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Autor: Ursu, Ioan / Turkevich, John

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Studies on the relation of catalytic properties of $LiAlH_4$ and its decomposition products and their magnetic resonance properties

by Ioan URSU and John TURKEVICH

Introduction.

The true nature of the active center of a heterogeneous catalyst is of great importance in understanding of the complex phenomenon of heterogeneous catalysis. On heating lithium aluminum hydride, centers active for hydrogen deuterium exchange and deuterium exchange with the $LiAlH_4$ catalyst can be gradually produced. The purpose of this investigation is to study how these centers arise and to characterize their nature by means of electron spin resonance of the electrons in the solid and the proton, lithium and aluminum nuclear resonances of the catalytically active material.

Furthermore the effect of ultraviolet radiation on the rate of the hydrogen-deuterium exchange and the deuterium exchange with the lithium aluminum hydride.

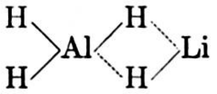
I. NUCLEAR MAGNETIC RESONANCE RESULTS

Materials.

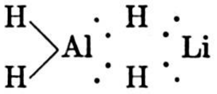
Lithium aluminum hydride.

Lithium aluminum hydride ($LiAlH_4$) was used as a catalyst in order to study the exchange between hydrogen and deuterium.

The lithium aluminum hydride used as catalyst in this study is a commercial compound from Metal Hydrides Incorporated, Beverly, Massachusetts. The lithium aluminum hydride is a microcrystalline solid which is stable in dry air at room temperature. It is extremely hygroscopic and reacts violently with moisture, liberating and igniting hydrogen. Lithium aluminum hydride has been postulated as a complex compound considered [1] as a double hydride $LiH.AlH_3$ given by a homopolar structure I, while a covalent structure II, has also been proposed [2]:



I



II

Lithium aluminum hydride may be heated without appreciable decomposition to temperatures below 100° C in vacuo.

According to Garner and Haycock [3] the thermal decomposition of $LiAlH_4$ occurs in three stages: (*a*) an initial reaction on the surface of the grains of the hydride, which is at first rapid and then slows down to a constant rate; (*b*) an interface reaction, the rate passing through a maximum and becoming very slow after two hydrogen atoms per mol. of $LiAlH_4$ have been liberated, corresponding to the reaction

$$LiAlH_4 \longrightarrow LiAlH_2 + H_2$$

and finally (*c*) a slow process during which a third hydrogen atom is liberated (at 150° C), giving as final products lithium hydride and aluminum, according to the equation

$$LiAlH_2 \longrightarrow LiH + Al + 1/2\ H_2\ .$$

The initial reaction which is rapid at first and then slows down to a constant rate, occurs to the extent of about 0.7% of the total decomposition and penetrates the surface to a depth of several molecular layers. In the surface reaction the loss of hydrogen results in the formation of surface defects which aggregate and collapse to give nuclei at which a normal interface reaction proceeds. Lithium aluminum hydride is an electrical conductor, with a positive temperature coefficient of conductivity.

The density of $LiAlH_4$ at 25° C is 0.917 gr./cc and the specific heat is 0.48 cal/gr./deg. [4].

Examination of the nuclear magnetic resonance of $LiAlH_4$ has shown that at room temperature the width of the resonance absorption line is 8.7 gauss [5].

Lithium aluminum hydride is soluble in compounds of the ether class.

The reported solubilities in grams per 100 gr. of solvent at 25° C are as follows [6]:

Diethyl ether	25-30; 0.83 molar [7]
Tetrahydrofuran	13
Dibutyl ether	2
Dioxane	0.1
Ethylene glycol dimethyl ether	1.1 molar [7]

Preparation of the samples.

The preparation of $LiAlH_4$ samples demand precautions necessitated by the moisture-sensitivity and reactivity of the complex metal hydride. In less humid atmospheres, the material was carefully crushed by wrapping the lumps in aluminum foil and tapping gently with a rubber hammer. All the operations were carried out in a well ventilated hood in order to remove dust and the small amount of hydrogen which may be evolved. Powdered $LiAlH_4$ prepared in this way, was introduced into a sample tube 1.5 cm. diameter × 17 cm. length. These dimensions were selected to permit insertion of the sample tube in the nuclear magnetic resonance instrument.

The amount of $LiAlH_4$ which was introduced in the sample tube was around 10 cc. Some glass wool was placed over the surface of the lithium aluminum hydride. Red sealing wax was placed around the joint to prevent leaks. For preliminary nuclear magnetic resonance measurements four samples were investigated and after these seven other samples were studied. The second set of samples was heated at various temperatures (from room temperature to 130° C) and pumped for various times (from 0.5 to 16 hrs.) at 10^{-3} mm. Hg. (Table 1).

TABLE 1.

I. Sample never pumped at room temperature.
II. Sample pumped for 6 hrs. at room temperature.
III. Sample pumped for 6 hrs. at 100° C.
IV. Sample pumped for 0.6 hr. at 130° C.
V. Sample pumped for 1 hr. at 130° C.
VI. Sample pumped for 6 hrs. at 130° C.
VII. Sample pumped for 6 hrs. at 130° C.

A standard vacuum apparatus was used for preparation of the samples.

Measurement procedure.

The nuclear magnetic resonance spectrum of $LiAlH_4$ was studied by means of Varian Nuclear Resonance Instrument (Model V4200 B-Spectrometer) [8]. The broad and narrow resonance lines were measured on the Varian Wide Line Spectrometer. For all measurements a fixed frequency of 40 megacycles was used, and the magnetic field was approximately 9,500 gauss.

The magnet had 12″ cylindrical pole faces and a gap width of 1¾″. In all the data reported, the homogeneity of the field was estimated to be less than .1 gauss over the sample. At first the proper conditions were determined for the measurement of the derivative of the absorption line. Various filters, various sweeps, and various scans, were investigated and the following best values were determined: for broad lines, filter number 4 (5.0 sec.), sweep L-8 (0.125) and scan 2-3 (785.0), and for narrow lines, no filter, sweep L-3 (4.0) and scan 1-3 (55.0). All during the measurements, the leakage was maintained at a constant value of 60.

The derivative spectrum of the proton resonance line was recorded for various values of the power of the radiofrequency-field, from 15.0 to 49. All the measurements were made at room temperature. Due to changes in the spectrometer sensitivity, a standard water sample was measured daily, and the values obtained for the $LiAlH_4$ samples were normalized to eliminate the influences of the changes of sensitivity. After every set of sample measurements, the standard water sample measurement was repeated. When the sensitivity was not changed (ΔH and ΔI were approximately constants) the data were considered acceptable. In order to obtain good reproducibility in data, approximately a one hour warm-up period of the instrument was required.

The peak derivative signal (S) at a value H_2 was plotted against the logarithm of the radio-frequency power to obtain a saturation curve for each sample. Because the line shape of the absorption curve is approximately Gaussian (the ratio between maximum negative slope and minimum positive slope of derivatives curves is approximately 2.2), then T_2 (spin-spin relaxation time) can be calculated directly from the width of the derivative curve. The spin lattice relaxation time T_1 was determined by the progressive saturation method [8, 9].

Experimental results.

The general appearance of the derivative of the broad and narrow resonance lines for $LiAlH_4$ is shown in Figure 1. It is seen that for every sample there are two peaks. The saturation curves $(S^{-2/3} = [k\Delta I\,.\,(\Delta H^2]^{-2/3})$ vs H_1^2 for $LiAlH_4$ samples are represented in Figure 2 (B*l*) and (N*l*). The proton signal value was determined for each $LiAlH_4$ samples, from saturation curve at $H_1^2 = 0$ (S^* for narrow and broad line) (Table 2). The proton signal value (S_i^*) is proportional with number of protons contained in a sample. For each sample T_1, T_2 and the slope (by the method described before) were also determined. The proton signal value (S_i^* for narrow and broad line) and the mobility (M_i, which is the ratio of area of narrow line to area of narrow and broad line), were also calculated by means of graphical integration. The shape of the integrated curves are shown in Figure 3 (A, B, C, D). The experimental condition for measurement and data, for each sample, are summarised in Table 2 and Table 3. Comparing the data for $LiAlH_4$ with data for standard water sample (.29% H_2) it is seen that:

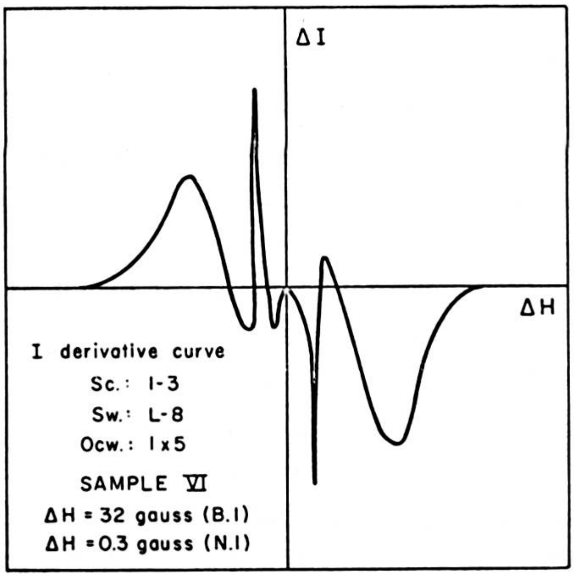


FIG. 1

The number of protons per cc (p) in $LiAlH_4$ sample are:

$$p = \frac{4 \times 0.917}{38} \times 6 \times 10^{23} \approx 6 \times 10^{22}.$$

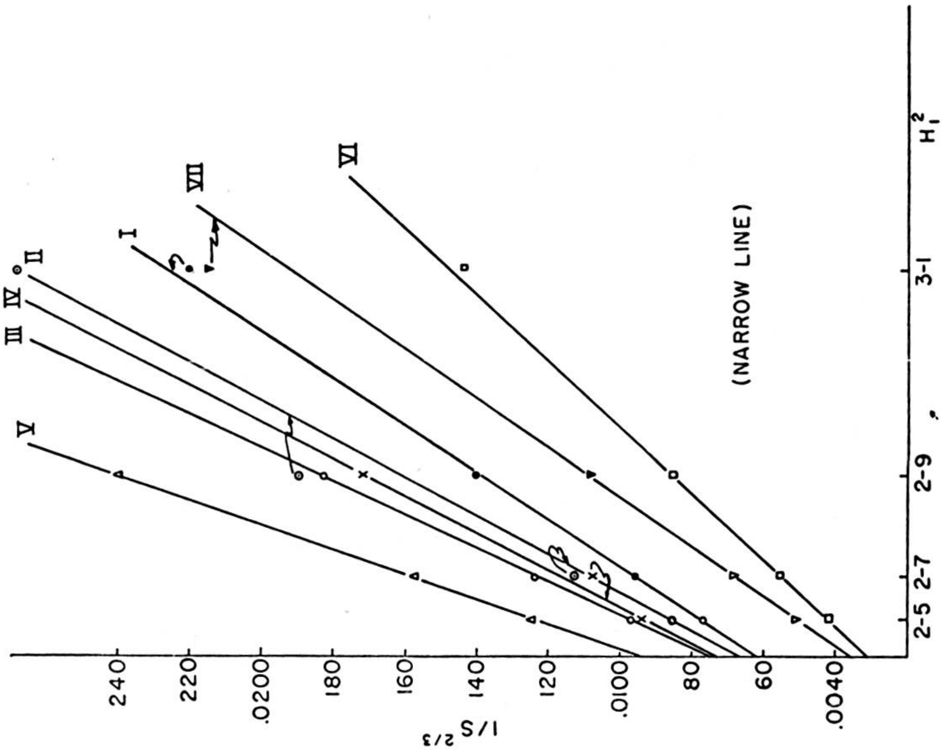


FIG. 2 (N.L.)

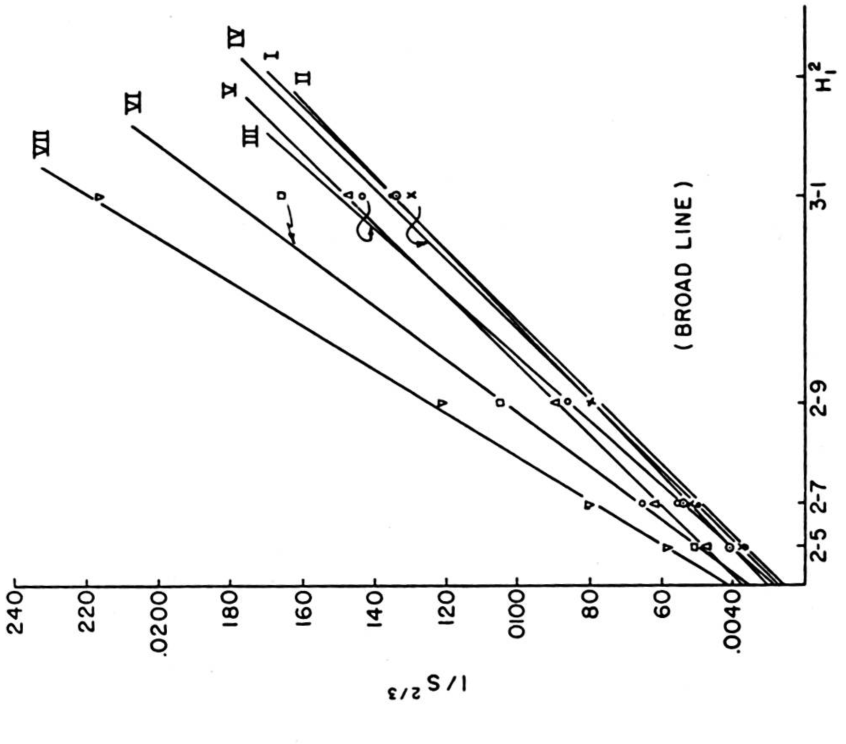


FIG. 2 (B.L.)

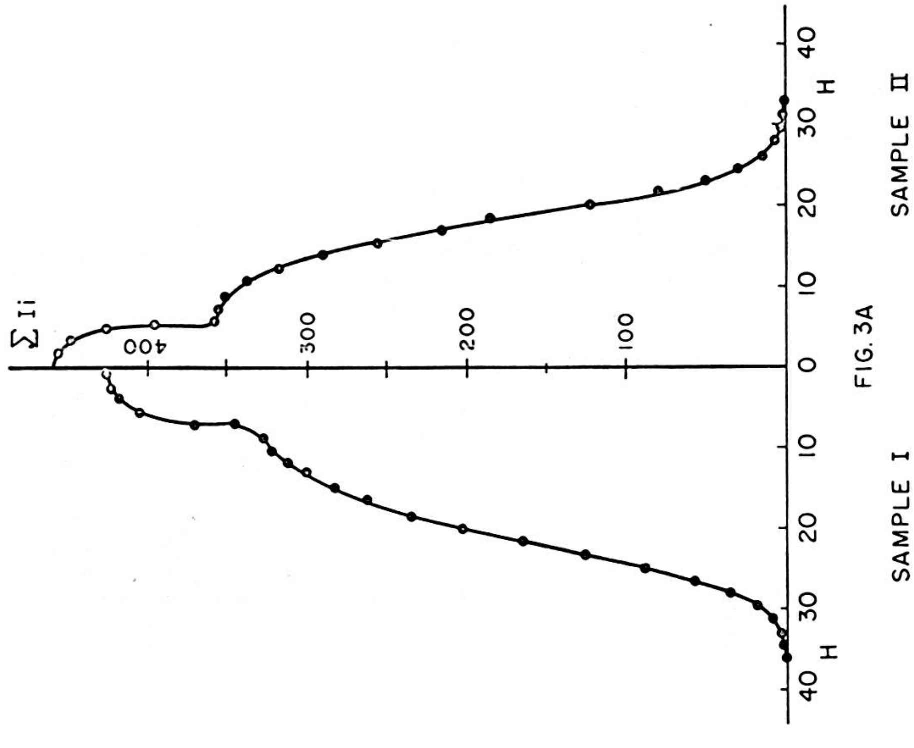

ΣI_i
400
300
200
100
0
10
20
30
40
H
SAMPLE I
SAMPLE II

FIG. 3A

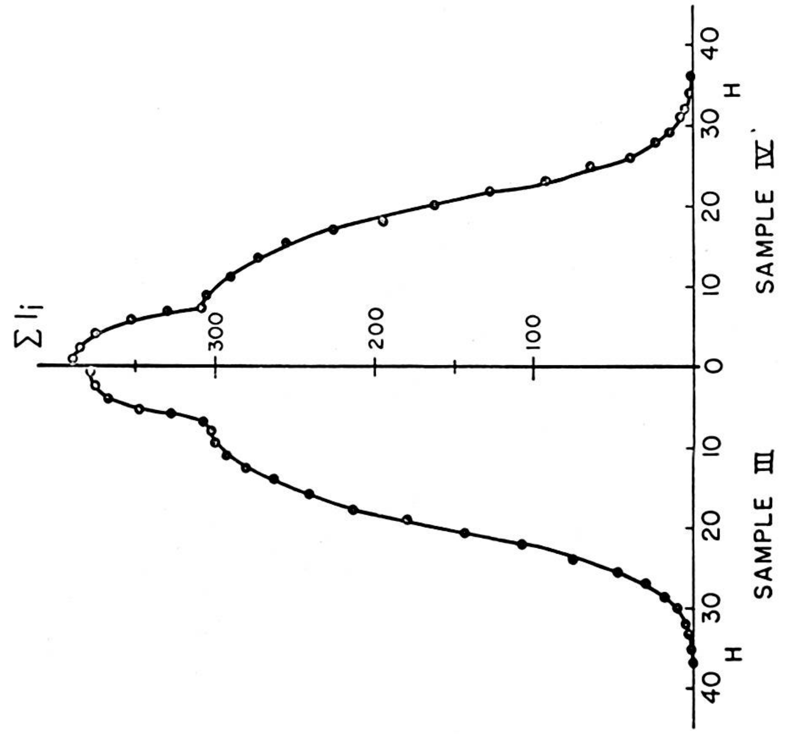

ΣI_i
300
200
100
0
10
20
30
40
H
SAMPLE III
SAMPLE IV

FIG. 3B

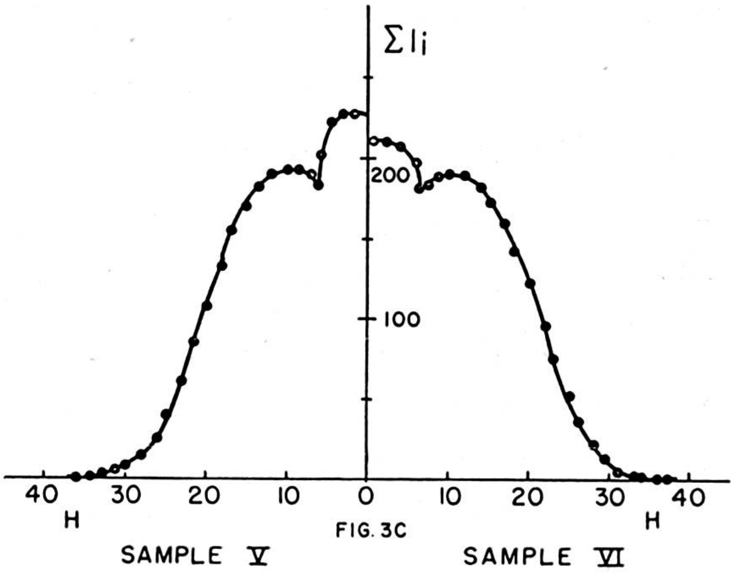


FIG. 3C

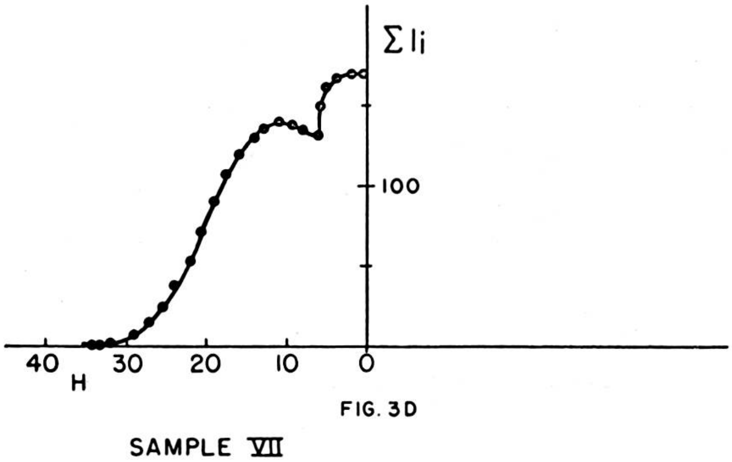


FIG. 3D

The number of protons per cc (p) in water sample (0.29% H_2) are:

$$p = \frac{2\times 0.29}{18} \times 6 \times 10^{23} \approx 1.9 \times 10^{22}.$$

From experimental data is known $S^*_{H_2O} = 60.0$ cycles. gauss^2 for water sample 0.29% H_2, and $S^*_t = 77.43$ cycles gauss^2 for $LiAlH_4$ sample 1 .

$$S^* K = P$$

k (the constant of proportionality) has the value:

$$k = \frac{1.9 \times 10^{22}}{60.0} \approx 3.2 \times 10^{20}$$

and then the relative value of number of protons in LiAlH$_4$ sample I are:

$$3.2 \times 10^{20} \times 77.43 = 2.45 \times 10^{22} ;$$

Using the value of 0.917 for the density of LiAlH$_4$ the ratio $\frac{2.45}{6.00} \times 100$ represents the percentage (40.5%) of protons from LiAlH$_4$ sample I, which interact with RF. The value of active protons (determined by means of saturation curve (*a*), and by means of integrated curve (*b*) decrease (except sample IV) with heating treatment and time of pumping (Table 3).

After the examination of experimental data, it is seen that:

1. For every sample, two peaks were found.
2. The shape of the proton resonance line may be considered (approximately) to be Gaussian.
3. The area for narrow and broad line, and total area (S^*, S_i^* and S_t^*) decrease (except sample IV) with the temperature treatment and time of pumping (in vacuo).
4. The spin lattice relaxation time T_1 and spin spin relaxation time T_2 may be considered constant for all the samples ($T_1 \approx 2.1 \times 10^{-9}$ sec. for narrow line, $T_1 \approx 2.9 \times 10^{-7}$ sec. for broad line, and $T_2 \approx 6.1 \times 10^{-4}$ sec. for narrow line, $T_2 \approx 6.0 \times 10^{-6}$ sec. for broad line).
5. The mobility from the saturation curve (M) and mobility from the integrated curve (M_i) may be considered constant also ($M \approx 1.5$ and $M_i \approx 5.5$).
7. The percentage of active protons from LiAlH$_4$ samples decrease (except sample IV) with temperatures increasing and the time of pumping.

II. The Exchange Reaction between Hydrogen and Deuterium on LiAlH$_4$ as Catalyst

The exchange between hydrogen (gas) and deuterium (gas) on LiAlH$_4$ (solid) at room temperature was measured in a static system. To date LiAlH$_4$ samples were used: sample 1 pumped for 6 hrs. at room temperature, sample 2 pumped for 6 hrs. at 100° C, sample 3 pumped for 0.6 hr. at 130° C, sample 4 pumped for 1 hr. at 130° C, sample 5 pumped for 4 hrs at 130° C, sample 6 pumped for 6 hrs. at 130° C and sample 7 pumped at 16 hrs. at 130° C. These samples were the same ones as were used for the NMR measurements.

TABLE 2.

Nuclear Magnetic Resonance Results.

Samples	S^*	S_1^*	T_1	T_2	Slope	S^*	S_1^*	T_1	T_2	Slope	S_l^*	S_{il}^*	M	M_i
	Narrow line					*Broad line*								
I	2.03	9.84	2.0×10^{-9}	6.1×10^{-4}	8.9×10^{-4}	75.4	158.52	2.7×10^{-7}	6.2×10^{-6}	1.2×10^{-3}	77.43	168.36	2.8 %	6.2 %
II	1.82	7.24	6.1×10^{-9}	2.3×10^{-4}	$6\ 9\times10^{-4}$	68.0	114.78	1.3×10^{-7}	7.2×10^{-6}	1.1×10^{-3}	69.82	122.02	2.6 %	6.3 %
III	1.18	7.00	2.1×10^{-9}	6.5×10^{-4}	9.4×10^{-4}	64.0	106.94	3.6×10^{-7}	6.5×10^{-6}	1.7×10^{-3}	65.20	113.94	1.8 %	6.5 %
IV	1.59	4.80	2.1×10^{-9}	6.1×10^{-4}	9.2×10^{-4}	73.3	118.80	2.6×10^{-7}	6.0×10^{-6}	1.2×10^{-3}	74.89	116.60	2.1 %	4.0 %
V	1.09	3.96	2.1×10^{-9}	6.1×10^{-4}	9.3×10^{-4}	41.4	68.48	2.2×10^{-7}	6.0×10^{-6}	0.94×10^{-3}	42.52	72.44	2.5 %	5.7 %
VI	0.58	2.16	2.5×10^{-9}	6.6×10^{-4}	1.2×10^{-3}	46.3	58.24	2.9×10^{-7}	5.7×10^{-6}	1.2×10^{-3}	46.88	60.40	1.2 %	3.7 %
VII	0.48	1.90	2.9×10^{-9}	6.6×10^{-4}	1.4×10^{-3}	37.4	44.0	2.9×10^{-7}	6.0×10^{-6}	1.2×10^{-3}	37.88	45.90	1.2 %	4.3 %

TABLE 3.

Samples	% *(no. of active prot.) from sat. curve*	% *(No. of active prot.) from integr. curve*	*Observation*
I	41.0 %	42.0 %	no exchange
II	37.1 %	31.0 %	no exchange
III	35.0 %	26.0 %	exchange
IV	40.1 %	30.2 %	exchange
V	22.6 %	18.0 %	exchange
VI	25.0 %	15.0 %	exchange
VII	20.6 %	11.4 %	exchange

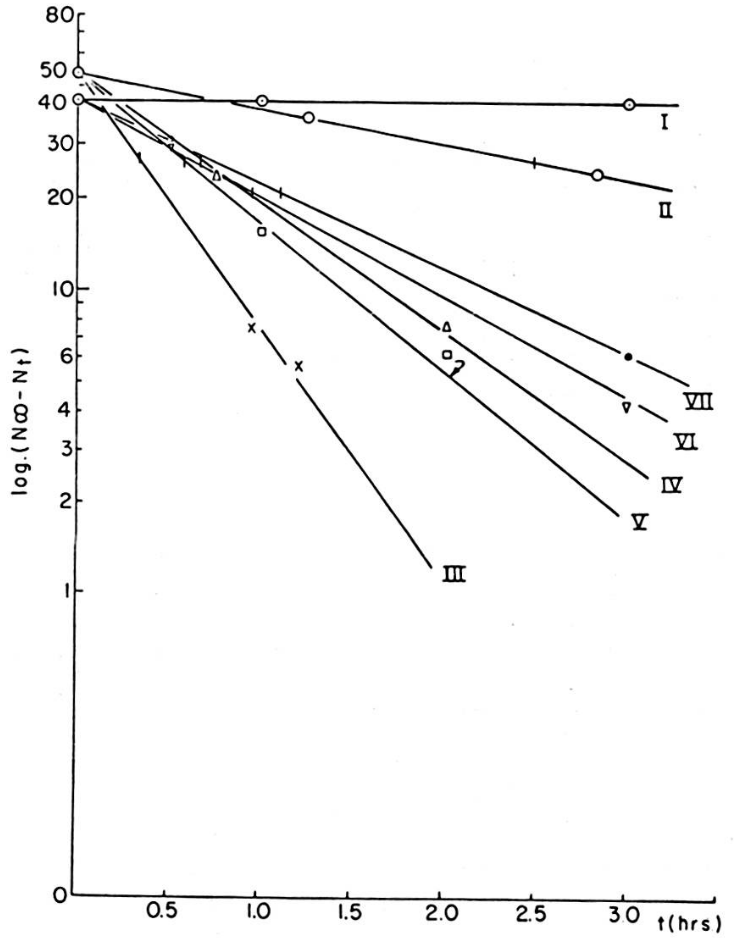


FIG. 4

The reaction vessel was then filled with a 1 : 1 volume deuterium-hydrogen mixture. The gases were purified by passage at room temperature over a commercial palladium-alumina (catalytic Deoxo, unit purifier from Engelhard Industries, Inc., Newark, New Jersey) and through a liquid air trap. At room temperature, after appropriate times gas samples were drawn off and the H_2, HD and D_2 analysis carried out on a Consolidated Engineering Corporation Mass Spectrometer No. 26-620 of the cycloid type. The respective sensitivities were 141.7 (H_2), 143.0 (HD) and 144.2 (D_2) mm. deflection per mm. Hg. For simplicity in calculation, they were assumed to have the same sensitivity.

The results obtained on the catalytic exchange of H_2-D_2 at room temperatures on the various $LiAlH_4$ samples are presented in Table 4. They are in agreement (Fig. 4) with the kinetic equation

$$N_t = N_\infty (1 - e^{-ct})$$

where N_t is the increase at time t in the concentration of HD over that originally present at time $t = 0$, N_∞ is the equilibrium cencentration of HD and c is the velocity constant in reciprocal hours. The hydrogen-deuterium reactions constant c (see $t_{\frac{1}{2}}$-half time) depends on the temperature and pumping treatment of the $LiAlH_4$ samples.

After the examination of experimental data, it was seen that:

1. For $LiAlH_4$ sample, never heated, pumped at room temperature, no exchange between hydrogen and deuterium ($t_{\frac{1}{2}} = \infty$).
2. For $LiAlH_4$ samples, heated at 130° C and pumped for various times, has been obtained a good exchange between hydrogen and deuterium ($t_{\frac{1}{2}} \neq \infty$).

TABLE 4.

Sample	Time in hours	% H_2	% D_2	% HD	$t_{\frac{1}{2}}$ (hrs.)	Observation
1.	0.0	49.6	41.7	8.7	—	no exchange
	1.0	50.0	41.5	8.7		
	3.0	50.8	40.5	8.7		
2.	0.0	49.1	49.7	1.2		
	1.25	41.8	42.3	15.9	2.4	exchange
	2.83	36.5	35.5	28.0		
3.	0.0	49.1	49.7	1.2		
	0.9	27.7	27.1	45.2	0.28	exchange
	1.2	28.4	24.5	47.1		
4.	0.0	49.1	49.7	1.2		
	0.75	35.6	35.1	29.3	0.68	exchange
	2.20	28.2	26.7	45.1		
5.	0.0	47.8	50.8	1.4		
	1.0	30.7	31.1	38.2	0.6	exchange
	2.0	26.6	27.0	46.4		
6.	0.0	49.1	41.7	9.1		
	0.5	44.2	34.3	1.4	0.95	exchange
	3.0	34.5	19.0	46.5		
7.	0.0	50.2	40.8	9.1		
	0.5	44.1	35.8	19.4	1.10	exchange
	3.0	32.2	23.2	44.5		

3. A minimum value of half time (maximum activity) has been obtained for $LiAlH_4$ sample, heated at 130° C for 0.6 hr. (in vacuo). (See Table 4.)

The exchange reaction data indicates a parallelism with the nuclear magnetic resonance data.

$LiAlH_4$ sample heated at 130° C for 0.6 hr. (in vacuo) which has a maximum activity ($t_{\frac{1}{2}} = 0.28$ hr.) has also a maximum value for narrow (1.59), broad (73.3) and total area (74.89).

III. THE EXCHANGE REACTION BETWEEN HYDROGEN AND DEUTERIUM ON LITHIUM ALUMINUM HYDRIDE AS CATALYST, AS FUNCTION OF THERMAL DECOMPOSITION OF LITHIUM ALUMINUM HYDRIDE

In order to check reproducibility, two samples of $LiAlH_4$ of known weight ($S_1 = 3.708$ gr. and 3.703 gr.) were used for detailed study of catalytic activity for $H_2 — D_2$, exchange reaction as a function of thermal decomposition.

A standard vacuum apparatus was used for preparation of the samples.

Twelve measurements were carried out on each of the duplicate samples. Prior to each measurement, each sample was thermally decomposed in vacuo set 130° C until 235 hydrogen was evolved.

After this pretreatment the hydrogen-deuterium exchange reaction was studied. Gas analyses were made after one and three hour periods at room temperature, with a C. E. C. Mass Spectrometer No. 26-620 of cycloid type. The experimental results which were obtained are represented in Table 5, and Figures 5 and 7 (curve *a*).

It is observed from the experimental data that:

1. For the unheated $LiAlH_4$ sample pumped at room temperature to remove the air, no exchange reaction occurs between hydrogen and deuterium ($t_{\frac{1}{2}} = \infty$).
2. For the same sample heated in vacuo at 130° C until 235 cc hydrogen was evolved, a exchange reaction was obtained ($t_{\frac{1}{2}} = 4.2$ hrs.).
3. Repeating the above pretreatment five times with a total hydrogen evolution of 5 × 235 cc, the maximum exchange rate obtained ($t_{\frac{1}{2}} = 0.45$ hr.).

TABLE 5.

Unirradiated samples.

Thermal pretreatment (cc. gas evolved)	Reaction time (hrs.)	% H_2	% D_2	% HD	$t_{\frac{1}{2}}$ (hrs.)	Observation
—	0.00	49.60	49.40	1.00	—	no exchange
	1.00	50.00	49.30	1.00		
	3.00	50.70	48.50	1.00		
1 × 235	0.00	49.60	49.40	1.00	4.30	exchange
	1.25	46.60	41.30	12.10		
	3.00	47.90	30.10	22.00		
2 × 235	0.00	49.60	49.40	1.00	1.90	exchange
	1.50	43.20	34.60	22.20		
	3.00	43.30	16.70	35.80		
3 × 235	0.00	47.10	52.00	0.80	0.90	exchange
	1.25	34.30	32.40	33.30		
	2.25	39.60	18.10	42.20		
4 × 235	0.00	47.10	52.00	0.80	0.70	exchange
	1.00	33.10	33.90	33.00		
	2.00	25.60	32.30	42.10		
5 × 235	0.00	43.90	55.50	0.60	0.45	exchange
	0.40	34.50	43.30	21.90		
	1.25	26.70	29.80	43.50		
6 × 235	0.00	43.90	55.50	0.60	0.82	exchange
	0.75	33.20	42.40	24.40		
	2.10	26.80	30.60	42.60		
7 × 235	0.00	43.90	55.50	0.60	1.00	exchange
	0.50	37.50	47.80	14.70		
	2.00	27.70	34.40	37.80		
8 × 235	0.00	44.90	54.20	0.90	0.80	exchange
	0.50	37.70	43.60	18.70		
	3.00	30.10	27.90	42.00		
9 × 235	0.00	44.90	54.20	0.90	1.06	exchange
	0.50	45.70	38.90	14.40		
	2.00	32.20	33.60	34.20		
10 × 235	0.00	48.80	50.62	0.58	0.90	exchange
	0.58	41.84	40.58	17.58		
	2.25	30.73	26.40	42.87		
11 × 235	0.00	48.80	50.62	0.58	1.10	exchange
	0.92	39.60	38.10	22.30		
	2.25	33.40	29.30	37.30		
12 × 235	0.00	48.80	50.62	0.58	1.15	exchange
	0.51	42.80	43.10	14.10		
	1.65	34.60	32.33	33.01		

4. Further continuation of this thermal pretreatment results in a gradual decrease in exchange rate to a near constant value of catalytic activity ($t_{\frac{1}{2}} \approx 0.95$ hr.).

These results obtained for hydrogen-deuterium exchange on the above consecutive thermal pretreatment are in agreement with the previous results which were obtained for different fresh samples with equal total thermal pretreatment.

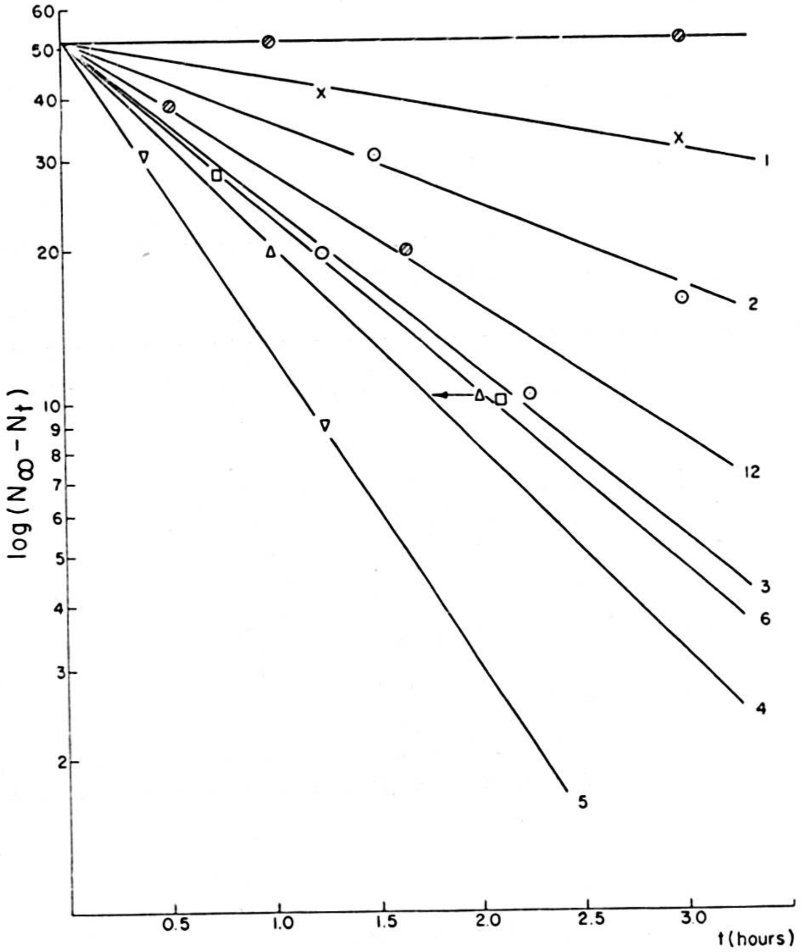


FIG. 5

At the same time, these results are in agreement with the results obtained by S. Weller and L. Wright (12, 13, 14) for the hydrogen-deuterium exchange on calcium and barium hydrides. These results show that the highest catalytic activity of $LiAlH_4$ for H_2-D_2 exchange occurs when the decomposition of $LiAlH_4$ to $LiAlH_2$ and H_2 occurs on pumping at elevated temperature (130° C) according to the equation:

$$LiAlH_4 \longrightarrow LiAlH_2 + H_2 .$$

Effect of ultra-violet light.

Since a color change of the $LiAlH_4$ particles was observed after long exposure to daylight, some attempts were made to determine the possible influence of ultra-violet irradiation on the catalytic activity of $LiAlH_4$ for this exchange reaction.

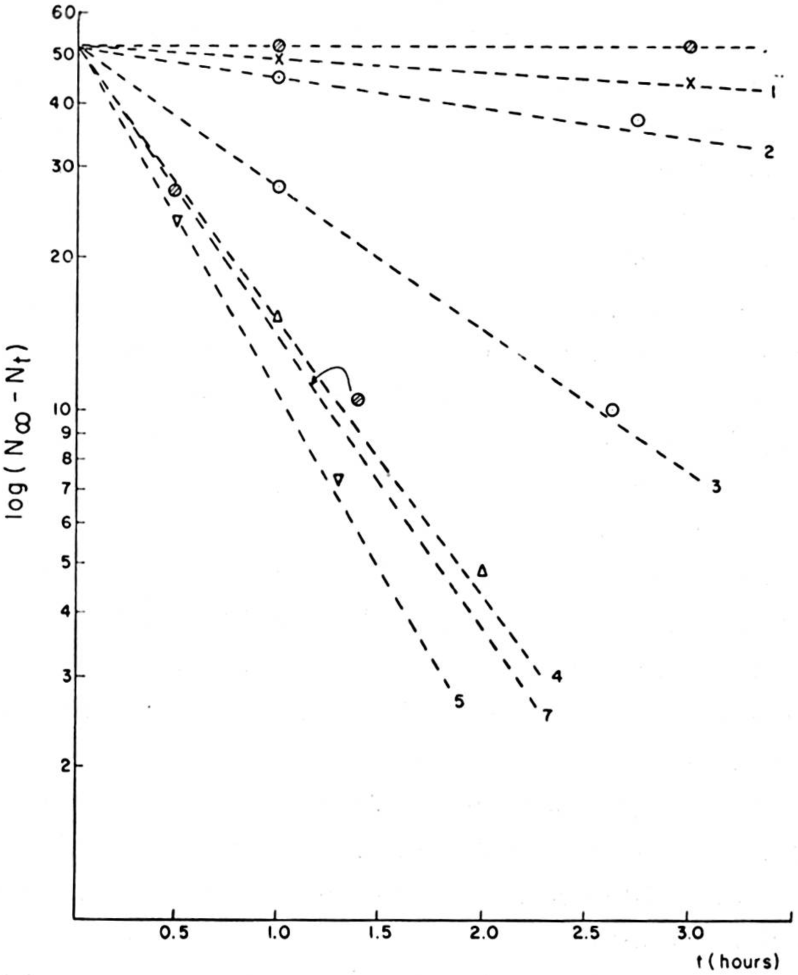


FIG. 6

A weighted amount of $LiAlH_4$ (S_2 = 3.052 gr. and 3.197 gr.) was introduced in quartz test tubes of the same dimensions as in the previous experiments. Two $LiAlH_4$ samples were studied in parallel under the same conditions as the above, unirradiated pair of samples. After the thermal pretreatment in vacuo, as described above, each sample was irradiated 0.5 hr. with a ultra-violet source with the following characteristics: General Electric, type A-H-6 lamp, 1,000 watts of 840 volts.

During the irradiation process the grams of lithium aluminum hydride became browned on the surface.

Following the irradiation the hydrogen-deuterium exchange rate was measured. Seven measurements were carried out for each sample and the results showed a similar reproducibility as the previous unirradiated samples.

The experimental results obtained under these conditions are summarized in Figures 6 and 7 (curve *b*) and Table No. 6.

From these experimental results it is observed that:

For $LiAlH_4$ sample without thermal pretreatment (pumped only at room temperature to remove the air) and after the irradiation process, at room temperature, no exchange reaction occurs between hydrogen and deuterium ($t_{\frac{1}{2}} = \infty$).

For the same $LiAlH_4$ sample heated at 130° C until 2 × 234.69 cc. hydrogen was evolved and then irradiated with ultra-violet light, a exchange reaction occurs between hydrogen and deuterium, but lower than those obtained for exchange for the unirradiated samples.

Repeating the above thermal and irradiation pretreatment, the exchange reaction between hydrogen and deuterium is more extensive than in the case of unirradiated sample.

These experimental results, which show that under the ultra-violet irradiation of $LiAlH_4$ samples, it may be possible to influence the isotopic exchange between hydrogen and deuterium, our presumption is strengthened that the active centers (created by means of thermal pretreatment) for this exchange reaction may be near the surface of the $LiAlH_4$ grains.

Magnetic Resonance measurements made on the above samples at certain stages of pretreatment were in agreement with the earlier Proton Magnetic Resonance results obtained on earlier individual samples with the same total thermal pretreatment.

The nuclear resonance of Li^7 and Al^{27} were found in both the unpumped and pumped samples. There were indications that the signal was greater for the Al resonance in the pumped sample.

It was not possible to observe a *Electron Spin Resonance* signal in $LiAlH_4$ samples (at room temperature) with thermal pretreatment history.

Only the unheated sample, pumped at room temperature was a very weak signal observed. This observation seems to be due to the increase in metallic character of the sample during the thermal pretreatment.

TABLE 6.

Irradiated samples.

Thermal pretreatment (cc. gas evolved)	Reaction time (hrs.)	% H_2	% D_2	% HD	$t_{\frac{1}{2}}$ (hrs.)	Observation
—	0.0	52.10	47.22	0.68	—	no exchange
	1.00	52.97	46.03	1.00		
	3.00	57.64	41.67	0.69		
1 × 235	0.00	52.10	47.22	0.68	25.00	exchange
	1.00	51.51	45.15	3.34		
	3.00	53.46	38.59	7.95		
2 × 235	0.00	52.10	47.22	0.68	4.40	exchange
	1.00	52.21	41.66	7.13		
	3.00	53.40	31.50	15.10		
3 × 235	0.00	52.10	47.22	0.68	1.08	exchange
	1.00	42.75	32.15	25.10		
	2.55	32.75	24.65	42.60		
4 × 235	0.00	51.44	47.25	1.31	0.58	exchange
	1.00	31.21	31.80	36.29		
	2.00	27.71	25.30	46.99		
5 × 235	0.00	51.44	47.25	1.31	0.43	exchange
	0.50	38.56	33.15	28.29		
	1.25	29.91	25.10	44.99		
6 × 235	0.00	51.44	47.25	1.31	0.51	exchange
	0.50	40.09	35.12	24.79		
	1.25	32.00	27.40	40.59		

IV. THE EXCHANGE REACTION BETWEEN DEUTERIUM GAS AND LITHIUM ALUMINUM HYDRIDE

During the study of the hydrogen and deuterium exchange reaction on $LiAlH_4$ at room temperature, an isotopic exchange has also been observed between deuterium gas and hydrogen from $LiAlH_4$.

S. Weller and L. Wright [12, 13, 14] also obtained a substantial isotopic exchange between deuterium gas and hydrogen from CaH_2 after a previous thermal treatment in vacuo of CaH_2.

These facts have led us to study the exchange reaction between deuterium gas and $LiAlH_4$. Two samples of $LiAlH_4$ has been investigated (under various conditions of temperature) in parallel and the experimental results obtained within the limits of experimental error are the same.

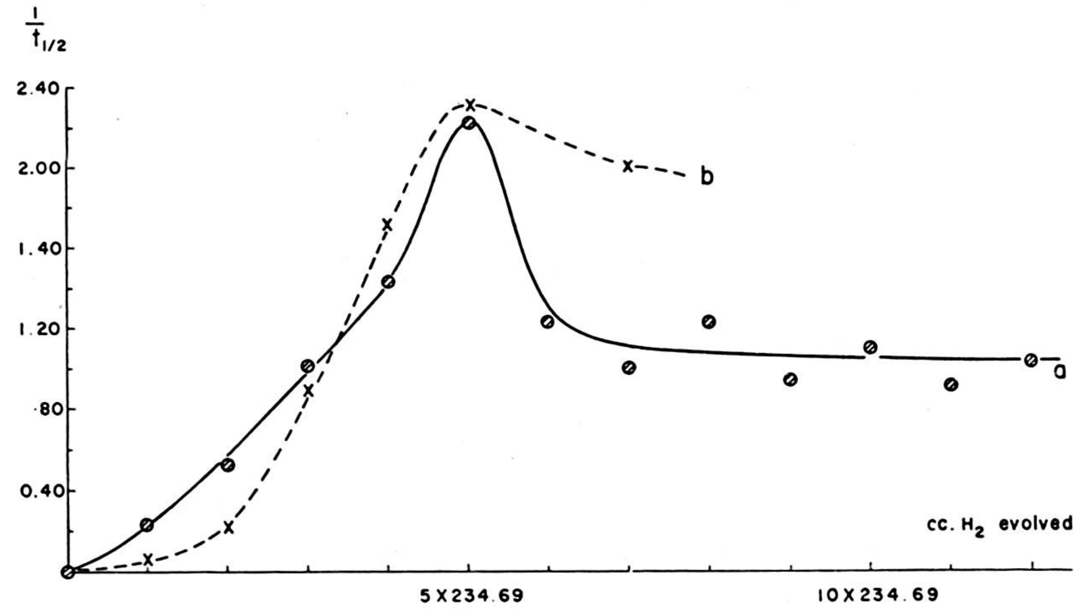


FIG. 7

The lithium aluminum hydride samples (S_3 = 3.472 gr. and 3.603 gr.) prepared by means of a standard vacuum installation, have been subjected before each exchange reaction to the same thermal treatment as in the case of hydrogen-deuterium exchange. Analysis of the gaseous reactants were carried out by means of a Consolidated Engineering Corporation Mass Spectrometer No. 26-620 of the cycloid type, after 1 hr. and 3 hr. reaction periods.

At 0° C (after 1 hr. and 3 hr. reaction periods) the exchange reaction between deuterium gas and $LiAlH_4$ are in general very slow (Fig. 8, curve a_1 and curve b_1) while at room temperature (Fig. 8, curve a_2 and curve b_2) the exchange reaction is more rapid.

The exchange reaction at 0° C has been studied by means of three series of measurements, while at room temperature seven series were conducted.

These experimental results have led us to investigate the exchange reaction at higher temperatures. After several preliminary attempts, it was found that the maximum exchange between deuterium gas and $LiAlH_4$ occurs at 75° C. For the investigation of this exchange reaction at 75° C eight series of measurements were carried out.

The experimental results obtained for the exchange reaction between deuterium gas and $LiAlH_4$ are summarized in Figure 8 and in Table 7.

c — represents the difference between the concentration of deuterium gas at time $t = 0$ and $t = 1$ or 3 hrs.

$D_0 - D$ — represents the difference between the concentration of deuterium gas at time $t = 0$ and $t = 1$ hr.

$H - H_0$ — represents the difference between the concentration of hydrogen gas at time $t = 1$ hr. and $t = 0$.

$D_0 - D'$ — represents the difference between the concentration of deuterium gas at time $t = 0$ and $t = 3$ hrs.

$H' - H_0$ — represents the difference between the concentration of hydrogen gas at time $t = 3$ hrs. and $t = 0$.

In general after all the exchange reaction measurements have been obtained $D_0 - D \approx H - H_0$ and $D_0 - D' \approx H' - H_0$, i.e. the amount of deuterium gas which appears as lithium aluminum deuteride is equal to the amount of hydrogen liberated from the hydride during the course of the exchange reaction.

After the analysis of these experimental results, it is observed that:

1. For $LiAlH_4$ sample without thermal pretreatment (pumped only at room temperature to remove the air) no exchange reaction between deuterium gas and $LiAlH_4$ occurs at 0° C ($c = 0$). For the same $LiAlH_4$ sample with thermal pretreatment, a small exchange reaction was obtained at 0° C which after attaining a maximum (after liberation of 235 cc. hydrogen) decreased to practically constant value ($c > 0$).

2. For $LiAlH_4$ sample without thermal pretreatment (pumped only at room temperature to remove the air) practically no exchange occurs again between deuterium gas and $LiAlH_4$ at room temperature. For the same $LiAlH_4$ sample heated at 130° C until 235 cc. hydrogen was evolved, a good exchange reaction occurs at room temperature. The exchange reaction with the same thermal pretreatment occurs at room temperature about 5.5 times more rapidly than at 0° C. With repetition of the above thermal

pretreatment, the isotopic exchange reaction at room temperature decreases gradually to a practically constant value ($c > 0$).

3. For $LiAlH_4$ sample without thermal pretreatment (pumped only at room temperature to remove the air), a small exchange reaction between deuterium gas and $LiAlH_4$ was obtained at 75° C ($c > 0$). For the same $LiAlH_4$ sample heated at 130° C until 235 cc. hydrogen was evolved, a very good exchange reaction occurs at 75° C ($c \gg 0$). The exchange reaction (at 75° C) after 3 hrs. reaction period is about 16 times more rapid than at 0° C and about 4.5 times more rapid than at room temperature.

TABLE 7.

Thermal pretreatment (cc. gas evolved)	Exch. cond.	Do-D	Do-D′	H-Ho	H′-Ho	Observation
—	0° C	0.00	0.00	0.00	0.00	Unirrad. samples
1 × 235	0° C	1.50	4.68	1.54	4.69	,,
2 × 235	0° C	0.90	3.00	0.93	3.16	,,
3 × 235	0° C	1.05	3.12	1.00	3.20	,,
—	room temp.	0.20	0.25	0.15	0.25	,,
1 × 235	room temp.	9.14	20.47	9.13	20.47	,,
2 × 235	room temp.	3.53	14.58	3.64	14.59	,,
3 × 235	room temp.	3.63	7.38	3.65	7.39	,,
4 × 235	room temp.	3.58	5.89	3.59	5.88	,,
—	75° C	0.90	2.30	1.15	2.60	,,
1 × 235	75° C	52.12	79.18	52.13	79.19	,,
2 × 235	75° C	55.38	78.61	55.30	78.62	,,
3 × 235	75° C	55.61	79.38	55.62	79.39	,,
4 × 235	75° C	49.66	75.66	49.66	75.61	,,
5 × 235	75° C	47.93	80.17	47.94	80.18	,,
6 × 235	75° C	41.43	80.65	41.44	80.66	,,
7 × 235	75° C	32.16	65.05	32.17	65.07	,,
—	75° C	1.32	7.28	1.32	7.29	Irrad. samples
1 × 235	75° C	47.20	82.72	47.21	82.90	,,
2 × 235	75° C	54.15	82.51	54.16	82.52	,,
3 × 235	75° C	43.36	74.63	43.37	74.64	,,
4 × 235	75° C	35.53	74.41	35.54	74.43	,,
5 × 235	75° C	29.60	70.20	29.65	70.20	,,

For the same $LiAlH_4$ sample, with repetition of the above thermal pretreatment the exchange reaction between deuterium gas and $LiAlH_4$ at

75° C, remains constant until 3 × 235 cc. hydrogen was evolved, for $t = 1$ hr. period of reaction and until 6 × 235 cc. hydrogen was evolved, for $t = 3$ hrs. period of reaction and then decreases ($c \gg 0$).

These experimental results show that only a fraction of the hydrogen in the $LiAlH_4$ participated in the exchange and this fraction increased with increasing reaction temperature and time. These results are consistent with the interpretation that hydrogen near the surface exchanges rapidly with gaseous deuterium (at 75° C), but that participation of all the hydride hydrogen in the exchange is limited by the time required for diffusion of hydride ions from the interior to the surface.

Effect of ultraviolet light.

The same indications (a color change of the $LiAlH_4$ particles was observed after long exposure to daylight) as in the case of hydrogen-deuterium exchange reaction have led us to the idea of study the influence of ultraviolet light of the hydride sample on the isotopic exchange between deuterium gas and $LiAlH_4$.

A known amount of $LiAlH_4$ ($S_4 = 2.955$ gr. and 2.930 gr.) was introduced in quartz test tubes of the same dimensions as in the previous experiments. Two $LiAlH_4$ samples were studied in parallel under the same conditions as the above unirradiated pair of samples used for the investigation of the exchange reaction between deuterium gas and $LiAlH_4$ at 75° C.

After each thermal pretreatment in vacuo, before the exchange reaction, each sample was irradiated 0.5 hr. with an ultra-violet source with the following characteristics: General Electric, type A-H-6 lamp, 1000 watts of 840 volts. During the irradiation process the grains of $LiAlH_4$ became browned on the surface.

Under these conditions for the investigations of the exchange reaction between deuterium gas and $LiAlH_4$, seven series of measurements were carried out, for each sample.

The experimental results obtained are summarized in Table No. 7 and Figure 8 (curve a'_s — reaction time $t = 1$ hr. and curve b'_3 — reaction time $t = 3$ hrs.).

After the analysis of these results, it is observed that:

1. For $LiAlH_4$ sample without thermal pretreatment (pumped only at room temperature to remove the air) and after the irradiation process at 75° C., a small exchange reaction occurs between deuterium gas and $LiAlH_4$

($c > 0$). For the same $LiAlH_4$ the sample heated at 130° C. until 234.69 cc. hydrogen was evolved and their irradiated with ultra-violet light for 0.5 hr., a very good exchange occurs between deuterium gas and $LiAlH_4$ at 75° C. The exchange reaction after a 1 hr. reaction period shows the same intensity as in the case of the unirradiated sample, but the exchange after a 3 hr. period of reaction is more extensive than in the case of the unirradiated sample ($c \gg 0$).

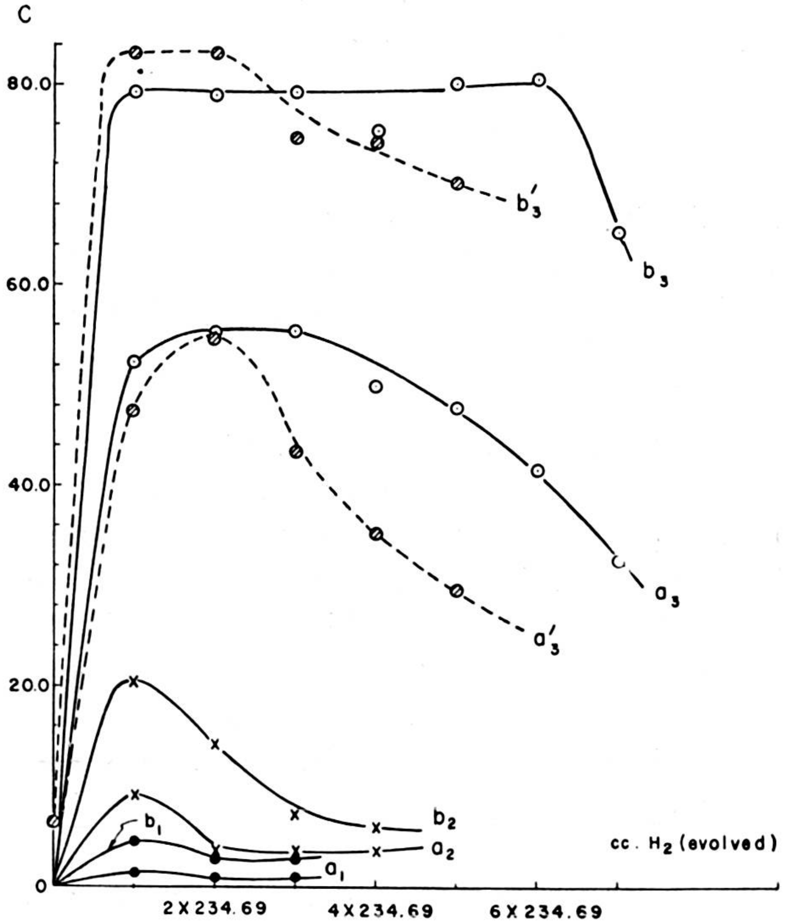


FIG. 8

For the same $LiAlH_4$ sample, with repetition of the above thermal and irradiation pretreatment, the exchange reaction between deuterium gas and $LiAlH_4$ at 75° C. decreases to values lower than those obtained for exchange for the unirradiated samples.

2. These experimental results show that for $LiAlH_4$ samples under irradiation with ultra-violet light, it may be possible to influence the

exchange between deuterium gas and $LiAlH_4$. While, after ultra-violet irradiation, the active centers for deuterium gas and $LiAlH_4$ exchange are increased during the beginning stages of thermal pretreatment (2 × 235 cc.) hydrogen was evolved, as the thermal pretreatment is continued, the active centers for deuterium gas and $LiAlH_4$ exchange are decreased.

These experimental results, which show that under the ultra-violet irradiation of $LiAlH_4$ samples it may be possible to influence the exchange reaction between deuterium gas and $LiAlH_4$, our presumtion is strenghtened that the active centers (created by means of thermal pretreatment) for this exchange reaction may be near the surface of the $LiAlH_4$ grains.

Magnetic Resonance Measurements.

As in the case of the hydrogen-deuterium exchange reaction, here also some parts of the protons Nuclear Magnetic Resonance measurements for $LiAlH_4$ samples have been repeated, and for the same conditions of the total pretreatment, the results are the same. Also, some qualitative diagnostic Nuclear Magnetic Resonance measurements were carried out to determine the concentration of Li^7 and Al^{27} in some $LiAlH_4$ samples.

The nuclear resonance of Li^7 and Al^{27} where found in both the unpumped and pumped samples. There where indications that the signal was greater for the Al resonance in the pumped sample.

By means of the same method, further trials were made in order to determine the concentration of deuterium in the hydride, but due either to the difficulty of determining the presence of deuterium in solids or because it is present in too low concentration, it was not possible to detect the presence of deuterium in the hydride.

Also, it was not possible to observe a *Electron Spin Resonance* signal in $LiAlH_4$ sample (at room temperature) with thermal pretreatment history. Only the unheated sample, pumped at room temperature, was a very weak signal observed. This observation seems to be due to the increase in metallic character of the sample during the thermal pretreatment.

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