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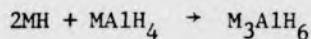
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UNIVERSITY ARCHIVES

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Studies of the thermal decomposition of tetrahydroaluminates, of formula MAH_4 ($M = Li, Na, K$), have shown that the decomposition proceeds through an intermediate of formula M_3AlH_6 . This hexahydroaluminate species has been synthesized by the addition of the metal hydride, MH to the MAH_4 compound:



($M = Li, Na, K$).

This is an initial report of the systematic synthesis of the complex aluminum hydride species using the above reaction. The products are of formula $M_2'MAlH_{6-n}X_n$ (M' may or may not be the same as $M = Li, Na, K$; $n = 0, 2$; $X = F, CH_3$).

The reactions were complete, synthesizing the nine products attempted. These hexahydroaluminates have the characteristics common to this species; they are air and moisture sensitive and insoluble in common solvents. They are also thermally more stable and less reactive than the corresponding tetrahydroaluminate.

X-ray powder and infrared data is given for each product. The X-ray powder patterns indicate that the structures of the products are isomorphous. Also in the mixed systems the infrared reveals some forbidden bands, indicating distortion in the octahedral lattice of the aluminum anion.

The kinetics of the complex aluminum hydrides are discussed. Three general kinetic models are used; A. W. Coates and J. P. Redfern, E. S. Freeman and B. Carroll, and Walter K. Tang. Thus, from thermal analysis, the activation energy and order of reaction is estimated for the hexahydroaluminate species.

A STUDY OF THE PREPARATION AND
CHARACTERIZATION OF SELECTED
COMPLEX ALUMINUM HYDRIDES


by

Charles L. Bratton

A Thesis Submitted to
the Faculty of the Graduate School at
The University of North Carolina at Greensboro
in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Greensboro
1970

Approved by


Thesis Advisor

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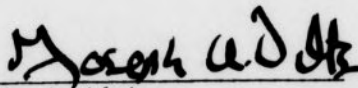
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INTRODUCTION

Complex Aluminum Hydrides. - Complex aluminum hydrides are well known as reducing agents in all areas of chemistry; these species are of the general formula MAH_4 ($M = Li, Na, K$). There are also six coordinate complex aluminum hydrides of form M_3AlH_6 ($M = Li, Na, K$). These, and related compounds, will be discussed in this study.

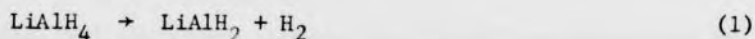
Thermal Decomposition of Complex Tetrahydroaluminates - Early Work. -

The first publication devoted to a study of the thermal decomposition of complex aluminum hydrides was published in 1952 by W. E. Garner and E. W. Haycock.¹ After this, there were few published studies until the 1960's through early 1970's. Although governments vigorously supported work in this area during the 1950's, the results of these studies are still classified because these compounds are potential solid rocket propellents, due to their high specific impulse¹⁸ resulting from the high hydrogen content.

The thermal decomposition of the MAH_4 species has been confirmed by latter work⁹⁻¹⁷ but this was not done without considerable research and initial misinterpretation of the actual route of decomposition.

Garner and Haycock did an isothermal decomposition study of $LiAlH_4$. These workers measured the hydrogen evolution and electrical conductivity at several temperatures between 100° and 150°. They proposed a three-step mechanism: first, a surface

reaction releasing unreproducible amounts of hydrogen, and second, a reaction releasing one-half of the hydrogen (equation 1).



This is then followed by a slow step (equation 2) to release the third hydrogen.



Thus the overall reaction being equation (3).



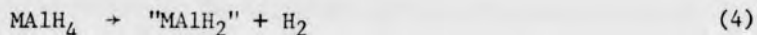
Wiberg and coworkers² also suggested a stoichiometry for the thermal decomposition of LiAlH_4 . Wiberg proposed a single-step decomposition to the lithium hydride product as in equation (3). These workers assumed this mechanism for the decomposition of several complex hydrides.

V. I. Mikheeva and coworkers³ used differential thermal analysis and effluent gas analysis to study the thermal decomposition of LiAlH_4 . They found an endothermic effect at 154°-161° with the loss of 50% of the hydrogen, a second endothermic effect at 197°-227° with loss of 25% of the hydrogen, and a final endotherm at 580°-586° with loss of the final hydrogen.

J. Block and A. P. Gray⁶ also studied the thermal decomposition of LiAlH_4 , using a differential scanning calorimeter (DSC). They found the three endotherms previously mentioned plus two exotherms. A low temperature (148°-158°) exothermic effect was attributed to

contamination of the sample. Later reports verified this affect due to impurities, and was in fact shown to be eliminated with pure samples.^{10, 11, 14-17}

T. N. Dymova and coworkers studied the thermal decomposition of NaAlH_4 ⁴ and KAlH_4 ⁵ and found they also displayed a thermal decomposition route similar to LiAlH_4 . This provides decomposition of general form:



In general, the thermal decomposition of complex aluminum hydrides follows the following sequence (M = Li, Na, K):

1. Phase change of the MAlH_4 compounds (with the exception of KAlH_4).
2. Loss of half of the hydrogen to form the "MAlH₂" species.
3. Formation of the MH species.
4. Decomposition to a non-characterized "MAI" species as proposed by Dilts and Asby.¹⁰

Early reports^{1, 3-7} agreed that the thermal decomposition of MAlH_4 compounds was essentially a similar, stepwise, process that proceeded through the postulated "MAlH₂" species.

Ehrlich's Preparation of Li_3AlH_6 . - Ehrlich and Young⁸ reported trillithium hexahydridoaluminate, Li_3AlH_6 , which was the first reported Lithium compound with more than four hydrogens bonded to the aluminum. This opened a whole new field of compounds and was initially used as the crux of the theory that MAlH_4 thermal decomposition went through the hexahydride intermediate.

Ehrlich's synthesis was accomplished by adding n-butyllithium to a solution of LiAlH_4 in a 1:2 ratio, using THF as a solvent.

These workers found that a white precipitate formed immediately upon combination. This white solid was insoluble in all common solvents, stable in a dry atmosphere and analyzed as Li_3AlH_6 .

This compound was assumed to be the hexahydride because its density was greater than the density of either LiH or LiAlH_4 . It was also thermally more stable and chemically less reactive than LiH or LiAlH_4 . It has a unique X-ray powder diffraction pattern⁸ which has since been substantiated to be different from a physical mixture of LiH and LiAlH_4 .⁹

Ehrlich reported that this compound decomposes without melting or subliming above 210° . This is consistent with the endothermic peak that occurs for the thermal decomposition of LiAlH_4 as earlier reports.

Hexahydro Intermediates and Preparation. - The report of Li_3AlH_6 by Ehrlich et al. made an intermediate of this type a definite possibility in the thermal decomposition of the MAlH_4 species.

The first report that reinvestigated the thermal decomposition of LiAlH_4 was by Mikheeva and Arkhipov⁹ in 1967. These workers found the three distinct endotherms and an exotherm in the thermal decomposition. Block and Gray had reported two exothermic effects. One of these exotherms is in the temperature region just below the phase change. This made the general thermal decomposition for LiAlH_4 as follows:

1. Phase change at 170°-endothermic.
2. Li_3AlH_6 formation at 190°-exothermic.
3. Li_3AlH_6 decomposition to LiH at 248°-endothermic.
4. LiH decomposition at 580°-endothermic.

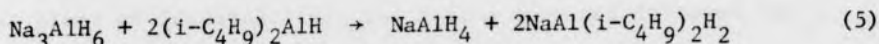
Therefore, this report by Mikheeva illustrated some important points in this solid state thermal decomposition.

1. Confirmed Block and Gray's report of the thermal decomposition.
2. Verified Li_3AlH_6 intermediate by X-ray diffraction.
3. Noted effect of impurities on thermal decomposition that accounted for one exothermic peak.
4. Suggested a solid state synthesis, as well as confirmed Ehrlich's report of Li_3AlH_6 .

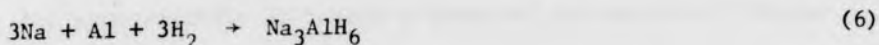
This work with the LiAlH_4 compounds is further supported by studies of the sodium and potassium analogs: NaAlH_4 and KAlH_4 , respectively.¹⁴

Zaharkin and Gavrilenko¹² in 1967 prepared Na_3AlH_6 by adding two moles of NaH to one mole of NaAlH_4 in heptane at elevated temperatures (160°). Proof of this hexahydride was given as:

1. Extraction with tetrahydrofuran (THF) did not result in the accumulation of NaAlH_4 (NaAlH_4 is very soluble in THF).
2. Reaction of the product with diisobutylaluminum hydride gave NaAlH_4 and sodium diisobutylaluminum hydride, as in equation (5).



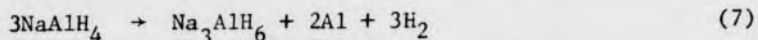
Ashby and Koebetz¹³ investigated the preparation of Na_3AlH_6 and associated research. By direct reaction they prepared Na_3AlH_6 (equation 6). This gave a 98% yield of Na_3AlH_6 with the reaction



of the elements under a sodium-aluminum ratio of 3:1, at 165° and

5000 psi. hydrogen pressure. The product was insoluble in hydrocarbon solvents and decomposed at 260°-280°. NaAlH_4 decomposes rapidly at 185°. Na_3AlH_6 exhibited a unique X-ray powder diffraction pattern which was similar to cryolite, Na_3AlF_6 . The product also gave an elemental analysis of Na:Al:H of 3:1:6.¹³ Additional reactions of the hexahydride with aluminum will be discussed later. But most important in this work was the fact that these workers also made Na_3AlH_6 from NaAlH_4 by controlled thermal conditions of 220° for 3 hours.¹³ Again, the product was insoluble in hydrocarbon solvents and gave an X-ray powder diffraction pattern identical to that of the product of the direct combination reaction.

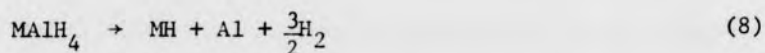
From this point it could be said that the formation of Na_3AlH_6 is an intermediate in the thermal decomposition of NaAlH_4 . This also accounted for a 50% loss of hydrogen in the first step of the decomposition as the stoichiometry of this reaction is identical to that proposed by Garner and Haycock (equation 7).



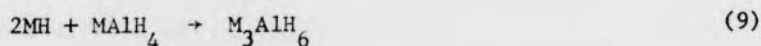
At this stage of decomposition, the sodium compound followed the pattern of decomposition previously mentioned. The mechanism of hexahydride formation will be discussed later.

In 1962, Dymova et al. also described the thermal decomposition of NaAlH_4 ⁴ and KAlH_4 ⁵ in the very same manner as had been for LiAlH_4 for approximately 15 years; a stepwise decomposition through a " MAlH_2 " species.

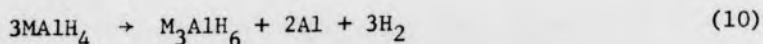
In 1969, Dymova¹⁴ reported a hexahydro intermediate for the thermal decomposition of NaAlH_4 and KAlH_4 . This added to the mounting evidence for the intermediate M_3AlH_6 species, whether it be exo- or endothermic in formation. These workers concluded that the hexahydridoaluminate species is formed during the thermal decomposition of the corresponding hydride. They also suggest that previous to the hexahydride formation there is a partial endothermic reaction which forms the metal hydride from the tetrahydride (equation 8).



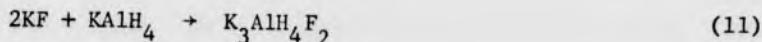
The metal hydride quickly reacts with the tetrahydride to form the M_3AlH_6 species (equation 9):



This is consistent with the report by Dilts and Ashby.^{15, 24} Therefore, the initial stoichiometry for the thermal decomposition of MAlH_4 species is as given in equation (10).



Study and Preparation of Complex Metal Hexahydridoaluminates. - The first reported deviation from the M_3AlH_6 species was by Chini, Baradel, and Vacca¹⁶ in 1966. This group successfully added an alkali metal halogen compound to an alkali-metal tetrahydroaluminate (i. e., KF with KAlH_4).



The significance here is that a new series of compounds of form $\text{M}_3\text{AlH}_{6-n}\text{F}_n$ has been experimentally verified. These compounds also exhibited the stability found in other six coordinate aluminum compounds. Chini *et al.* also successfully added sodium and potassium hydrides to their respective potassium tetrahydroaluminate.

As seen with the above work, the very reactive metal hydride species will combine with an alkali metal tetrahydroaluminate to form a six coordinate aluminum compound.

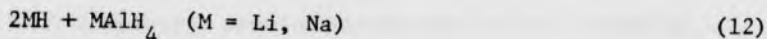
Dilts and Ashby found that for the alkali metals Li, Na, and K, the thermal decomposition of MAlH_4 is generally predictable. There are appropriate amounts of hydrogen released during decomposition and the formation of the hexahydrido intermediate, with a high temperature reaction between the metal and aluminum.

In summary, the thermal decomposition of MAlH_4 follows the order below with increasing temperature:

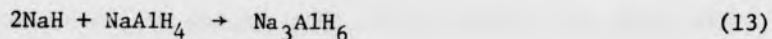
1. Phase change (except potassium).
2. M_3AlH_6 formation with release of 50% of the hydrogen.
3. M_3AlH_6 decomposition to MH species with loss of 25% of the hydrogen.
4. MH decomposition, which probably has some solid state reaction between the metal and aluminum (probably unstable species).^{15,17}

In the three alkali metal cases previously mentioned, the M_3AlH_6 species was formed following the phase change. This reaction is irreversible and is exothermic for Li, and endothermic for Na.

Dilts and Ashby²⁴ also studied the solid state reaction of complex metal hydrides (equation 12).



Differential thermal analysis traces showed that there is hexahydride formation immediately following the phase change. This hexahydride formation was exothermic in both cases, even though the formation of Na_3AlH_6 was endothermic in $NaAlH_4$ thermal decomposition.



The information in the preceding three paragraphs is essentially the accumulation of many years of work. But this is also the basis for the synthetic and kinetic studies of the six coordinate aluminum species. Therefore, a systematic study of the synthesis of complex alkali-metal aluminum compounds of formula M_3AlH_6 , M'_2MAlH_6 , or $M_3AlH_{6-n}X_n$ ($M', M = Li, Na, K$ and $X = F$) is presented.

Kinetics of Thermal Decomposition. - Thus far, there has been no study of the non-isothermal kinetics of the decomposition of these compounds.

Three general models of decomposition are used to point out conflicting or analogous steps of the decomposition of M_3AlH_6 compounds. The first model to be used is that of E. S. Freeman and B. Carroll.¹⁹ This was first proposed in 1958 and derives the kinetic parameters (order of reaction and activation energy) from the weight loss and the derivative of the weight loss. Also a very important point about this method is that the activation energy and order of reaction may both be determined.

The second kinetic model is that of A. W. Coates and J. P.

Redfern.²⁰ With this method a previous knowledge of the reaction order is assumed. This may be of the theoretically possible types of 0, $\frac{1}{2}$, $\frac{2}{3}$, and first order. Therefore, the order and rate constant come from an equation that is essentially a plot of the log of the fractional sample weight loss vs. $\frac{1}{T}$.

The third model is proposed by Walter K. Tang.²¹ It is derived by using the differences in weight. This plot assumes the order of reaction is one, and uses the specific rate constant. All of the authors noted the difficulty in doing kinetic studies on a solid state system, and the error necessarily involved.

T. Ozawa²² is very much against a single equation to determine kinetic parameters. Instead he feels that in order to get the proper activation energy and order of reaction, one must confirm data at different heating rates and different models. Ozawa points out that Coates and Redfern's calculations neglect higher order reactions, although he does show that this calculation does give an excellent correlation for the pre-exponential factors in an Arrhenius type plot.

The Tang calculation is relatively simple compared to that of Freeman and Carroll because the latter not only requires the thermal gravimetric analysis (TGA) curve, but also weight derivative TGA (DTGA). This calculation has been held as reliable since 1958 as many other models have been tested against it.

For the lower order reactions (one or less) the Coates and Redfern calculation seems to be the most successful and widely accepted simple kinetic decomposition model.

All of the above methods are dynamic kinetic models. For the solid state reaction some invalid assumptions must be made. The discussion of kinetic equations is connected with the following processes: (1) movement of phases, (2) boundaries diffusion, (3) nucleation, (4) growth of nuclei.²³ Here the kinetic parameters (rate constant, pre-exponential term, activation energy, activation entropy) normally used with the homogeneous reactions are described and used in the same manner as the heterogeneous reaction (solid state). For the solid state, kinetic parameters for an equilibrium situation are being derived from non-equilibrium situations, which is not truly sound. The basic problem areas are: (1) constant surface reaction, (2) size of sample, (3) particle size, (4) packing of sample, (5) pressure, (6) atmosphere around reaction, and (7) heating rate. But relative to experimental error and factors not so obvious, most incongruities are neglected and relative activation energies or reaction orders became relevant. Most of the above factors, by the nature of the experiment design, will be highly reproducible or error minimized, therefore resulting in a consistent set of kinetic parameters which may be compared.

STATEMENT OF THE PROBLEM

When Ehrlich synthesized the first reported hexahydroaluminate, another aspect of chemistry was initiated. These complex aluminum compounds have since been synthesized in a variety of ways and are still under study.

There has been no systematic study of some of the compounds, particularly complex alkali metal aluminum hydrides and halides, of formula M'_2MAlH_6 , $M_3AlH_nX_{6-n}$ or $M'_2MAlH_nX_{6-n}$ ($M' \neq M = Li, Na, K,$ and $X = F$).

The first purpose of this study was to synthesize the aforementioned compounds and characterize them. A second purpose was to study the kinetics by thermal analysis in order to gain some insight of the solid state reaction.

EXPERIMENTAL

Source of Materials and Purification of Solvents. - The compounds used in these studies are: sodium aluminum hydride, potassium fluoride, lithium fluoride, and sodium hydride (Alfa Inorganics, Beverly, Massachusetts). The above were used without further purification. There were two sources of methyl lithium. The first, recrystallized (commercial source) from ether did not remove all of the impurities. Therefore, CH_3Li was obtained from the reaction of methyl mercury, $(\text{CH}_3)_2\text{Hg}$, with metallic lithium.²⁴

The lithium aluminum hydride (Alfa Inorganics) was recrystallized from an ether-toluene solvent system under a nitrogen atmosphere.

All of the above and subsequent products were stored in an inert-atmosphere box (Vacuum Atmospheres Co., Los Angeles, Calif.). This dry box is equipped with a regeneration and purification unit for the N_2 atmosphere.

The KH is received in a 50% oil dispersion and had to be washed with dry hexane and dried under N_2 vacuum.

Solvents. - The initial reactions were performed in mineral oil. The mineral oil had been boiled with molten sodium metal and allowed to cool under partial vacuum.

The tetrahydronaphthalene (Eastman Organic Chemical Co., Rochester, N.Y.) was dried under nitrogen atmosphere by boiling the solvent with sodium metal. The solvent was then distilled (140°)

and stored in the dry box, over sodium metal. Initially, the tetrahydronaphthalene was a dark liquid, but after distillation and drying, the solution was colorless.

By hydrogenation of 1-decene (Eastman Organics), decane was prepared. The hydrogenation was done under N_2 and using a platinum catalyst. Commercial decane (MCB Co., Norwood, Ohio) was also dried and stored with sodium metal under nitrogen atmosphere.

The ether and toluene (Fisher Scientific Co., Fair Lawn, N.J.) were both dried by refluxing with Na/K alloy-benzophenone and stored under nitrogen. These solvents were kept in the dry box when possible.

The tetrahydronaphthalene and decane were recycled by distilling, drying, and kept in a nitrogen atmosphere over molecular sieves.

Preparation and Purification of Compounds. - Air-sensitive compounds were handled in an inert atmosphere box, Schlenk-type glassware, or on a standard vacuum line²⁵ with mechanical pump.

The $LiAlH_4$ was added to anhydrous Et_2O (0.285 M) so that it might be recrystallized.

For the $LiAlH_4$ recrystallization, approximately half of the Et_2O was removed by reducing the pressure in the vacuum line and trapping the ether in a liquid N_2 cold trap. An equal amount of toluene was added to the $LiAlH_4$ - Et_2O solution (toluene refluxed over calcium hydride for approximately one and one-half hours). The pressure was again reduced to remove the remaining ether. The vacuum was continued until solid began to precipitate. The toluene

suspension of LiAlH_4 was then filtered through a Schlenk-type, glass frit filter, connected to the reaction flask (see Figure 1). After filtration, the LiAlH_4 was evacuated for approximately 36 hours in order to remove any traces of Et_2O . The flask was then sealed and placed in the dry box.

A Noreleco-Phillips X-ray source was used for the X-ray powder data. The camera was 114.6 mm and a $\text{CuK}\alpha$ -Ni radiation filter was used. The infrared spectra were obtained on a Perkin Elmer 457 grating infrared spectrometer.

Complex Alkali-Metal Six Coordinate Aluminum Compounds. - The preparation of these complex aluminum compounds is essentially the same. The products of this preparation were unaffected by the three saturated hydro-carbon solvents used.

The general procedure will be described. Then for each set of reagents there will be a short paragraph giving the reactants, reaction conditions, and notable characteristics of the reaction.

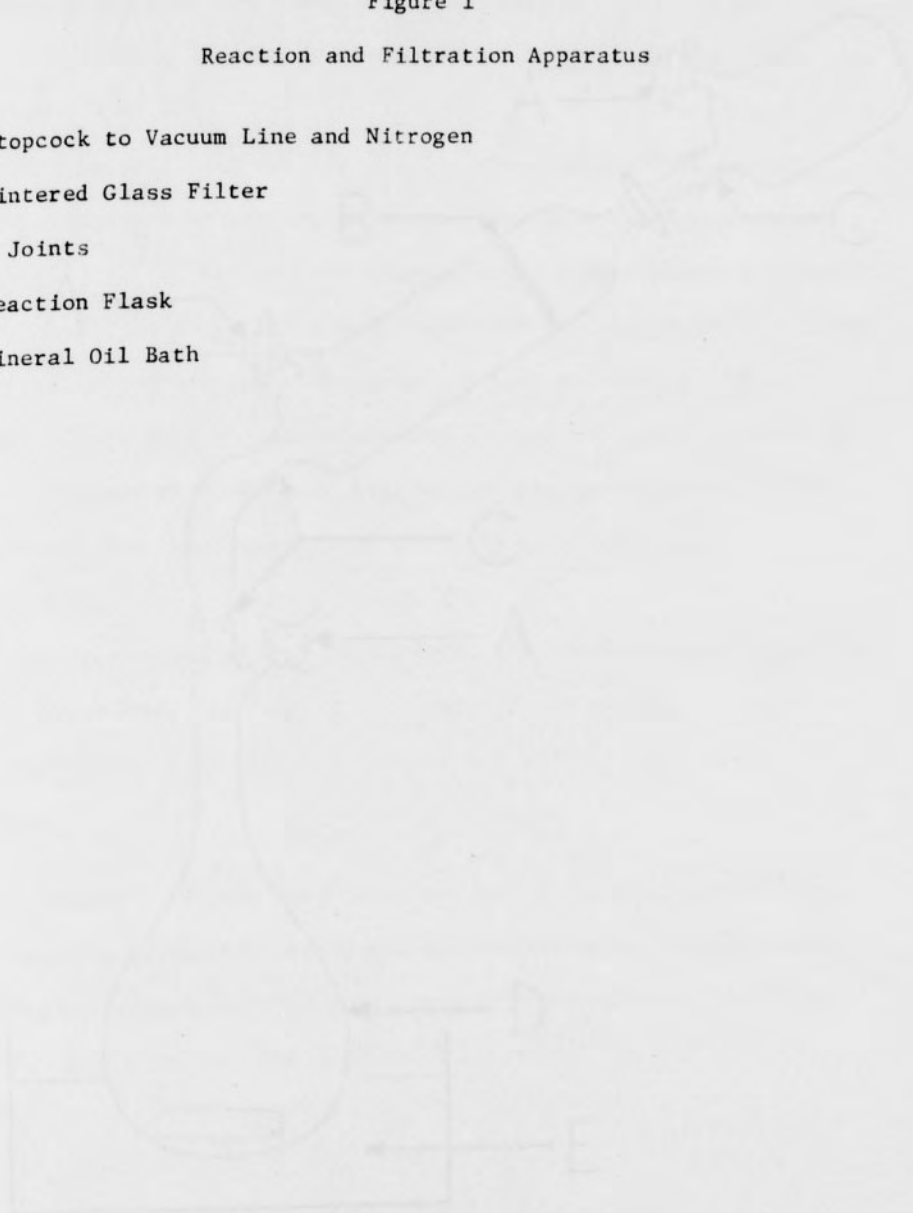
The metal halide or metal hydride was reacted with the complex aluminum hydride in a two to one mole ratio. These reactants were ground together with mortar and pestal in the dry box. Then approximately one-half of the solid was placed in a Schlenk flask which contained a small magnetic stir bar. The remaining sample was stored in a stoppered ampul in the dry box.

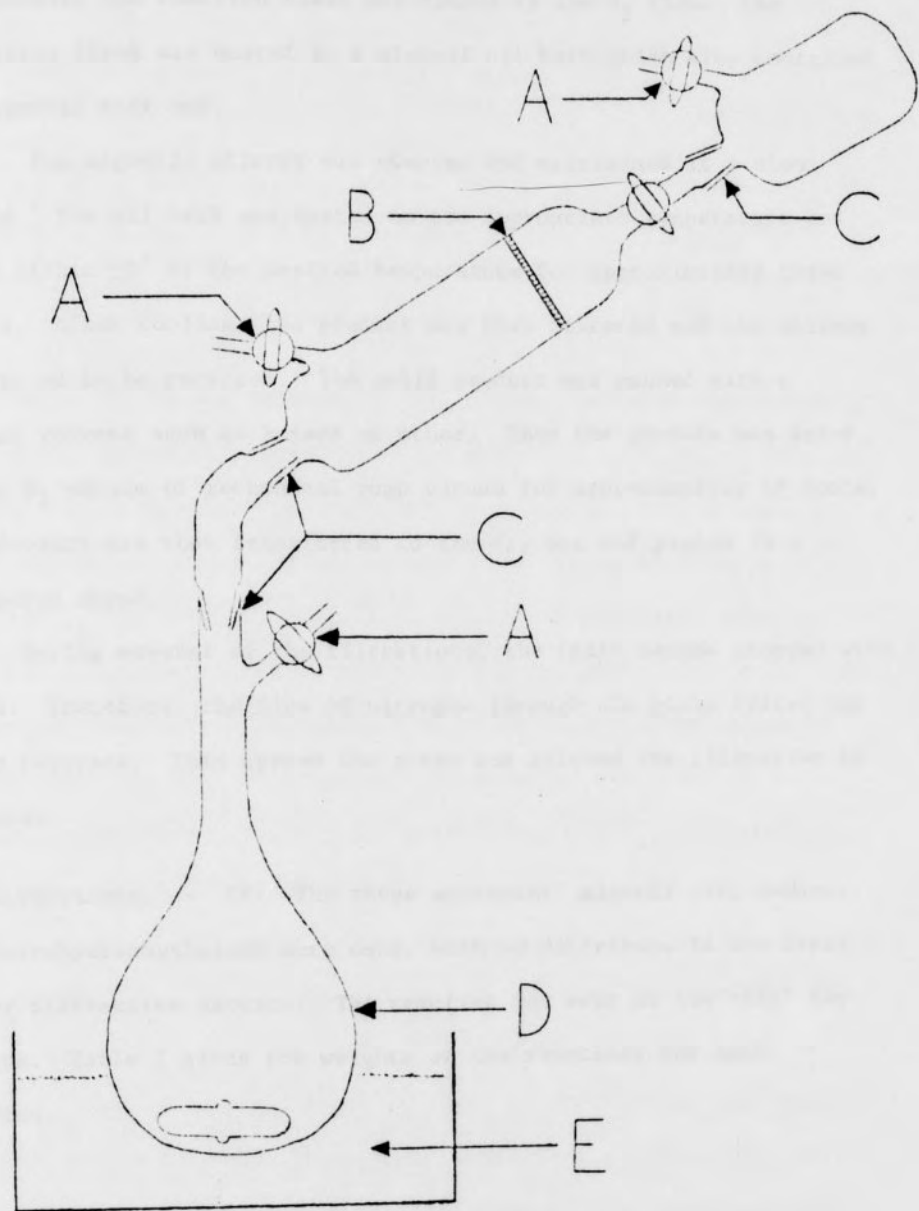
Enough solvent was added to just cover the reagents. Then the reaction flask was sealed, removed from the dry box, and connected to a constant flow of N_2 . After flushing the connecting tubing and

Figure 1

Reaction and Filtration Apparatus

- A Stopcock to Vacuum Line and Nitrogen
- B Sintered Glass Filter
- C T Joints
- D Reaction Flask
- E Mineral Oil Bath





N_2 bubbler the reaction flask was opened to the N_2 flow. The reaction flask was heated in a mineral oil bath which also contained a magnetic stir bar.

The magnetic stirrer was started and maintained at a slow speed. The oil bath was heated to the appropriate temperature and held within $\pm 5^\circ$ of the desired temperature for approximately three hours. After cooling, the product was then filtered and the solvent collected to be recycled. The solid product was washed with a common solvent such as hexane or ether. Then the product was dried under N_2 vacuum or mechanical pump vacuum for approximately 18 hours. The product was then transferred to the dry box and placed in a stoppered ampul.

During several of the filtrations, the frit became stopped with solid. Therefore, the flow of nitrogen through the glass filter had to be reversed. This opened the pores and allowed the filtration to continue.

$NaAlH_4$ reactions. - KF: The three solvents: mineral oil, decane, and tetrahydronaphthalene were used, with no difference in the X-ray powder diffraction pattern. The reaction was kept at 150° - 155° for 3 hours. Table 1 gives the weights of the reactants for each reaction.

Table 1. KF-NaAlH₄ Reactions

<u>weight - grams</u> <u>NaAlH₄ (moles)</u>	<u>weight - grams</u> <u>KF (moles)</u>	<u>Solvent</u>
0.62 (0.011)	1.38 (0.0238)	mineral oil
0.54 (0.0100)	1.11 (0.0191)	mineral oil
0.39 (0.0072)	0.81 (0.014)	decane
0.76 (0.014)	1.62 (0.0279)	decane
0.43 (0.0080)*	0.92 (0.016)	tetrahydronaphthalene

*temperature of reaction was approximately 190° for 3 hours.

KH: The KH was kept in the oil dispersion until approximately five hours before the reaction. The solid was then washed with dry hexane and dried under N₂ vacuum and in a dry box. There appeared to be an unusual amount of gas evolution at temperatures greater than 140°. The material solidified into dense crystals, stopping the stir bar at times. No large pieces or unusual amounts of solid formed during the reaction. The NaAlH₄-0.81 grams (0.015 mole) smoothly reacted with the KH-1.20 grams (0.0300 mole) at 160°-165° in tetrahydronaphthalene for 3 hours. The product was washed with toluene.

LiF: NaAlH₄ (0.54 grams, 0.010 mole) was combined with LiF-0.52 grams (0.020 mole) in tetrahydronaphthalene. Within one-half hour the oil bath temperature was greater than 180° and clumps of solid started to form. The reaction was held at 190°-192° for 2½ hours. Some of the solid was sticking to the stir bar and some to the sides of the reaction flask, but the solvent stayed clear. At lower temperatures there appeared to be a good homogeneous mixture of reagents. The product was washed with hexane.

LiH: NaAlH₄ (1.65 grams, 0.0306 mole) was combined with

LiH-0.47 grams (0.059 mole) in tetrahydronaphthalene. The reaction temperature was greater than 170° for 3 hours and held at 190° for $1\frac{1}{2}$ hours. The reactants formed a firm solid greater than 180°, and fixed firmly to reaction flask for brief periods of time. The stir bar kept most of the solid from being stationary or accumulating, but it could still not break some of the solid pieces. The product was washed with ether and dried under vacuum.

CH₃Li: NaAlH₄ (1.08 grams, 0.0200 mole) was combined with CH₃Li-0.88 grams (0.040 mole) in decane. The reaction temperature was held at 97°-99° for 3 hours. After the reaction some heterogeneous dark gray colored particles settled in the bottom of the flask. Therefore, the reaction was run for another hour at 110°. The CH₃Li used in this reaction was recrystallized from Et₂O. Therefore, the reaction was run again using CH₃Li prepared from (CH₃)₂Hg.

The NaAlH₄ (0.81 grams, 0.015 mole) was combined with CH₃Li-0.66 grams (0.030 mole) in decane. The reaction temperature was 106°-109° for 3 hours. After the second reaction there was a good homogeneous mixture with no solid settling out of solution. The product was a white solid, not light gray as in previous reactions. The latter CH₃Li reaction was used for X-ray and DTA data.

LiAlH₄ reactions. - KF: LiAlH₄ (0.38 grams, 0.10 mole) was combined with KF-1.16 grams (0.20 mole) in decane. The reaction temperature was kept at 130° for 3 hours. The decane could not be filtered because the glass fritt became stopped with solid. Therefore, the solution was allowed to sit under N₂ for approximately 18 hours.

The product did settle to the bottom of the flask leaving a partially clear solution that could be decanted from the product. The product was washed with ether, but still had problems with the glass frit becoming stopped. The solid was dried as before, transferred to a dry box, and spread on a watchglass to dry.

KH: The LiAlH_4 (0.57 grams, 0.015 mole) was mixed with KH-1.20 grams (0.0300 mole) in decane. The solution was heated slowly to 128° for $2\frac{1}{2}$ hours (greater than 124° for 3 hours). There was no noticeable change in solution upon cooling. The decane had to be removed by reducing the pressure and trapping the solvent in a liquid nitrogen cold trap, because the filter again became stopped with the solid. The product was washed with dry hexane and dried as usual.

LiF: LiAlH_4 -0.57 grams (0.015 mole) was combined with LiF-0.78 grams (0.030 mole) in decane. The LiF was dried immediately prior to the reaction by N_2 vacuum and hot air blown over the LiF flask. The reaction proceeded smoothly at 125° - 128° . The product was washed with dry hexane.

NaH: LiAlH_4 -0.57 grams (0.15 mole) was combined with NaH-0.96 grams (0.040 mole) in decane. The decane had to be removed by reduced pressure and trapped in a liquid N_2 cold trap. The product was washed with dry hexane and dried under vacuum.

Thermal Analysis Equipment. - The basic thermal analysis equipment used was the commercial Perkin-Elmer DSC-1b differential scanning calorimeter, and the TGS-1 thermal balance. Because of the extreme

sensitivity of the materials involved and special demands on analog data output, several modifications of this equipment and operating procedures were necessary. These are described below.

TGS 1. - The screw cap closures on the gas inlet and tareloop of the TGS 1 were replaced with teflon needle valves to provide improved integrity of the atmosphere within the balanced bottle. A modified furnace mount assembly, consisting of a small platinum heater with fixed thermocouple was fabricated after the suggestions of Etter and Smith.²⁵ A second satisfactory solution to avoiding the screw closures used by Perkin-Elmer involves sealing these closures at room temperature with a vulcanizing silicon elastomer.

The platinum sample pans provided by Perkin-Elmer were replaced by micro crucibles (approximately 150 mg in weight) made of hot pressed Al_2O_3 . This allowed for reasonable size samples (5 to 10 mg) with a low density hydride. To provide maximum thermal equilibrium, helium was used as inert gas (argon could be used alternatively but nitrogen must be excluded because of formation of Li_3N in some cases). Although the rated rings of the Cahn RG balance is 20 micrograms full scale (0.1 microgram sensitivity), in practical terms, the 0.4 mg range (0.4 microgram sensitivity) represents a maximum sensitivity of this system (due in part to the low percentage weight loss of hydrogen in the compounds being studied). The output from the Cahn RG balance was recorded on either a Texas Instrument 2 channel recorder (Servo-Riter II, 1 millivolt range) or a multiplexed 4 channel Heath Recorder.

The derivative of the primary (attenuated) TG signal is fed into a Cahn Mark II Time Derivative computer (classical RC differentiation) and the output of this device was recorded on the second channel of the TI recorder or a second multiplex channel on the Heath Recorder (1 or 10 mv respectively). The approximate ranges on the time derivative computer were calibrated by determining weight loss due to diffusion of water vapor from a Kneudsen cell that controlled the temperature. The balance weighing ranges were calibrated class M (NBS) standard 10 mg weights.

Temperature calibration of the thermal balance was accomplished by means of the Curie point magnetic transitions in the method described in the TGS 1 manual. Agreement between the observed and actual temperature was found to be within 1° over the temperature range from 100°-500°.

Auto Range Expander. - The function of the auto range expander was to allow for recording an analog signal at the higher sensitivity without the fear of losing information on the recorder. For example, suppose one was anticipating a 100 mg weight loss. Without the use of this device, one would then have to use at least the 100 mg full scale range of the recorder. This would limit the sensitivity of the recorder, the approximately 0.5 mg. By using the auto range expander one could perform this same experiment using a much more sensitive 10 mg full scale range. Each time the recorder pen neared zero, indicating 10 mg of weight loss, the precision calibrated off-set would be superimposed on the balance signal, turning the pen to the

100 position on the chart (up to 10 times). Now our resolution would be 10 times greater than one would have without using this device. The auto range expander was also useful when observing small weight losses in the presence of large ones. In addition, this does not require the specificity in selecting ranges for a run, or in cases where it is not possible to anticipate the magnitude of the weight loss associated with the decomposition reaction.

Sample Loading Procedure. - The sample crucible was initially fired with a temperature of approximately 800°, allowed to cool to room temperature, and suspended from hangdown wire on the balance. Once an atmosphere of helium had been re-established in the balance chamber, the mass dial of the RG balance was adjusted so that zero deflection was noted on a recorder scale. The sample crucible was then transferred in a weighing bottle to the dry box so the sample could be loaded into the crucible under an atmosphere of nitrogen.

The sample was then loaded on the balance being protected from the atmosphere by increasing the flow of helium. An Al_2O_3 top on the crucible prevented this excess flow of helium from blowing the sample out of the crucible. Once the sample was in place and the hangdown tube was returned to its normal position, the helium flow was maintained at 2.0 l. per minute for approximately 5 minutes at which time the balance chamber again contained a pure helium atmosphere. The sample weight could then be read directly from the recorder.

The above system has been evaluated using $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and

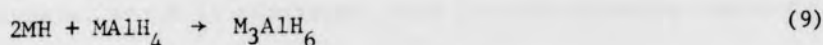
NaS_2O_5 . Both cases gave reproducible kinetic results.

DSC. - The methods used to prepare samples for the DSC have been discussed in detail elsewhere.^{15, 24}

All of the TGA equipment for this study was set up and modified by Dr. J. A. Dilts, research director.

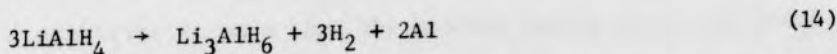
RESULTS AND DISCUSSION

Formation and Stability of Six Coordinate Aluminum Compounds. - This study stems from the thermal decomposition of complex aluminum hydrides, in particular, the formation of the six coordinate aluminum compound during the thermal decomposition of the corresponding tetrahydroaluminate (MAlH_4 , $\text{M} = \text{Li, Na, K}$). In general, this decomposition goes through the the first two steps¹⁵ which form the hexahydride (equation 8, 9). Equation (8) is essentially the initiating step,



and equation (9) is the actual formation of the hexahydride. As previously mentioned, the MH species is very reactive and combines with the MAlH_4 . Attempts to synthesize or isolate the M_2AlH_5 species have not been successful. Due to the nature of MH and MAlH_4 , rapid combination, a mechanism such as that of equations (8) and (9) is assumed to be correct reaction.

The thermal decomposition of LiAlH_4 proceeds as following:



This study uses the above as a possible synthetic route to the six-coordinate aluminum compound. As previously cited, $M_3AlH_{6-n}X_n$ compounds have been synthesized in a variety of ways, although, thus far, there has been no report of a systematic study of this type of reaction.

The hexahydrides, Li_3AlH_6 ²⁴ and Na_3AlH_6 ¹⁰, are documented and synthesized by controlled pyrolytic reaction. This study covers substitution of the cations Li, Na, and K in the crystal lattice and substitution of fluoride and methyl groups for a hydride in the anion structure.

The products obtained from our study are stable at room temperature. They are also air and moisture sensitive and insoluble in common solvents, which is consistent with hexahydroaluminum compounds in general. The thermal stability of these compounds appeared to increase with increasing cation size (Li < Na < K). This is agreeable with reports by Dilts and Ashby¹⁵ of the stability of the corresponding tetrahydroaluminates. These workers showed that this class of compounds behaves in the same manner.

The general relationship between stability and relative cation to anion size is well documented.

For the AlH_6^{3-} species, larger cations would fit into the crystal lattice and stabilize it more than the smaller cation (i.e., Li ionic radius is 0.68 Å vs. K ionic radii of 1.33 Å). Selected examples of this may be seen by the decomposition temperature of the six-coordinate species, using DSC. In the DSC spectra, $K_2NaAlH_4F_2$

decomposed at 320°, $\text{Li}_2\text{NaAlH}_6$ at 277°, and $\text{Na}_2\text{LiAlH}_6$ at 273°.

Literature values for the onset of decomposition for Li_3AlH_6 is 220° and for Na_3AlH_6 262°. ¹⁵ One would expect the $\text{Li}_2\text{NaAlH}_6$ value to be closer to its parent compound, but the behavior of the alkali metal combinations, particularly the anomalous behavior of Li precludes any justification of the close values of $\text{Na}_2\text{LiAlH}_6$ and $\text{Li}_2\text{NaAlH}_6$.

All of our Li_3AlH_6 and Na_3AlH_6 or LiAlH_4 and NaAlH_4 thermal decomposition data was in agreement with earlier works. ⁹⁻¹⁶

Infrared Analysis. - Infrared spectra were run on all products. For the AlH_6^{3-} octahedral species, there should be two active infrared stretching bands, ν_3 and ν_4 . Previous reports by Beach and Ashby¹¹ give strong, broad bands at 700 cm^{-1} and 1400 cm^{-1} for Li_3AlH_6 , and 800 cm^{-1} and 1300 cm^{-1} for Na_3AlH_6 . These bands shifted little if at all for the varied compounds (see Table 2). This would be expected for molecules with anions of the AlH_6^{3-} type. Because infrared frequencies are so dependent on the weights and relative cation-anion size for the stretching and bending, replacing one of alkali metal with another, or substituting a fluorine for a hydride should not create a large shift.

Some characteristics of a particular compound tend to be revealed with replacement in the ionic lattice or substituting a fluorine. Beach and Ashby noted that there could be infrared active bands suppressed in the spectra. In the $\text{K}_2\text{LiAlH}_4\text{F}_2$, K_2LiAlH_6 , and $\text{Na}_2\text{LiAlH}_6$ spectra the broad band at 1400 cm^{-1} splits (hexachlorocyclopentadiene mull). Previously this had exhibited only a single band at 1400 cm^{-1} .

Table 2

Infrared Data of the Complex Aluminum Hydrides (cm^{-1})*

<u>Li_3AlH_6</u>	<u>NaAlH_6</u>
740 s, b	800 s, b
1400 s, b	1370 s, b
<u>$\text{Li}_3\text{AlH}_4\text{F}_2$</u>	<u>$\text{Li}_2\text{NaAlH}_6$</u>
800 m	790 s, b
1400 m	1400 w
<u>$\text{Na}_2\text{LiAlH}_6$</u>	<u>$\text{Li}_2\text{NaAlH}_4(\text{CH}_3)_2$</u>
750 m, b	730 m, b
1375 w	1530 m, b
1450 w	
<u>K_2LiAlH_6</u>	<u>$\text{Li}_2\text{NaAlH}_4\text{F}_2$</u>
750 m, b	800 m
1380 w	1390 w
1460 w	
<u>$\text{K}_2\text{LiAlH}_4\text{F}_2$</u>	<u>K_2NaAlH_6</u>
750 m, b	730 s, b
1380 w	1410 m
1430 w	1450 m
	<u>$\text{K}_2\text{NaAlH}_4\text{F}_2$</u>
	790 s, b
	1440 m
	1550 s, b

*s, strong; m, medium; w, weak; b, broad

The Li definitely plays an important role in these spectra and what appears to be the identification of two bands at 1380 cm^{-1} and 1480 cm^{-1} . The differences in size and ionic potential, particularly Li, would serve as a powerful source to distort or deform the crystal lattice positions and allow forbidden bands to be seen.

With the $\text{Li}_3\text{AlH}_4\text{F}_2$ spectra the band at 1400 cm^{-1} becomes much more sharp, but not as strong as Li_3AlH_6 . This is probably due to decreased electron density from the fluorine. The fluoride-hydride size and weight difference allow the Al-H stretching frequency to become more pronounced.

Variations of the alkali metals tend to also bring out three bands which Beach and Ashby noticed upon reaction of LiAlH_4 with $(\text{C}_2\text{H}_5)_2\text{NH}$.¹¹ By substituting an alkali metal, or metals, the degeneracy would be lost and could distort the O_h lattice. For the octahedral AlH_6^{3-} species, there are six vibrational bands of which only two are infrared active. But the distorted octahedral would make it possible for the forbidden bands to become active.²⁵

All of the spectra indicate that the complex aluminum compounds tend to deviate from the pure O_h and that a compound of type M_2LiAlH_6 does tend to go towards its parent compound, i. e., MAlH_4 . This is mentioned in previous works, with amine reactions and aluminum hydrides.^{15, 24} The AlH_6^{3-} anion is more symmetrical and more susceptible to deviations in the lattice than the AlH_4^{1-} anion. Therefore, cleavage or substitution should be more sensitive and show the trend towards the MAlH_4 compound. Lack of structural and general

knowledge of these compounds makes such arguments open for debate. But the infrared spectra do indicate that the two basic bands previously reported appear to indicate the deformation of the crystal lattice site placement when the compound is perturbed by substitution. Yet, this reaction goes to completion of the six-coordinate aluminum anion.

These substitutions of the alkali metals indicate that the number of vibrational modes seen in the infrared spectra is dependent on the symmetry of the lattice surrounding the AlH_6^{3-} anion. Both Beach and Ashby¹¹ and this study give evidence of some of the forbidden bands appearing in the infrared spectrum.

Fluoride and methyl substitutions also change the symmetry around the aluminum. This will accordingly affect the electron density, lattice symmetry, and local symmetry.

For the compounds with trans substitution of the fluoride ion, such as $\text{K}_2\text{NaAlH}_4\text{F}_2$, the symmetry would be D_{4h} . The fluorines would decrease the electron density allowing more pronounced Al-H stretching. This was particularly noticeable for $\text{Li}_3\text{AlH}_4\text{F}_2$, with the peak at 1400 cm^{-1} decreasing in amplitude but increasing the sharpness of the peak. This should also have six infrared active bands.

Other changes in the lattice around the aluminum, i. e., cis substitution (C_{2v}), substitution would tend to distort the symmetry even further. This would induce more Al-H bending and far less stretching.

The methyl substitution did give a relative strong band at 1600 cm^{-1} and made the spectra more spread out and less intense, indicating that the CH_3 groups made it difficult for any strong Al-H stretch. This is due to increased steric factors and the added hydrogens in the molecule.

X-Ray Powder Analysis. - The X-ray powder patterns indicate that these compounds are isomorphous (Tables 3 and 4). There is much variation in the intensities of the lines, but there appears to be enough consistency in all nine compounds to conclude that they are isomorphous. Although, even more important, even if our conclusion is not sound, in all cases the patterns did not compare with the parent compounds, indicating the reaction had occurred.

There was some problem evaluating the X-ray patterns involving KF, because the KF dominated the powder pattern.

Differential Scanning Calorimetry Results. - The DSC was used to confirm a reaction, but it was not used as the main source of information. When there were doubts about reaction completion the DSC provided another means of testing the reaction, particularly for solid state reactions.

Consistently the reaction:



would give an exotherm at approximately the temperature of the phase change for the tetrahydroaluminate, or just below that temperature.

Table 3

X-Ray Powder Diffraction Patterns of LiAlH_4 Reactions

LiF		NaH		KH		KF	
$d, \text{\AA}$	I/I_0^*	$d, \text{\AA}$	I/I_0^*	$d, \text{\AA}$	I/I_0^*	$d, \text{\AA}$	I/I_0^*
4.1	m	4.6	vw	4.08	w	4.0	vw
3.93	m	4.25	m	3.65	w	3.5	vw
2.95	vw	4.04	m	3.54	m	3.35	vw
2.82	w	3.00	vs	3.41	w	3.17	vw
2.33	vs	2.80	vs	3.30	vs	3.08	mw
2.25	vw	2.60	ms	3.17	mw	2.90	w
2.02	s	2.50	m	2.93	mw	2.65	vs
1.81	vw	2.42	vs	2.82	s	2.40	vw
1.77	vw	2.31	s	2.72	vw	2.32	mw
1.52	vw	2.21	w	2.53	w	2.20	vw
1.50	vw	2.13	vw	2.33	ms	2.13	vw
1.426	ms	2.02	s	2.20	w	2.03	w
1.224	m	1.87	ms	2.12	w	1.88	s
1.16	mw	1.84	mw	2.01	s	1.72	vw
1.01	vw	1.77	m	1.88	vw	1.61	w
		1.72	s	1.80	vw	1.54	m
		1.66	m	1.72	s	1.43	w
		1.53	ms	1.69	vw	1.335	w
		1.50	ms	1.65	m	1.225	vw
		1.46	s	1.59	vw	1.195	m
		1.425	ms	1.53	vw	1.09	w
		1.40	ms	1.43	m	1.03	vw
		1.305	w	1.31	m		
		1.250	w	1.277	m		
		1.230	w	1.222	mw		
		1.116	s	1.167	mw		
		1.087	s	1.097	mw		
		1.040	w				
		1.01	w				

* d values read from transparent scale obtained from N. P. Nies, Laguna Beach, California. s, strong; m, medium; w, weak; v, very.

Table 4

X-Ray Powder Diffraction Patterns of NaAlH_4 Reactions

LiH		LiF	
d, Å	I/I ₀ *	d, Å	I/I ₀ *
4.6	vw	3.95	w
4.3	w	3.40	vw
3.71	vw	3.00	w
3.34	vw	2.70	vw
3.0	vs	2.65	w
2.80	ms	2.33	vs
2.60	s	2.01	vs
2.50	s	1.89	w
2.34	w	1.64	w
2.23	vw	1.425	s
2.04	mw	1.225	mw
1.88	ms	1.215	m
1.85	w	1.165	m
1.77	m		
1.67	ms		
1.53	s		
1.51	s		
1.445	vw		
1.415	vw		
1.31	w		
1.255	w		
1.235	w		
1.217	mw		
1.171	w		
1.159	w		
1.148	w		
1.125	w		
1.109	w		
1.080	w		
1.069	vw		
1.043	w		
1.003	vw		

*d values read from transparent scale obtained from N.P. Nies, Laguna Beach, California. s, strong; m, medium; w, weak; v, very.

LiCH ₃		KH		KF	
<u>d,A</u>	<u>I/I₀*</u>	<u>d,A</u>	<u>I/I₀*</u>	<u>d,A</u>	<u>I/I₀*</u>
4.6	w	4.05	vw	4.00	vw
3.15	s	3.7	vw	3.50	w
2.96	vs	3.5	w	3.37	w
2.82	m	3.28	s	3.15	w
2.72	ms	3.15	w	3.09	w
2.50	m	2.99	s	2.90	w
1.93	m	2.82	s	2.66	vs
1.87	ms	2.70	mw	2.50	vw
1.77	m	2.50	m	2.32	w
1.65	s	2.20	vw	2.20	vw
1.58	mw	2.17	vw	2.13	vw
1.52	m	2.02	ms	1.89	s
1.50	m	1.93	w	1.79	vw
1.41	vw	1.87	m	1.71	vw
1.37	w	1.77	ms	1.64	w
1.255	m	1.66	m	1.61	w
1.23	m	1.64	m	1.545	mw
1.21	m	1.59	vw	1.337	w
1.16	w	1.53	ms	1.227	vw
1.15	w	1.50	m	1.190	mw
1.12	mw	1.42	w	1.088	w
1.11	w	1.31	m	1.038	vw
1.08	vw	1.27	m	1.025	vw
1.055	mw	1.235	w		
1.04	mw	1.215	mw		
1.00	w	1.165	mw		
		1.15	vw		
		1.098	w		
		1.08	w		
		1.042	w		
		1.008	vw		

*d values read from transparent scale obtained from N. P. Nies, Laguna Beach, California. s, strong; m, medium; w, weak; v, very.

The DSC verification became particularly important with the KF reactions. For the reaction $\text{KF} + \text{NaAlH}_4$ the exotherm was sharp and very distinct. The peak occurred at 176° , suppressing the endothermic effect of the phase change (literature 183°).¹⁵ The base of the peak had approximately a 20° spread, but the reaction appeared to have taken place within a 10° - 15° span. There would be approximately three minutes or less in the solid state.

We were able to reproduce the reactions of Chini, *et al.*,¹⁶ in which a fluoride was substituted for a hydride. In addition, a methyl group was substituted for a hydride ion. There has not been a previous report of an alkyl group substitution in these classes of compounds or the tetrahydroaluminates.

The infrared spectra indicated two broad peaks centered at 690 cm^{-1} and 1600 cm^{-1} . The compound is stable and X-ray powder data are given in Table 4. Because $\text{Li}_2\text{NaAlH}_4\text{Me}_2$ forms at such a low temperature (95° - 100°) and also appears to begin decomposition at less than 100° , a good DSC run is very difficult to get.

The X-ray powder pattern of $\text{Li}_2\text{NaAlH}_4(\text{CH}_3)_2$ compares well with Na_3AlH_6 and may be considered isomorphous.

Thermal Analysis. - Sharp and Wentworth²⁷ give three kinetic models that are suitable for general application of thermogravimetric data; (1) integral model, (2) difference model, and (3) difference differential model. This study incorporates one model from each category for comparison of results. The author of each model that we used is given in the order corresponding to the above classifications;

(1) A. W. Coates and J. P. Redfern, (2) Walter K. Tang, and (3) E. S. Freeman and B. Carroll.

The above are dynamic kinetic models vs. the isothermal kinetic model (e.g., Garner and Haycock). There are several advantages to a dynamic method of study, which J. Simon²³ has previously noted;

(1) they are rapid and results are easier to calculate, (2) they have a wide temperature range and the sample may be followed over the entire range, (3) informatory experiments, often necessary with isothermal models are not needed, (4) several decomposition steps can be followed by a single curve, and (5) the theory and methods of evaluation have already been developed for the interpretation of curves obtained at linear heating rates.

From the kinetic study of the thermal decomposition of LiAlH_4 and Li_3AlH_6 , we found that the kinetic model of Coates and Redfern gave the most consistent results. J. Zsako likewise found the integral approximation of Coates and Redfern superior in determining kinetic parameters from thermogravimetric data.

There has been some criticism of kinetic studies by TGA on exothermic systems, but samples of CaC_2O_2 and NaS_2O_5 both gave results consistent with documented results. Thus, we have no reservation of the validity of our data of the aluminum hydrides.

We have tried to eliminate error in the TGA in several ways. The sample size is kept small (i.e., less than 10 mg) and ground before analysis to reduce particle size. An inert atmosphere of He gas is used at a constant flow rate through the balance system. And

the samples were run at different heating rates. Also, as previously mentioned, the results were applied to the different kinetic models and compared.

The decomposition of LiAlH_4 appears to be first order, with an activation energy of 60 ± 5 kcal per mole.

The Li_3AlH_6 also appears to be first order with an activation energy of 65 ± 5 kcal per mole. Large samples (greater than 75 mg) tend to lower the activation energy, but the reaction order appears to remain first order.

The activation energy for the Li_3AlH_6 is in agreement with Block and Gray, being 64 kcal per mole. But this is low relative to that given by the Freeman and Carroll method, i.e. 159 kcal per mole.

In this study the Freeman-Carroll calculation varied the most compared to the other two methods (approximately 95 kcal variation vs. 20 kcal variation for the Coates and Redfern method and 15 kcal variation for the Tang method). Therefore, such a large difference between values of activation energy could be expected with such a large fluctuation for the Freeman and Carroll calculations.

The Na_3AlH_6 compound has an activation energy of 48 ± 2 kcal and appears first order.

There was no TGA data collected on the complex aluminum hydride systems.

SUMMARY

This study has systematically synthesized and characterized a new class of compounds; the six-coordinate alkali metal aluminum hydrides.

From the fundamental AlH_6^{3-} anion, fluoride or methyl groups have been substituted for the hydride ion. Formerly, there has not been an alkyl group substituted in this aluminum anion. The anions formed are $\text{AlH}_4\text{F}_2^{3-}$ and $\text{AlH}_4(\text{CH}_3)_2^{3-}$.

The cations in the ionic lattice are the alkali metals Li, Na, or K. Substitution of the cations destroys the degeneracy of the compounds M_3AlH_6 and forces distortion of the octahedral symmetry around the AlH_6^{3-} anion, thus revealing some of the forbidden infrared bands.

The X-ray powder diffraction patterns indicate that these compounds are indeed isomorphous with the unsubstituted parent compounds. Since we have found M_3AlH_6 ($\text{M} = \text{Li}, \text{Na}$) to follow first order kinetics, the complex aluminum hydrides are probably the same.

Finally, as with all previous reports of M_3AlH_6 ($\text{M} = \text{Li}, \text{Na}, \text{K}$) compounds, we have also found that the complex alkali metal aluminum hydrides are less reactive, insoluble in common solvents, and thermally more stable than the corresponding tetrahydroaluminate.

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APPENDIX

This computer program basically calculates x and y points according to the methods of Coates and Redfern, W. K. Tang, and Freeman and Carroll. It also performs a least squares regression analysis from which the activation energy may be determined, and in the case of Freeman and Carroll, the order of reaction may be calculated.

The thermogravimetric data may be entered directly into the computer or the data may be typed on computer cards and read into the computer. This data may be saved for later use.

The program is written in the Basic language and is compatible with the Systems 72 and Hewlett-Packard computer.

```

100 REM ***THIS PROGRAM CALCULATES KINETIC PARAMETERS FROM THERMAL
110 REM ***ANALYSIS DATA USING THE FREEMAN-CARROLL, TANG, AND
120 REM ***COATS AND REDFERN METHODS. NOTE IT IS POSSIBLE TO
130 REM ***DO ONLY THE COATS AND REDFERN METHOD BY ENTERING
140 REM ***ZERO FOR THE DTG RANGE.
150 REM ***PROGRAMED FOR SYS72 0N10/13/75 BY JAD
160 FOR I=1 TO 5
170 PRINT
180 NEXT I
190 PRINT "SAMPLE-"
200 PRINT
210 PRINT
220 PRINT "DATE="
230 LET T5=0
240 PRINT
250 REM ***DATA INPUT
260 LET E=0
270 LET I=0
280 LET T=0
290 LET W=0
300 LET P=0
310 LET T2=0
320 LET C=0
330 LET W2=0
340 IF T5=5 THEN 820
350 IF T5=1 THEN 820
360 PRINT
370 PRINT
380 PRINT
390 DIM A(50),Z(50),Q(50),V(50)
400 DIM X(50),Y(59)
410 DIM K(50),L(50),U(50)
420 PRINT "INPUT NUMBER OF DATA POINTS, ZERO TO TERMINATE"
430 PRINT "FOR COATS-REDFERN ONLY ENTER 0 FOR DTG RANGE"
440 INPUT N
450 IF N=0 THEN 9999

```

```

460 PRINT "INPUT SAMPLE WT. IN MG"
470 INPUT D
480 PRINT "WHAT IS THE FINAL WT IN MG"
490 INPUT G
500 PRINT "WHAT IS THE INITIAL TG (OTØ 1.0)"
510 INPUT H
520 PRINT "DTG RANGE?"
530 INPUT J
540 PRINT "TG RANGE?"
550 INPUT F
560 PRINT "HEATING RATE IS"
570 INPUT A5
580 IF J=0 THEN 600
590 GØTØ 620
600 GØSUB 3030
610 GØTØ 2160
620 PRINT "INPUT DATA ØN FØRMAT TG,DTG,T(IN C)"
630 FØR I=1 TØ N
640 PRINT "DATA"
650 INPUT K(I),L(I),U(I)
660 NEXT I
670 FØR I=1 TØ 3
680 PRINT
690 NEXT I
700 PRINT "FREEMAN CARRØLL CALCULATION";A5;"DEG/MIN";D;"MG SAMPLE"
710 FØR I=1 TØ N
720 LET V(I)=1/(U(I)+273.15)
730 LET L(I)=L(I)*J*.866667
740 LET Ø(I)=((D-G)-(H*F-K(I)*F))
750 NEXT I
760 FØR I=1 TØ N-1
770 LET Y(I)=(LØG(L(I))-LØG(L(I+1)))/(LØG(Ø(I))-LØG(Ø(I+1)))
780 LET X(I)=(V(I)-V(I+1))/(LØG(Ø(I))-LØG(Ø(I+1)))
790 NEXT I
800 LET N=N-1

```



```

810 REM ***LEAST SQUARES CALCULATION
820 FOR I=1 TO N
830 LET T=T+X(I)
840 LET T2=T2+X(I)^2
850 LET W=W+Y(I)
860 LET P=P+X(I)*Y(I)
870 LET W2=W2+Y(I)^2
880 NEXT I
890 LET A=0
900 REM ***SOLVE OF COEFFICIENTS
910 LET B=(W*T2-T*P)/(N*T2-T^2)
920 LET M=(N*P-T*W)/(N*T2-T^2)
930 IF T5=5 THEN 960
940 PRINT "Y=MX+B"
950 PRINT "B=";B;"M=";M
960 LET A1=0
970 LET A1=((M*1.987)/(1000))
980 IF T5=5 THEN 1040
990 PRINT
1000 PRINT "THE ACTIVATION ENERGY IS";A1;"KCAL/MOLE"
1010 IF T5=1 THEN 1030
1020 PRINT "THE APPARENT ORDER IS";B
1030 PRINT
1040 LET S=0
1050 FOR I=1 TO N
1060 LET Z(I)=B+M*X(I)
1070 LET Q(I)=Y(I)-Z(I)
1080 LET S=S+Q(I)^2
1090 NEXT I
1100 LET R=SQR(S/(N-2))
1110 LET M1=R*SQR(N/(N*T2-T^2))
1120 LET B1=R*SQR(T2/(N*T2-T^2))
1130 IF T5=5 THEN 1160
1140 PRINT "THE STANDARD DEVIATIONS ARE"
1150 PRINT "SB=";B1;"SM=";M1

```

```

1160 LET C=(N*P-T*W)
1170 LET C=C/SQR((N*T2-T^2)*(N*W2-W^2))
1180 PRINT
1190 IF T5=5 THEN 1210
1200 GOTO 1220
1210 RETURN
1220 PRINT "THE CORRELATION COEFF. IS";C
1230 PRINT
1240 PRINT
1250 PRINT "OBSERVED X      OBSERVED Y      CALCULATED Y      RESIDUAL"
1260 PRINT
1270 FOR I=1 TO N
1280 PRINT X(I),Y(I),Z(I),Q(I)
1290 NEXT I
1300 PRINT
1310 GOSUB 1550
1320 IF T5=5 THEN 1340
1330 GOTO 1350
1340 RETURN
1350 IF T5=1 THEN 2140
1360 PRINT "TANG CALCULATION? 1=YES"
1370 LET N=N+1
1380 INPUT T5
1390 IF T5=1 THEN 1420
1400 GOTO 2140
1410 REM ***TANG CALCULATION
1420 FOR I=1 TO 5
1430 PRINT
1440 NEXT I
1450 PRINT "TANG CALCULATION";A5;"DEG/MIN"
1460 FOR I=1 TO N
1470 LET Y(I)=LOG(L(I)/((D-G)-(H*F-K(I)*F)))
1480 LET X(I)=1/(U(I)+273.15)
1490 NEXT I
1500 GOTO 250

```

```

1510 FOR I=1 TO 5
1520 PRINT
1530 NEXT I
1540 RETURN
1550 REM ***PLOT SUBROUTINE
1555 IF ABS(C)<0.975 THEN 2125
1560 LET X2=X(N)-.1*(ABS(X(1)-X(N)))
1570 LET X3=X(1)+.1*(ABS(X(1)-X(N)))
1580 LET Y2=Y(1)-.1*(ABS(Y(1)-Y(N)))
1590 LET Y3=Y(N)+.1*(ABS(Y(1)-Y(N)))
1600 LET X1=ABS(X(N)-X(1))/30
1610 LET X8=INT(X2/X1)
1620 LET X9=INT(X3/X1+.5)
1630 LET D5=(Y3-Y2)/57
1640 PRINT "X-MIN";X2;"X-MAX";X3
1650 PRINT "X-INC";X1
1660 PRINT
1670 PRINT "Y-MIN=";Y2;"Y-MAX=";Y3
1680 PRINT "Y-INCR=";D5
1690 PRINT
1700 IF T5=1 THEN 2010
1710 GOSUB 2050
1720 REM ***SCALES AND INTEGERIZES THE DATA POINTS
1730 DEF FNI(X)=INT(X/X1+.5)
1740 DEF FNJ(Y)=INT((Y-Y2)/D5+.5)+1
1750 FOR I=1 TO N
1760 LET X(I)=FNI(X(I))
1770 LET Y(I)=FNJ(Y(I))
1780 NEXT I
1790 GOSUB 2970
1800 REM ***PLOT GENERATION
1810 FOR X=X8 TO X9
1820 PRINT ".";
1830 FOR I=1 TO N
1840 IF X(I)<>X THEN 1930
1850 IF Y(I)>60 THEN 1930

```

```

1860 IF Y(I)<1 THEN 1930
1870 REM *** PRINTS POINT
1880 FOR Q=1 TO Y(I)
1890 PRINT " ";
1900 NEXT Q
1910 PRINT "*";
1930 NEXT I
1940 PRINT
1950 NEXT X
1960 GOSUB 2970
1970 FOR I=1 TO 3
1980 PRINT
1990 NEXT I
2000 RETURN
2010 PRINT "                *TANG*"
2020 PRINT
2030 PRINT "                Y-AXIS"
2040 GOTO 1720
2050 IF T5=5 THEN 2100
2060 PRINT "                FREEMAN-CARROLL"
2070 PRINT
2080 PRINT "                Y-AXIS"
2090 RETURN
2100 PRINT "                COATES-REDFERN-"; A6; "ORDER"
2110 PRINT
2120 PRINT "                Y-AXIS"
2124 GOTO 2130
2125 PRINT "PLOT SUPPRESSED"
2126 GOTO 2130
2130 RETURN
2140 PRINT "COATES-REDFERN CALCULATION? I=YES"
2150 INPUT T5
2160 IF T5=1 THEN 2190
2170 LET T5=0
2180 GOTO 160
2190 LET T5=5

```

```

2200 REM ***COATES-REDFERN CALCULATION FIRST ORDER
2210 LET A6=1
2220 PRINT
2230 PRINT
2240 PRINT
2250 FOR I=1 TO N
2260 LET Ø(I)=(((D-G)-F*(H-K(I)))/(D-G))
2270 NEXT I
2280 FOR I=1 TO N
2290 LET X(I)=1/(U(I)+273.15)
2300 LET Z7=-(LØG(Ø(I)))
2310 LET Z8=(U(I))2
2320 LET Y(I)=LØG(Z7*Z8)
2330 NEXT I
2340 GØSUB 250
2350 GØSUB 2650
2360 GØSUB 1230
2370 LET Z9=2/3
2380 REM **** ZERO AND FRACTIONAL CR COMPUTATION
2390 IF A6=1 THEN 2430
2400 IF A6=0 THEN 2490
2410 IF A6=.5 THEN 2550
2420 IF A6=Z9 THEN 2610
2430 LET A6=0
2440 GØSUB 2880
2450 GØSUB 250
2460 GØSUB 2650
2470 GØSUB 1230
2480 GØTØ 2380
2490 LET A6=.5
2500 GØSUB 2880
2510 GØSUB 250
2520 GØSUB 2650
2530 GØSUB 1230
2540 GØTØ 2380

```

```

2550 LET A6=Z9
2560 GOSUB 2830
2570 GOSUB 250
2580 GOSUB 2650
2590 GOSUB 1230
2600 GOTO 2380
2610 LET T5=0
2620 LET A6=0
2630 GOTO 160
2640 REM *** REPORTS LEAST SQUARE RESULTS FOR C-R
2650 FOR I=1 TO 3
2660 PRINT
2670 NEXT I
2680 PRINT "C-R CALCULATION"; A6; " IS ORDER, "; A5; " DEG/MIN"; D; " MG SAMPLE"
2690 PRINT
2700 PRINT "Y=B+AX"
2710 PRINT "B="; B; "M="; M
2720 LET A1=((M*1.987)/(1000))
2730 PRINT "ACTIVATION ENERGY IS "; A1; " KCAL"
2740 PRINT "CORRELATION COEFF IS "; C
2745 PRINT "STANDARD DEVIATIONS ARE SB= "; B1; "SM= "; M1
2750 PRINT
2760 PRINT
2770 LET A3=0
2780 LET A9=1-((2*(1.987)*(U(1)+273.14))/A1)
2790 LET A3=EXP(B)
2800 LET A3=A3/A9
2810 LET A3=(A3*A1*A5)/1.987
2820 LET A3=-A3
2830 PRINT "THE PRE-EXPONENTIAL FACTOR IS "; A3
2840 LET A3=LOG(A3)/LOG(10)
2850 PRINT "LOG(10) OF PRE-EXP FACTOR IS "; A3
2860 RETURN

```

```

2870 REM ***CALC Y(I) VALUES FOR FRACTIONAL C-R CASE
2880 FOR I=1 TO N
2890 LET X(I)=1/(U(I)+273.15)
2900 LET Ø(I)=(((D-G)-F*(H-K(I)))/(D-G))
2910 LET Y9=EXP((1-A6)*LOG(Ø(I)))
2920 LET Y9=((1-Y9)*((X(I))2)/(1-A6)
2930 LET Y(I)=LOG(Y9)
2940 NEXT I
2950 RETURN
2960 REM ***AXIS SUBROUTINE
2970 PRINT " ";
2980 FOR I=1 TO 60
2990 PRINT ".";
3000 NEXT I
3010 PRINT
3020 RETURN
3030 PRINT "INPUT DATA ON FORMAT TG,T(IN C)"
3040 FOR I=1 TO N
3050 PRINT "DATA"
3060 INPUT K(I),U(I)
3070 NEXT I
3080 LET T5=1
3090 RETURN
9999 END

```