be indistinguishable.

B. Linear-Polymer Model

If the structure of AlD_3 is a linear one, then the following calculations may be made for the second moment of the absorption curve that such a model would have. (See Fig. 10.) For this model, there are two types of protons--bridge protons and terminal protons. In order to calculate an absorption-curve second moment for this model, four assumptions must be made:

- (a) The aluminum bonding is sp^3 and that the bond angles are tetrahedral;
- (b) The Al-D bond distance is the same for both types of protons;
- (c) The Al-D-Al angle for the bridge protons is 180° ;
- (d) The only important interactions are those between deuterons bonded to a common aluminum atom.

On the basis of these assumptions, the following summations may be made.

1. Deuteron-deuteron interactions

- a. Terminal deuterons accounting for 2/3 of the total:

$$\sum_k \left(R_{jk} \right)^{-6} = (3R_0)^{-6} = 3/(2 R_0 \sin 54^\circ 44')^6 \\ = 0.202 R_0^{-6}.$$

- b. Bridge deuterons accounting for 1/3 of the total:

$$\sum_k \left(R_{jk} \right)^{-6} = 6 R_0^{-6} / (2 \sin 54.73^\circ)^6 \\ = 0.404 R_0^{-6}.$$

2. Deuteron-aluminum interactions:

- a. Terminal deuterons accounting for 2/3 of the total:

$$R_{a1} = R_0,$$

$$R_{a2} = R_0 \sqrt{2^2 + 1^2} = 2 \times 2 \times 1 \times \cos 109^\circ 28',$$

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Fig. 10. Section of the linear AlH_3 polymer.

$$R_{a2} = 2.62 R_0 ,$$

$$\begin{aligned} \sum_f \left(R_{jf} \right)^{-6} &= R_0^{-6} + 2 R_0^{-6} / (2.62)^6 \\ &= 1.006 R_0^{-6} . \end{aligned}$$

b. Bridge deuterons accounting for 1/3 of the total:

$$\sum_f \left(R_{jf} \right)^{-6} = 2 R_0^{-6} .$$

Substituting these four summations into Eq. (5'), one obtains

$$\begin{aligned} \langle \Delta H_2 \rangle^2 &= [22.5 (2/3 \times 0.202 + 1/3 \times 0.404) + 126.0 (2/3 \times 1.006 + 1/3 \times 2)] R_0^{-6} \\ &= 174.5 R_0^{-6} \text{ gauss}^2 . \end{aligned} \quad (7)$$

Hence the ratio is

$$\frac{\langle \Delta H_2 \rangle^2_{\text{tot}}}{\langle \Delta H_2 \rangle^2_{\text{D only}}} = \frac{174.5 R_0^{-6}}{6.05 R_0^{-6}} = 29. \quad (8)$$

Apparatus

At the time when this study of AlH_3 was started, there became available a commercial NMR unit built by Varian Associates.²⁴ The main features of the apparatus (Fig. 11) are as follows.

- (a) It is of the nuclear-induction type developed by Felix Bloch.²⁵⁻²⁷
- (b) It has a frequency range of 2 to 16 Mc covered by one receiver-transmitter and three probes with the ranges 2 to 4 Mc, 4 to 8 Mc, and 8 to 16 Mc.
- (c) These probes, constructed of aluminum, contain the transmitter coils, receiver coils, and modulation coils along with the necessary capacitors for tuning. There are also paddles to direct the flow of radio-frequency flux for the proper adjustment of the leakage from the transmitter coil to the receiver coil. These paddles are also used to select the mode of interest, i. e., whether the absorption curve or the dispersion curve of the nuclear paramagnetism is recorded.
- (d) A phase detector is used for recording the signal, and for this reason the derivative rather than the curve itself is the information obtained.
- (e) An electromagnet with a 12-in. pole face and a 1-3/4-in. gap, capable of producing 10,000 gauss is used.

A disadvantage of the Varian equipment was the difficulty of obtaining the absorption curves of samples at temperatures below room temperature. Low-temperature work was necessary because the time-average magnetic field produced at a given point by a nucleus in motion is different from that of a motionless nucleus, and the theoretical second moments were calculated on the basis of models involving no motion. Thus it is necessary to eliminate or substantially reduce these motions. This is particularly true if the molecule involved contains rotating groups with magnetically active nuclei. Hence the use of low temperatures is necessary in order to compare experimental data with the theoretical calculations. For this reason it was necessary to adapt the existing equipment for low-temperature work.

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Fig. 11. Block diagram of Varian variable-frequency NMR unit.

It was decided that for low-temperature experiments a single-coil apparatus would be the simplest solution. Thus the experiments performed would involve nuclear resonance absorption rather than nuclear induction.²⁸ In theory, the nuclear resonance absorption technique involves the measurement of the energy absorbed from a resonant circuit by a spin system at resonance. The nuclear induction technique, however, measures the voltage induced in a receiver coil by the dipole moment of precessing nuclei. The precession of the nucleus is caused by the radio-frequency magnetic field produced by the energy in the transmitter coil.

The nuclear signal resulting from either of these two methods is of the order of a few microvolts or less, so that a large amount of amplification of the nuclear signal is necessary. In order to amplify these weak signals a millionfold, it is necessary to reduce the power-level input to the amplifier (receiver is the term most commonly used) to the magnitude of the nuclear signal. Since the source of the driving radio-frequency magnetic flux, the power from the transmitter, is many orders of magnitude larger than the nuclear signal, it is necessary to neutralize most of this power before amplification. In a nuclear induction apparatus, this neutralizing is accomplished mainly by using a transmitter coil that is orthogonal to the receiver coil. Fine balance is obtained by paddles which direct small amounts of the radio-frequency flux of the proper phase and amplitude from the transmitter coil to the receiver coil. In nuclear absorption apparatus, involving only one coil, the neutralizing is accomplished with a balanced electrical bridge.

Figure 12 shows the circuit diagram of the nuclear absorption apparatus. Figures 13 and 14 show the sample coil and cooling assembly. The coil assembly of Fig. 13 was cemented into the dewar of Fig. 14. A coaxial cable passing through the side arm was connected with the leads that passed up through the porcelain tubes. Cooling was accomplished by passing nitrogen gas through coiled

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Fig. 12. Circuit diagram of the nuclear absorption bridge.

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Fig. 13. Construction of the nuclear absorption sample coil support.
a. teflon, b. porcelain tube $5/32 \times 9\frac{1}{2}$ in., c. porcelain tube $5/32 \times 9\frac{1}{2}$ in., d. teflon, e. pyrex tube 17.4 mm i.d., f. teflon.
Coil: 11 turns No. 20 copper wire, close-wound internally.
Bonding agent: araldite cement.

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Fig. 14. Dewar for nuclear absorption bridge.

copper tubing, immersed in liquid nitrogen, and then into the dewar at the bottom.

When this apparatus was constructed and tested, it was found that the signal-to-noise ratio for samples with weak nuclear absorption (of which AlD_3 was one) was inferior to that of which the nuclear induction method was capable. In order to improve on the signal-to-noise ratio, a preamplifier was constructed utilizing a cascode-type circuit.²⁹ The circuit diagram is shown in Fig. 15. However, even though some improvement was noted, the sensitivity of this method was still inadequate for observing the weak nuclear signals to be encountered with AlD_3 .

Since the nuclear induction method was more sensitive than the nuclear absorption method, it was necessary to design and build a nuclear induction assembly that could be used for low-temperature studies.

The design decided upon was a unit consisting of a transmitter coil, a receiver coil, and a third coil for introducing a high-power saturation frequency. The coils were mounted on a pyrex tube with araldite cement and the tubes rigidly supported by an aluminum body. Figures 16 to 19 show the construction. This unit, along with the sample, was cooled by passing precooled nitrogen gas through the special dewar (see Fig. 20). The necessary tuning capacitor and balancing controls were contained in a box outside the dewar (see Fig. 21).

In this design the transmitter and receiver coils, on separate forms, were made as close to orthogonal as possible to reduce the coupling. A Faraday shield was placed between the two sets of coils to eliminate electrostatic coupling. The receiver coil was wound on its own form and connected to the rest of the unit with a modified BNC connector (Fig. 16). Thus the form could be rotated to reduce the coupling between the two sets of coils. In this manner it was possible to reduce the pickup of the receiver coil to about 1% of the voltage in the transmitter coils. Since the voltage in the transmitter coil was of the order of tenths of volts whereas

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Fig. 15. Circuit diagram of the preamplifier used with the nuclear absorption bridge.

T_1 6AK5, T_2 6J6, T_3 OB2

L_1 7.5 μ h, L_2 14 μ h, L_3 20 μ h, L_4, L_5 10 μ h, L_6 RFC

C_1, C_3, C_4, C_5 0.005 μ f, C_2, C_7 50 μ mf, C_6 5 μ mf,

C_8, C_9 0.01 μ f

R_1, R_3 100 Ω , $\frac{1}{2}$ watt, R_2, R_4 1000 Ω , $\frac{1}{2}$ watt, R_5 6000 Ω , 10

watts, R_6 23 Ω , 10 watts.

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Fig. 16. Construction of the nuclear induction receiver-coil insert.

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Fig. 17. Nuclear induction probe--transmitter coils and form.

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Fig. 18. Nuclear induction probe--complete assembly.

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Fig. 19. Nuclear induction probe--cross section.

Fig. 20. Dewar for nuclear induction probe.

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Fig. 21. Nuclear induction probe--circuit diagram.

L_1 2.2 μ h, L_2 11 μ h, L_3 19 μ h

C_1 1 pf, C_2 50 pf, C_3 300 pf, C_4 140 pf, C_5 2000 pf,

C_6 600 pf, C_7 30 pf, C_8 2000 pf, C_9 0.001 μ f

R 1 meg.

the voltage in the receiver coil had to be of the order of microvolts in order to prevent saturation of the receiver, further reduction of the receiver-coil voltage was necessary. This was accomplished by tapping off some of the power from the transmitter, attenuating it to the proper level, passing it through a continuously variable phase shifter,* and coupling the resultant voltage to the receiver coil with a small capacitor. In this manner, the voltage amplitude in the receiver coil could be reduced to about 1 microvolt even though the voltage level in the transmitter coil was of the order of volts. (see Fig. 21). The output of the receiver coil was then put through a preamplifier to a receiver of a special design, where the necessary amplification and selection of modes was made. A block diagram of this unit is shown in Fig. 22. This special receiver was constructed to operate at a frequency of 6 Mc/sec. This apparatus was, in fact, more sensitive than nuclear absorption apparatus.

Results, Discussion, and Interpretation

For reasons explained above, AlD_3 was studied rather than AlH_3 . A sample of AlD_3 was prepared in the same manner as AlH_3 preparation No. 5. Analysis showed that this AlD_3 sample had approximately the same composition as No. 5. It was found, however, that no deuterium signal was observable for AlD_3 although the deuterium signal was observable for LiAlD_4 . Therefore it was not possible to study AlD_3 directly.

Since AlH_3 and AlD_3 are chemically and physically identical compounds, it was reasoned that the hydride protons in AlH_3 might be detectable if the contribution of the ether protons as observed in AlD_3 were subtracted. This could be accomplished by obtaining the proton spin resonance signals for AlH_3 and AlD_3 under the exact same conditions. Figures 23 and 24 show respectively the curves

* A 2.5- μsec continuously variable delay line was used.

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Fig. 22. Block diagram of the special-type transmitter-receiver used for the nuclear induction probe.

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Fig. 23. The derivative curve of the proton spin resonance curve of AlH_3 at $300^\circ K$. This curve represents the proton of both the hydride and the ether. The units for the abscissa are in gauss. The units for the ordinate are arbitrary.

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Fig. 24. The derivative curve of the proton spin resonance curve of AlD_3 at 300°K . This curve is due to the presence of protons of the ether in AlD_3 . The units for the abscissa are in gauss. The units for the ordinate are arbitrary.

obtained for each of these compounds at room temperature. Figure 25 shows the curve resulting from the algebraic subtraction of the AlD_3 curve from the AlH_3 curve. Figure 26 shows the same series of curves at about -200°C .

It is quite obvious from Figs. 25 and 26 that there is a definite fine structure to these absorption curves. This type of fine structure is usually observed in compounds containing a methyl group or other symmetrical-top groups with hydrogen, and is characteristic of "three-proton spin systems."³⁰ However, it was not possible to construct a model for AlH_3 , incorporating such a three-proton system, that would have the known physical and chemical properties.

There is, however, another possibility. The lines to be expected from the interactions of a four-proton spin system, such as the ammonium ion, have been calculated.³¹ It appears from these calculations that if such a system rotates about its C_3 axis so that the rotation takes place about a given proton, a pattern of lines as shown in Fig. 27 can be expected. However, since such a system is never isolated, there is a sizable contribution from neighboring protons. These contributions tend to smear out the fine structure, leaving only the most prominent features of such structure. To a good approximation, such contributions may be represented by a Gaussian broadening function which is superimposed on the fine structure.³² A typical result of such a broadening on the fine structure is shown in Fig. 27. This curve has the same general characteristics as the integrated curves (shown in Figs. 28 and 29) of Figs. 25 and 26 respectively. Such a comparison can be only qualitative because the algebraic subtraction performed in order to obtain the curves of Figs. 25 and 26 does not take into account the difference in ether content between AlH_3 and AlD_3 , the broadening effect of the hydride protons on the ether protons, nor the small difference in sample size due to a slight difference in the size of the container for each. Nor is the exact nature of the Gaussian function to be superimposed on the lines of Fig. 27 known.

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Fig. 25. The derivative curve of the proton spin resonance curve of AlH_3 at 300°K obtained by subtracting the curve of Fig. 22 from the curve of Fig. 23. This curve approximately represents the protons of AlH_3 only. The fine structure shows up clearly in two smaller maxima and two smaller minima.

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Fig. 26. Derivative curves obtained at -200° K.
Solid curve: AlH_3
Dashed curve: AlD_3
Dotted curve: $(AlH_3) - (AlD_3)$.

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Fig. 27. Theoretical absorption curve. The vertical lines indicate the expected energies of transitions and their relative intensities for an isolated tetrahedral four-proton spin system rotating about its C_3 axis. The dashed curve represents a possible broadening function due to the neighboring nuclei. The solid curve shows the probable result of the superposition of the dashed curve on the lines. The units of the abscissa are gauss-cm³. The actual values change with the rate of rotation.

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Fig. 28. The room-temperature absorption curve obtained by integrating Fig. 25.

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Fig. 29. The -200°C absorption curve obtained by integrating the dotted curve of Fig. 26.

The similarity between the curves of Figs. 28 and 29 and of Fig. 27 is sufficiently close to warrant investigating models for AlH_3 based on a four-proton spin system. There are also other factors that should be considered in constructing such a model. They are (a) the inevitable presence of ether in AlH_3 to the extent of 1/4 mole ether per mole AlH_3 ; (b) the apparent existence of the species $\text{Li}(\text{Al}_2\text{H}_7)$.^{*} The most logical structure for this compound would be

so that possibly AlH_3 may contain similar hydrogen bridges; (c) the apparent instability of AlH_3 when attempts are made to completely remove the ether; (d) the reaction for the formation of AlH_3 , i. e.,

The model proposed here to explain the observations listed above is shown in Figs. 30 and 31. This structure is essentially made of 4 $[\text{AlH}_4]^-$ bonded through hydrogen bridges to a central aluminum atom. The central aluminum atom also has a molecule of ether bonded to it through the oxygen atom to partially fill the otherwise vacant orbital on this aluminum atom. Such a model would allow the $[\text{AlH}_4]^-$ groups to rotate and would account for the fine structure noted in the NSR absorption curve. It also accounts for the inevitable presence of ether in AlH_3 . If this is the structure then Eq. (9) might be more correctly written

Such a model is also consistent with the postulated species $\text{Li}[\text{Al}_2\text{H}_7]$, to be described below.

^{*}To be treated below.

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Fig. 30. A top view of the proposed model for AlH_3 . The aluminum atoms are filled in. The hydrogen atoms are plain.

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Fig. 31. A side view of Fig. 30. The ether molecule is shown attached to the aluminum atom at the top.

Although the original program included double-resonance experiments, it was not possible at the time of conclusion of this investigation to generate a sufficiently intense saturating frequency to appreciably affect the aluminum nuclei. This difficulty is due to the very short relaxation time of the aluminum nuclei spin system, i. e., this spin system is able to transfer its energy readily to the lattice and remain in temperature equilibrium with the lattice. Under these circumstances it is very difficult to heat up such a spin system. This difficulty was not considered serious because the fine structure exhibited by the proton spin resonance absorption curves gave directly some definite clues to the molecular structure.

III. HIGH-RESOLUTION NUCLEAR SPIN RESONANCE STUDIES OF AlH_3

High-resolution NSR is dependent upon the very narrow line widths observable in solutions and liquids. Whereas solids may exhibit line widths on the order of gauss, liquids exhibit line widths on the order of milligauss or less. The reason for this difference is that, in liquids, molecules and ions are in very rapid motion and hence static magnet-field contributions at a given nucleus from other nuclei is time-averaged to zero. Therefore it is possible to observe the diamagnetic effect of the shell electrons on the field at the nucleus. The result of the diamagnetic effect of the shell electrons is to counteract the applied magnetic field to a small degree. For this reason the nucleus "sees" a magnetic field that is slightly less than the applied field. The size of the counteraction is dependent upon the electron density around the nucleus. Thus the nucleus of a given atom "sees" a magnetic field that is determined by the chemical bonding. This causes the resonant frequency of the nucleus to differ slightly, for a given nucleus, in various chemical compounds. This effect is referred to as chemical shift. It was hoped that application of this chemical shift for the proton to a study of the reaction

would yield some information on the structure of AlH_3 .

Experimental Procedure

This investigation was carried out in the following manner: Stock solutions of AlCl_3 and LiAlH_4 were made up. These were kept in serum bottles that were stoppered. Measured amounts were then withdrawn by means of hypodermic syringes and inserted into a 5-mm capillary tube through a serum-bottle stopper.*

*The size of the tube was dictated by the NSR apparatus.

When the solutions had been added, the tube was placed in the NMR probe and the signal was observed and recorded. When solutions were to be observed before they reacted, one was frozen after it had been placed in the tube, then the other solution was added to the tube and also frozen. Thus it was possible to place the tube in the probe and begin observations before the solutions had thawed and reacted.

Since the reactants were dissolved in ethyl ether, peaks due to the ether were also observed; however, they did not usually interfere.

Results and Discussion

Figures 32 to 37 illustrate some characteristic traces. The results of several experiments in which the ratio of LiAlH_4 to AlCl_3 is varied are as follows (see Table III).

1. Neither LiAlH_4 nor AlCl_3 solution produced a peak other than those attributed to the diethyl ether.

2. If the amount of LiAlH_4 solution added was equal to or less than that demanded by the stoichiometry, no signal other than the ether peaks was observed, indicating one or more of the following possibilities:

(a) AlH_3 was never in solution in sufficient concentration to be observable;

(b) it is possible but not probable that an AlH_3 peak was obscured by the ether peaks, because one of the peaks would then be distorted but no such effect was usually observed;

(c) the hydride nuclei had a very long spin lattice relaxation, so that observable quantities of energy were not absorbed.

It is also possible that the line width was very broad which would make detection very difficult.

3. If LiAlH_4 was present in excess, a signal other than the ether peaks was observable. It was found to have the following characteristics:

(a) over a period of seconds, minutes and sometimes hours, it shifted in the direction of lower magnetic field, i. e., toward the

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Fig. 32. (upper) Peaks due to diethyl ether.
 (lower) Additional undetermined peak.
 Also shown is the means to determine the position of the
 undetermined peak.

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Fig. 33. Typical sample in which the fifth peak is observed.
Top: # 4; $d = 0.59$
Bottom: # 11; $d = 0.88$.

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Fig. 34. Top: Peaks observable for Li Al H_4 in ether.
Bottom: Peaks observable for Al Cl_3 in ether.

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Fig. 35. # 1. Top: Peaks observed after the reaction has taken place.
Li AlH₄ in excess. $d = 0.66$
Middle: Same sample, 2 days later. $d = 1.10$
Bottom: Same sample, 3 days old. $d = 1.16$.

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Fig. 36. # 6; Top: Sample which contained Li AlH_4 in excess.
Bottom: Same sample with AlCl_3 added.

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Fig. 37. An example in which the fifth peak has shifted. Top: 80 seconds after reaction: $d = 0.51$; Bottom: 720 seconds after reaction: $d = -0.12$.

ether peaks. Over a period of days, the shift was to higher magnetic fields, i.e., away from the ether peaks.

(b) the initial and final positions were dependent upon the initial concentration ratio of LiAlH_4 to AlCl_3 .

Interpretation of Results

When chemical exchange can occur at a rapid rate, as of protons between water and an acid, a given proton will have exchanged positions a number of times during an observation. A single line will then appear at a position that is the number average of the positions in the two compounds, since the protons "see" an effective field intermediate between the two fields that prevail if there is no exchange.

For example, consider the equilibrium

The proton that is part of the molecule HA "sees" a different field than the proton of HB. If there were no exchange, two NSR peaks would be observed, one for each species. If there is exchange and if the lifetime of each species is very short compared with the line width, the two peaks coalesce into one peak that is intermediate. The position of this one peak depends upon the relative concentrations of the two species and varies linearly with relative concentration. Thus if the chemical HA is present initially and then HB is added in increasing amounts, the peak is observed to shift toward the position of pure HB. Since this type of behavior is what is observed in the LiAlH_4 , AlH_3 system, then undoubtedly this behavior is best explained by some equilibrium exchange reaction.

If an equilibrium reaction is the correct explanation for the shifts of the NSR peaks of the AlH_3 , LiAlH_4 system, then by making some assumptions about this equilibrium, one should be able to derive a relationship between the magnitude of the observed shift and the relative concentrations of LiAlH_4 and AlCl_3 . It was decided that the following assumptions would be the most logical.

Table III

Summary table showing the time-dependent behavior of the hydride peak

$$r = \frac{(\text{LAH})}{(\text{AlCl}_3)}$$

Stoichiometry: $r = 3$

No.	r	Time				Position d ^a	Remarks
		d	h	m	s		
1 ^b	>3		0			0.66	
			48			1.10	
			53			1.16	Very noticeable increase in the amplitude of the peak relative to the previous two.
2 ^b	>3		0			--	
			2			0.81	
			7			0.89	Very noticeable increase in the amplitude of the peak relative to the previous two.
3 [†]	>3		0			0.22	
			1			0.29	
			2			0.37	
			3			0.56	
			4			0.61	
4 [†]			0			--	
			3			0.17	
			4			0.24	
			5			0.31	
			6			0.31	
			7				

^aSee Fig. 32.

^bSolutions mixed at room temperature.

† Solutions prefrozen.

No.	r	Time				Position d ^a	Remarks
		d	h	m	s		
4 [†]				8½		0.46	
				9½		0.48	
				10		0.53	
		1				0.53	
		2				0.59	
		3				1.26	Very weak and broad peak
5 [†]	<3						No signal
6 [†]	>3						Signal observed, AlCl ₃ then added in excess, causing signal to vanish.
7 [†]						0.55	
			23			0.55	
			44			0.70	
8 [†]	5		0			-0.16	
			16				Signal vanished
9 [†]	7				37	0.89	
					47	1.0	
					56	0.89	
					65	0.64	
					73	0.33	
					82	0.33	
					117	0.16	
					126	0.15	
					150	0.11	Beyond 150 sec, signal becomes unresolvable from ether peak.
10 [†]	11.5				100	- -	No signal observed
					140	- -	No signal observed
					150	0.24	Weak

No.	r	Time				Position d ^a	Remarks
		d	h	m	s		
10 ⁺	11.5				200	0.37	
					228	0.30	
					320	0.31	
					440	0.33	
				10		0.34	
				15		0.36	
				23		0.38	
				30		0.46	
11 ⁺	23				40	- -	No signal observed
				1	40	0.95	Broad and weak peak
				2	10	0.83	
				2	49	0.89	
				3	23	0.86	
				4	18	0.72	
				5	09	0.91	
				7	21	0.92	
				10	51	0.88	
				15	24	0.91	
				20	-	0.91	
				22	18	0.88	
12 ⁺	725				40	- -	No signal
				1	15	1.02	
				1	40	0.85	
				3	23	0.95	
				3	46	0.94	
				4	36	0.96	
				4	54	0.88	
				7	48	0.89	

No.	r	Time				Position d ^a	Remarks
		d	h	m	s		
13 [†]	725				30	- -	No signal
				1	-	- -	No signal
				1	21	1.12	
				1	42	1.09	
				3	17	1.08	
				3	30	1.12	
				6	44	0.97	
				7	09	0.95	
				8	10	0.98	
14 [†]	11.5			-	56	1.11	
				1	13	1.12	
				1	40	0.86	
				2	06	0.64	
				2	27	0.66	
				2	49	0.58	
				3	11	0.62	
				3	52	0.61	
				4	15	0.60	
				4	27	0.63	
				5	11	0.62	
				7	57	0.64	
15 [†]	7				50	- -	No signal
				1	02	0.75	
				1	14	0.83	
				2	08	0.55	
				2	19	0.51	
				3	04	0.46	
				3	13	0.49	
				3	57	0.45	
				5	56	0.42	

No.	r	Time				Position d ^a	Remarks
		d	h	m	s		
15 [†]	7			9	02	0.42	
				11	13	0.45	
16 [†]	5			1	-	- -	No signal
				1	12	0.51	Weak
				1	27	0.54	Weak
				1	46	0.46	Weak
				3	05	- -	No signal
				4	27	0.43	Weak
				5	00	- -	No signal
				6	-	- -	No signal
				6	20	-0.04	Just resolvable from ether peak
				7	04	-0.07	
				7	52	-0.085	
				8	40	-0.12	
				9	23	-0.12	
				10	54	-0.12	
				11	51	-0.12	
				12	20	-0.12	
				15	51	-0.13	
				18	46	-0.14	
17 [†]	4				45	- -	No signal
				1	-	- -	No signal
				1	20	- -	No signal
				2	40	0.22	Weak
				2	54	0.21	Weak
				3	54	0.16	
				3	51	0.16	
				4	19	0.12	
				4	43	0.12	

No.	r	Time				Position d ^a	Remarks
		d	h	m	s		
17 ⁺	4			5	20	0.11	
				5	33	0.10	
				6	14	0.10	
				6	29	0.09	
				7	-	- -	Not resolvable
				7	30	- -	Not resolvable
				8	-	- -	Not resolvable
				10	-	- -	Not resolvable
				14	-	- -	Not resolvable
				18	20	- -	Not resolvable
				22	-	- -	Not resolvable
				23	13	-0.10	Weak
				24	41	-0.12	Weak
				25	34	-0.11	Weak
				26	09	-0.11	Weak
				26	44	-0.15	Weak
				27	07	-0.12	
				28	37	-0.15	
				30	52	-0.15	
				31	57	-0.14	
				33	00	-0.18	
				36	30	- -	Very possible that the signal has moved into the large peak and is no longer resolvable.
18 ⁺	3.2			-	-	- -	No signal observed.

Assumption 1. The equilibrium described by Eq. (12) exists.

Assumption 2. The signal observed is due to one or more of the protons in the species LiAl_2H_7 , and its position is dependent upon the average environment that a given proton is subjected to between LiAl_2H_7 and AlH_3 .

Assumption 3. The precipitation of AlH_3 is irregular and variable.

Assumption 4. A portion of the AlH_3 is prevented from precipitating as it is stabilized in solution by the formation of the complex. The amount of AlH_3 that remains in solution is approximately constant over wide concentration of LiAlH_4 .

Assumption 5. $(\text{LiAl}_2\text{H}_7) \ll (\text{AlH}_3)$.

If these assumptions are valid, then a relationship between the shift and the initial concentration of LiAlH_4 can be derived.

The magnitude of the shift should be proportional to the concentration of protons of the species LiAl_2H_7 .

Using the notation $()$ = concentration,

$()_0$ = initial concentration,

d = position of the undetermined peak

relative to the ether peaks (see Fig. 32)

then one can write

$$d \sim \frac{7 (\text{LiAl}_2\text{H}_7)}{3(\text{AlH}_3) + (\text{LiAl}_2\text{H}_7)7} \quad (13)$$

$$(\text{LiAl}_2\text{H}_7) = k(\text{LiAlH}_4)(\text{AlH}_3), \quad (14)$$

$$(\text{AlH}_3) + (\text{LiAl}_2\text{H}_7) = m(\text{AlH}_3)_0 \quad (15)$$

* This equilibrium has also been proposed to explain the results of conductrimetric studies of the system. ³³

The stoichiometry of Eq. (1) shows

$$(\text{AlH}_3)_0 = 4(\text{AlCl}_3)_0 \quad (16)$$

Substituting Eqs. (15) and (16) into (14) and rearranging, one obtains

$$(\text{LiAl}_2\text{H}_7) = \frac{4 k m (\text{LiAlH}_4)' (\text{AlCl}_3)_0}{1 + k (\text{LiAlH}_4)} \quad (17)$$

Substituting Eqs. (15), (16), (17) into (13) and rearranging, one has

$$d \sim \frac{7k (\text{LiAlH}_4)}{3 + 7k (\text{LiAlH}_4)} \quad (18)$$

Assume $(\text{LiAl}_2\text{H}_7) \ll (\text{LiAlH}_4)$;

one then can say

$$(\text{LiAlH}_4) \approx (\text{LiAlH}_4)_0 - 3(\text{AlCl}_3), \quad (19)$$

$$r = \frac{(\text{LiAlH}_4)_0}{(\text{AlCl}_3)_0} \quad (20)$$

Substituting Eqs. (19) and (20) into (18) and rearranging, one gets

$$d \sim \frac{7k (r - 3)}{\frac{37}{(\text{LiAlH}_4)_0} + 7k (r - 3)} \quad (21)$$

Since (LiAlH_4) is 3.30 M, the result is

$$d \sim \frac{7k (r - 3)}{.91r + 7k (r - 3)} \quad (21'')$$

The graph of Fig. 38 shows a plot of the final position of the undetermined peak relative to the ether peaks versus the function given by Eq. (21'). We take k to be 0.1 as a matter of convenience for obtaining numbers. Other functions of r were obtained by assuming

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Fig. 38. Dependence of the final position of the undetermined peak on $f(r) = [7k(r-3)/0.91r + 7k(r-3)]$ for $k = 0.1$.

$$(a) \quad d \sim \frac{7(\text{LiAl}_2\text{H}_7)}{3(\text{AlH}_3) + 7(\text{LiAl}_2\text{H}_7) + 4(\text{LiAlH}_4)}$$

$$(b) \quad d \sim \frac{7(\text{LiAl}_2\text{H}_7)}{4(\text{LiAlH}_4) + 7(\text{LiAl}_2\text{H}_7)}$$

$$(c) \quad (\text{LiAl}_2\text{H}_7) > (\text{LiAlH}_4) ;$$

however, they yielded curves, when plotted, that were far from being linear.

The initial values of d were also plotted against the function given by Eq. (21') as shown by the graph in Fig. 39. The points scatter badly, probably owing to the variable precipitation of AlH_3 and the fact that the solutions were prefrozen. Unless prefrozen solutions warmed up at the same rate each time, the time of the reaction and its rate would be inconsistent from one sample to the next. The time-dependent shift can also be attributed to these two factors, of which the variable precipitation is the more important.

If the precipitation of AlH_3 is the primary cause of this shift and if the rate of precipitation of AlH_3 is proportional to its concentration, then the shift should be of first order. A plot of $\log d$ versus time for a solution for which sufficient data were available is shown on Fig. 40. The points scatter but do imply a linear pattern. This suggests that the shift is dependent on the precipitation of AlH_3 and that rate of this precipitation is of first order. The shift away from the ether peaks, i. e., increasing d over the period of days, can be attributed to the increasing concentration of LiAlH_4 due to the evaporation of ether.

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Fig. 39. Dependence of the initial position of the undetermined peak on $f(r) = 7k(r-3)/0.91r + 7k(r-3)$.

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Fig. 40. Dependence of $\log d$ on time for Sample 9.

CONCLUSION

At the beginning of this research project, it was believed that the structure of AlH_3 was polymeric and that the main object would be to determine the type of polymer. However, the negative results of many attempts to prepare AlH_3 free of ether under various conditions hinted that the structure probably was not a simple polymer, but in some way incorporated ether.

When nuclear spin resonance curves for AlH_3 were obtained, they showed definitely that the structure of AlH_3 was more complicated than originally supposed. Indeed it was found that the model that best explained the information about AlH_3 was not a polymer but a molecule of definite composition: $\text{Et}_2\text{O} \cdot \text{Al} \equiv [\text{H} - \text{AlH}_3]_3$.

It was hoped that high-resolution studies of the LiAlH_4 , AlH_3 system in ether would give some evidence as to the molecular structure of AlH_3 . The only information obtained however was that indicating probable existence of the species LiAl_2H_7 . Even so the existence of such a compound would give some indirect support for the molecular structure proposed in that both compounds must contain hydrogen bridges connecting two aluminum atoms.

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