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AFPTC-TR-61-34
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A STUDY OF PENTABORANE

ANDREAS V. JENSEN

BERGE B. GOSHGARIAN

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A STUDY OF PENTABORANE

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This report has been reviewed and approved

A handwritten signature in cursive script, reading "Harold W. Norton". The signature is written in black ink and is positioned above the printed name and title.

HAROLD W. NORTON
Colonel, USAF
Director, Rocket Propulsion
and Missiles

ABSTRACT

There have been several research programs undertaken in recent years to obtain all of the energy available from boron hydrides in rocket engine applications with various oxidizers. The work performed at Edwards AFB with pentaborane -9 in support of an engine project is the basis of this report.

The density, vapor pressure, and freezing point of pentaborane -9 may all be determined in the quality control laboratory with one basic transfer apparatus and test vessels of 1-5 milliliter volume. These physical properties plus a determination of dissolved and total solids are sufficient to certify that the pentaborane is suitable for use in a rocket engine.

The best method found to decontaminate entire missile systems after use with pentaborane is to flush with a hydrocarbon solvent such as a kerosene to remove most of the material, followed by a flush with a mixture containing 80 percent methylene chloride and 20 percent ethyl alcohol and purge dry with gaseous nitrogen.

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INTRODUCTION

There have been several research programs undertaken in recent years to obtain all of the energy available from boron hydrides in rocket engine applications with various oxidizers. The work performed at Edwards AFB with pentaborane -9 in support of an engine project is the basis of this report.

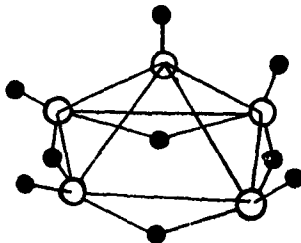
The reactivity and extreme toxicity of this potential storable rocket fuel presented technical problems in handling, quality control analysis, detection in air and the disposal of portions of fuel after sampling and analysis were completed. Solutions to these problems, developed analytical procedures, typical analytical results and handling recommendations are given in this report.

References to other work in the field of boron hydride chemistry are quoted where this data is pertinent to the scope of this paper.

STRUCTURE

Pentaborane is a boron hydride having the empirical formula B_5H_9 . It is the most stable of the lower molecular weight boron hydrides. Another boron hydride consisting of 5 boron atoms also exists but is relatively unstable. The two Pentaboranes must be distinguished; therefore, the stable B_5H_9 is designated Pentaborane -9 and the unstable B_5H_{11} is designated Pentaborane -11. Discussion in this report will be limited to Pentaborane -9 since it is of particular interest due to its stability in storage.

The structure of the Pentaborane molecule has been published by Dulmage and Lipscomb.⁽¹⁾ The structure is represented by the diagram shown below:



The skeleton of the molecule is comprised of five boron atoms in a tetragonal pyramid. The boron atom at the apex of the pyramid is bonded to each of the other 4 boron atoms through boron-boron bonds, and to a single hydrogen atom.

Four of the hydrogen atoms form single hydrogen-bridge bonds between the four boron atoms at the base of the pyramid and each of these borons also is linked to a single hydrogen atom by a normal boron-hydrogen bond. The boron-boron bond distances range from 1.66 to 1.77 A. U., depending upon the position of the bond in the molecule; boron-hydrogen distances similarly range from 1.20 to 1.35 A. U., depending upon whether the hydrogen is bonded normally to one boron atom or is acting as a bridge between two atoms.

PHYSICAL PROPERTIES

Pentaborane, in a pure state, is a clear, water-white, low viscosity liquid. Impurities, such as dissolved polymeric boron hydrides formed from decomposition of other lower boron hydrides present in commercial grade B_5H_9 , will impart a slight yellow coloration to the liquid if present in concentrations greater than 0.5 percent by weight. These polymeric boron hydrides are discussed further in the Section on Stability. Pentaborane must be considered pyrophoric, although under certain conditions it has been exposed to the atmosphere without ignition.

Reactions of B_5H_9 with O_2 in air are many and cover a wide range of conditions and products formed. Detailed $B_5H_9-O_2$ reaction conditions will be given in the Section on Reactions.

Pentaborane must be transferred and handled in leak-tight vacuum systems using vacuum or inert gas for transferring. Transfer and handling systems will be discussed in the Section on Sampling and Analysis.

Pentaborane is extremely toxic in both the liquid and vapor state. Its characteristic pungent odor can be used to warn of its presence. However, reliance on odor detection is a dangerous practice since sensory adaptation quickly occurs. (Refer to the Section on Detection and Toxicity for details). If not properly decontaminated a spill will create a long-term toxicity problem, due to the relatively high boiling point and low vapor pressure of Pentaborane at atmospheric conditions. (For adequate decontamination procedures see the Section on Handling).

The physical properties of pentaborane currently available are summarized on the following page:

PROPERTIES OF PENTABORANE

		<u>Reference</u>
Molecular Formula	B ₅ H ₉	
Molecular Weight	63.17	
Boiling Point, 760mm	58.4°C	
Melting Point	-46.6°C	(2)
Density at 0°C	.638 gm/cc	(3)
Density at 20°C	.623 gm/cc	(3)
Index of Refraction n _D ²⁴	1.4445	(4)
Vapor Pressure at 0°C	65mm	(5)
Vapor Pressure at 20°C	174.5mm	(5)
Heat of Formation, gas, 25°C	15.0 Kcal/mole	(8)
Heat of Formation, liquid, 25°C	7.8 Kcal/mole	(8)
Free Energy, gas, 25°C	39.6 Kcal/mole	(8)
Free Energy, liquid, 25°C	38.8 Kcal/mole	(8)
Entropy, gas, 25°C	65.88 cal/deg mole	(8)
Entropy, liquid, 25°C	44.16 cal/deg mole	(8)
Heat Capacity, gas, 25°C	19.00 cal/deg mole	(8)
Heat Capacity, liquid, 25°C	35.8 cal/deg mole	(8)
Heat of Vaporization, 58°C, 760mm	7.7 Kcal/mole	(8)
Entropy of Vaporization, 58°C, 760mm	23.3 cal/deg mole	(8)
Heat of Fusion	1.466 Kcal/mole	
Heat of Combustion	1026.4 Kcal/mole	
Dipole Moment, Vapor	2.13 debyes	(6)
Dipole Moment, liquid, at 24°C	3.37 debyes	(4)
Dipole Moment, liquid, at -46.7°C	4.45 debyes	(4)

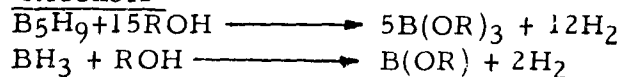
REACTIONS

Pentaborane reacts in a manner similar to that of diborane since it has the same empirical formula, B_5H_9 and the ability to liberate the reactive BH_3 group. However, for Pentaborane containing a boron structure which must be broken to liberate BH_3 groups, symmetrical cleavage requires more vigorous conditions with a greater possibility of destructive secondary reaction (12). In many of its reactions with hydrocarbons the borine group behaves like a very strong acid comparable to such materials as boron trifluoride and aluminum chloride (13).

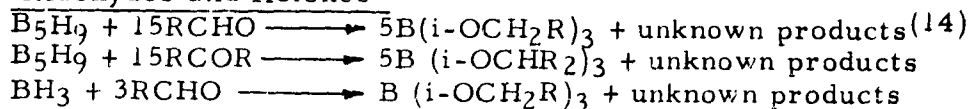
Some of the important reactions of Pentaborane are listed below. The analogous BH_3 group reactions are also listed.

REACTIONS

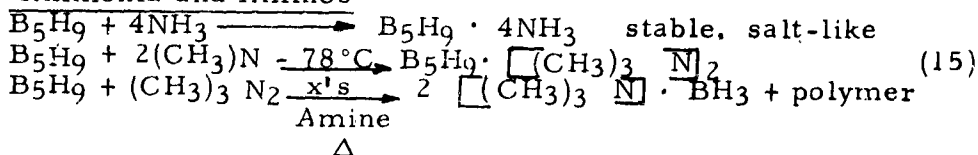
1. Alcohols



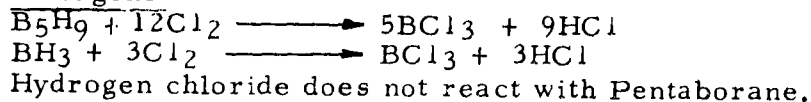
2. Aldehydes and Ketones



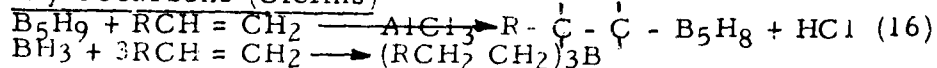
3. Ammonia and Amines



4. Halogens

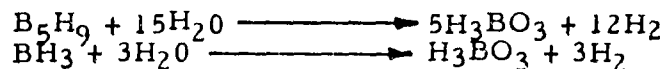


5. Hydrocarbons (Olefins)



Pentaborane can cause cross-linking and vulcanization of chloroprene and butadiene-acrylo-nitrile rubbers and possibly also butadiene-styrene and natural rubbers (13).

6. Water

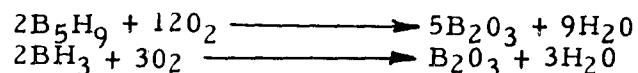


Reaction is slow since Pentaborane is immiscible with water. The addition of dioxane to the mixture greatly enhances the hydrolysis and a vigorous reaction occurs. At a concentration of 80 percent dioxane and 20 percent water the hydrolysis is complete in a few minutes at room temperature (17).

7. Oxygen

Under certain conditions Pentaborane will react explosively with oxygen. Our primary interests were Pentaborane reactions in air. Pentaborane-air flash point studies gave erratic results. However, these results did indicate that high humidity reduces the likelihood of an explosive reaction of Pentaborane-air.

The reaction of Pentaborane with Oxygen:



However, a number of complex products may form depending upon speed of mixing, system temperature and pressure, system wall conditions, and moisture.

For example, air slowly entering a partially evacuated Pentaborane system containing liquid Pentaborane may not cause ignition. Yet, intermediate oxidation products of variable branching are forming. These intermediate oxidation products may be of the form of unstable $\text{B}_4\text{H}_{12}\text{O}$. (18) An explosion may then result when the system pressure is changed causing a rapid breaking of the chain. We have found that these unstable Pentaborane-Oxygen products form at ambient as well as liquid nitrogen temperatures. They seem to be stable at the pressure at which they are formed; however, as the pressure is lowered an explosion occurs. Our system pressures both at ambient and liquid nitrogen temperatures approached 500mm when the explosions occurred. Further work on the Pentaborane-Oxygen reaction can be found in other literature. (19, 20)

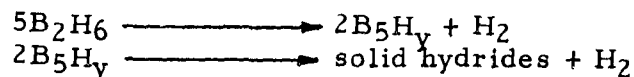
PREPARATION

Much work has been done in the preparation of boron hydrides. Stock⁽⁹⁾ reported the preparation and identification of B_4H_{10} , the first boron hydride definitely characterized. This was prepared

by the hydrolysis of reactive metal borides such as magnesium boride in acid solutions. However, poor yields were obtained. By 1924 Stock and his co-workers had prepared and identified all of the other presently known hydrides: B_2H_6 , B_5H_9 , B_5H_{11} , B_6H_{10} and $B_{10}H_{14}$. The first isolation of B_5H_9 by Stock (5) was made by chance, in tubes of B_4H_{10} which had been preserved for years. During this time another boron hydride in the B_4H_{10} had disintegrated and disappeared, allowing the separation of B_5H_9 .

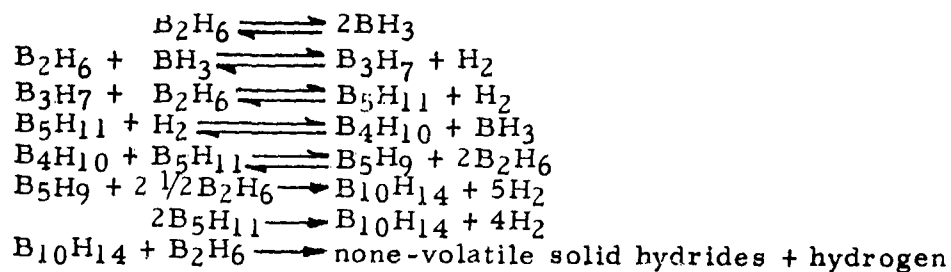
Schliesinger and Brown (10) prepared B_2H_6 , the present starting material for B_5H_9 preparation, by the reaction of boron trifluoride with lithium hydride in ether.

Owen (11) prepared B_5H_9 from B_2H_6 in a multi-stage reactor with good yields. A 12-unit reactor operating at 240 degrees C with a flow rate of 400cc/min, and a B_2H_6/H_2 ratio of 1/5 was used in the preparation. Under these conditions 57.0 percent B_2H_6 was converted into B_5H_9 , 14.1 percent solid hydrides, and 29.0 percent B_2H_6 recovered. The solids are formed by the following reactions:



The composition of the B_5 intermediate is dependent on temperature of the reactions. It is mainly B_5H_{11} at 170 degrees C and B_5H_9 at 230-280 degrees C.

The pyrolysis of B_2H_6 is summarized by Owen in the following equations:



From the above one can see that not only B_2H_6 , but B_4H_{10} and B_5H_{11} can be pyrolyzed to B_5H_9 , either alone or in conjunction with one or more other boron hydrides.

SAMPLING AND ANALYSIS

Pentaborane can be handled with no difficulty providing precautions are taken to eliminate all air and moisture contamination from systems. The systems must be leak-tight to prevent Pentaborane from leaking into the atmosphere and creating a dual problem of toxicity and fire hazard.

Sampling of 500 pound Pentaborane shipping cylinders has been accomplished with no difficulty using the sampler shown in Figure 6. Pentaborane is vacuum transferred from the shipping cylinder to sample cylinder. The system is purged with nitrogen prior to cylinder connection to displace the air. Evacuation then removes any traces of air or water vapor. The system is then vacuum leak-checked prior to each transfer thus eliminating the possibility of sample contamination. An alcohol scrubber-vacuum system, shown in Figure 7, is used to remove excess Pentaborane (2cc) in the transfer lines after transfer is complete. This scrubber system eliminates the possibility of atmospheric contamination since all the B_5H_9 reacts with the alcohol forming a stable alkoxyborane and hydrogen.

The sample cylinders are constructed of 316 series Stainless Steel and are manufactured by Hoke, Incorporated. They are low pressure cylinders of 30cc volume. The cylinder valve is a Hoke Model 1241 and was checked periodically for tightness. Personnel invariably tend to tighten valves too tightly, thus galling the needle valve or seat and allowing vapor to leak through the seat. Blunt stem valves were used since high velocity flow liquid transfer from sample cylinder to the reaction vessels was necessary, particularly for solids analysis.

Analysis of Pentaborane calls for the same precautions as sampling a clean, leak-tight system. The system with which all our analyses are done is pictured in Figure 8. A metal system is advantageous since any explosions will be contained. The valves eliminate use of stopcock lubricants which will continually absorb Pentaborane until they dissolve. The metal system can be easily dismantled and cleaned. Connection of any type of reactor or apparatus to the metal system is easily accomplished by using swageloks and polyethylene ferrules supplied by Swagelok, Incorporated. This makes the metal system very versatile. We have used it to determine freezing points, thermal stabilities, non-filterable solids, vapor pressure, density, solubility, compatibility and to make sample withdrawal for standards preparation. The related apparatus is shown in Figures 9, 10, 11 and 12. The metal system was designed such that liquid Pentaborane is transferred directly into the

test apparatus, thus eliminating any distillation step which would change the composition of the sample for analysis. Distillation can be accomplished after initial liquid transfer or, fraction samples may be taken by the use of the alternate system shown in Figure 3.

Analysis techniques for purity of B_5H_9 by freezing point method, thermal stability and non-filterable dissolved solids using the metal system have been reported^(2, 21, 22). Most of the transfers were accomplished under a partial vacuum equivalent to the vapor pressure of B_5H_9 at the transfer temperature (200mm at 20 degrees C). Nitrogen to 1 atmosphere was then introduced to prevent air from leaking into the system in event of leaks.

Vapor pressure studies were conducted using a mercury manometer in place of the compound gauge for more accurate determinations. A calibrated thermocouple in a temperature regulated circulating bath was used for obtaining temperature vs. pressure data. The mercury manometer was read using a cathotometer.

Density of commercial grade B_5H_9 was determined using the procedure described by Reaction Motors. ⁽²³⁾

Solubilities and compatibilities were determined similarly by weighing or measuring known amounts of sample, chilling the sample, removing air by vacuum and transferring a given amount of Pentaborane.

In case of liquid samples, a small magnetic stirrer in the vessel was used for agitation. Any reaction between the sample specimen and Pentaborane can be determined by visual inspection of the sample, system pressure rise, changes in a physical or chemical property of the specimen, and weight change.

Samples of Pentaborane were withdrawn for preparation of standard dilution mixtures by using the apparatus shown in Figure 12, and the following procedure:

A glass tube with a rubber diaphragm on the bottom covered with 2-5mm mercury was attached to the system and evacuated. Pentaborane was transferred to the tube and pressurized to 1 atmosphere with nitrogen. The pressurization is necessary since pricking of the rubber diaphragm with the needle will cause air to enter the system if it is under vacuum. The syringe was cleaned and filled with mercury to remove all air. The mercury was then removed until a small quantity was left in the needle and syringe. The needle was inserted into the tube, excess mercury removed and the required amount of Pentaborane was withdrawn. The needle tip was

lowered into the mercury and a small volume withdrawn into the needle to seal off Pentaborane from air during the needle removal. Excess Pentaborane and mercury were removed by displacing under alcohol. Dilute standards were prepared in double distilled, dried hydrocarbons for detector calibration. (see Section on Detection and Toxicity)

STABILITY

Pentaborane B_5H_9 can be considered as a stable, storable boron hydride when pure. Its decomposition at room temperature is slow and nearly negligible if the material is pure and not exposed to light. It is stable to 180 degrees C (24); however, above this temperature it decomposes to hydrogen, non-volatile solids and traces of decaborane. Norton (25) states that the order of stability of the boron hydrides is represented as follows: B_5H_9 greater than B_2H_6 by a factor of 100; B_2H_6 greater than B_5H_{11} by a factor of 10, B_5H_{11} greater than B_4H_{10} by a factor of 5.

Impurities such as B_2H_6 , B_4H_{10} and B_5H_{11} present in production of B_5H_9 will tend to decompose on storage forming other boron hydrides, including non-volatile polymeric boron hydride and hydrogen. However, the polymeric boron hydrides will not react with B_5H_9 as do some of the more volatile boron hydrides to form more solids and hydrogen. Since appreciable amounts of hydrogen are liberated upon decomposition of volatile boron hydrides, system pressures will increase. Excess pressure can be vented through a flare (see Section on Handling).

The formation of polymeric boron hydrides must be kept at a minimum since precipitation of these solids will tend to clog filters and valves during transfer. We have found that these non-volatile solids precipitate out at a concentration of 3 percent by weight at 110 degrees C and 1.3 percent by weight at 80 degrees C. The amount of solids found in series of samples is quite variable due to the original impurities present in the B_5H_9 and the temperatures to which the B_5H_9 has been exposed.

Dissolved solids in commercial grade Pentaborane have been found as high as 1.3 percent by weight (22). It is interesting to note

that the yellow coloration imparted to the liquid Pentaborane by the dissolved solid boron hydride polymers can be detected by eye when the concentration approaches 0.5 percent by weight. The solids formed during long-term storage of B_5H_9 contain on an average 14 percent by weight $B_{10}H_{14}$ with the remaining 86 percent non-volatile (150 degrees C, 10mm) boron hydrides. (22)

The $B_{10}H_{14}$ concentration in the non-volatile solids tended to increase as temperature was increased. The average $B_{10}H_{14}$ concentration in the non-volatile solids after a stability test of commercial Pentaborane for 3 hours at 90 degrees C was found to be greater than 25 percent by weight, indicating the reactions favor $B_{10}H_{14}$ formation at elevated temperatures (100 degrees C).

Hydrogen tends to inhibit decomposition of volatile boron hydrides. Decomposition of volatile boron hydrides in commercial grade B_5H_9 during thermal stability tests is rapid during the first hour at elevated temperatures (80-90 degrees C)⁽²¹⁾ (see Figure 14). The decomposition rate decreases considerably after this time. Hydrogen liberated during the initial decomposition steps appears to inhibit further decomposition.

The Pentaborane procured for storage was at least 99 mole percent pure. Pentaborane of this purity has been stored for periods of up to 3 years at -20 degrees F to +100 degrees F with no change (26). A check of solids increase was not made.

It is recommended that periodic checks by vacuum evaporation techniques of Pentaborane storage cylinder samples be made to determine any increase in non-volatile boron hydrides in the storage cylinders. When solubility limits of solids in Pentaborane are accurately determined, one will be able to determine the solids precipitation point in a storage cylinder.

If high ambient temperatures are anticipated it is advantageous to store cylinders in a sheltered area to keep cylinders cool and preclude the possibility of rapid decomposition occurring. If a sheltered area cannot be provided, a water spray on the cylinders will retard decomposition.

COMPATIBILITY AND SOLUBILITY

SOLUBILITY

In general, Pentaborane is soluble without reaction in inert hydrocarbon solvents as hexane, pentane, benzene, toluene, kerosene and petroleum base lubricants and greases which do not contain fatty acid salts.

Solvents with reactive carbonyl groups and highly halogenated or highly oxygenated solvents must not be employed for use with Pentaborane. Olin Mathieson Chemical Corporation⁽²⁶⁾ has found that these solutions are shock-sensitive. Solvents of this nature which definitely must not be used are carbon tetrachloride, aldehydes and ketones. Solutions of Pentaborane in hydrocarbon solvents must not exceed 5 percent at ambient temperatures. It has been our experience that Pentaborane in higher concentrations or at elevated temperatures in hydrocarbons will ignite in air.

Solubility studies were conducted by this laboratory on inert hydrocarbon solvents. We found that the solvents must be dried through a 2' X 1" activated silica gel column. If this precaution was not taken the small amount of dissolved water present in the solvents reacted with Pentaborane, forming fine, white precipitate, probably different forms of boric acids. It is also advisable to vacuum-distill the solvent to remove dissolved oxygen which will also react with Pentaborane to form solid oxides.

Distilled and dried toluene was used for standards preparation. Mixtures of up to 5 percent Pentaborane in toluene were prepared as described in the Section on Sampling and Analysis. The ullage space above the standards was rendered inert with dry nitrogen prior to storage. Toluene which had been vacuum-distilled only, gave white precipitate almost immediately after addition of 5 percent Pentaborane, indicating dissolved water was not removed. Solubility of gaseous nitrogen, hydrogen and helium in Pentaborane at temperatures of from 30-150 degrees C and pressures of from 500-1500 psig have been reported by Callery Chemical Company. This work has been done under Navy Contract No. a(s 58-454).⁽²⁷⁾

COMPATIBILITY

Much work has been done in the compatibility of solids and liquids with Pentaborane.⁽²⁶⁾⁽²⁸⁾ We have determined compatibility

of materials used in transfer and storage systems by the technique described in the Section on Sampling and Analysis.

Pentaborane is a strong reducing agent. Its reaction in terms of determining compatibility with materials are as follows:⁽²⁶⁾

1. Pentaborane will react with any organic compound containing a reducible functional group. The rate of reaction will depend on the type and concentration of functional groups.

2. Pentaborane will hydrolyze slowly in the presence of water to form boric acid and hydrogen. Any process material containing free or bound water will show some degree of reaction with Pentaborane.

3. Because of its strong reducing potential, Pentaborane will reduce some metal oxides and also precipitate some heavy metals from solutions of their salts.

4. Pentaborane is miscible with many inert organic compounds. In this respect it may cause failure of a process equipment component by extracting the inert material from a gasket or packing.

Many lubricants are compatible with Pentaborane as listed below. However, Pentaborane is soluble in these lubricants, thus creating a problem of disposal and cleaning of lubricated parts which have been used in Pentaborane service.

For example, silicon oil which has been in contact with Pentaborane for 24 hours flashed when removed from the reaction vessel. Despite the removal of Pentaborane by prolonged exposure to vacuum, a flash still occurred. This emphasizes the difficulty of removal of Pentaborane from lubricants. The silicon oil had not changed in its structure as substantiated by Infra-red analysis. Cleaning and disposal of Pentaborane contaminated materials is summarized in the Section on Handling.

Most metals appear to be compatible with Pentaborane. However, oxides of the metals which may form from surface action with water or oxygen will react with Pentaborane.

Many of the elastomers are not compatible with Pentaborane due to their reactive functional groups. The dissolution of the plasticizer will cause the elastomers to become brittle.

Material Compatibility

The following is a list of more common materials and lubricants found to be compatible with Pentaborane. Further compatibility data has been published:

Asbestos, Dry	Silicone Grease
Asbestos, Graphite-Impregnated	Teflon
Fluoroflex T	Viton, Viton A
Fluorosilicon Rubber	Aluminum, Anodized
Glyptal Sealant	Foil; 17S-T; 24S-T
Halocarbon 4-11 V Oil	Brass
Pure Hydrocarbon Lubricants and Greases	Copper
Hycar	Glass
Kel-F Number 550	Monel
Molybdenum Disulfide	Nichrome
Polyethylene	Steel, Mild and Stainless
Polystyrene	Iron and Titanium Alloy

The following have been found incompatible with Pentaborane:

Geon Plastic					
Mylar					
Nylon					
Plexiglas					
Rubber,	Buna	Butyl	GR-S	Natural	
	Neoprene	Silicone	Thiokol		
Saran					
Tygon					

HANDLING

DECONTAMINATION

Decontamination of laboratory equipment used in Pentaborane handling is necessary due to the toxicity of boron hydrides.

The maximum average atmospheric concentration to which humans may be exposed to Pentaborane for an 8-hour working day is tentatively set at 0.005ppm.⁽²⁹⁾ However, decaborane and polymeric boron hydrides vapors are generally encountered in cleaning borane systems. Decaborane MAC has been set at 0.05 ppm for an 8-hour day. Therefore, materials used in Pentaborane service must be thoroughly decontaminated before removal from Pentaborane work area. Long-Term exposure may result if spatulas, glassware, protective equipment and other materials contaminated with boron hydrides are allowed to accumulate in open laboratory areas.

All items used in Borane handling and/or analysis, must be completely decontaminated after use. A 3 percent NH_4OH solution is good; however, it reacts slowly with the solid boron hydrides which are generally found on lab equipment after borane contact. An alcohol rinse of articles is more advantageous since it will react with all boron hydrides rapidly. The alcohol rinse can be followed by the 3 percent NH_4OH , then a final alcohol rinse will remove the water. All liquids used for decontamination purposes must be dumped into a prescribed sink and washed away with copious amounts of water.

Alcohol has been useful in decontaminating lab systems since it readily reacts with all boranes to liberate hydrogen and form alkoxyboranes which are soluble in excess alcohol or water. It will also dissolve boron hydride oxidation products which will form when air is allowed in contact with them. The contaminated material is immersed in alcohol or an alcohol-water solution, and any gas evolution indicating boron hydride-alcohol reaction, is observed. As long as gas is evolved, boron hydrides are present on the material. After evolution ceases the material is removed, rinsed with clean alcohol and allowed to dry. If the material is to be used in a vacuum system it should be placed in a 50 degree C vacuum oven to remove traces of alcohol.

Boron hydrides will be absorbed by materials such as seal assemblies, packing, greases, etc.; therefore, these materials must be decontaminated prior to use in open areas. Immersion in a 50-50-alcohol-water solution will completely react all the boron hydrides. When gas evolution ceases, all the boron hydrides can be assumed to have reacted. Further wash with alcohol will remove traces of alkoxyboranes which may have deposited on the materials.

It has been found that a hasty washing of contaminated skin with soap and water will not remove all the absorbed boranes. A thorough washing with soap and water is necessary. An ammonium hydroxide solution wash, followed by soap and water, appears to be effective. A water soluble ammoniated soap can be used for washing. Alcohol rinse and a soap wash will also remove boron hydrides.

SCRUBBER SYSTEMS

Alcohol scrubber systems, together with water aspirators and vacuum pumps, have been used in this laboratory for Pentaborane removal and disposal. (see Figures 7, 15)

The volume of alcohol to Pentaborane for complete reaction is 10 to 1. The reaction readily evolves hydrogen and can be controlled by the Pentaborane disposal rate. Pentaborane vapor is evaporated through the scrubber system to prevent excess gas evolution. The alkoxyborane formed is dumped down a drain with a water wash when the alcohol-Pentaborane ratio approaches 10 to 1. The hydrogen is removed through the aspirator, thus eliminating the possibility of hydrogen ignition.

Silica gel scrubbers have been used in Pentaborane systems and have worked well. However, as in alcohol scrubbers, care must be taken not to saturate the scrubbers. Limits of scrubber efficiencies must be established and a log of the amount of Pentaborane disposed through the scrubber must be kept. In the case of silica gel scrubbers, saturation will allow Pentaborane to be transferred directly into the vacuum pump and will ignite at the exhaust outlet. Contamination and toxicity problems also arise if this occurs.

The alcohol scrubber system is advantageous since all the Pentaborane is disposed of by reaction. Also, with knowledge of the volume of Pentaborane disposed of, one can easily determine the change time for the alcohol.

Dilution of the scrubber alcohol with an equal amount of water will reduce the possibility of scrubber ignition in the event of system failure.

DISPOSAL AND CLEANING

Large scale disposal of Pentaborane can readily be accomplished by the use of a flare as a propane torch or a kerosene dump pit. The propane torch is considered favorable for use since all the boron hydrides are burned, thus eliminating the possibility of atmospheric contaminations. However, a flame arrestor and nitrogen gas purge must be used to prevent backflash.

The kerosene dump pit is useful since all the volatile boron hydrides are readily soluble in the organic solvent. The total amount of boron hydrides added should not exceed 5 percent by weight of boron hydrides in a hydrocarbon since the mixture will become pyrophoric in air somewhat above this concentration. The hydrocarbon mixture must be burned immediately after use since the dissolved boron hydrides exhibit a substantial vapor pressure on a warm day and will contaminate the area downwind of the burn pit. Another procedure used for cleaning contaminated boron hydride systems consists of flushing with kerosene, followed by a mixture of 80 percent CH_2Cl_2 -20 percent alcohol. The methylene chloride dissolves remaining kerosene while the alcohol reacts with remaining polymers and dissolves boron oxides for easy removal. The system pressure must be continually monitored to observe pressure rises due to heat and hydrogen evolution. As soon as the system pressure remains constant the boron hydrides can be assumed to have completely reacted. This mixture is then removed by an ambient temperature nitrogen purge, followed by pre-heated nitrogen to remove all traces of liquids. Steam, followed by an alcohol flush and nitrogen purge may also be used.

The cleaning liquids must be dumped into a burn pit removed from the general area. A steady nitrogen purge must be maintained on the transfer line from the system to the burn pit. The pit should contain kerosene or other organic solvents which will dissolve any unreacted boron hydrides. The contaminated solvents are then burned to complete the disposal.

The Olin Mathieson Chemical Corporation Technical Bulletin-LF 202 has further procedures for decontamination of boron hydrides systems.

All liquids or gases which have been used in decontaminating, flushing, disposal and purging of boron hydride systems must be treated as toxic until they are disposed of by burning.

SPILLAGE

A satisfactory procedure for handling Pentaborane spills is reported by OMCC.⁽²⁶⁾ In essence, the spill is soaked with kerosene to decrease the possibility of spontaneous ignition and then reacted with a 10 percent aqueous alcohol solution or 10-30 percent aqueous solution of sodium hydroxide. The reaction products are then flushed away with large quantities of water. Adequate ventilation is necessary when destroying spillages and all sources of ignition must be avoided. A final treatment of the area with 5 percent aqueous ammonia solution containing a good detergent and followed by a water wash will completely decontaminate the area.

Adequate respiratory safety equipment must be worn when decontamination of spills is conducted. In cases of relatively large spills, self-contained respiratory equipment must be worn since cannister type equipment is not efficient under conditions where the oxygen content in the immediate vicinity is less than 16 percent.

In case of spillage ignition, the area should be deluged with water. The water will not extinguish the fire but is of value in cooling surrounding equipment and facilities.

In conclusion, the best way to decontaminate a spill area is ignition of the Pentaborane. However, if heat and flame should endanger equipment the procedure described above using kerosene is recommended. Following the fire the area must be treated with an aqueous ammonia solution before allowing personnel to return to the area.

All protective clothing which has been used in field boron hydride systems must be physically removed from areas where personnel frequent. A well ventilated room with decontamination facilities is recommended.

A periodic check of protective equipment with a borane detector will reveal any contamination. If contamination is detected the equipment must immediately be decontaminated - a 3 percent aqueous ammonia solution is good for this purpose.

DETECTION

Since Pentaborane is a highly toxic compound it is imperative that low concentrations of this material in air be detected and quantitatively measured.

The laboratory method which has proven most successful is a combination freeze-out and colorimetric method developed by Rocketdyne, a Division of North American Aviation, Incorporated. (32) This method utilizes a U-tube trap 15 to 20 inches long and 1 inch in diameter packed $\frac{1}{3}$ full with n-heptane wetted glass helices. The trap is immersed in a -80 degrees C cold bath and a calibrated flow of air is drawn through the U-tube. It has been determined in this laboratory that 100 percent of the Pentaborane will be trapped and retained at flow rates as high as 15 liters per minute and in concentrations from 0.01ppm to 1500ppm. The resulting n-heptane-Pentaborane mixture is warmed to room temperature and 5cc of a 10 percent pyridine in toluene mixture is added. The intensity of the color developed is measured on a standard colorimeter at 400m μ . If high concentrations of Pentaborane are suspected, then aliquots of the n-heptane-Pentaborane mixture are taken prior to addition of the color developing mixture. The range of the colorimeter adequately covers 0.1 to 12ppm total Pentaborane in 25cc of heptane-Pentaborane-pyridine mixture. Analyses of very low levels of Pentaborane in air are obtained by passing large volumes of air through the U-tube trap to obtain the proper amount of Pentaborane.

Several commercial instruments have been developed to detect Pentaborane in air. All of these instruments are extremely limited in range (0.01 to 10 ppm) unless the air stream can be diluted with pure air prior to admission to the instrument.

The Mine Safety Appliances Company has developed three instruments for boron hydride detection:

1. A portable hand pump type (Part No. MSA 82100) aspirates air through a specially treated filter paper. The boron hydride concentration is obtained by comparing the colored complex formed on the paper with a standard color chart.

2. An instrument which performs a continuous coulometric titration of reducing agents in the air aspirated through the titration vessel is also available from MSA as Part No. 82600. The current flow between the two platinum electrodes is recorded continuously and is proportional to the amount of reducing agent in the air stream.

3. Mine Safety Appliance Co., has developed a detector under AF Contract 04(611)-3738. This detector has been made to be specific for Pentaborane by proper choice of reagents to be added to the pyrolyzed incoming Pentaborane-air stream to produce a fine particle smoke in the ionization chamber. The amount of reduction in ion drift current is proportional to Pentaborane concentration in air up to 0.2ppm on low range and 6 to 8ppm on high range. This instrument is adaptable to almost all toxic gases and vapors with the proper choice of particulate producing reagents and the removal of the pyrolyzer tube which is required only to convert the boron hydrides to boron oxides prior to addition of the reagent.

The Olin Mathieson Chemical Corporation developed a Boranes-in-Air (Demon type) detector. Reducing or oxidizing agents in an air stream are detected by a specially treated electrolytic cell and the potential difference between this sample cell and a reference cell is displayed on a microammeter. This instrument operates over three ranges: 0-.04, 0-4 and 0-40ppm Pentaborane full scale. Its usefulness, however, is reduced due to excessive zero drift and a long recovery time. It is not specific for Pentaborane and responds to cigarette smoke, ammonia, carbon monoxide and hydrazine.

American Systems Incorporated is producing a fuel detector which incorporates a coulometric titrator to measure reducing agents drawn through the titration cell. The operating principle of this instrument should apply to the detection of Pentaborane in air over a broad range of conditions.

All of these instruments have been or are being evaluated in this laboratory for use in low level detection of Pentaborane in air.

CONCLUSIONS

The density, vapor pressure and freezing point of pentaborane -9 may all be determined in the quality control laboratory with one basic transfer apparatus and test vessels of 1-5 milliliter volume.

These physical properties plus a determination of dissolved and total solids are sufficient to certify that the pentaborane is suitable for use in a rocket engine.

Observations of cylinder storage pressure changes and visual inspection for yellow color changes are useful criteria for determining the degree of decomposition during storage.

The purity of pentaborane may be determined to ± 0.1 mole percent using the freezing point depression technique and the apparatus described. The dissolved solids present may be determined to ± 2.0 percent of the amount present within the range 0.1 to 3.0 weight percent. Proximate analyses for decaborane ($B_{10}H_{14}$), boron hydrides polymer and boron oxides may be made conveniently by using the sample obtained from the dissolved solids determination.

The best method found to decontaminate entire missile systems after use with pentaborane is to flush with a hydrocarbon solvent such as a kerosene to remove most of the material, followed by a flush with a mixture containing 80 percent methylene chloride and 20 percent ethyl alcohol and purge dry with gaseous nitrogen.

The most specific and accurate method for the determination of pentaborane concentration in air has been devised by Rocketdyne. This volumetric colorimetric method is accurate to at least 10 percent of the amount of pentaborane present in a range from 0.01 ppm to 1500 ppm in air.

APPENDIX I

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ILLUSTRATIONS

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FIGURE 1
DENSITY vs TEMPERATURE
(Ref. 3)

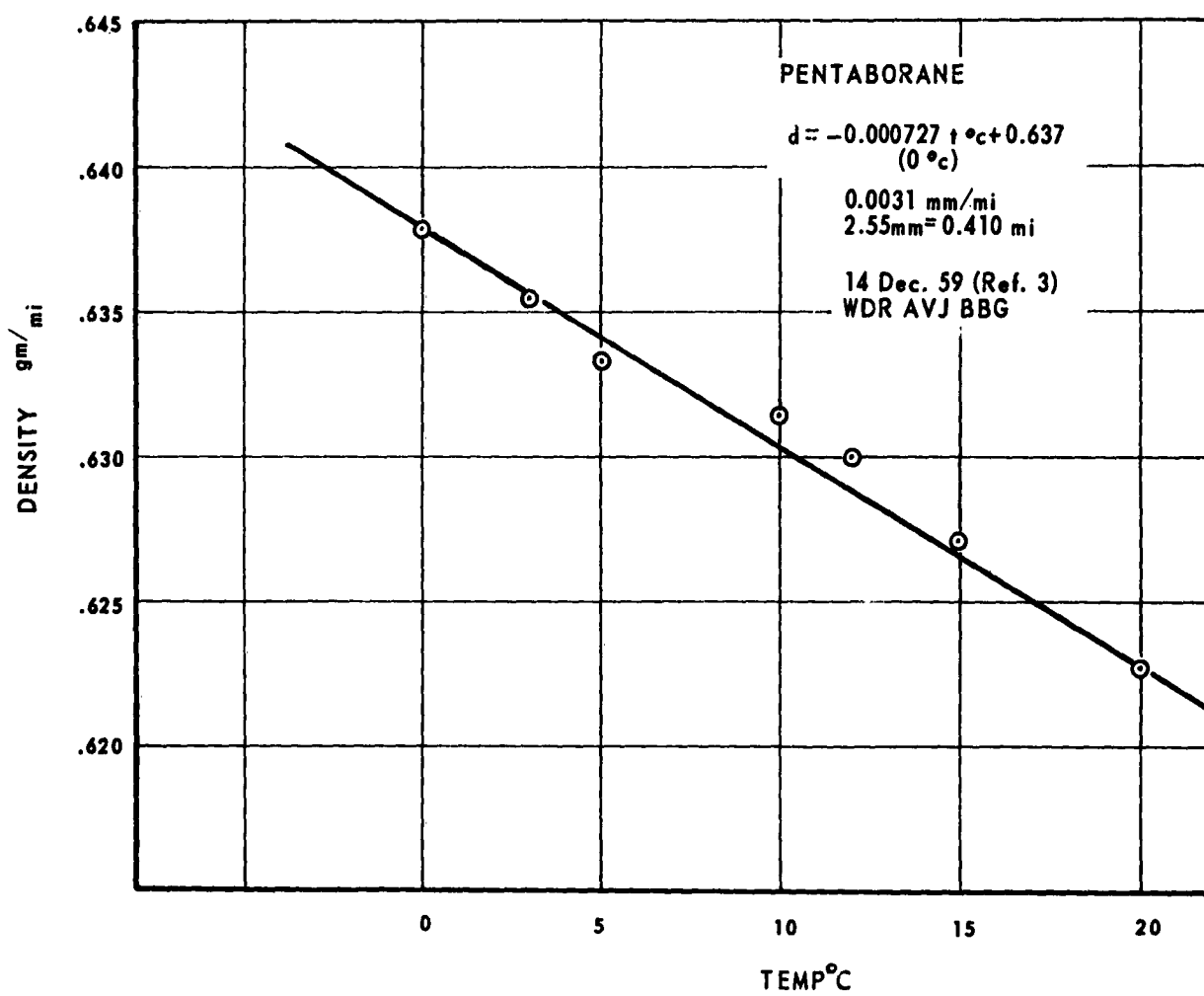


FIGURE 2
DIELECTRIC CONSTANT
vs TEMPERATURE (Ref. 4)

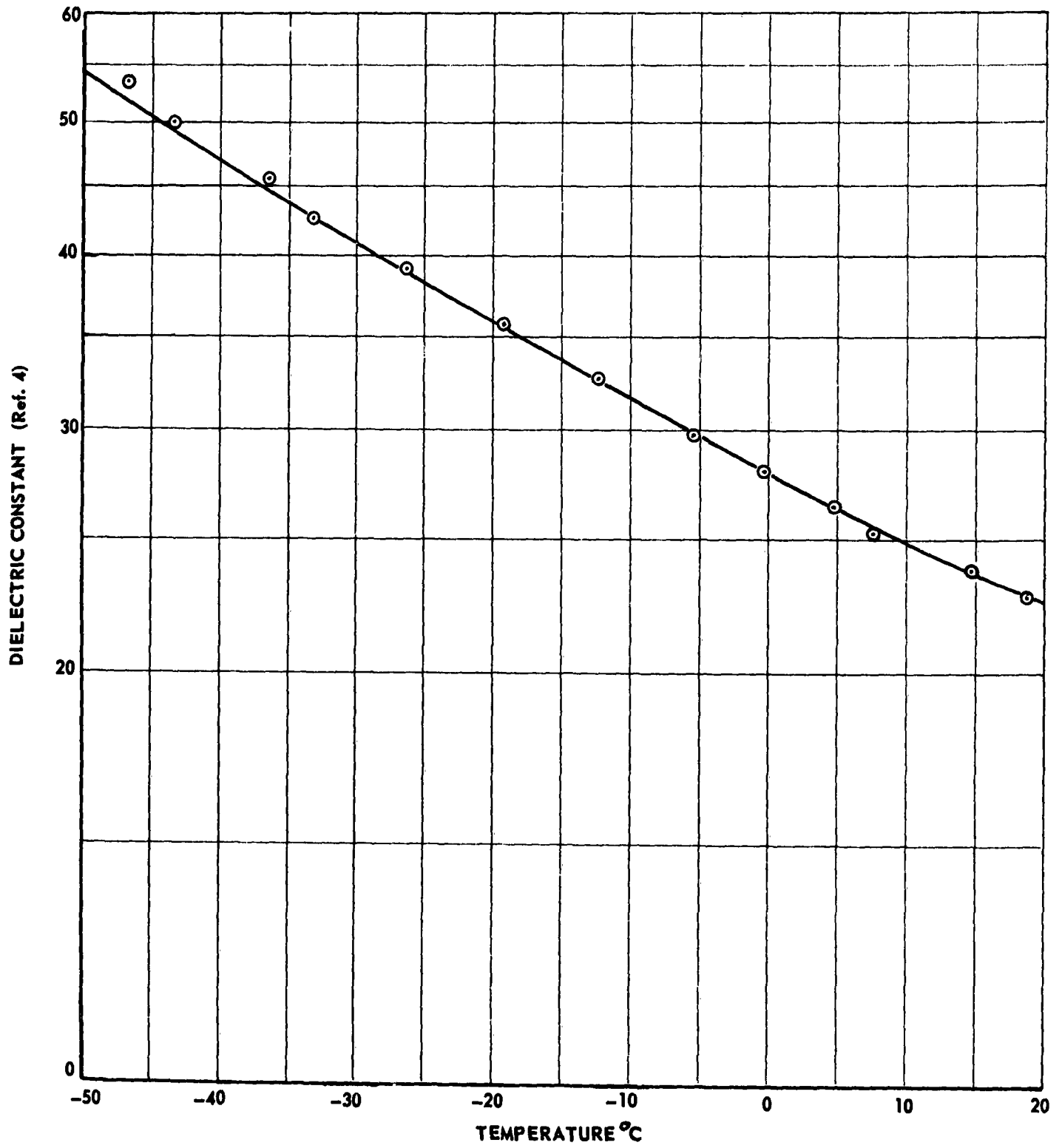


FIGURE 3
SURFACE TENSION
vs TEMPERATURE (Ref. 7)

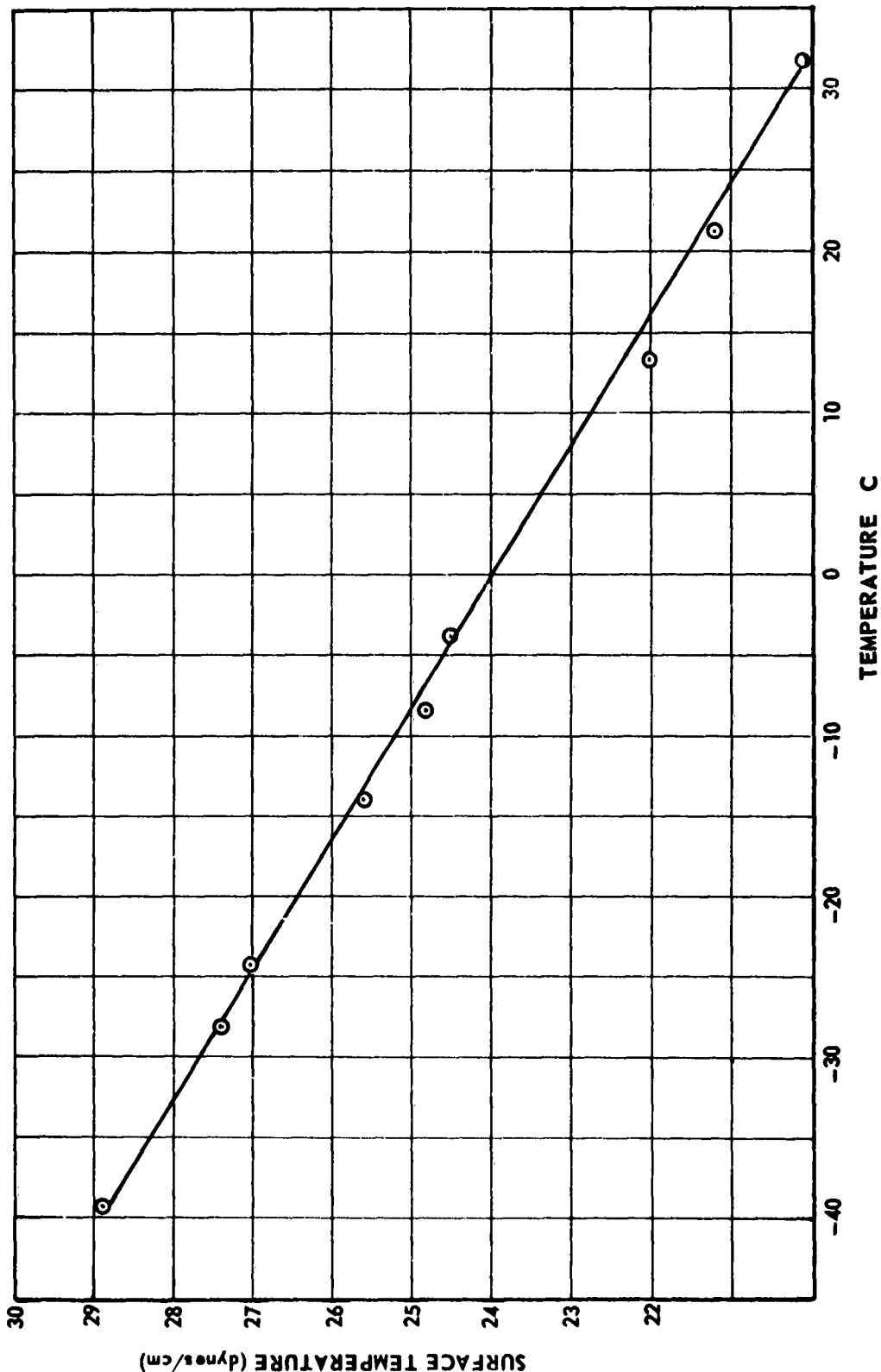
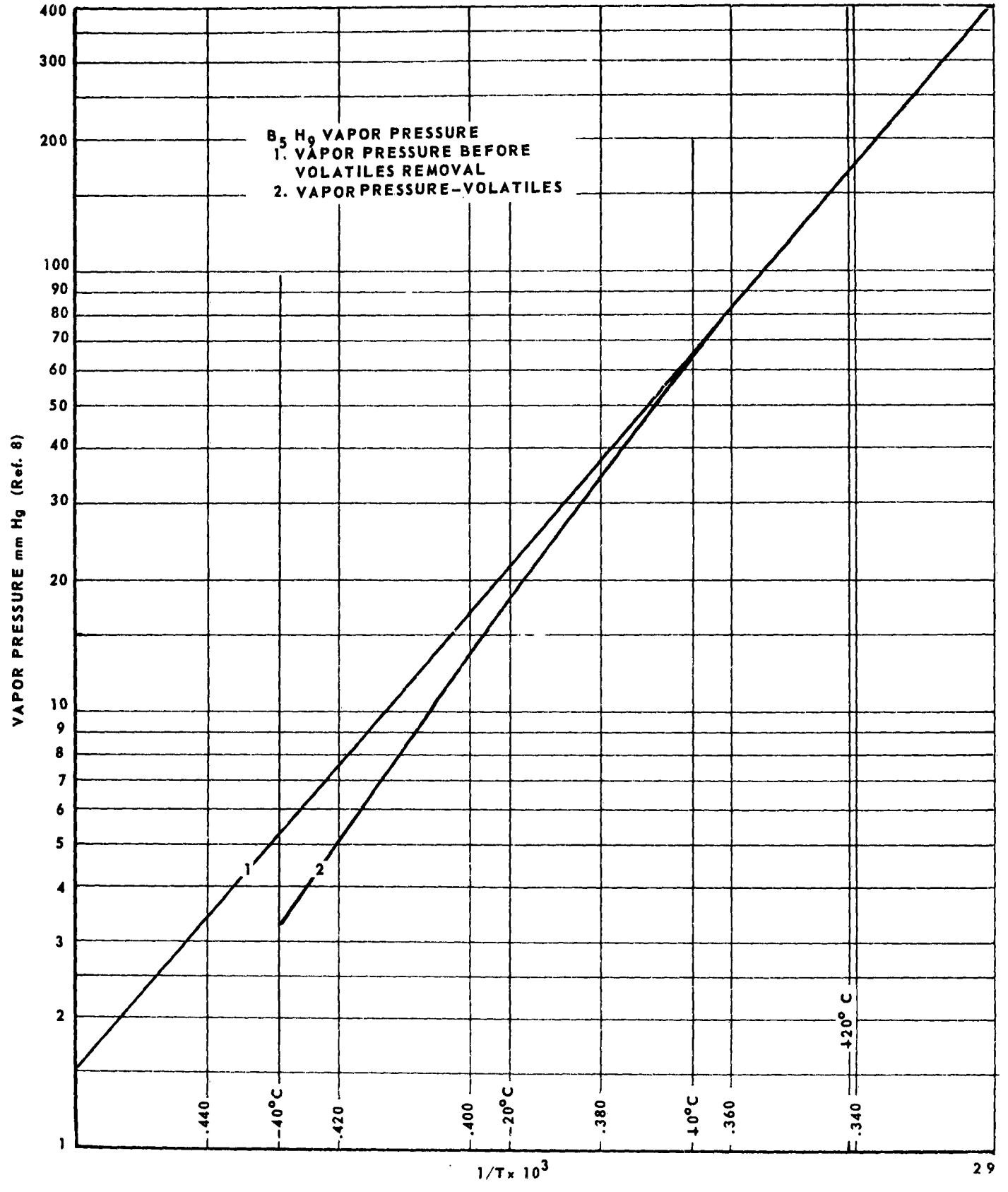


FIGURE 4
VAPOR PRESSURE
vs TEMPERATURE (Ref. 8)



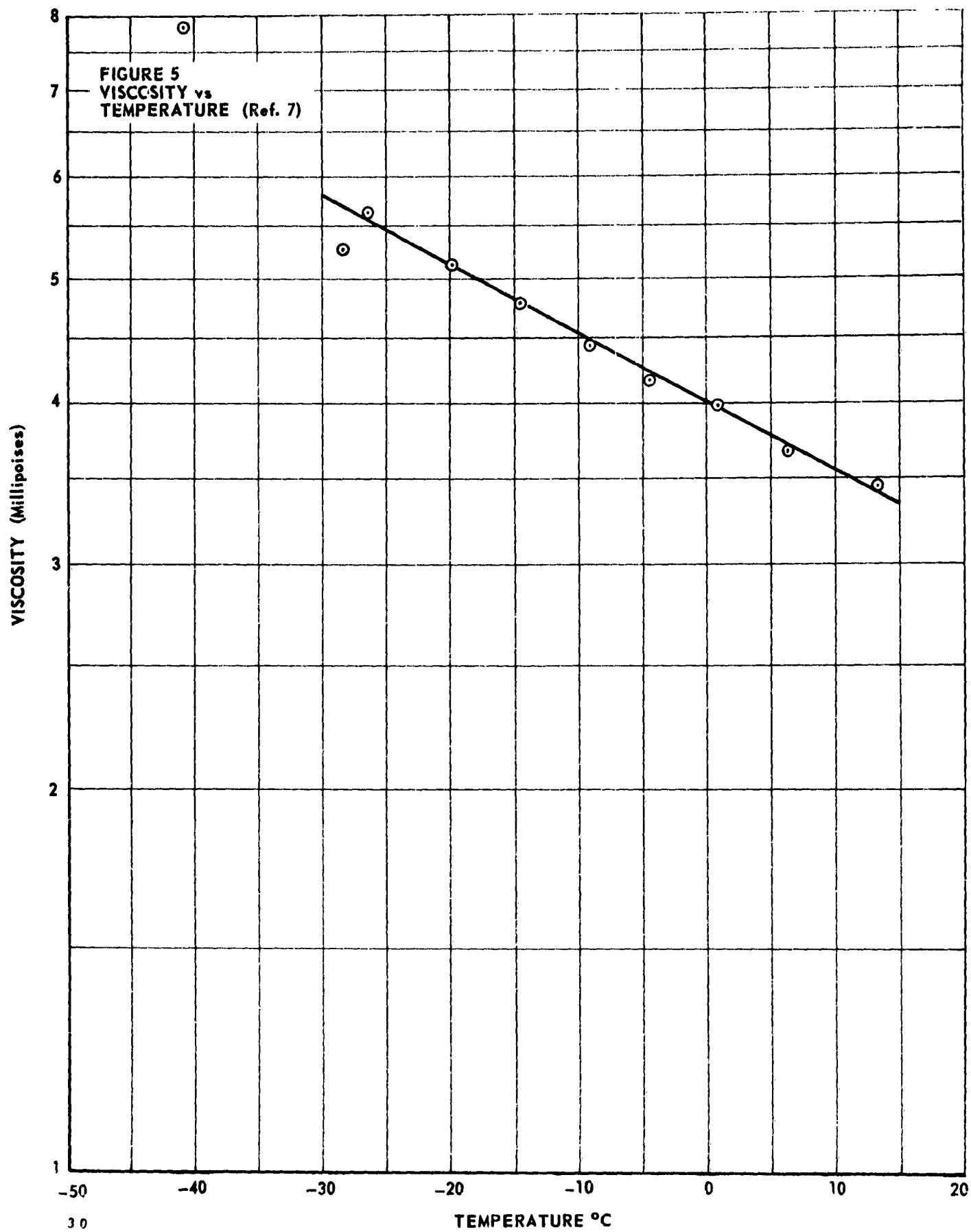
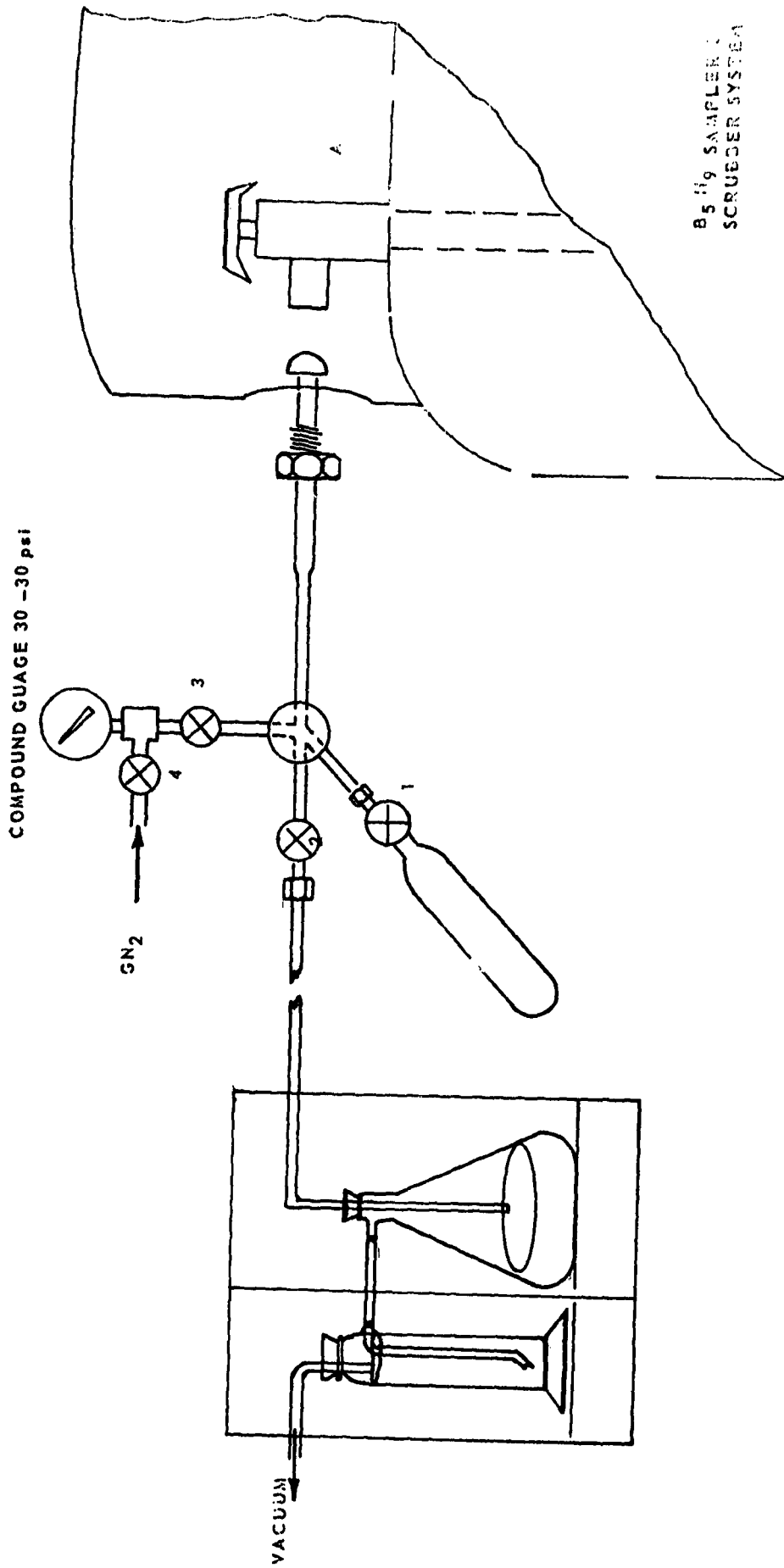
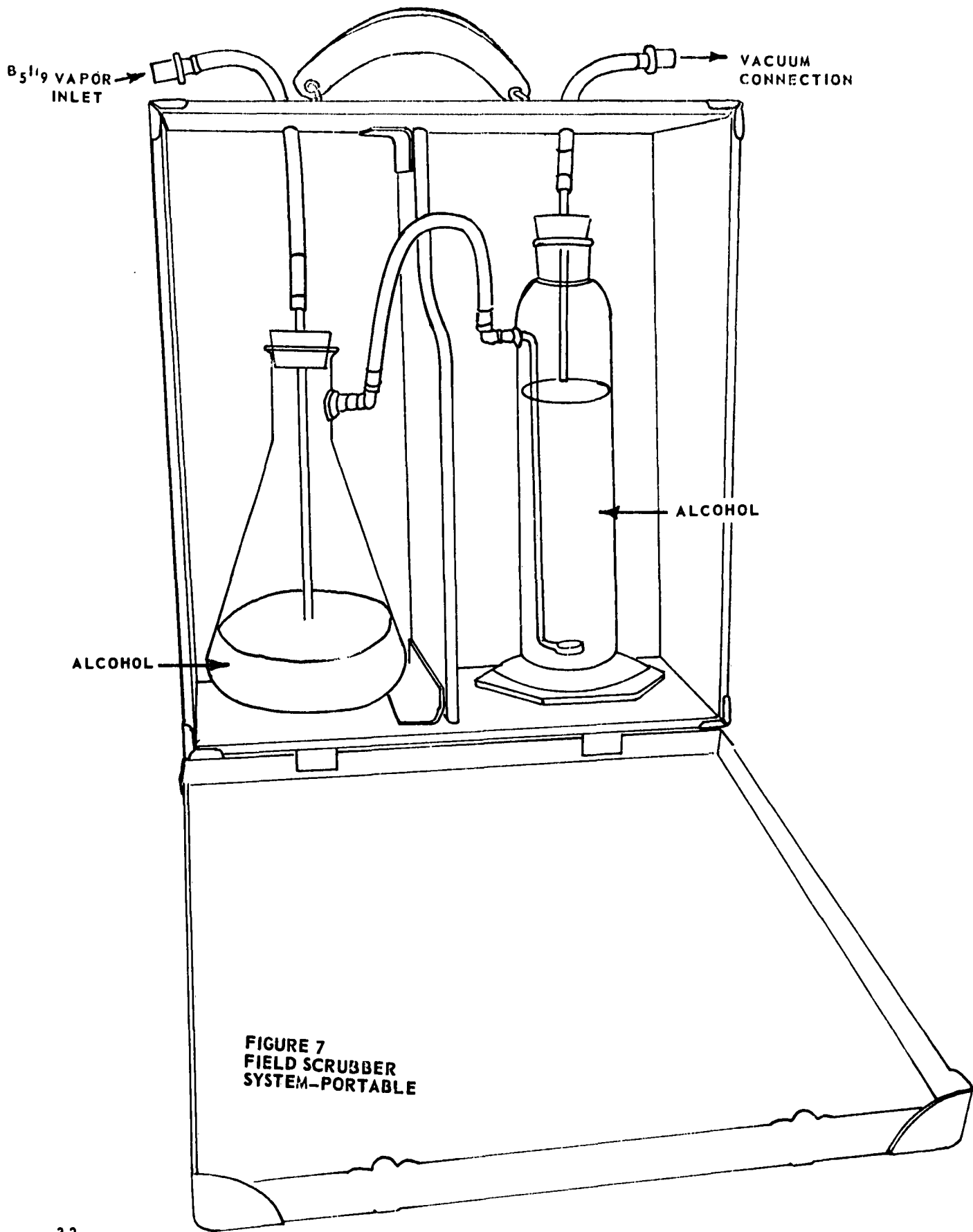


FIGURE 6
FIELD SAMPLER &
SCRUBBER SYSTEM





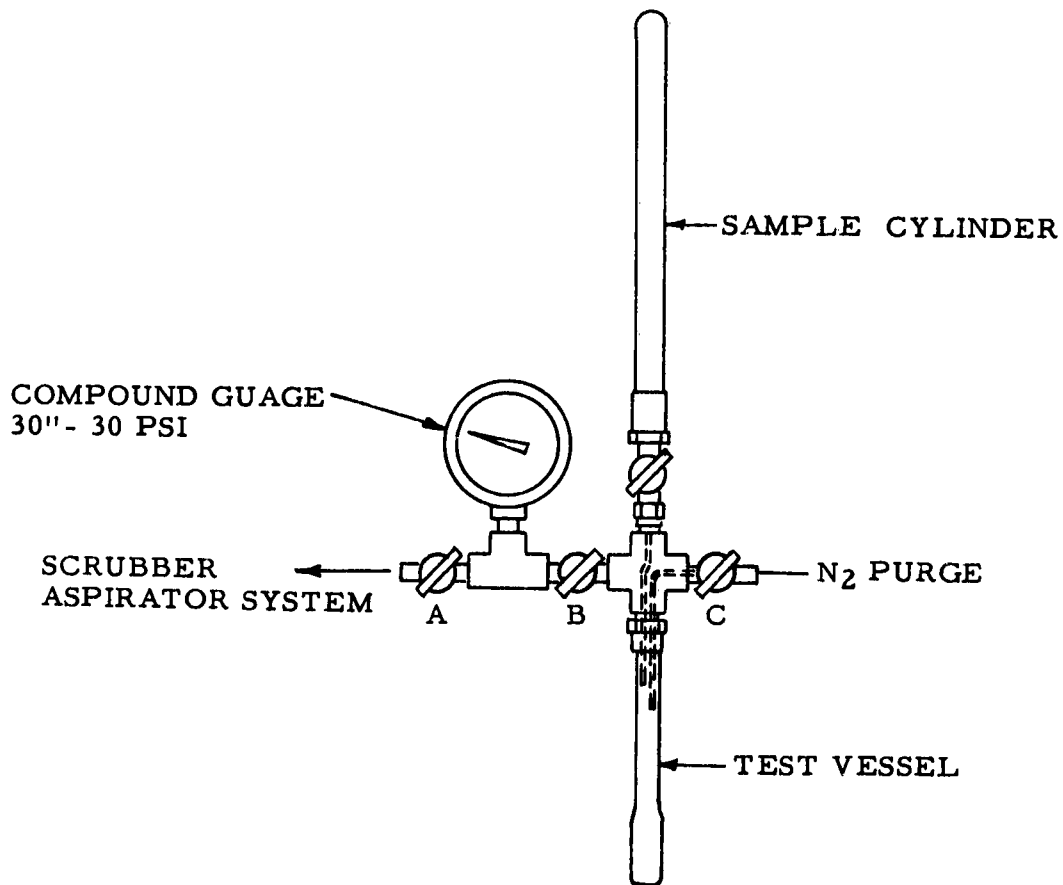


FIGURE 8
METAL VACUUM SYSTEM
W/ATTACHER TEST VESSEL

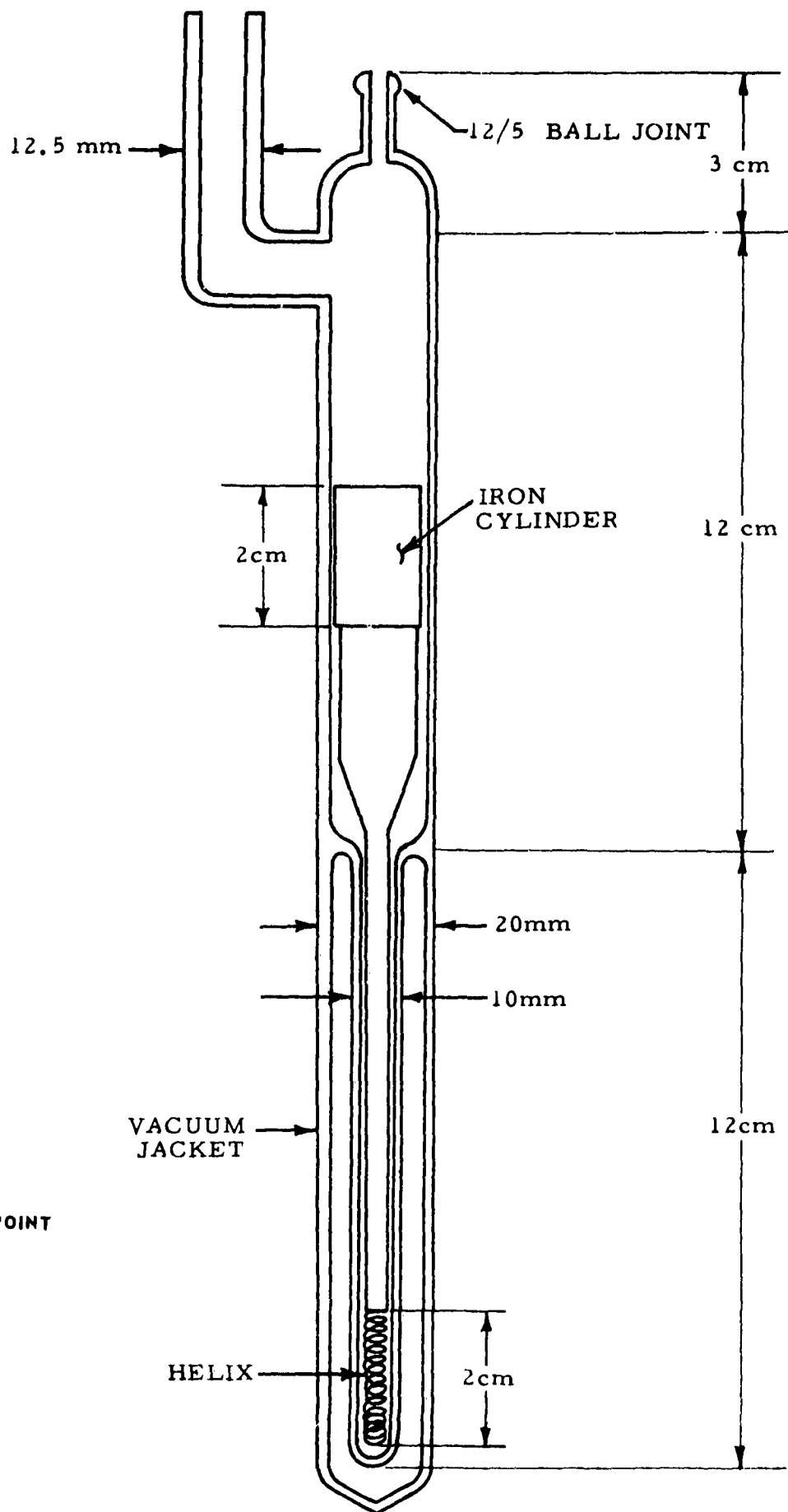


FIGURE 9
FREEZING POINT
APPARATUS

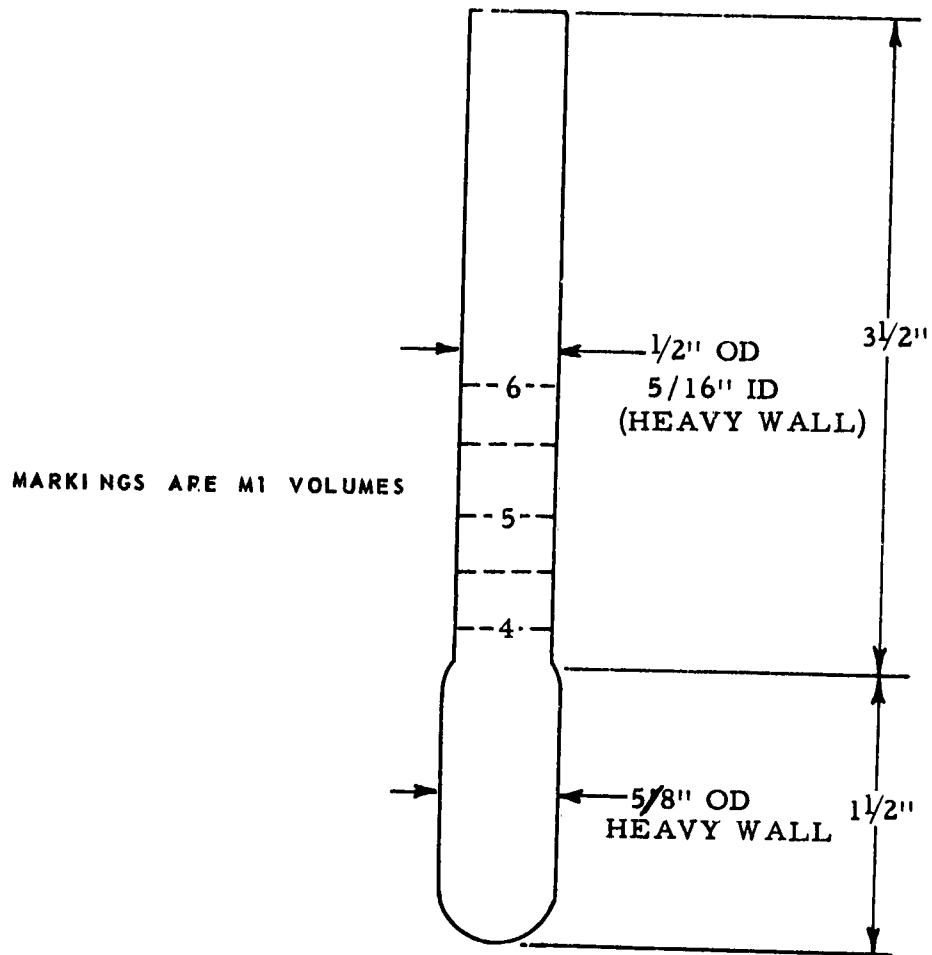
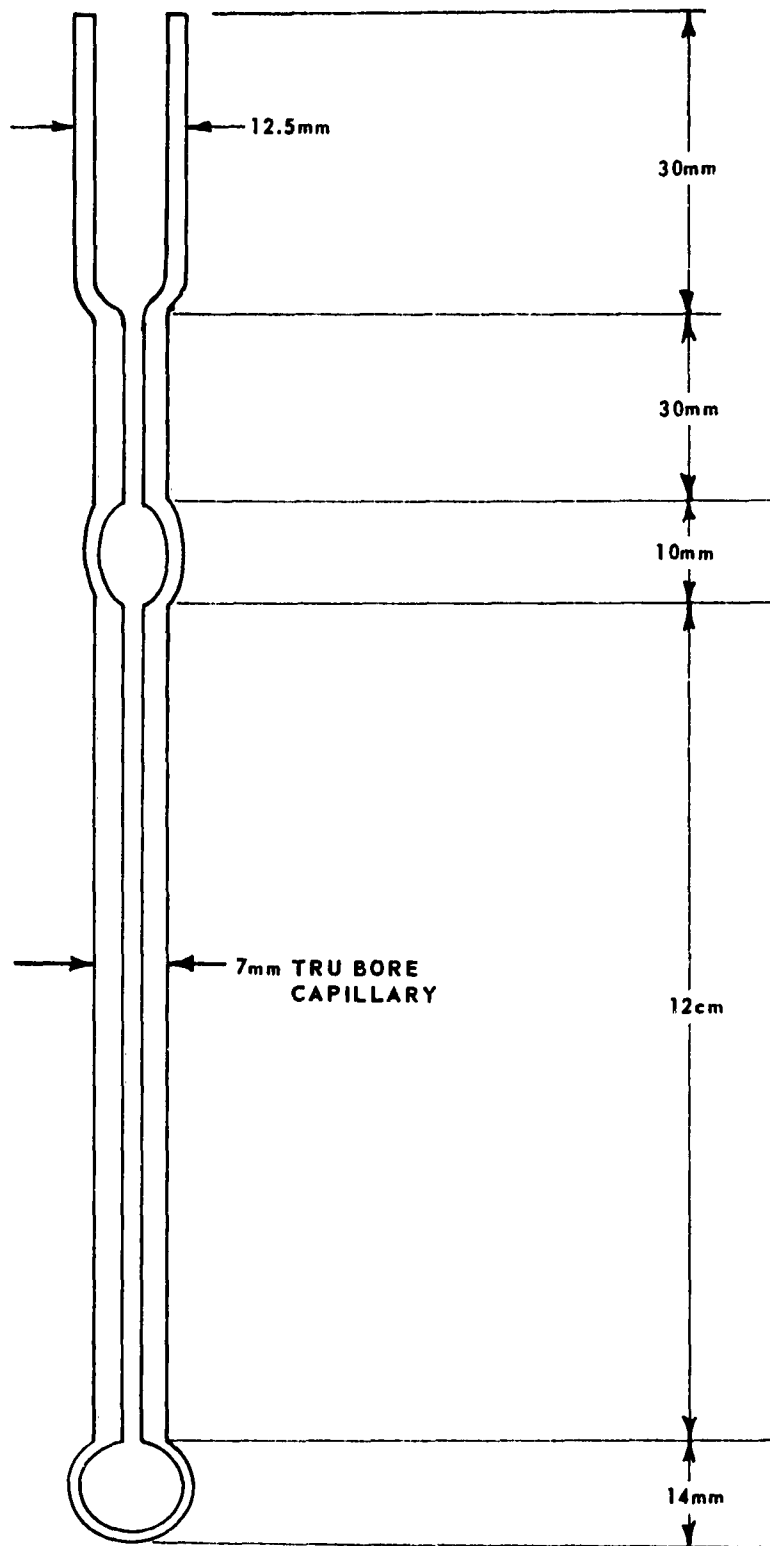
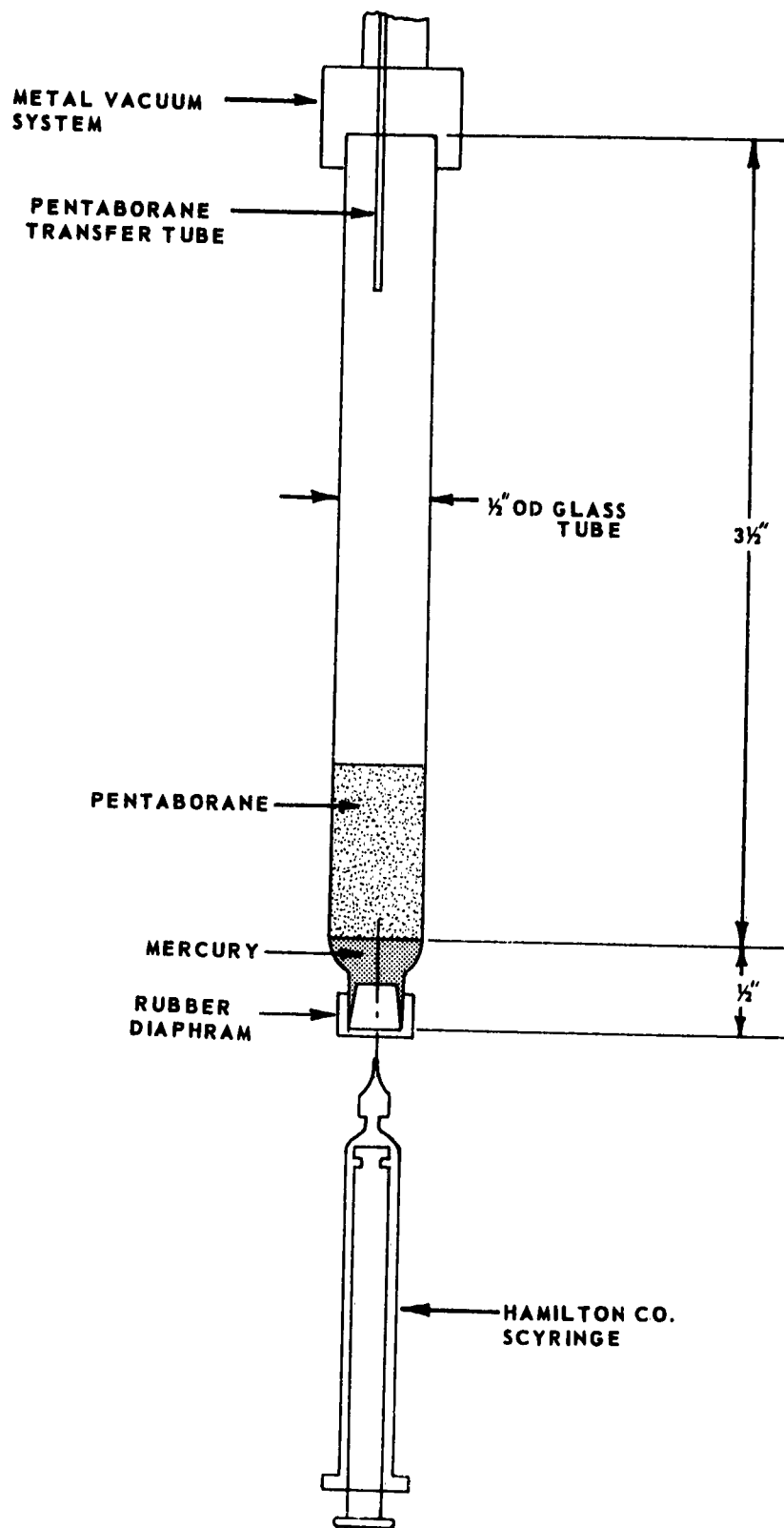


FIGURE 10
UNIVERSAL TEST
VESSEL

**FIGURE 11
PYCNOMETER TUBE
DENSITY DETERMINATION**



**FIGURE 12
LIQUID SAMPLE
EXTRACTION**



**FIGURE 13
METAL VACUUM SYSTEM
MODIFIED FOR LIQUID
& GAS SAMPLING**

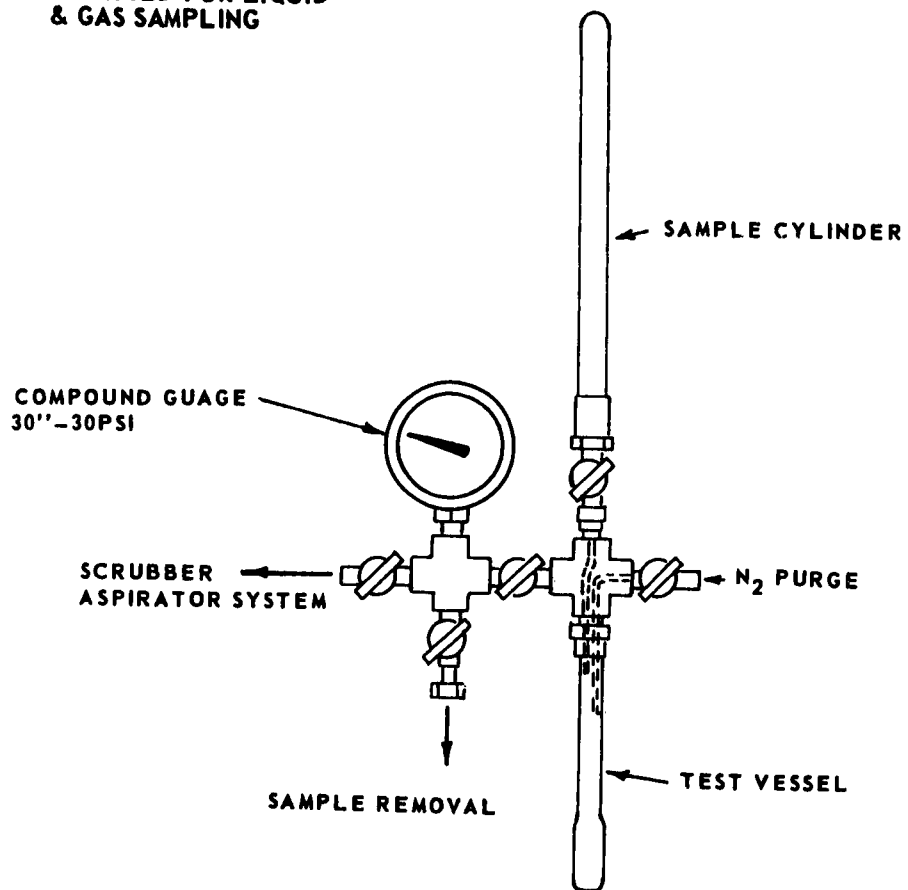
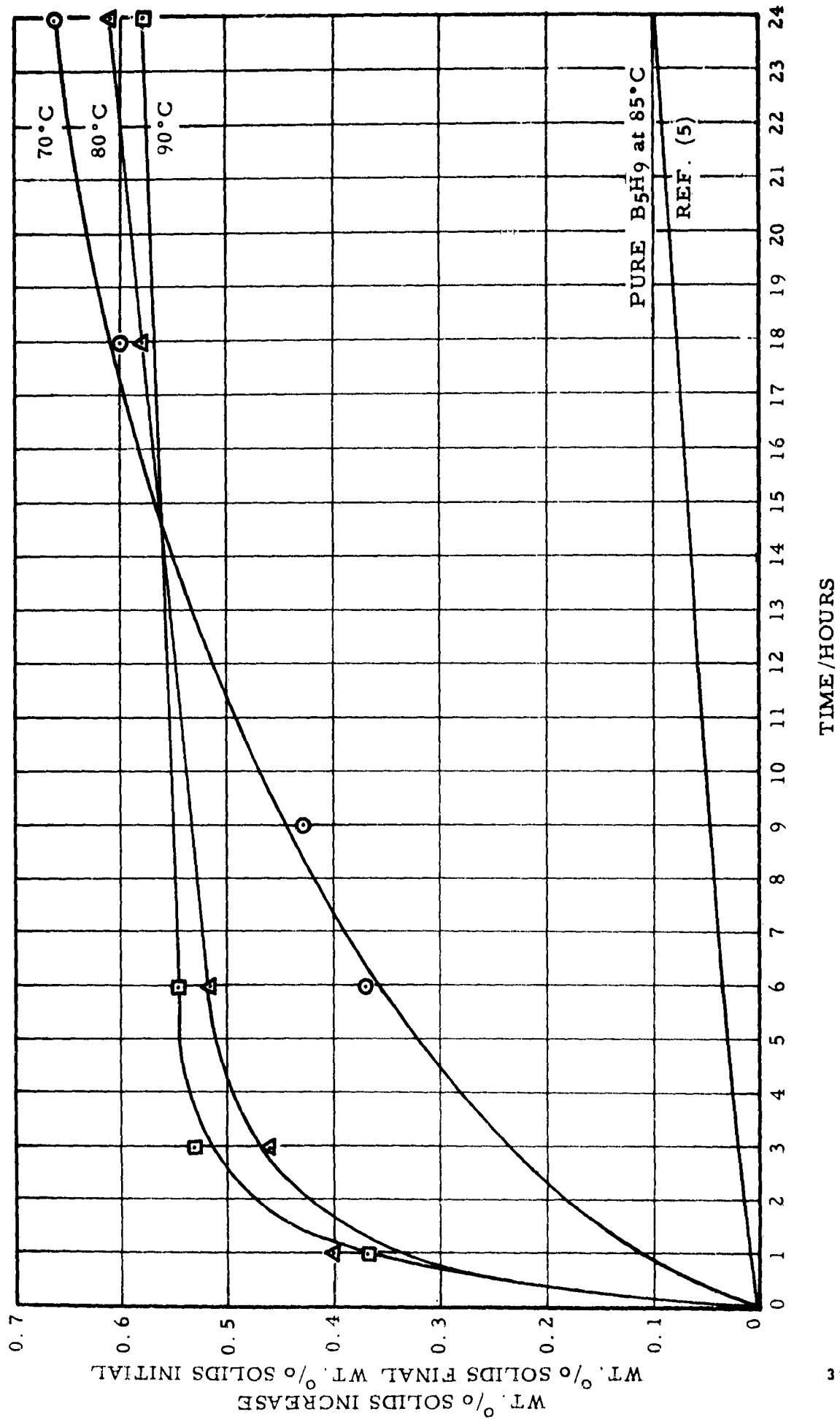


FIGURE 14
 SOLIDS INCREASE IN B₅H₉ AT
 ELEVATED TEMPERATURES vs TIME



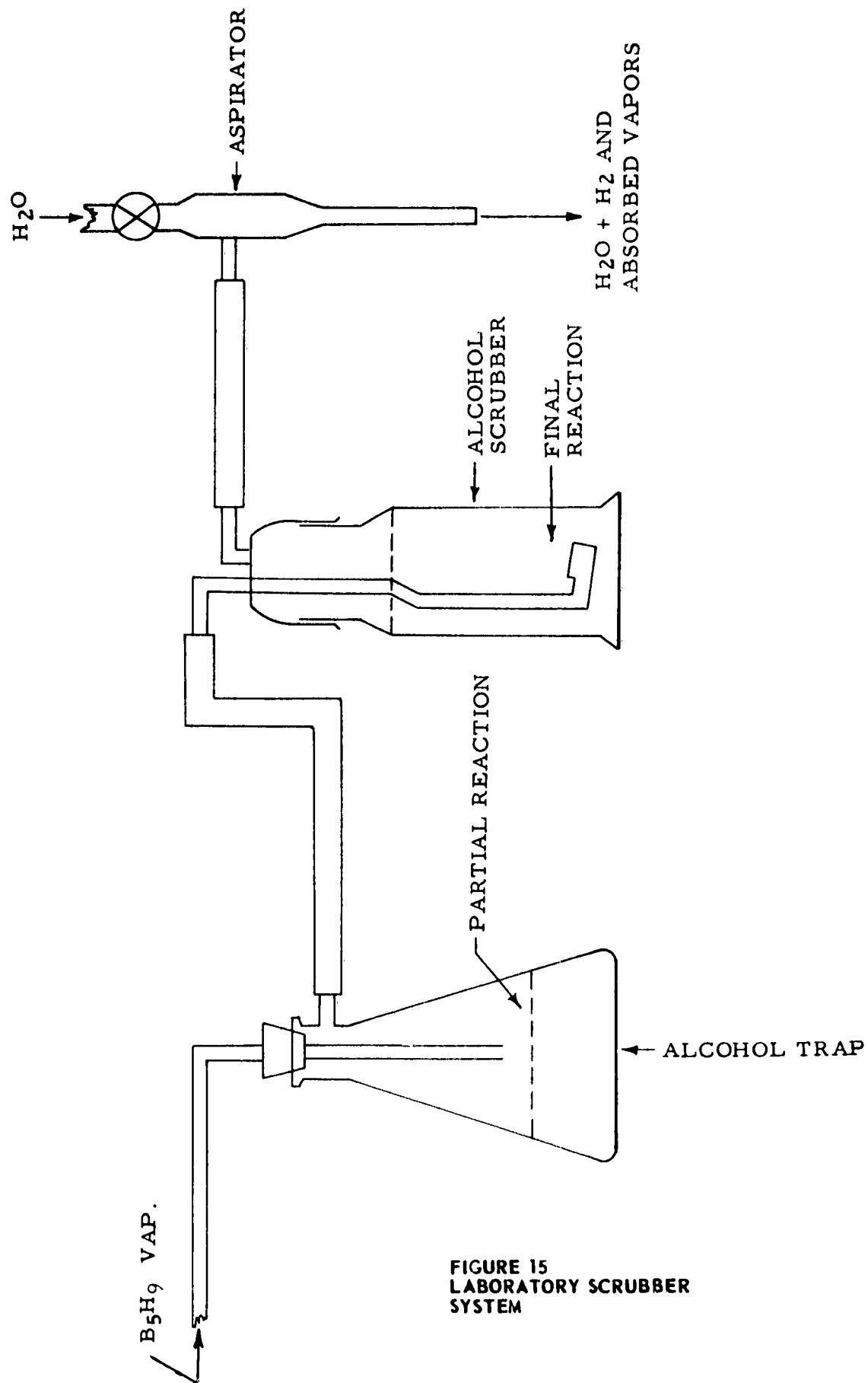


FIGURE 15
LABORATORY SCRUBBER
SYSTEM

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A Study of Pentaborane. By A. V. Jensen and B. B. Goshgarian. May 1961. 40 Pages. (AFFTC-TR-61-34).

There have been several research programs undertaken in recent years to obtain all of the energy available from boron hydrides in rocket engine applications with various oxidizers. The work performed at Edwards AFB with pentaborane -9 in support of an engine project is the basis of this report. The density, vapor pressure, and freezing point of pentaborane -9 may all be determined in the quality control laboratory with one

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