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CHEMISTRY DIVISION - PHYSICAL & INORGANIC SECTION

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AN INVESTIGATION OF METHODS FOR THE PREPARATION OF DIBORANE

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\- Report No. P-2571 -

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NRL Problem P-95

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ABSTRACT

A comparison has been undertaken of the various hydrogen-source materials which might serve useful in the preparation of diborane. Although various types of reactor were used in preliminary tests, the general preparative method of Dr. H. I. Schlesinger, including boron trifluoride etherate as a boron source, was used in all final comparisons. Lithium hydride seems more satisfactory than any other metal hydride, borohydride, or trimethoxyborohydride tested. Smooth reaction, however, requires the use either of a catalyst such as methyl borate or of specially controlled temperature conditions as employed by the Lithaloys Corporation.

The results of diborane storage tests, previously unreported, are appended.

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INTRODUCTION

1. Authorization. This report covers a part of the investigation authorized by Bureau of Aeronautics TED No. NRL 3401. Locally identified as P-95.

2. Statement of Problem. General Problem. Investigate and prepare specific metal organic compounds. This phase of the problem was the study of the chemical and physical properties of diborane along with a study of methods of production in usable quantities.

3. Known Facts Bearing on the Problem. Diborane is a colorless gas, b. p. -92°C, f. p. -165°C, with physical properties close to those of ethane and ethylene. In its contemplated uses, the material was to be handled as a compressed gas, the critical pressure and temperature of which are approximately 670 psi at 20°C. Early workers had encountered violent reaction of the material when mixed with air and oxygen; though the hazards are now thought to be less serious, all diborane preparations must be made with rigid exclusion of oxygen and moisture. Diborane has been made numerous times in small quantities and reported in scientific literature. Considerable is known concerning its general nature. However, certain factors were unknown, such as storage stability in metals at varying temperatures, heats of oxidation and hydrolysis, rates of hydrolysis and large scale methods of production. Arrangements were made to collect the desired information on this compound and related compounds partly by research at this Laboratory and partly through contracts with other interested groups. Dr. H. I. Schlesinger, University of Chicago, has directed a group on the preparation and study of properties of desirable compounds. His work is reported in progress reports on Contracts numbered N173s 9820 and N173s 9058. Information has also been obtained from work done on a production contract Number N173s 9661 with the Lithaloys, Inc., New York City. Unreported information from this contract is included in part of this report.

4. At the time this series of experiments was started, considerable interest had been expressed in diborane, both as a high energy fuel and as an intermediate in the preparation of other boron compounds. The reported value of the heat of combustion of diborane was 18.6 kg cal/gram (ref.a) as compared to 11.5 kg cal/gram for gasolene; moreover, diborane had been used as an intermediate in the preparation of sodium and lithium borohydrides (ref.b), the two compounds of the type which were well known at that time.

5. Preparation of diborane had been reported by the University of Chicago (ref. b) and by the Lithaloys Corporation (ref. d). In addition, the same type of work was going on at this Laboratory. All successful preparations used boron trifluoride ethyl

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etherate as the source of boron. The experiments of the three groups, however, were so varied as to conditions of reaction, size of batch, duration of run, etc. that no comparison could be made of the relative merits of the reducing agents advocated. The object of the work reported here was to compare the various reactions under comparable conditions and then to study the more promising ones on a pre-pilot plant basis.

6. The compounds considered as sources of hydrogen in the preparation were the hydrides, borohydrides, and trimethoxyborohydrides of lithium, sodium, and calcium. Of these, the calcium trimethoxyborohydride could not be prepared, and calcium borohydride was never obtained in sufficient quantity and purity for a good test. Of the materials tried, lithium compounds appeared generally more effective than sodium compounds; as to the hydrogen-carrying groups, the order of effectiveness was borohydride, trimethoxyborohydride, hydride. (See Table I). Lithium hydride, however, proves the most satisfactory from a practical and economical standpoint, and the two methods of generation below are the most strongly recommended.

(a) $6LiH(100\ mesh) + 2BF_3.Et_2O \xrightarrow[Et_2O]{B(OCH_3)_3} B_2H_6 + 6LiF + 2Et_2O$

(b) Developed by the Lithaloys Corporation (See Para.24)

$6LiH(100\ mesh) + 2BF_3.Et_2O \xrightarrow[Et_2O]{\text{"surge"}} B_2H_6 + 6LiF + 2Et_2O$

Good results have been obtained with both of these reactions, and only large scale operations can indicate which one is the better. The only problems anticipated are grinding of the hydride and generation of boron trifluoride. A ball mill reactor may solve the grinding problem. The boron trifluoride may be generated from fluorspar, boric anhydride, and sulphuric acid at the plant site. The reason for generating boron trifluoride on the spot is that a large percentage of the cost of the commercially available product is in compressing it in cylinders.

EXPERIMENTAL DATA

7. Reactions Investigated. (No. on left refers to paragraphs).

11 $6LiH + 8BF_3.Et_2O \xrightarrow[Et_2O\ 34^{\circ}]{} B_2H_6 + 6LiBF_4 + 8Et_2O$

11 $6LiH + 2BF_3.Et_2O \xrightarrow[Et_2O\ 34^{\circ}]{} B_2H_6 + 6LiF + 2Et_2O$

12 $6LiH + 6B(OCH_3)_3 + 2BF_3.Et_2O \xrightarrow[Et_2O\ \ 34^{\circ}]{\text{copper shaker}} B_2H_6 + 6LiF + 6B(OCH_3)_3 + 2Et_2O$

[redacted]

12 $6LiHB(OCH_3)_3+2BF_3.Et_2O \xrightarrow[Et_2O\ 34^\circ]{} B_2H_6+6LiF+6B(OCH_3)_3+2Et_2O$

14 $6LiHB(OCH_3)_3+3F_2BOCH_3 \xrightarrow[B(OCH_3)_3]{} B_2H_6+6LiF+7B(OCH_3)_3$

15 $6LiH+4F_2BOCH_3 \xrightarrow[FB(OCH_3)_2\ 50^\circ]{} B_2H_6+6LiF+2FB(OCH_3)_2$

16 $6LiHB(OCH_3)_3+10F_2BOCH_3 \xrightarrow[FB(OCH_3)_2\ 55^\circ]{} B_2H_6+6LiF+14FB(OCH_3)_2$

17 $6LiHB(OCH_3)_3+2BF_3.\text{dioxanate} \xrightarrow[\text{dioxane}\ 75^\circ]{} B_2H_6+6LiF+2\ \text{dioxane}$

18 $6LiH+2BF_3.Et_2O \xrightarrow[Et_2O\ 34^\circ]{B(OCH_3)_3} B_2H_6+6LiF+2Et_2O$

19 $6LiH+2BF_3.Et_2O \xrightarrow[\text{benzene}\ 65^\circ]{B(OCH_3)_3} B_2H_6+6LiF+2Et_2O$

20 $6LiH(30\text{-}80\ \text{mesh})+2BF_3.Et_2O \xrightarrow[Et_2O\ 34^\circ]{B(OCH_3)_3} B_2H_6+6LiF+2Et_2O$

20 $6LiH(200\ \text{mesh})+2BF_3.Et_2O \xrightarrow[Et_2O\ 34^\circ]{B(OCH_3)_3} B_2H_6+6LiF+2Et_2O$

21 $6LiH+2BF_3 \xrightarrow[Et_2O\ 34^\circ]{B(OCH_3)_3} B_2H_6+6LiF$

22 $6LiH+2BF_3.Et_2O \xrightarrow[\text{pressure}\ Et_2O\ 34^\circ]{B(OCH_3)_3} B_2H_6+6LiF+2Et_2O$

27 $6NaHB(OCH_3)_3+2BF_3But_2O \xrightarrow[But_2O\ 107^\circ]{} B_2H_6+6NaF+2But_2O$

27 $6NaHB(OCH_3)_3+8BF_3.Me_2O \xrightarrow[\text{toluene}\ 50^\circ]{} B_2H_6+6NaBF_4+8Me_2O$

27 $6NaHB(OCH_3)_3+8BF_3.Et_2O \xrightarrow[\text{toluene}\ 75^\circ]{} B_2H_6+6NaBF_4+8Et_2O$

27 $6NaHB(OCH_3)_3+2BF_3.Et_2O \xrightarrow[\text{CU shaker, dioxane}]{} B_2H_6+6NaF+2Et_2O$

26 $6NaH+8BF_3.Et_2O \xrightarrow[Et_2O\ 65^\circ]{\text{copper shaker}} B_2H_6+6NaBF_4+8Et_2O$

28 $3NaBH_4+4BF_3.Et_2O \xrightarrow[Et_2O\ 34^\circ]{LiBF_4} 2B_2H_6+3NaBF_4+4Et_2O$

28 $3NaBF_4+4BF_3.Et_2O \xrightarrow[Et_2O\ 34^\circ]{\text{isopropylamine}} 2B_2H_6+3NaBF_4+4Et_2O$

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28 $3CaH_2+2BF_3.Et_2O \xrightarrow[Et_2O]{} B_2H_6+3CaF_2+2Et_2O$

28 $3CaBH_4+2BF_3.Et_2O \xrightarrow[Et_2O]{} 4B_2H_6+3CaF_2+2Et_2O$

Discussion of Reactions and Experimental Data

8. All the reactions investigated involved practically the same physical considerations. The hydrogen source compound was suspended in a solvent, and boron trifluoride was added as a gas or an organic complex. (High temperature gas reactions -- 300°C -- were found in preliminary tests to be impractical, since the diborane formed was decomposed to great extent in the reactor). The greatest difficulty lies in finding the solvent for the hydrogen source compound, it being relatively easy to form an etherate or a substitution product of boron trifluoride.

9. A copper shaker (Plate II) was constructed for use on some of the reactions investigated. Several copper balls about an inch in diameter were placed inside. The purpose of this arrangement was to provide a grinding as well as stirring action. It was thought that in some of the reactions the reacting material became coated with reaction product early in the run. For all other runs, unless specified, the reactor in Plate I was used.

10. In all experiments using lithium hydride, it was ground to between one hundred and two hundred mesh (U.S.Standard sieve series), unless otherwise specified. Boron trifluoride was always added in slight excess of the amount theoretically necessary. The amount of suspending medium was in most cases more than the minimum necessary for suspension; this was because the reactor was too big for the particular charge used and good stirring could not be obtained with less liquid.

11. Lithium hydride was investigated extensively. The first reaction tried, run #1A was analogous to one devised by Dr. H. I. Schlesinger (ref.c) using sodium hydride.

$$6LiH+8BF_3.Et_2O \xrightarrow[Et_2O\ \ 45^\circ]{} B_2H_6+6LiBF_4+8Et_2O$$

This had been the best diborane reaction using sodium hydride, but the above run gave only 22% of the theoretical yield in seven and one quarter hours. At about this time, the Lithaloys Corporation (ref.d) reported that the reaction would go to lithium fluoride. This would affect a 75% reduc-

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tion in the amount of boron trifluoride etherate required.

$$6LiH+2BF_3.Et_2O \xrightarrow[Et_2O \quad 34°]{} B_2H_6+6LiF+2Et_2O$$

The reaction was tried in run #1 to verify the yield of 99% in twenty-four hours claimed by the Lithaloys Corporation. Only 56% of the theoretical yield was realized in twenty-four hours, but the test was not conclusive because of failure of the stirrer early in the run.

12. The compound sodium trimethoxyborohydride was found by Dr. Schlesinger to give a good yield of diborane (ref.c). Therefore, it was decided to try the corresponding lithium compound. It was prepared in a high pressure bomb under hydrogen pressure from methyl borate and approximately ten mesh lithium hydride. It was then tried as a diborane source in run #6A according to the reaction:

$$6LiHB(OCH_3)_3+2BF_3.Et_2O \xrightarrow[Et_2O \quad 34°]{\text{copper shaker}} B_2H_6+6LiF+6B(OCH_3)_3+2Et_2O$$

In three hours, the yield was 73%; in four hours it was 87%. The purity of the product was 99%. Thus the reaction appears to be very good but for the fact that lithium trimethoxyborohydride hasn't been prepared by ordinary means (i.e. above method) with a purity better than 75% on the basis of available hydrogen. In an attempt to avoid this loss of hydrogen, a run was made wherein the trimethoxy compound was made in the reactor, and boron triflauride etherate added immediately afterward (run #4A).

$$6LiH+6B(OCH_3)_3+2BF_3.Et_2O \xrightarrow[Et_2O \quad 34°]{} B_2H_6+6LiF+6B(OCH_3)_3+2Et_2O$$

The lithium hydride and methyl borate were placed in the reactor and allowed to react completely. The reaction did not take place at 26°C. in one hour but did when the temperature was raised to about 35°. It was allowed four hours to go to completion before the boron trifluoride etherate was added. The diborane yield was 54% in four and one quarter hours, and had only reached 59% after seven hours. Roughly, this is about the same yield as that obtained from previously prepared lithium trimethoxyborohydride, taking into account the 25% hydrogen loss suffered in its preparation.

13. It is desirable to avoid the use of ether in a plant because of the fire hazard, physiological hazard, and evaporation loss. Therefore, it was decided to investigate other possible suspending media for the reaction.

[redacted]

14. In run #8A the reaction was

$$6LiHB(OCH_3)_3+3F_2BOCH \xrightarrow[B(OCH_3)_3]{} B_2H_6+6LiF+7B(OCH_3)_3$$

Difluoromethylborate is formed by bubbling boron trifluoride through methyl borate. This run made it apparent that monofluoromethylborate was more stable than the difluoro compound; the monofluoromethylborate released boron trifluoride much more slowly. Also the following reaction was ~~believed~~ proved to have taken place:

$$F_2BOCH_3+B(\cancel{OCH_3})_3 \longrightarrow 2BF(OCH_3)_2 + BF_3$$

The yield of diborane from this run was 12% in one hour and 55% in five and two thirds hours. insufficient BF₂OMe since above rx.

15. On the basis of the above results, the following run, #9A was made:

$$6LiH+4F_2BOCH_3 \xrightarrow[FB(OCH_3)_2\ 50°]{} B_2H_6+2FB(OCH_3)_2+6LiF$$

Lithium hydride was used because in a continuous plant process the methyl borate liberated from lithium trimethoxyborohydride would continually dilute the reaction medium and the problem of separating methyl borate from monofluoromethylborate would arise. The yield of this run was only 18% in six and one half hours.

16. In run #4 the above reaction was tried using lithium trimethoxyborohydride in spite of the undesirable feature mentioned above.

$$6LiHB(OCH_3)_3+10F_2BOCH_3 \xrightarrow[FB(OCH_3)_2\ 55°]{} B_2H_6+6LiF+14FB(OCH_3)_2$$

This reaction looked as if it might have possibilities, but there were so many angles to be worked out that further work on it was postponed. In the first place, a violent reaction on giving diborane was observed when the suspending medium was poured on the trimethoxy compound; this diborane was lost. In the second place, mercury from the stirrer seal was accidentally sucked into the reactor; this seemed to have some effect on the reaction. The solids in the reactor became black, and the mercury appeared tarnished. The product, according to hydrolysis and vapor density measurements, seemed to be tetramethyl diborane. It smelled a little like hydrogen sulphide. Altogether the data on the reaction is inconclusive.

[redacted]

17. In run #7A dioxane was used as the suspending medium, and the boron trifluoride was added as the dioxanate.

$$6LiHB(OCH_3)_3+2BF_3\ \text{dioxanate}\ \xrightarrow[\text{dioxane }75^\circ]{} B_2H_6+6LiF+6B(OCH_3)_3+2\text{dioxane}$$

The reason for the use of dioxane is its higher boiling point.+ to avoid ethane. The yield was practically zero until a small amount of ether was added. Even then only about 2% of the theoretical yield was realized. It was concluded that dioxane is too basic to give up boron trifluoride to the hydride.

18. Since lithium trimethoxyborohydride had proved to be more reactive than lithium hydride, it was thought that a small amount of methyl borate might catalyze the lithium hydride reaction by forming momentarily lithium trimethoxyborohydride and then being liberated again. This was tried with success in run #5.

$$(a)\quad 6LiH+6B(OCH_3)_3\ \xrightarrow[Et_2O\quad 34^\circ]{}\ 6LiHB(OCH_3)_3$$

$$(b)\quad 6LiHB(OCH_3)_3+2BF_3.ET_2O\ \xrightarrow[31^\circ]{Et_2O}\ B_2H_6+6LiF+6B(OCH_3)_3+2Et_2O$$

$$(a)+(b)\quad 6LiH+2BF_3.Et_2O\ \xrightarrow[Et_2O\quad 34^\circ]{B(OCH_3)_3}\ B_2H_6+6LiF+2Et_2O$$

About 16% of the methyl borate necessary to carry reaction (a) to completion was used; this amount was chosen at random, and further tests were not made to determine the optimum amount. The yield of the run approached 90% in three and one half hours with a purity of 96%.

19. Benzene was tried in run #11 as the suspending solvent for the catalysed lithium hydride - boron trifluoride reaction.

$$6LiH+2BF_3.Et_2O\ \xrightarrow[\text{benzene }65^\circ]{B(OCH_3)_3}\ B_2H_6+6LiF+2Et_2O$$

An attempt to make a boron trifluoride - benzene substitution compound for this run failed, although boron trifluoride is soluble in benzene to some extent. The run was unsuccessful, giving a yield of 21% and a purity of 86%.

20. A series of runs was made to determine the effect of mesh size on the rate of the catalyzed lithium hydride - boron trifluoride reaction. Three different mesh sizes were used, namely thirty to eighty, one hundred to two hundred, and finer than two hundred (U.S.Standard seive series). The one hundred to

[redacted]

two hundred mesh material gave the best yield per unit time, although theoretically the finer the mesh is the faster the reaction should be. (The solubility of lithium hydride in ether is very low.) The finer than two hundred mesh material went through a viscous, gummy stage during the run and finally solidified; it could not be dislodged from the stirrer or broken up. A ball mill type of stirring might prevent this and enable the increased surface to have its full effect on the rate of reaction. For a set of curves plotted from the results of this series of runs refer to Plate IV.

21. One run was made using gaseous boron trifluoride to see if any chemical difficulties were involved. Judging by the quality and quantity of product the method involves problems, the solutions of which were not apparent in this run. The yield was only 20% of theoretical for the amount of boron trifluoride added. Only about a fourth of the necessary boron trifluoride was added because the bubbler became clogged; this difficulty could be overcome. However, the product was only 47% pure and had some boron trifluoride in it in spite of the fact that there was a dry ice condenser followed by an ether scrubber and two more dry ice condensers between the generator and diborane traps.

22. One high pressure bomb reaction was tried using the catalysed lithium hydride - boron trifluoride reaction. The product was 98% pure, but the yield was only 35% in five and two thirds hours. Also the maximum pressure developed was only 33 psi; a higher pressure might slow the reaction still more. However, the fact that this sort of procedure would require no attention except to charge and empty the bomb, weighs considerably in its favor. Experiments and calculations to determine the merit of this method were beyond the scope of this work, but it is presented as a possibility.

23. In run #10A, lithium borohydride was checked for reaction rate and completeness of reaction.

$$3LiBH_4+BF_3.Et_2O \xrightarrow[Et_2O\ rm.Temp.]{} 2B_2H_6+3LiF+Et_2O$$

The yield was 99.5% in forty-five minutes, and the purity was 95%.

24. In run #17, a reaction originating in the laboratory of the Lithaloys Corporation was verified (ref.e)

$$6LiH+2BF_3.Et_2O \xrightarrow[Et_2O]{\text{"surge"}} B_2H_6+6LiF+2Et_2O$$

[redacted]

The procedure is to place a relatively small charge (about 12 grams) of lithium hydride in the reactor and add half the theoretical amount of boron trifluoride etherate. There is a slight evolution of diborane while the etherate is being added, followed by a period of complete inactivity. After about half an hour, the reaction continues with great vigor and must be controlled by cooling. When it has again subsided, the full charge of lithium hydride can be added as an ether slurry, and the addition of etherate continued. Two different procedures can be followed from this point on; the reaction can continue at room temperature or higher and give diborane rapidly and smoothly as etherate is added or the reactor can be cooled to about ten degrees centigrade or less and yield lithium borohydride. The exact mechanism of the "surge" is not known, but it is believed due to the presence of a catalyst. The reaction for lithium borohydride is as follows:

$$4LiH+BF_3.Et_2O \xrightarrow[Et_2O\ 5-15°]{} LiBH_4+3LiF+Et_2O$$

25. Sodium compounds were investigated briefly. The experience of Dr. Schlesinger had been that relatively high temperatures (80°C) were necessary, and that sodium borofluoride rather than sodium fluoride always formed. At high temperatures the purity of the product is lowered; the formation of the borofluoride quadruples the amount of boron trifluoride necessary.

26. In run #2A sodium hydride was tried in the copper shaker with excess boron trifluoride etherate to form sodium borofluoride. In twenty-four hours the yield was 69% and the purity 75%.

27. Sodium trimethoxyborohydride was tried in several different combinations. In run #2 it was suspended in butyl ether, and boron trifluoride butyl etherate was added. In run #15 it was suspended in toluene and boron trifluoride methyl etherate was added. In run #16 it was again suspended in toluene, but boron trifluoride ethyl etherate was added. In the latter two runs, boron trifluoride etherate was added to form the borofluoride of sodium rather than the fluoride. In run #5A sodium trimethoxyborohydride was suspended in dioxane and boron trifluoride ethyl etherate was added - first in the amount to give sodium fluoride and finally to give sodium borofluoride (in the copper shaker. The solvent was chosen in all these runs to make possible a high reaction temperature. None of the runs was successful; the yield was negligible, and the purity of the product was low. In fact, run #15 using methyl etherate gave dimethyl-ether-borine, from which diborane could not be reclaimed by the usual methods of purification.

[redacted]

28. Sodium borohydride was used in two runs. In run #13, it was suspended in ethyl ether with a small amount of lithium borofluoride, and boron trifluoride etherate was added. It was thought that lithium borofluoride might cause a favorable change in the solubility of sodium borohydride in ether. The result was negative. In run #9, the same principle was tried using isopropylamine. The yield was negligible and the product only 30% pure.

29. Calcium compounds gave no promise as diborane sources. Calcium hydride was tried in a test tube reaction and gave practically no smell of diborane. An attempt to make calcium trimethoxyborohydride by methods used with sodium and lithium compounds was unsuccessful. Calcium borohydride was made by metathesis, but it was of such low purity that no diborane run was made with it.

[redacted]

RECOMMENDATIONS

30. There is little interest at this time in diborane. Its low density (ref. d) and poor storage stability (Appendix A) are sufficient reason for disqualification as a fuel in itself; its use as an intermediate for metal borohydrides is no longer necessary since the Lithaloys Corporation has been able to prepare lithium borohydride from lithium hydride in one step (Paragraph 24).

31. Present plans, however, call for study of the higher boron hydrides such as B_5H_9. In the event that any of these materials prove valuable, diborane may again be important as an intermediate. In this case, the two reactions of Paragraph 6 would be worth study on a larger scale.

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TABLE I

COMPARISON OF DIBORANE PRODUCING EFFICIENCIES WITH BF_3 ETHERATE AT 34°C.

Compound		Metal		
		Lithium	Sodium	Calcium
borohydride	yield	99.5%	2.2%	Not available
	time	3/4 hrs.	6 hrs.	
	purity	95%	30%	
trimethoxy-borohydride	yield	87.1%	18.7%	No compound
	time	4 hrs.	5-3/4 hrs.	
	purity	98.8%		
hydride	yield	89%	68.6%	0%
	time	3-1/2 hrs.	24 hrs.	
	purity	95.8%	75%	

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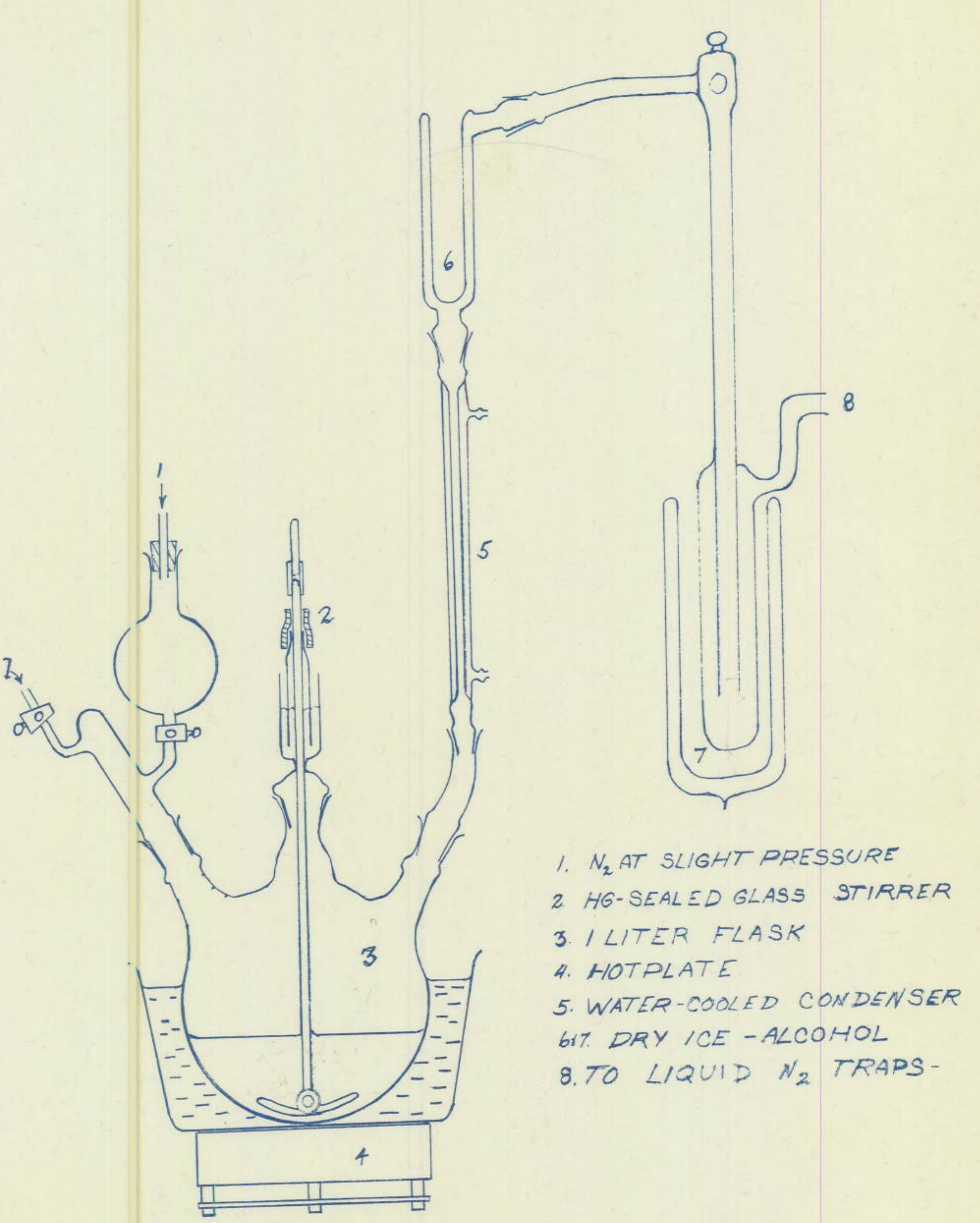

1. N_2 AT SLIGHT PRESSURE
2. HG-SEALED GLASS STIRRER
3. 1 LITER FLASK
4. HOTPLATE
5. WATER-COOLED CONDENSER
6&7. DRY ICE - ALCOHOL
8. TO LIQUID N_2 TRAPS -

REACTOR

PLATE I

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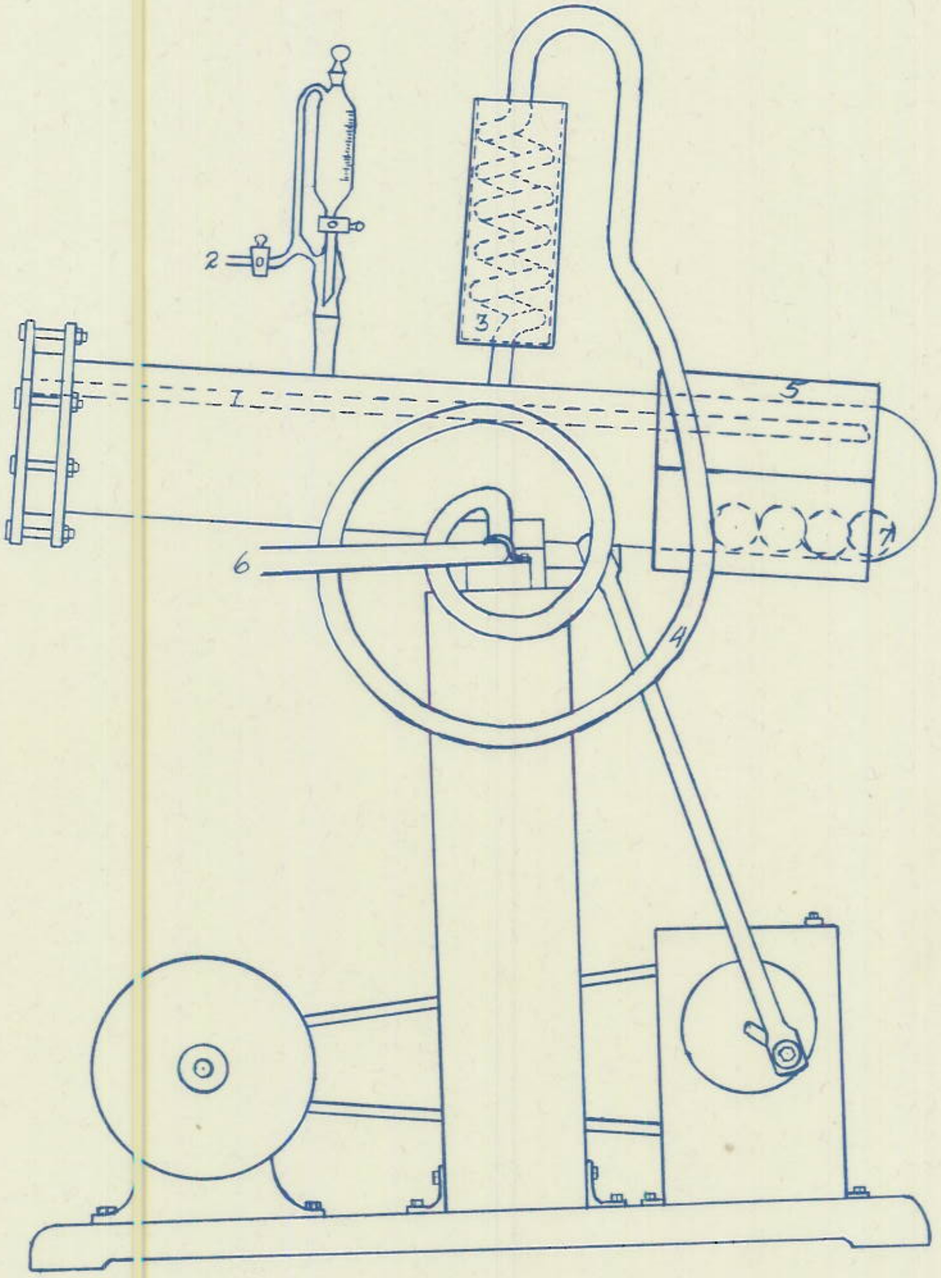

1 THERMOMETER WELL
2 N_2 AT SLIGHT PRESSURE
3. DRY ICE CONDENSER
4. TORSION ABSORBING SPIRAL
5. HEATING ELEMENT
6. TO GLASS LINE
7. COPPER BALLS

COPPER SHAKER

PLATE II

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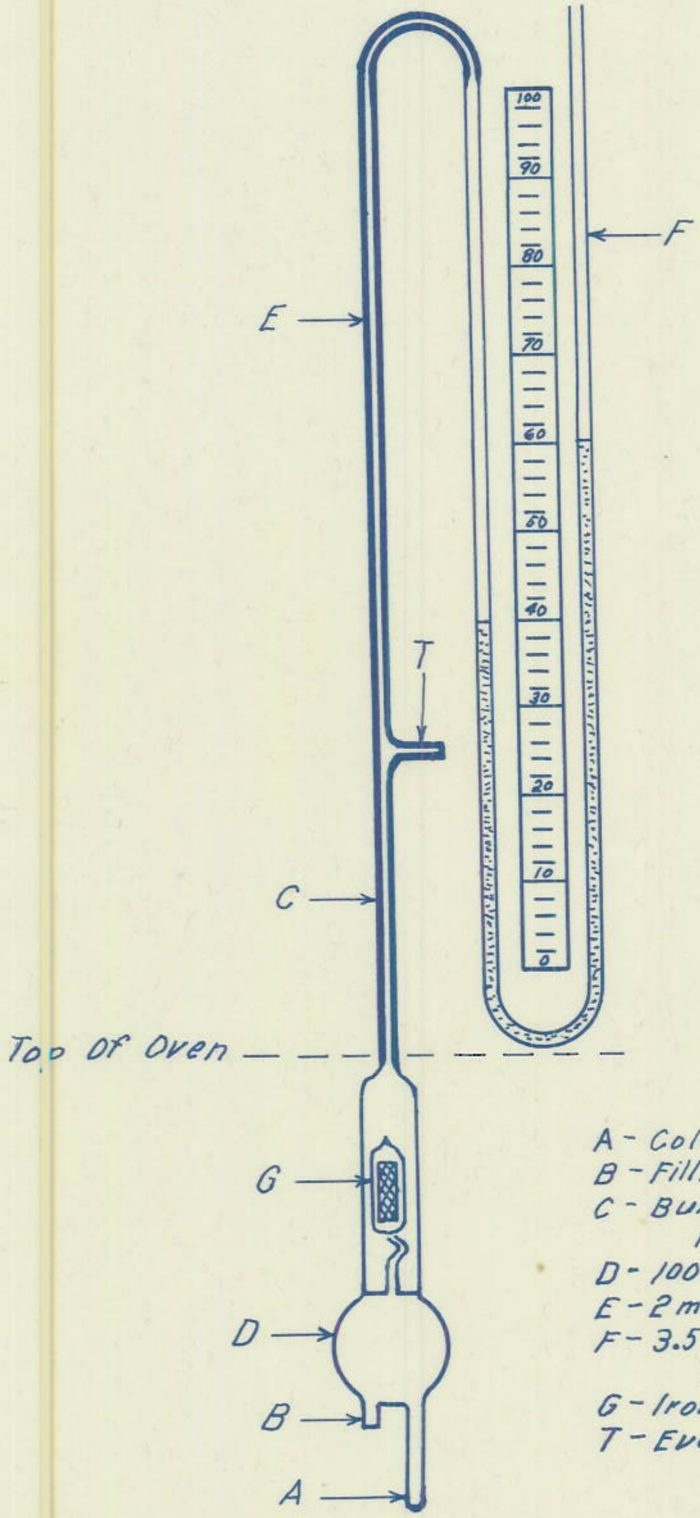
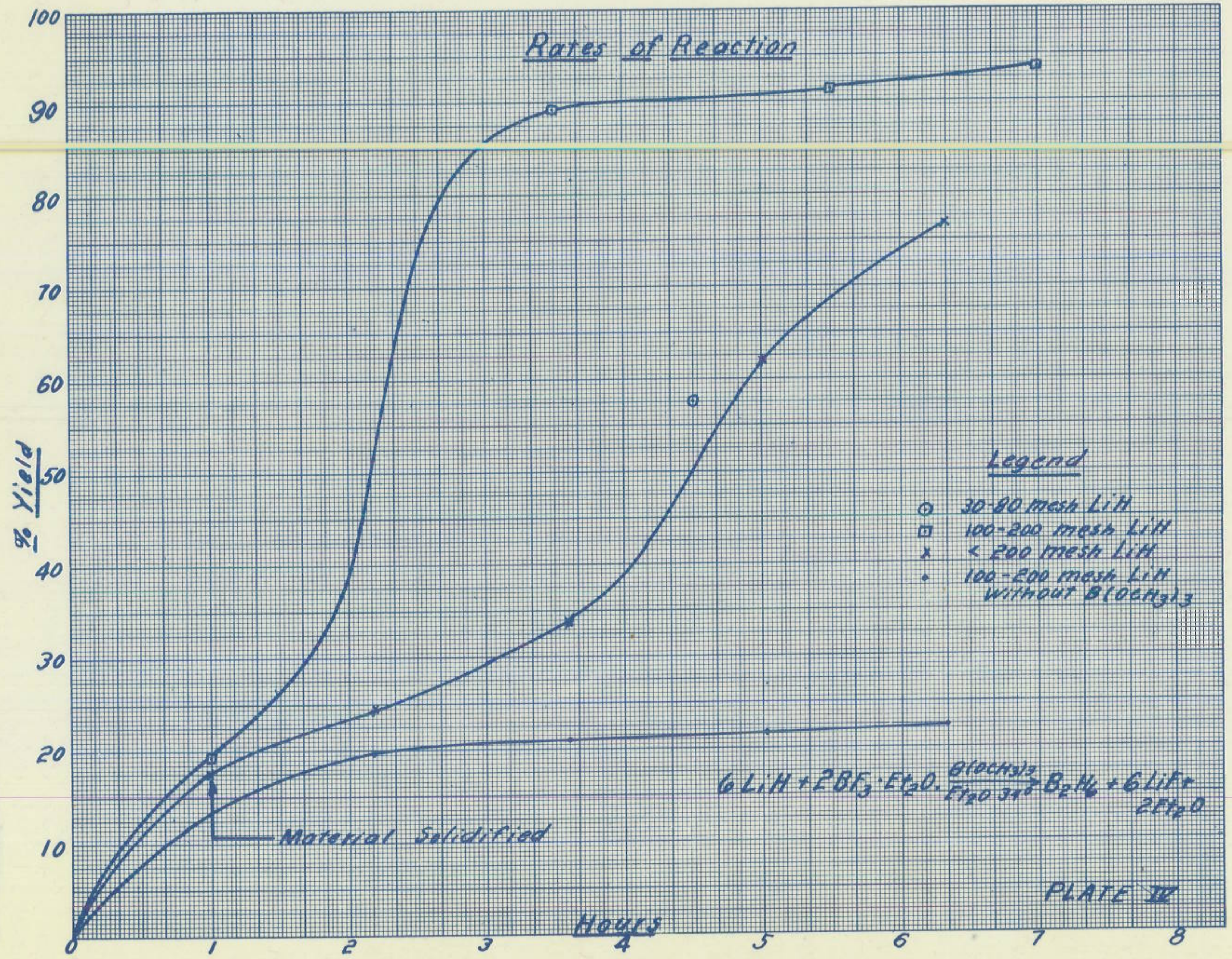


Legend

A - Cold Finger
B - Filling Tube
C - Bulb Sealed To Manometer Here
D - 100 cc Flask
E - 2 mm ID Capillary
F - 3.5 mm ID Heavy Wall Tubing
G - Iron Rod Sealed In Glass
T - Evacuation Lead From Manometer

Storage Test Apparatus

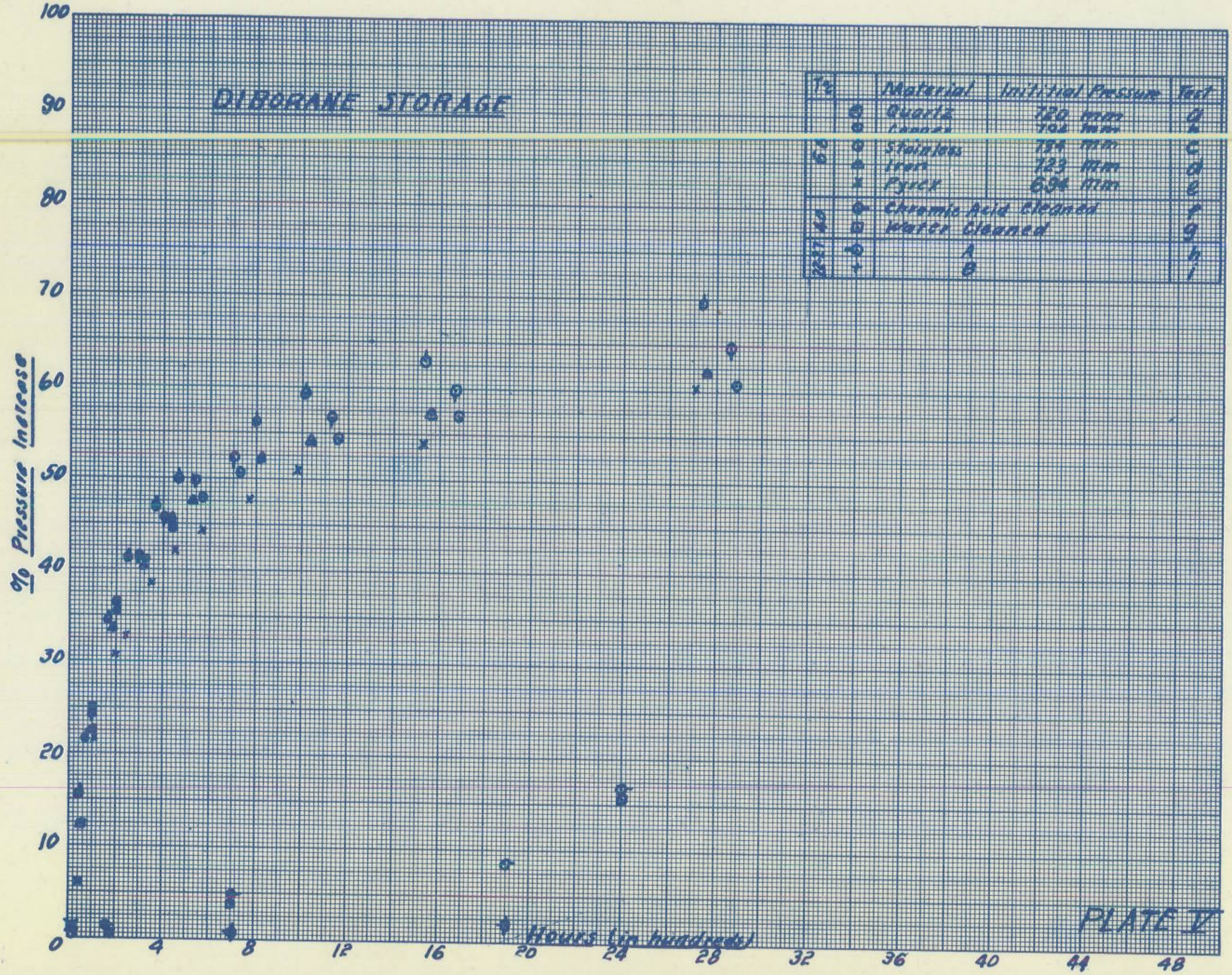
Plate III



Rates of Reaction

$6\,LiH + 2BF_3 \cdot Et_2O \xrightarrow[Et_2O\ 34°]{B(OCH_3)_3} B_2H_6 + 6\,LiF + 2Et_2O$

PLATE IV



DIBORANE STORAGE

PLATE V

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STORAGE TESTS OF DIBORANE

Storage tests of diborane in contact with different materials at 66°C., 40°C., and room temperature, 22-27°C., have been in progress for approximately four months. Five tests have been conducted at 66°C. as follows: B_2H_6 in (a) quartz, (b) pyrex with copper turnings, (c) pyrex with stainless steel turnings, (d) pyrex with iron wire, and (e) Pyrex. All bulbs in the above tests were carefully cleaned with hot chromic acid solution, tap water, and distilled water and dried. The copper turnings were washed with alcohol and ether, and reduced by hydrogen at 400°C. The stainless steel turnings were washed with alcohol and ether, and dried. The iron wire was pickled in dilute HCl, washed, and dried. Two tests were carried out at 40°C. in Pyrex, one of the bulbs having been cleaned with hot chromic acid solution, tap water, distilled water, and dried (f) while the chromic acid treatment was omitted with the second bulb (g). Identical cleaning procedures, hot chromic acid, etc., were used to clean the two bulbs (h,i) used in tests at room temperature. The bulbs at room temperature were the only ones constantly exposed to daylight during the test.

The methods of filling with diborane and observation of pressures have been the same for each bulb. Plate III shows the construction details for the storage bulbs. Tube B served as a filling tube for the metals and the diborane. As much metal as possible was put into the 100 cc. bulbs. The bulb was then sealed to the diborane generating system at B, and sufficient diborane condensed in A with liquid nitrogen to give approximately one atmosphere at the storage test temperature. Hydrolysis of the diborane used indicated a purity of 98%. The bulb was sealed off at B with no evidence of decomposition and sealed on to a capillary mamometer lead at C. The manometers were of the open end type. The manometer lead contained a T through which it was evacuated to 10^{-4} mm., and then sealed off. The diborane was allowed to expand into the evacuated mamometer by lifting the glass-covered iron rod magnetically and letting it fall against the thin glass tip.

The data obtained are presented in Plate V which is a plot of percent pressure increase versus time at constant temperature and volume. In all of the tests, diborane decomposed to yield a gas non-liquified at -194°C. (assumed to be hydrogen), and a white crystalline solid, which in the tests at 66 ° C. and 40°C, sublimed from the storage bulb into the manometer leads. In the tests at room temperature, the crystals

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remained in the storage bulb. The crystals resemble Stock's (Alfred Stock, "Hydrides of boron and Silicon", Cornell University Press) description of the crystals of dekaborane, $B_{10}H_{14}$, the only solid, volatile hydride of boron. Stock also states that when B_2H_6 is kept at ordinary temperatures for a long time a certain amount of $B_{10}H_{14}$ is formed; it is produced more rapidly, however, when B_2H_6 is exposed to ultraviolet light, and also at higher temperatures. The bulbs stored at 66°C. and 40°C. also became coated with an extremely thin layer of condensate showing brownish iridescence, which is the result of the formation of small amounts of solid, non-volatile hydrides in which the ratio of hydrogen to boron atoms is less than the corresponding ratio in dekaborane.

Examination of Plate V shows that the rate of percent pressure increase and the maximum percent pressure increase observed after storage for approximately four months are nearly independent of the containing materials. The rate of decomposition, however, is shown to be greatly accelerated by increase in temperature. At 66°C. the maximum, limiting percent pressure increase is approximately 60%, with the test using stainless steel showing the greatest deviation from this value. The equation for the decomposition of diborane into hydrogen and dekaborane is as follows:

$$5B_2H_6(g) \longrightarrow B_{10}H_{14}\ (s) + 8H_2(g)$$

Since the vapor pressure of $B_{10}H_{14}$ is less than 0.3 mm. at room temperature, the percent pressure increase for complete decomposition at constant volume according to the above reaction is 60%. Percent pressure increase multiplied by 1.666 gives the percentage decomposition in this reaction. Percent pressure increases greater than 60% are no doubt caused by the formation of the brownish, non-volatile, hydrogen-poor hydrides previously mentioned.

Different methods of cleaning the bulbs used in the tests at 40°C. had no significant effect on the rate of decomposition. The tests at room temperature show that diborane can be stored at room temperature for a considerable length of time with only slight decomposition.

[redacted]

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(a) Progress Report On "Heat of Combustion of Diborane" National Bureau of Standards March 23, 1945.

(b) Progress Reports I, II, and III University of Chicago Contract No. N173 S--9058 BuAero TED-NRL No. 3401

(c) Ibid. Report II.

(d) Report No. 1 (Preliminary) Lithaloys Corporation Contract NOa (S)-3744 BuAero TED-NRL No. 3401

(e) Conference involving NRL representatives at Lithaloys Corp. in New York, April 9, 10, 11, 1945.

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