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PRODUCTION OF METHANOL-C^{14} BY THE LITHIUM ALUMINUM HYDRIDE PROCESS

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ABSTRACT

A procedure has been developed for the routine production of high activity methanol-C^{14} in 90-95% yields and of high purity by the reduction of carbon dioxide-C^{14} with lithium aluminum hydride. The process consists of (1) introducing carbon dioxide into a solution of lithium aluminum hydride in diethyl carbitol at atmospheric pressure and room temperature, (2) treating the resulting product with n-butyl carbitol and (3) removing the liberated methanol by distillation.

A number of modifications have been made in the original procedure in order to prevent the contamination of the product by diethyl ether and other volatile impurities.

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PRODUCTION OF METHANOL-C^{14} BY THE LITHIUM ALUMINUM HYDRIDE PROCESS

R. F. Nystrom, W. J. Skraba and R. G. Mansfield

I. Introduction

The conversion of isotopically labeled carbon dioxide to methanol by means of lithium aluminum hydride has been described in a preliminary publication from this Laboratory(1). Further experience with this process has shown the need for some modifications of the original process if methanol of high purity is to be obtained. This has resulted in a procedure considerably more elaborate than the original but still comparing favorably with high-pressure catalytic hydrogenation(2) or with the indirect process used by Melville, Rachele and Keller(3).

(1) Nystrom, Yanko and Brown, J. Am. Chem. Soc., 70, 441 (1948).

(2) Tolbert, J. Am. Chem. Soc., 69, 1529 (1947).

(3) Melville, Rachele and Keller, J. Biol. Chem., 169, 419 (1947).

Basically, the process consists of introducing carbon dioxide into a solution of lithium aluminum hydride in diethylcarbitol, treating the resulting product with n-butylcarbitol and removing the liberated methanol by distillation.

First Stage:

$$4CO_2 + 3LiAlH_4 \longrightarrow LiAl(OCH_3)_4 + 2LiAlO_2$$

Second Stage (R = n-butylcarityl)

$$LiAlH_4 + ROH \longrightarrow LiAl(OR)_4 + 4H_2$$

$$LiAl(OCH_3)_4 + 4ROH \longrightarrow LiAl(OR)_4 + 4CH_3OH$$

In theory, methanol is the only volatile material present in the system and should therefore be readily separable in pure form by a simple distillation. In practice, however, difficulties arise due to the presence of traces of diethyl ether which are present in commercial lithium aluminum hydride and also because, notwithstanding the large difference in boiling points of diethylcarbitol and methanol, a clean separation is not too easily achieved. The latter difficulty is aggravated by the fact that the mixture must be heated to relatively high temperatures to effect complete recovery of the methanol. Because of these factors, the product initially obtained from the reaction mixture is not pure methanol but a mixture containing substantial amounts of diethylcarbitol, together with traces of diethyl ether. A more elaborate process has been designed to remove these impurities.

II. Discussion of Impurities and Their Removal

A. Possible Sources of Contaminants

It is conceivable, in view of the manufacturing process for lithium aluminum hydride, that the hydride may contain significant amounts of lithium aluminum ethoxide, which would give rise to contamination of the synthetic methanol by ethanol. This ethanol could be derived from impurities in the commercial ether used in the manufacture of the hydride or from cleavage of ether by aluminum chloride which is present at high concentration during the formation of lithium aluminum hydride. Moreover, if aluminum chloride is present in the reducing agent, cleavage of diethylcarbitol, forming eventually ethanol as one product, could perhaps occur during, and subsequent to the carbonation reaction. However, in control experiments, carried out under conditions simulating the methanol synthesis, the presence of ethanol could

not be detected although traces of inactive methanol were found (vide infra). Moreover, the radiochemical assay of the methanol produced in tracer runs, agreeing with that of the carbon dioxide used, to within experimental error, leaves room for the presence of inactive ethanol to the extent of not more than 2-3%.

The report[4] that the presence of ethanol in synthetic methanol-C^{14}

(4) M. Calvin, personal communication.

was shown by the recovery of acetic acid from the oxidized product, cannot be properly evaluated. The ethers, diethyl ether and diethylcarbitol, which may have been present, could also give acetic acid on oxidation. Further work will be required to determine whether inactive ethanol is present in trace quantities or to the extent of our upper limit, 2-3%.

B. Analysis of Lithium Aluminum Hydride

The material used throughout the work dealing with inactive and tracer-level syntheses of methanol, was the commercial material supplied by Metal Hydrides, Inc.

Analysis for active hydrogen, based on hydrogen gas evolved upon hydrolysis, showed 95.5% $LiAlH_4$. The chlorine content, determined by the Volhard method on the residue after hydrolysis, was 1.2%. Oxidizable volatile organic matter determined by hydrolysis of a solution of the hydride in diphenyl ether, oxidation of the distillate therefrom by excess potassium permanganate, and back-titration with oxalic acid, was present to the extent of 0.8%.

C. Removal of Diethyl Ether

Solid lithium aluminum hydride retains traces of diethyl ether so tenaciously that complete removal by vacuum drying is not feasible. Likewise

it is not possible to remove the last traces of diethyl ether from a solution of the hydride in diethylcarbitol by sweeping with an inert gas. This behavior, together with the high solubility of the hydride in diethyl ether indicates strong coordination and suggests that the ether would be more effectively removed after the reaction with carbon dioxide and after the excess hydride had been destroyed by the addition of n-butylcarbitol. Accordingly, it is the usual practice to pass helium through the mixture, maintained at 40°C, for a period of about 45 minutes at this point, discarding the small quantity of distillate, which consists largely of diethyl ether and contains virtually no methanol. In later experiments using high-purity lithium aluminum hydride the quantity of distillate obtained in this step was so small as to be negligible. Separation of the diethyl ether at this point is made possible by the fact that the alcohol interchange reaction, in which methanol is liberated, does not occur until high temperatures have been reached.

D. Separation of Methanol and Diethylcarbitol

The product which is obtained as distillate from the reaction mixture, even after purification by successive bulb-to-bulb vacuum distillations, may contain as much as 1% diethylcarbitol, if the distillation is conducted so as to secure substantially quantitative recovery of the methanol. This estimate is based on the observed refractive indices, namely n_D^{20} 1.330 - 1.332 (pure methanol, n_D^{20} 1.3279; diethylcarbitol, n_D^{20} 1.6860), assuming the impurity to be diethylcarbitol.

Experiments were conducted on known mixtures of methanol and diethylcarbitol in order to determine appropriate conditions for achieving a better degree of separation without at the same time making too large a sacrifice in

yield. A mixture, having n_D^{20} 1.3517, on a simple bulb-to-bulb distillation under high vacuum, the receiver being cooled in liquid nitrogen, and the still being allowed to warm up to room temperature, furnished a distillate having n_D^{20} 1.3352. Inserting between still and receiver a trap maintained at 0°C, resulted in a product having n_D^{20} 1.3306. Lowering of the temperature of the trap to -25°C resulted in further improvement distillate n_D^{20} 1.3292. Pure methanol (n_D^{20} 1.3280) was recovered in yields of 95-97% from the mixture by two distillations at -30°C.

These experiments show clearly the necessity for purification of the product under rigorously prescribed conditions.

E. Purification of Solvents

Diethylcarbitol from two commercial sources, Carbide and Carbon Chemicals Corporation and City Chemical Company, has been used. They were purified before use by treatment with sodium wire for a period of about five days at room temperature, then by distillation of the filtered material. The distillations were carried out with a 25 mm x 48" Podbielniak Heligrid column (cat. no. HC-701-A) operating at 7 mm. pressure. A fore-fraction, amounting to approximately 50 ml. out of a charge of 750 ml., was discarded and the still-head temperature, thereafter remained constant at 65°C (pot temperature, 100°C) during the collection of approximately 600 ml. of useful product at the rate of 25 ml. per hour.

In earlier work, this solvent was purified by treatment of the commercial product with lithium aluminum hydride, followed by vacuum distillation. This procedure was abandoned in favor of that described above because of the relatively large quantities of hydride required for purification.

The commercial products (from both sources) showed large variations in purity from one lot to another, as evidenced by the amounts of lithium aluminum hydride needed for purification. The product obtained from City Chemical Company was of poorer quality; it formed a heavy brown sludge on treatment with sodium.

Commercial n-butylcarbitol (Carbide and Carbon Chemicals Corporation) was purified by fractional distillation through the Podbielniak column. A forerun of over 10% was discarded, the useful fraction being taken, at 9 mm. pressure, at a still-head temperature of 110°C and a pot temperature of 148°C.

F. Generation and Assay of Radioactive Carbon Dioxide

The tracer-level syntheses of methanol, which served as model experiments for later high-level production runs, were carried out with carbon dioxide generated by the addition of perchloric acid (30%) to barium carbonate. The active barium carbonate had been assayed by generating carbon dioxide from a weighed sample, and determining the activity of the carbon dioxide in an ionization chamber using the dynamic condenser electrometer. Nitrogen gas was used to fill the chambers to atmospheric pressure. A similar procedure was used in the assay of the carbon dioxide formed by the oxidation of methanol, so that the radiochemical results from this series of tracer-level experiments are on a self-consistent basis.

In the high-level methanol syntheses conducted subsequently, the active barium carbonate was not analyzed either chemically or radiochemically by us, nor have we, as yet, sacrificed any of the product methanol for such analyses. Earlier work on the production of methanol by catalytic hydrogenation had shown satisfactory agreement between the specific activity of the methanol,

as determined by ionization chamber measurements, and the assay furnished with the barium carbonate which was based on solid counting. However, the uncertainty of the latter was of the order of 10%. The chemical yield of the high-activity methanol produced by the lithium aluminum hydride process is likewise subject to uncertainty since it is based on the weight of barium carbonate taken, and involves the assumption that the barium carbonate was pure. At the time of these experiments steps had been taken to improve the quality of the barium carbonate; nevertheless the uncertainty as to the quantity of carbon dioxide introduced into the reactor is of the order of 10%.

G. Assay of Radioactive Methanol (Tracer levels)

The assay of the methanol produced in experiments conducted at tracer concentrations of C^{14} was carried out by wet oxidation to carbon dioxide, and assay of the latter in an ionization chamber. The experimental technique described by Neville[5] for the radioactive assay of organic

(5) Neville, J. Am. Chem. Soc., 70, 3501 (1948).

materials by van Slyke oxidation was modified to permit (a) introduction of the sample by vacuum distillation, the reaction vessel being cooled in liquid nitrogen during this operation, and (b) collection and volumetric determination of the amount of carbon dioxide produced. To accomplish the latter, a stream of helium was used to carry the carbon dioxide into a trap, cooled in liquid nitrogen, which could later be isolated, evacuated and then allowed to warm to room temperature while forming part of a system of calibrated volume. A later modification consisted of passing the effluent gas from the reactor through a trap containing 20-mesh zinc metal for the purpose of re-

moving acidic materials carried over as vapor or spray from the oxidizing mixture. In the analysis of 50 mg. samples of methanol, the quantity of carbon dioxide as measured approximated theoretical but fluctuated rather widely above and below theoretical. In view of the relatively large blank corrections (10%), the radioactive assays were based upon the weight of methanol taken, rather than the quantity of carbon dioxide measured. The results of duplicate assays agreed to within 4%.

In later work with acetic acid and with ethanol, the oxidation to carbon dioxide was incomplete and consistent results could not be obtained by this procedure; therefore it was eventually abandoned in favor of dry oxidation methods.

H. Assay of High-activity Methanol

Some effort has been directed toward the development of a method for the assay of high-activity methanol in which methanol vapor, in millicurie quantities, is introduced directly into an ionization chamber of conventional design using an electron-tube electrometer as the current measuring instrument. These experiments have shown that highly reproducible results are obtainable, but a detailed description of the apparatus and procedure will be deferred pending completion of calibration experiments with carbon dioxide and further study of performance.

One use of the instrument, which does not depend upon a calibration, and which has been of value as an indication of the purity of methanol preparations, has been to take a series of readings on samples vaporized successively from a given preparation. This provides a sensitive indication of the presence of either more or less volatile inactive impurities.

III. Experimental Methods in the Lithium Aluminum Hydride Reductions of Carbon Dioxide

A. Control Experiments

Control experiments were carried out on the same scale, and under experimental conditions simulating the synthetic runs to be described. In a typical experiment, 60 ml. of n-butylcarbitol was added dropwise to a solution of 0.9 g. of $LiAlH_4$ in 140 ml. of diethylcarbitol while passing helium gas through the system. The mixture was heated at 145°C for four hours and the resulting distillate, collected in the cold trap was then vacuum distilled furnishing 31 mg. of volatile product. On adding α-napththyl isocyanate and fractionation of the resulting material, sym-di-α-naphthylurea and methyl-α-naphthyl-urea (7 mg.), m.p. 123°C., were isolated. The volatile product therefore contained water and methanol, the latter probably resulting from incidental exposure of the lithium aluminum hydride to atmospheric carbon dioxide during manufacture and subsequent handling.

B. Tracer-level Experiments

In a series of experiments carried out on a 10 m. mole scale at tracer levels of radioactivity (1-5 μc./m. mole), variations in chemical and radiochemical yields were encountered which were eventually traced back to the various factors which have been enumerated above. The apparent dilution of the radiocarbon, observed in the first tracer runs, was the result of the presence of inactive impurities, diethyl ether and diethylcarbitol. The low chemical yields were the result of heating the reaction mixture at too low a temperature, or for too short a time. Thus in one experiment in which 10.2 m. moles of barium carbonate, containing 58.8 microcuries of C^{14}, was reduced and the mixture, after adding n-butylcarbitol, was heated at 140°C

for two hours, methanol of substantially the same activity (5.73 μc./m. mole) as the starting material (5.75 μc./m. mole) was isolated, but the chemical yield was 252 mg. (7.9 m. moles) of methanol, or 79% of theoretical. Analysis of the mixture remaining in the reactor vessel showed the presence of 11.0 microcuries, leaving 1.3 microcuries unaccounted for. The low yield was thus largely due to incomplete recovery from the reactor, and not to incomplete reduction or losses in purification.

The final experiment in this series represents nearly optimum conditions for the production of methanol and will be described in detail. Carbon dioxide was generated from 2.011 g. of barium carbonate (5.15 μc./m. mole) by the slow addition of 30% perchloric acid, using a stream of helium gas as carrier, dried by passage through a Dry Ice-cooled trap, and introduced under the surface of a solution of 0.9 g. of lithium aluminum hydride in 100 ml. of diethylcarbitol. The solution was stirred continuously by a magnetic bar. This operation required ninety minutes. The mixture was allowed to stand at room temperature for one hour, and then 70 ml. of n-butylcarbitol was added dropwise and with care to ensure that the temperature does not rise above 50°C. Thereafter the temperature was maintained at 40°C for a period of forty-five minutes, with continued flow of helium, in order to remove traces of diethyl ether. The temperature was then raised to 140°C and liquid nitrogen was applied to the last two of a series of four traps attached to the reaction vessel on the effluent side. The first two of these traps, remaining at room temperature, served to collect the major portion of the diethylcarbitol carried over from the reactor. After maintaining these conditions for four hours, the last two traps were isolated

by sealing at a constriction, evacuated under high vacuum, and the contents subjected to a series of four successive distillations in which the receiver was cooled in liquid nitrogen and the trap serving as still-pot was maintained at -45°C. These distillations proceeded slowly, the first requiring about forty-five minutes, the later ones taking somewhat less time. During the distillations the system was isolated from the high-vacuum pump, and the pressure of non-condensable gases, registered by a McLeod gage, did not at any time exceed 10^{-5} mm. The resulting product showed a vapor pressure, measured at 0°C of 29.0 mm. (identical, within experimental error, with that of pure methanol) and amounted to 296 mg., or 92% of theoretical yield. Radioactive assay, by the van Slyke oxidation procedure previously described, showed 5.00 μc./m. mole), i.e. 3% lower than that of the starting material (5.15 μc./m. mole). The difference is within the limits of experimental error in the analytical procedures employed.

C. High-level Synthesis

The apparatus which has been used in the routine production runs, and which was developed on the basis of experience acquired during the series of tracer-level experiments just described, is shown in the accompanying figure (Figure 1). A carbon dioxide generator, shown on the extreme left of the figure, leads through a trap which is cooled by a Dry Ice freezing mixture to the reactor. This consists of a 300 ml. round-bottomed flask, equipped with a thermometer well and a side-arm with stopcock closure, used for the introduction of lithium aluminum hydride solution, and a magnetic stirring bar. The upper part of the reactor, through which the incoming gas enters and is conducted into the solution, is provided with a device for

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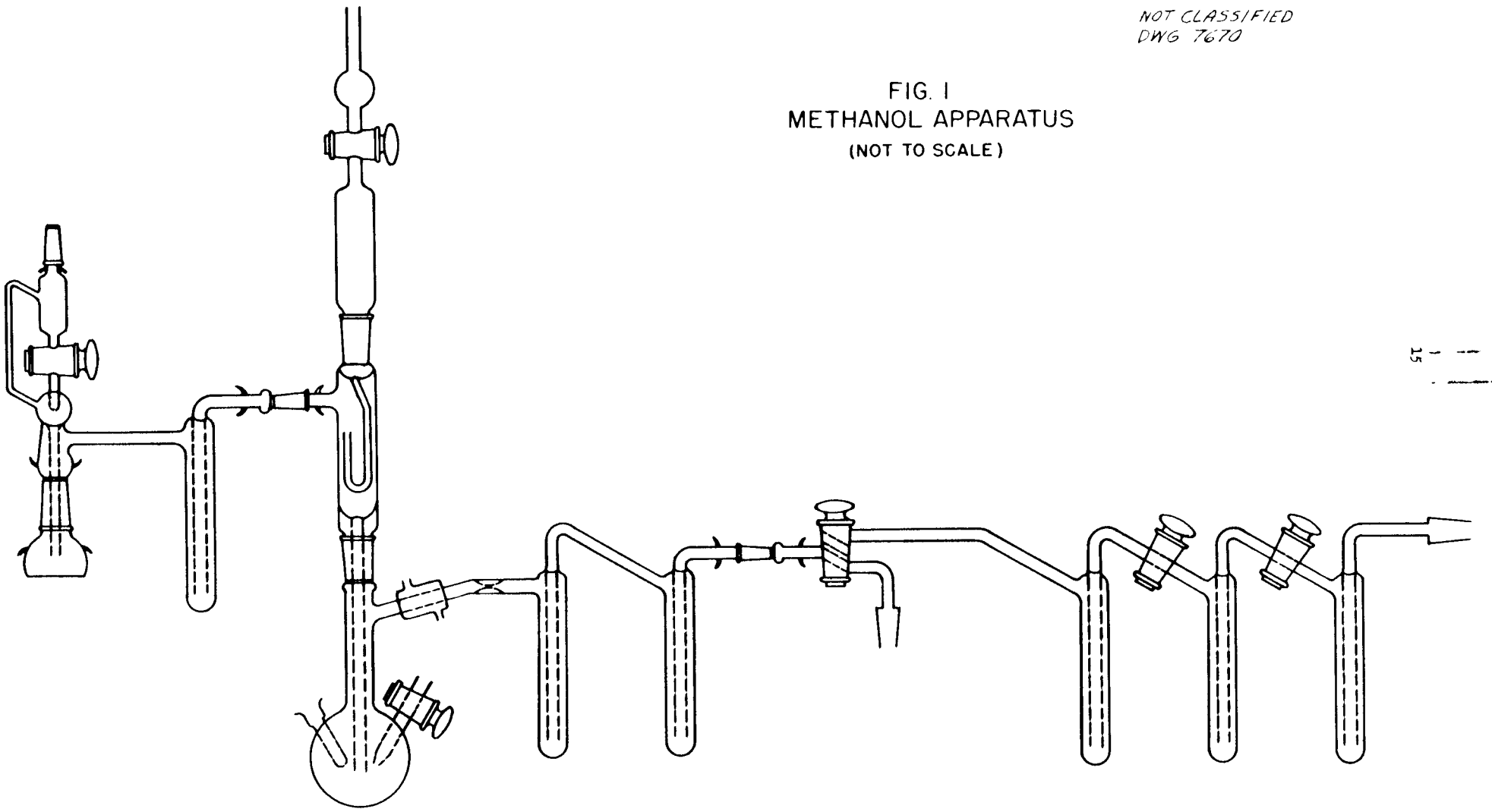
FIG. 1
METHANOL APPARATUS
(NOT TO SCALE)



introducing liquids which avoids their contact with a greased stopcock. During the reduction, this device contains diethylcarbitol which is added if and when necessary to clear stoppage of the delivery tube leading into the hydride solution. Later it is used for the introduction of n-butylcarbitol. On the exit side, the gas passes first through a small water-cooled reflux condenser, then through two traps in series, which are cooled by liquid nitrogen during collection of the product, and is discharged through an ascarite absorber connected at the two-way stopcock. The two traps containing the product are isolated from the reactor by sealing at a constriction (at present a stopcock is used at this location) and after evacuation to a pressure below 10^{-5} mm, the product is distilled successively through the series of traps shown on the extreme right. In each of these distillations the material distills from a trap maintained at -45°C into one cooled with liquid nitrogen.

The entire apparatus, including the associated vacuum-line equipment, is housed in a hood which can be completely enclosed except for such openings as are necessary for the manipulations. Other details of procedure are essentially the same as have been recorded for operations at tracer levels of radioactivity.

The chemical yields of methanol obtained in a series of high-level syntheses, shown in the accompanying table show a higher degree of variability than was to be anticipated on the basis of the tracer-level experiment. In part this is attributable to the questionable purity of the active barium carbonate, and in the case of the first experiment shown in the table to the inadvertent use of an old sample of lithium aluminum hydride of dubious

quality. It is doubtless true, however, that an important factor, if not the most important factor, is represented by the personal equation. The course of this development has shown repeatedly that a rather high degree of skill and experience must be developed before consistently good results can be obtained.

Table 1

Yields of Methanol Obtained in High-level Runs

Barium Carbonate			Methanol	
Weight, g.	Activity mc./mmole	Milli-curies	Weight	Yield, %
2.236	1.94	21.9	0.177	49
1.701	2.76	23.7	0.244	88.7
2.083	1.66	17.5	0.268	79.5
1.616	4.53	37.0	0.262	100
2.087	4.00	42.4	0.253	74.5

A radiochemical balance sheet covering these experiments cannot be given at this time since, as a result of the continuing urgent need for methanol, the reaction mixtures and other residues were set aside for later recovery.