



# AEROJET NUCLEAR SYSTEMS COMPANY

A DIVISION OF AEROJET-GENERAL 

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Space Nuclear Propulsion Office  
Cleveland Extension  
National Aeronautics and Space Administration  
21000 Brookpark Road  
Cleveland, Ohio 44135

Attention: Mr. R. W. Schroeder

Subject: Final Report, Project 396, Contract SNP-1

Gentlemen:

Two (2) copies of Report No. FT02-W396, Carbon Compounds/Liquid Hydrogen Fuels dated October 1970 are enclosed. This document covers the period through September 30, 1970 and is the final report of the work performed under Project 396, Contract SNP-1.

Distribution of this report has been made in accordance with Enclosure (2).

Very truly yours,

AEROJET NUCLEAR SYSTEMS COMPANY

*for J. Ryland*  
G. L. Ryland  
Manager, Administration  
NERVA Rocket Operations

Enclosure:

(1) Report No. FT02-W396 (2 copies)

cc: M. M. Carness, SNPO-C/Sacto

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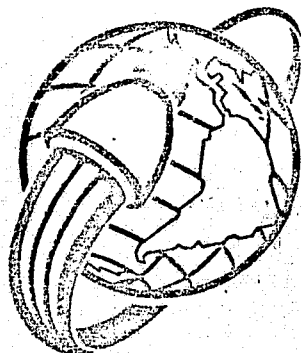
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**CARBON COMPOUNDS/LIQUID HYDROGEN FUELS**

**FINAL REPORT**

**TECHNICAL REPORT FR02-W396**

**OCTOBER 1970**



**AEROJET LIQUID ROCKET COMPANY**

A DIVISION OF AEROJET-GENERAL 

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CARBON COMPOUNDS/LIQUID HYDROGEN FUELS

FINAL REPORT

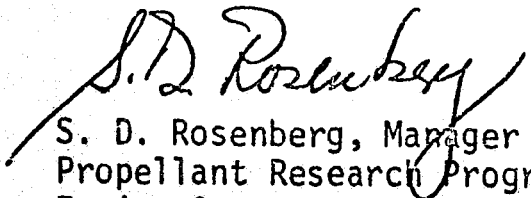
TECHNICAL REPORT FR02-W396

OCTOBER 1970

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Approved:



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## FOREWORD

The investigation "Carbon Compounds/Liquid Hydrogen Fuels" was conducted by personnel of the Research Chemistry Laboratory, Research Laboratories Section, Engine Components Department, Aerojet Liquid Rocket Company. The Program Manager was Dr. S. D. Rosenberg. The Principal Investigator was Dr. E. M. Vander Wall who was supported by R. L. Beegle, Jr. and Dr. R. E. Yates.

## ABSTRACT

An experimental program was conducted to determine the feasibility of preparing suspensions of colloidal-size hydrocarbon particles in liquid hydrogen. The ultrafine hydrocarbon particles were prepared in-situ by injecting hydrocarbon/hydrogen gas mixtures into liquid hydrogen under static and flowing conditions. Several hydrocarbons were evaluated for use in the suspensions; cyclopropane proved to be the most attractive candidate. Eventually agglomeration of the hydrocarbon particles led to the settling of the suspensions.

Concurrently, the use of very small particles of hydrocarbons as particulate gelants for liquid hydrogen was investigated. The particles were prepared in-situ using similar techniques; ethane was found to possess the greatest gelling capacity for liquid hydrogen. Stable gels were prepared with as little as 10 weight percent ethane. A stable gel of slush hydrogen required no more than 4 weight percent ethane. The flowability of the gels was demonstrated and the viscosity and yield stress values determined.

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## I. INTRODUCTION

The addition of small quantities of hydrocarbons, such as methane, to the liquid hydrogen used as the propellant in nuclear propulsion systems offers a potentially beneficial method for reducing erosion in the flow channels of the nuclear reactor. Prior to the current program, no simple method was available for incorporating the hydrocarbons at an appropriate concentration level in the liquid hydrogen fuel, ca. 5000 ppm.

The primary objective of this investigation was to initiate development of a liquid hydrogen fuel which contained a carbon-containing compound at a concentration level corresponding to 5000 ppm methane. In order to achieve the objective, the investigation was conducted to determine whether the carbon-containing compound can be prepared in the form of sufficiently small particles so that they remain suspended in the form of a colloidal solution in liquid hydrogen. An alternative route of investigation was also pursued, i.e., to gel liquid hydrogen with a minimum quantity of carbon-containing particles.

The experimental investigation was directed towards (1) the preparation of small hydrocarbon particles which remain uniformly suspended in liquid hydrogen either because of their colloidal size or as a result of gelation of the liquid, (2) characterization of the colloidal and gelled suspensions, and (3) evaluation of the stability of the hydrocarbon suspensions in liquid hydrogen as related to time. The results of the program are presented in this report.

The report is organized as follows: (1) Introduction, (2) Theoretical Background, (3) Experimental Procedures and Apparatus, (4) Discussion of The Experimental Results, (5) Implications of the Experimental Results, and (6) Conclusions and Recommendations.

## II. THEORETICAL BACKGROUND

The theoretical background section is divided into two major topics: (1) theoretical specific impulse performance of a suspension of hydrocarbons in liquid hydrogen, and (2) particle size requirements for a stable suspension in liquid hydrogen. The topics are presented in this order.

### A. THEORETICAL SPECIFIC IMPULSE PERFORMANCE OF A SUSPENSION OF HYDROCARBONS IN LIQUID HYDROGEN

Researchers concerned with the core erosion problem encountered in the operation of the NERVA engine hypothesize that a concentration of 5000 ppm (0.5 wt%) of methane in hydrogen will significantly inhibit the erosion process. Thus, the formulation of a uniform suspension of a carbon-containing compound in liquid hydrogen at a concentration level corresponding to 5000 ppm of methane is the major goal of the experimental program. Theoretical calculations indicate that, at an operating temperature of 4500°R, a chamber pressure of 450 psia, and an expansion ratio of 100, 0.5 weight percent of methane in liquid hydrogen will produce a specific impulse loss of 1.9 sec out of 876 sec, or 0.22% degradation in performance.

If gelation is required to maintain a uniform suspension of hydrocarbon particles in liquid hydrogen, appreciably larger quantities of hydrocarbons are required. Because of the extremely low molecular weight of hydrogen, the addition of relatively small amounts of hydrocarbon will cause some degradation in performance. For illustrative purposes, the weight and volume concentration relationships of solid methane in liquid hydrogen at its normal boiling point and in 50% slush hydrogen are presented in Figure 1.

Data obtained during this investigation indicated that approximately 17 weight percent methane is required to produce stable liquid hydrogen gels. This corresponds to approximately a 5.6% degradation of performance as

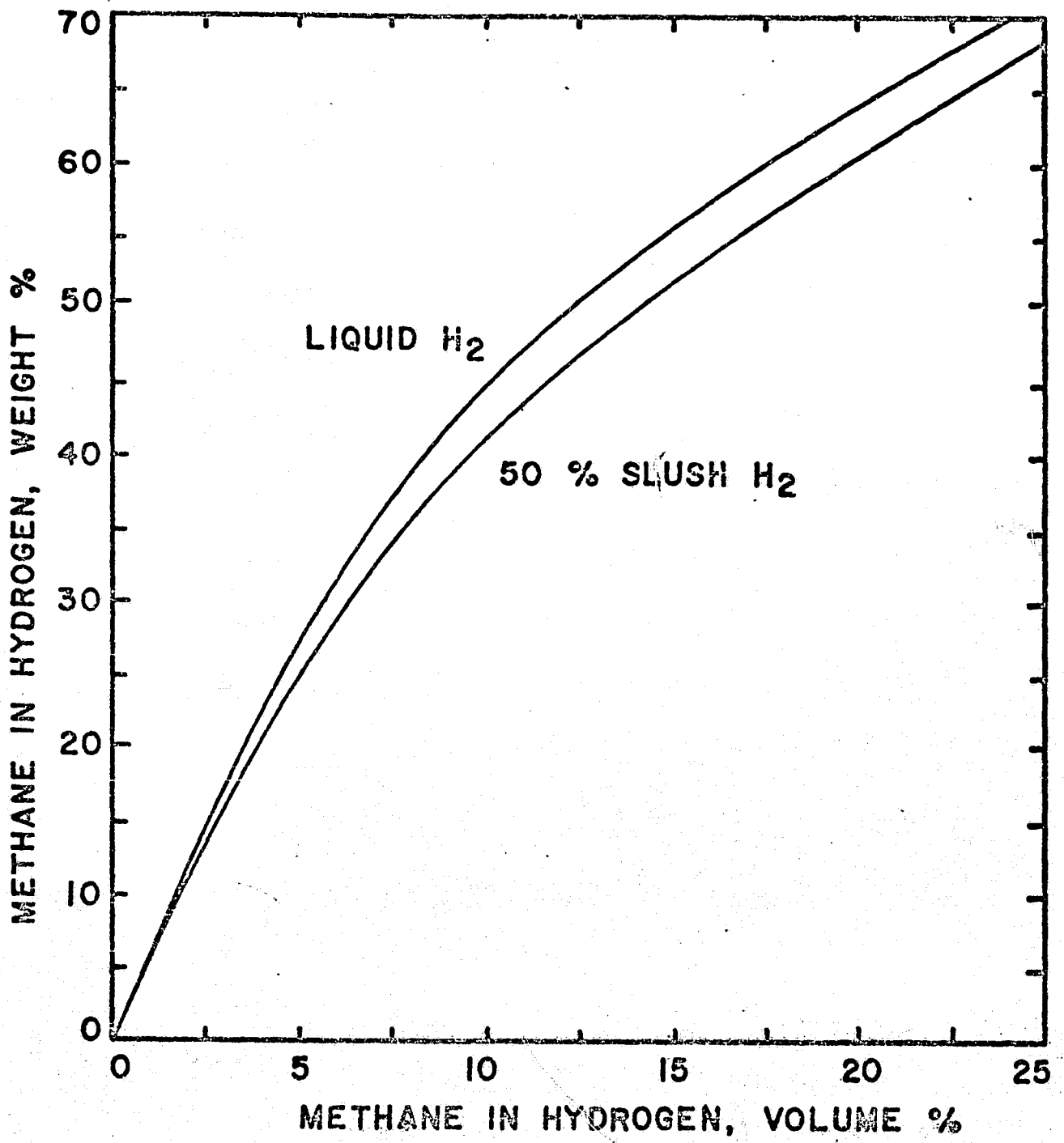


Figure 1. CONCENTRATION RELATIONSHIPS OF SOLID METHANE IN LIQUID AND SLUSH HYDROGEN

## II, A, Theoretical Specific Impulse Performance of a Suspension of Hydrocarbons in Liquid Hydrogen (cont.)

measured by the theoretical specific impulse. This loss can be reduced significantly if the liquid hydrogen is replaced by slush hydrogen. Based on a conservative approximation, 50% slush hydrogen can be gelled with 8.5 weight percent methane, i.e., approximately 1.5 volume percent methane. This concentration, while greater than the hypothesized value of 5000 ppm, provides a suitable beginning. According to the theoretical performance data plotted in Figure 2, a loss in specific impulse of 32 sec (3.65% loss) results from the addition of 1.5 volume percent methane to the hydrogen under standard engine operating conditions, i.e., at a chamber temperature of 4500°R. Note, however, that operation of the engine at 4740°R (5.33% increase) compensates for the presence of methane and no performance loss results. The sensitivity of these three parameters, one-to-another, is indicated in Table I.

TABLE I

EFFECT OF METHANE CONCENTRATION IN HYDROGEN AND OPERATING TEMPERATURE ON SPECIFIC IMPULSE LOSSES

Methane Concentration In Slush Hydrogen		$I_{sp}$ Loss at 4500°R (sec)	$T_c$ Required For Zero $I_{sp}$ Loss (°R)	$T_c$ Increase Required For Zero $I_{sp}$ Loss (%)
(vol%)	(wt%)			
1.5	8.5	32	4740	5.33
1.0	6.0	24	4678	3.96
0.5	2.5	14	4607	2.38
0.1	0.75	3	4524	0.53

The tabulation is presented as an example of how the parameters may be varied to minimize performance losses. The experimental results obtained during the program indicate that significantly smaller quantities of hydrocarbons other than methane can be used to produce stable liquid hydrogen gels and uniform slush hydrogen.

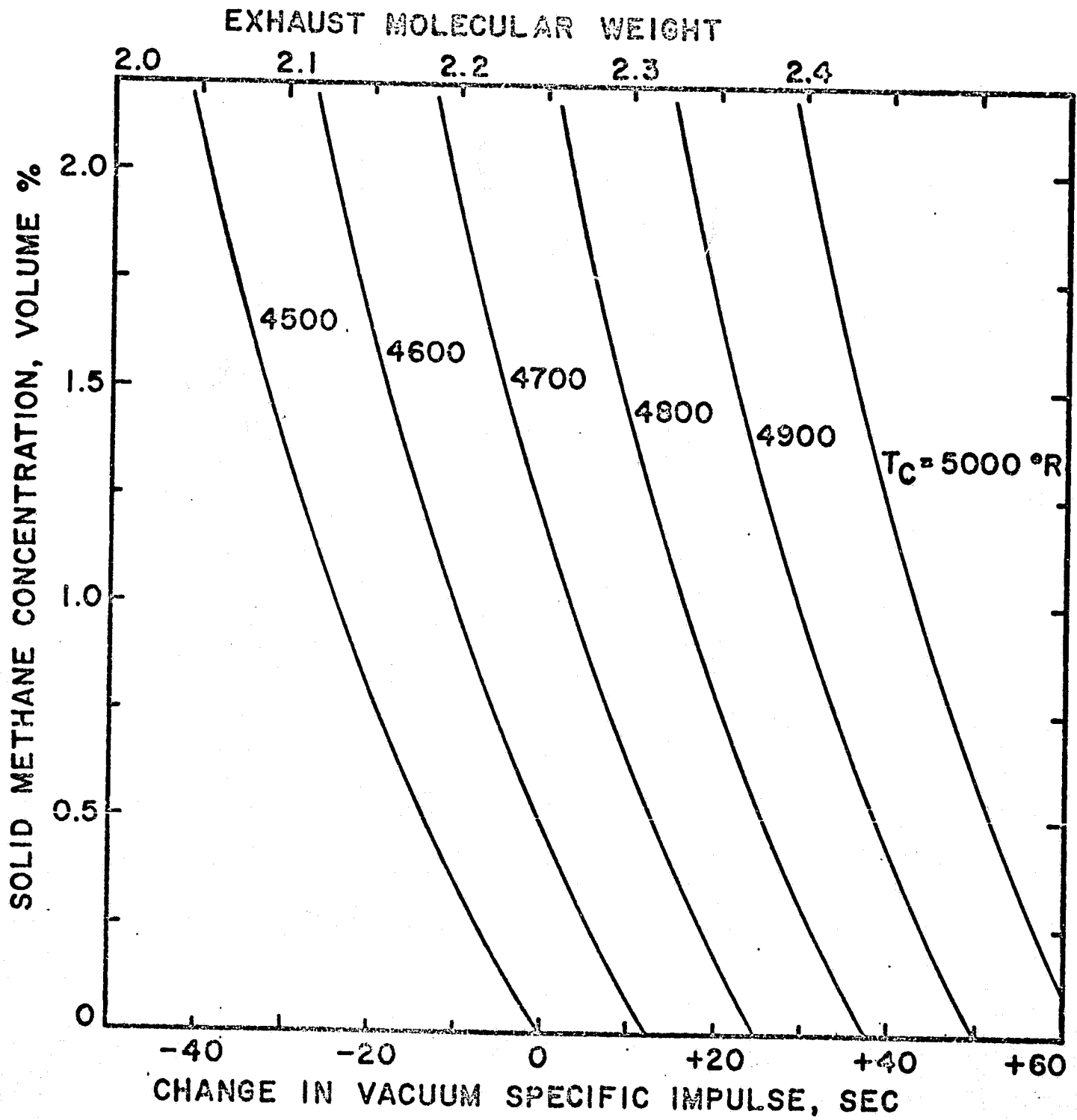


Figure 2. THE RELATIONSHIP AMONG THEORETICAL SPECIFIC IMPULSE, GELANT CONCENTRATION, AND CHAMBER TEMPERATURE  
 STANDARD CONDITIONS:  $I_{sp}$ , 876 sec;  $P_C$ , 450 psia;  
 $T_C$ , 4500°R;  $\epsilon = 100$



## II, Theoretical Background (cont.)

### B. PARTICLE SIZE REQUIREMENTS FOR A STABLE SUSPENSION IN LIQUID HYDROGEN

Theoretically, if one prepares solid particles of a sufficiently small size, they will remain suspended uniformly in a liquid medium because the kinetic energy which the particles possess is sufficient to overcome the gravitational effect which causes the particles to settle. One can calculate the terminal velocity or settling rate of spherical particles in a liquid using Equation (1).

$$\mu = \frac{4r^2(\rho - \rho^1)g}{18\eta} \quad (1)$$

where

- $\mu$  = the settling rate, cm/sec
- $r$  = particle radius, cm
- $\rho$  = density of the particles
- $\rho^1$  = density of liquid hydrogen at NBP = 0.071 g/cc
- $g$  = gravitational constant = 980.6 cm/sec<sup>2</sup>
- $\eta$  = viscosity of liquid hydrogen at NBP = 132.8 x 10<sup>-6</sup> g/cm-sec

As examples, the settling rate for amorphous carbon and for solid methane with densities of 2.0 and 0.52 g/cc, respectively, are presented in Table II as a function of the particle radius.

TABLE II

SETTLING RATE OF CARBON AND METHANE PARTICLES OF VARIOUS SIZES IN LIQUID HYDROGEN

Particle Size, Radius in cm	Settling Rate			
	Carbon		Methane	
	(cm/sec)	(in/day)	(cm/sec)	(in/day)
10 <sup>-3</sup>	3.2	1.1 x 10 <sup>5</sup>	7.4 x 10 <sup>-1</sup>	2.5 x 10 <sup>4</sup>
10 <sup>-4</sup>	3.2 x 10 <sup>-2</sup>	1.1 x 10 <sup>3</sup>	7.4 x 10 <sup>-3</sup>	2.5 x 10 <sup>2</sup>
10 <sup>-5</sup>	3.2 x 10 <sup>-4</sup>	1.1 x 10 <sup>1</sup>	7.4 x 10 <sup>-5</sup>	2.5
10 <sup>-6</sup>	3.2 x 10 <sup>-6</sup>	1.1 x 10 <sup>-1</sup>	7.4 x 10 <sup>-7</sup>	2.5 x 10 <sup>-2</sup>
10 <sup>-7</sup>	3.2 x 10 <sup>-8</sup>	1.1 x 10 <sup>-3</sup>	7.4 x 10 <sup>-9</sup>	2.5 x 10 <sup>-4</sup>

## II, B, Particle Size Requirements for a Stable Suspension in Liquid Hydrogen (cont.)

The significant item to be noted from the data in Table II are that particles with a radius of  $10^{-5}$  cm ( $0.1\mu$ ) settle rather slowly even if the kinetic energy of the particles is neglected and that methane, because of its low density, settles at a rate approximately 4 fold less than that for solid carbon particles.

A calculation of the root-mean-square velocity of the particle is the starting point to obtain an approximate estimate of the particle size required to avert settling if one makes allowances for the kinetic energy of the particle. The root-mean-square velocity of a particle can be calculated from Equation (2).

$$v = \sqrt{\frac{9kT}{4\pi\rho_s r^3}} \quad (2)$$

where

$v$  = root-mean-square velocity, cm/sec

$k$  = Boltzman constant

$T$  = temperature, °K

$\rho_s$  = density of the particle, g/cc

$r$  = radius of the particle, cm

The root-mean-square velocities for carbon and methane particles at the normal boiling point of liquid hydrogen are presented in Table III as a function of the particle radius.

TABLE III

ROOT-MEAN-SQUARE VELOCITIES OF PARTICLES OF  
CARBON AND METHANE IN LIQUID HYDROGEN

Particle Size, Radius in cm	Root-Mean-Square Velocities			
	Carbon		Methane	
	(cm/sec)	(in/day)	(cm/sec)	(in/day)
$10^{-3}$	$1.0 \times 10^{-3}$	34	$2.0 \times 10^{-3}$	78
$10^{-4}$	$3.2 \times 10^{-2}$	$1.1 \times 10^3$	$6.2 \times 10^{-2}$	$2.1 \times 10^3$
$10^{-5}$	1.0	$3.4 \times 10^4$	2.0	$7.8 \times 10^4$
$10^{-6}$	32	$1.1 \times 10^6$	62	$2.1 \times 10^6$
$10^{-7}$	$1.0 \times 10^3$	$3.4 \times 10^7$	$2.0 \times 10^3$	$7.8 \times 10^7$

## II, B, Particle Size Requirements for a Stable Suspension in Liquid Hydrogen (cont.)

The significant items to be noted from the data in Table III are that the root-mean-square velocities of methane particles are twice that of carbon particles of comparable size and that particles with a radius of  $10^{-4}$  cm ( $1\mu$ ) possess root-mean-square velocities that are equal to the settling rate of carbon particles and greater than the settling rate of methane particles. For methane, the particle size at which the settling rate and root-mean-square velocity are equal is calculated to be  $1.8\mu$ .

Because the root-mean-square velocities are omni-directional while the settling rate is unidirectional, a significantly greater root-mean-square velocity than settling rate is required to maintain a uniform suspension of particles. However, on the basis of the preceding calculations, it is apparent that, if the particles of methane or carbon can be prepared in the size range between  $0.1$  and  $1.0\mu$  and dispersed in liquid hydrogen, the particles should remain suspended in a uniform manner. If agglomeration of the particles occurs after dispersion, the particles will behave as if their size is much larger and settling may occur. To overcome such behavior, gelation of the suspension may be necessary to maintain the uniformity of the suspension. One encouraging aspect of gelation is that the gelling capacity of the particles increases with decreasing particle size and, therefore, the preparation of small particles is desirable regardless of whether or not gelation is required.

### III. EXPERIMENTAL PROCEDURES AND APPARATUS

#### A. PREPARATION OF HYDROCARBON PARTICLES

##### 1. Static Liquid Hydrogen System

A method for the preparation of micron-size particles of solid chlorine trifluoride used to gel liquid nitrogen and liquid oxygen difluoride was developed under Contract NAS 7-473 (Reference 1). The general technique, with proper modification, can be used for preparation of small particles of energetic oxidizers and fuels. In the current investigation, the technique was used to prepare small hydrocarbon particles in liquid hydrogen.

The basic method involves the dilution of the vapor of the candidate particles with an inert carrier gas, followed by the injection of the gaseous mixture through a suitably heated tube and orifice directly into a cryogenic liquid so that condensation occurs immediately within the bulk of the liquid. The direct dispersion of the particles in the liquid avoids condensation of particles on the walls of the vessel and eliminates the necessity of additional mixing normally required to disperse particles in the liquid.

During the current investigation, various hydrocarbons were diluted with hydrogen and helium as the carrier gas and injected directly in liquid hydrogen. A schematic of the heated injection tube is shown in Figure 3. The size of the orifice, and the pressure drop across the orifice were varied in an effort to vary the ultimate size of the particles. The results are discussed in Section IV.

The apparatus in which the hydrocarbon particles were prepared is shown in Figure 4. The tube in the center of the vacuum-jacketed glass flask is the heated injection tube; the tube in the right hand side of the flask was

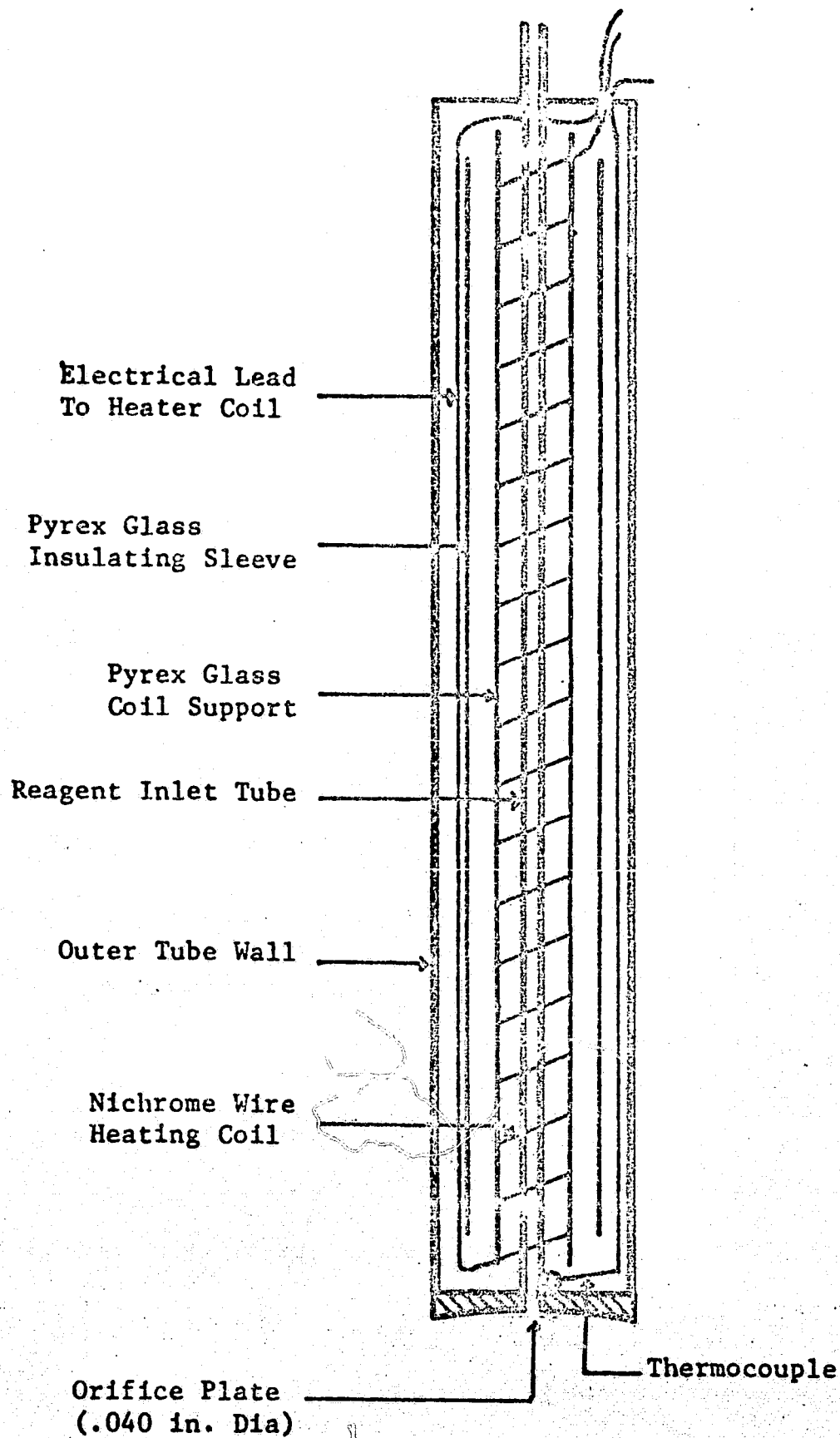


Figure 3. SCHEMATIC OF HEATED INJECTION TUBE

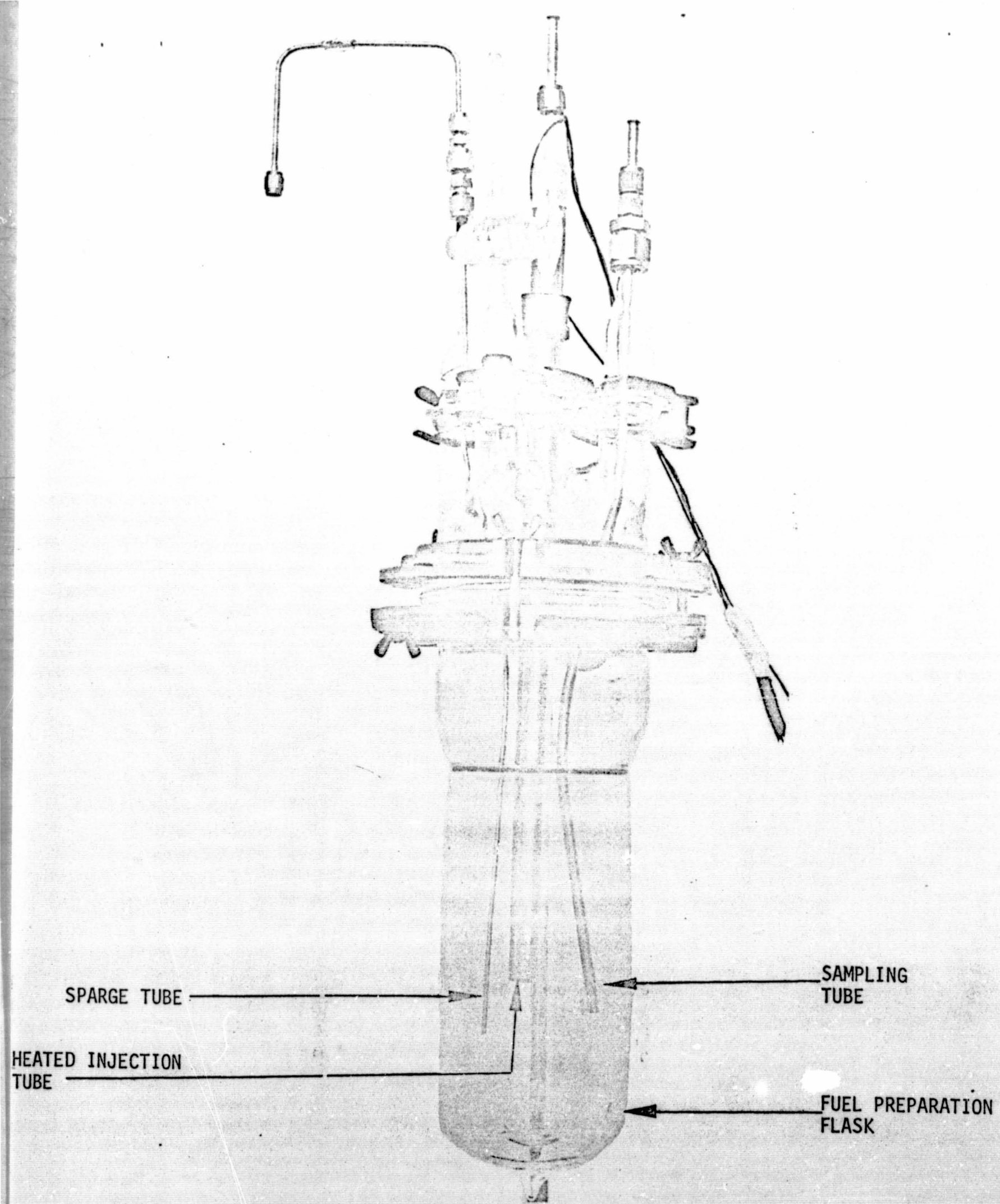


Figure 4. BASIC APPARATUS FOR PREPARATION OF HYDROCARBON SUSPENSIONS IN LIQUID HYDROGEN

### III, A, Preparation of Hydrocarbon Particles (cont.)

used for withdrawing liquid samples for chemical analysis; and the tube on the left hand side was used for mixing the resulting mixture with helium or for sparging the products from the flask. A clear-glass Dewar is used externally to the particle preparation flask to minimize heat losses. The apparatus assembly, with the external Dewar, is shown in Figure 5.

The experiments were conducted in a box fabricated with Lucite panels to allow visual observation of the experiments. The box was used to provide an inert atmosphere around the experimental apparatus so that contamination by oxygen is prevented. A photograph of the box is shown in Figure 6. The liquid hydrogen is supplied to the particle preparation flask through a vacuum jacketed line which appears in the upper portion of the box. The control valves for adding the various gases to the test apparatus were mounted external to the box.

#### 2. Flowing Liquid Hydrogen System

A more attractive method of preparing very small particles of hydrocarbons in liquid hydrogen is direct injection of a hydrocarbon/carrier gas mixture into a flowing stream of liquid hydrogen. This approach should avoid condensation of hydrocarbon on particles already present in the vicinity of the injection orifice and the overall result should be the formation of smaller hydrocarbon particles. An apparatus was designed, constructed, and operated to determine whether this approach is feasible. Data generated during the initial phase of the program was used for the design of the approach.

A discussion of the design and operation of the apparatus follows and the experimental results are presented in Section IV.

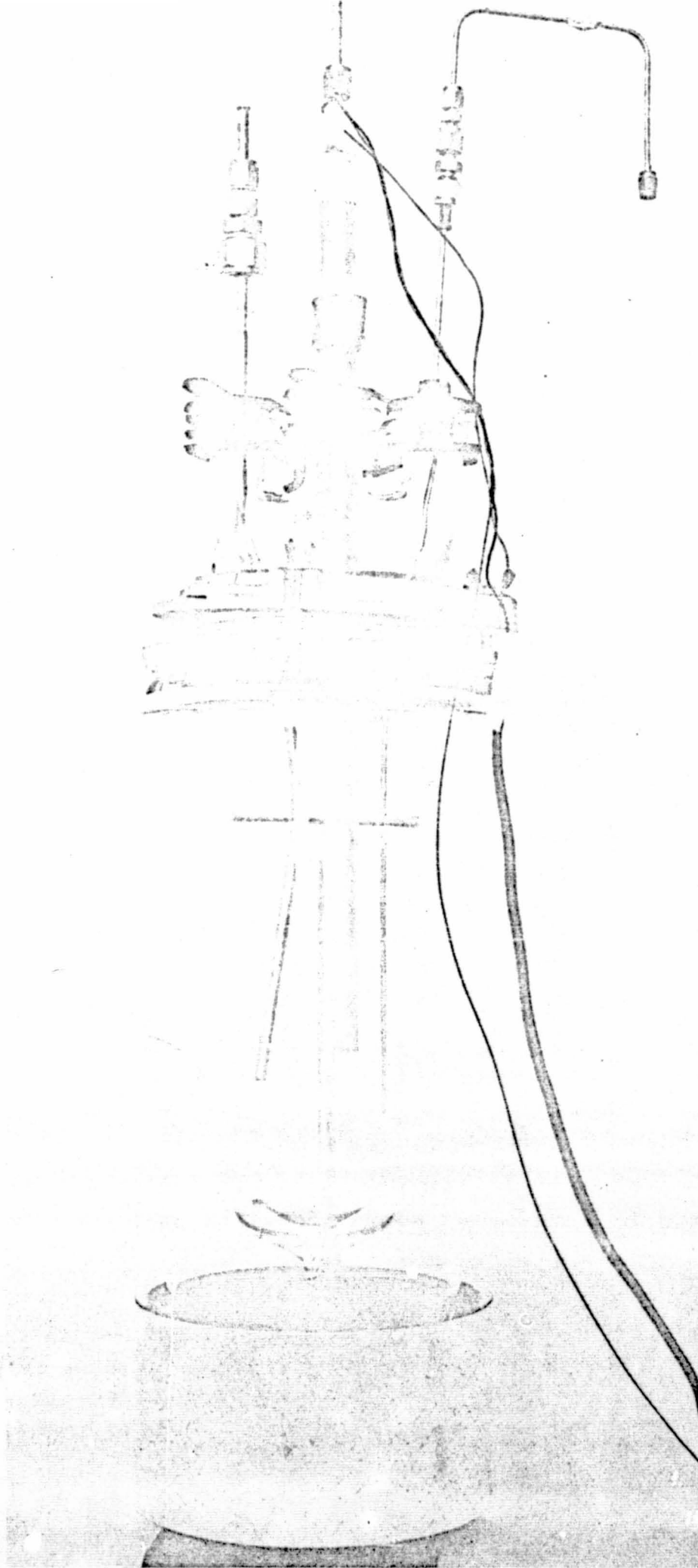


Figure 5. BASIC APPARATUS FOR PREPARATION OF HYDROCARBON SUSPENSIONS  
IN LIQUID HYDROGEN WITH EXTERNAL COOLING DEWAR



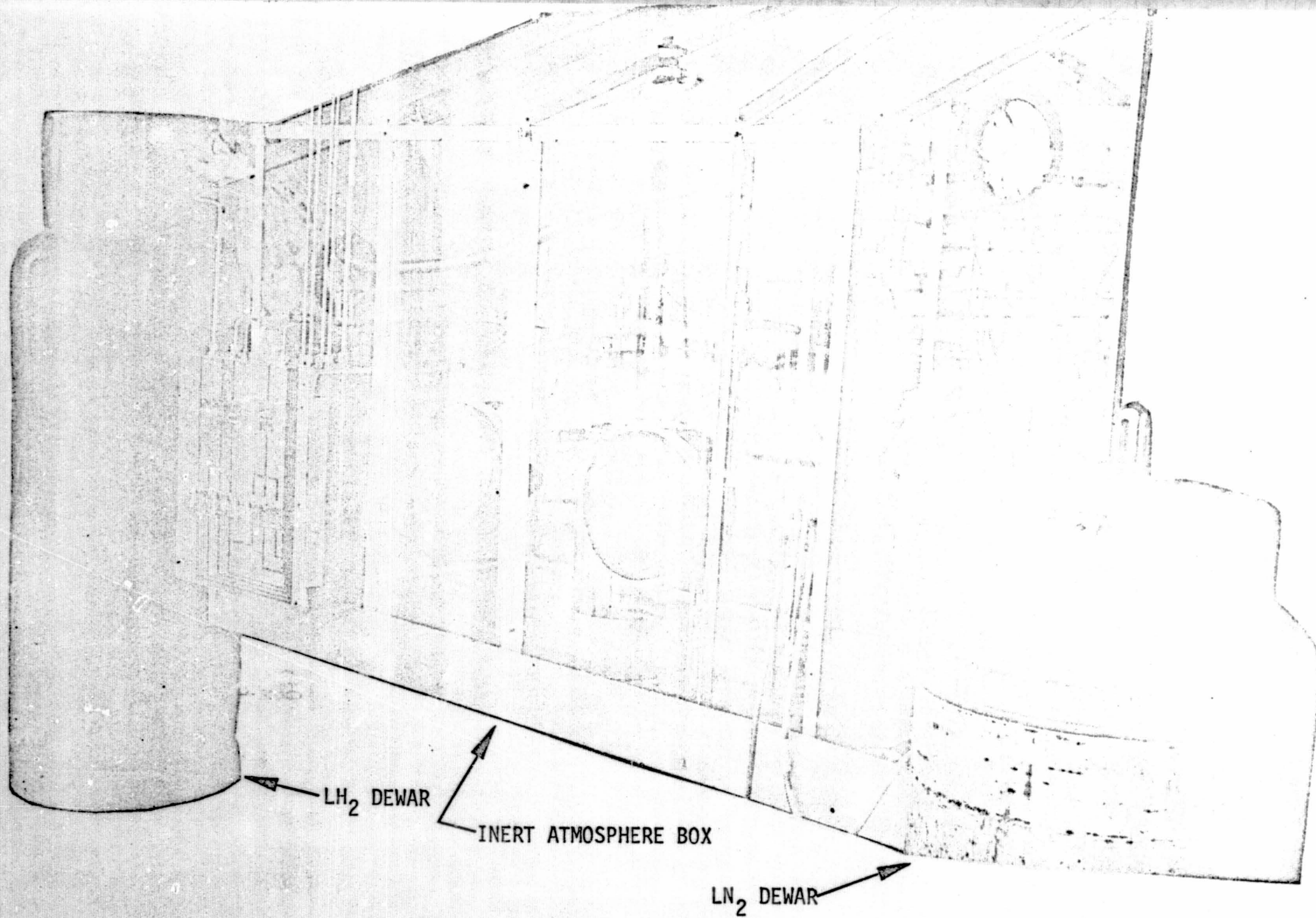


Figure 6. ASSEMBLY OF EXPERIMENTAL APPARATUS FOR HYDROCARBON PARTICLE PREPARATION

### III, A, Preparation of Hydrocarbon Particles (cont.)

The process of forming the particles involves the rapid condensation of a hydrocarbon compound in  $\text{LH}_2$  and requires the exchange of energy from the hydrogen/hydrocarbon gas mixture to the  $\text{LH}_2$  acting as a refrigerant. The thermal cycle involved in the process of condensing the hydrocarbon gelant and evaporating a portion of the  $\text{LH}_2$  provides the basic equation which is required for the development of the system design.

The amount of  $\text{LH}_2$  vaporized in the gelation process is dependent on the hydrocarbon compound used as the gelling agent, its concentration in the hydrocarbon/hydrogen gas mixture and the temperature at injection. This  $\text{LH}_2$  boiloff rate is an important factor in the design of the system and the economics of the gelation process.

The sizing of the various apparatus components, particularly the flow metering and controlling devices, requires a knowledge of the gas and liquid flow rates. Similarly, the design of the gas heater used to control the gas-mixture injection temperature requires a knowledge of the gas flow rates. Thus, the flow rates and heating requirements were established on the basis of the projected experimental requirements.

The physical characteristics of the flow system were then established in such a manner that the experiments would provide the requisite data.

#### a. Boiloff Rate of $\text{LH}_2$

The thermal cycle involved in the gelation process was utilized to determine the rate of  $\text{LH}_2$  boiloff (in grams of  $\text{LH}_2$  evaporated/gram of gelant), assuming total capture of the hydrocarbon. These determinations, shown graphically in Figure 7, were performed for both cyclopropane

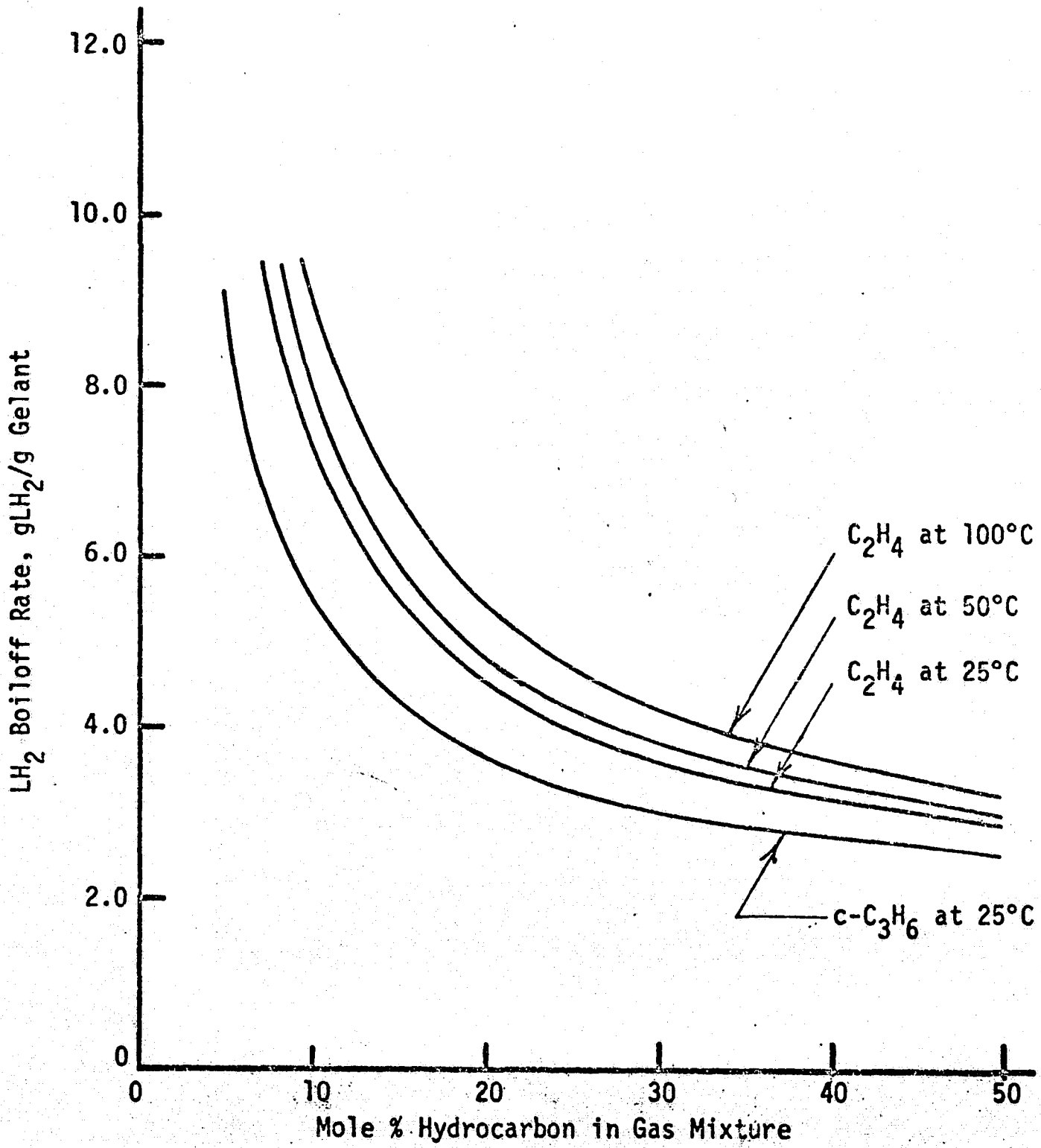


Figure 7. BOILOFF RATE OF LH<sub>2</sub> AS A FUNCTION OF HYDROCARBON CONCENTRATION

### III, A, Preparation of Hydrocarbon Particles (cont.)

and ethylene, at concentrations (in the injected gas mixture) in the range 10-50 mole % and at gas-injection temperatures in the range 25-100°C.

The figure shows that the  $\text{LH}_2$  boiloff is greater for ethylene than for cyclopropane under equivalent conditions. Also, the figure shows that as the concentration of hydrocarbon in the gas mixture increases the  $\text{LH}_2$  boiloff rate decreases. This results from the fact that, as the hydrocarbon concentration increases, less total gas mixture is required to supply a given quantity of hydrocarbon and less  $\text{LH}_2$  refrigerant is required.

#### b. Gas and Liquid Flow Rates

It is apparent from a consideration of the process that the flow rate of  $\text{LH}_2$  must be high enough to allow for  $\text{LH}_2$  boiloff as well as for the formation of a suspension of hydrocarbon particles in  $\text{LH}_2$ . Thus, the flow rate of  $\text{LH}_2$  will be dependent on the boiloff rate and on the desired final concentrations of hydrocarbons in the  $\text{LH}_2$ . For purposes of apparatus and experimental design, the concentration of hydrocarbon in the gas stream was established to be in the range 10-50 mole % and the maximum allowed concentration of hydrocarbon in the  $\text{LH}_2$  product was established to be 0.5 mole% (9.5 wt% cyclopropane or 6.5 wt% ethylene).

These criteria were used to determine the relationship of gas mixture flow rate and  $\text{LH}_2$  flow rate at a gas injection temperature of 25°C. The flow rates of gas mixtures (of cyclopropane concentration 10-50 mole%) and the corresponding  $\text{LH}_2$  flow rates are presented in Table IV. Also included are the anticipated flow rates of hydrocarbon/ $\text{LH}_2$  products. The ranges of the respective gas mixture and  $\text{LH}_2$  flow rates are such that the experiments could be performed on a scale consistent with the size of the equipment available.

III, A, Preparation of Hydrocarbon Particles (cont.)

TABLE IV

GAS MIXTURE AND LIQUID HYDROGEN FLOW RATES

<u>Gas Mixture Flow Rate (cc/min)</u>	<u>Cyclopropane Concentration (mole %)</u>	<u>LH<sub>2</sub> Flow Rate (g/sec)</u>	<u>Hydrocarbon/LH<sub>2</sub> Fuel Production Rate* (g/sec)</u>
10,000	10	0.43	0.27
	20	0.76	0.55
	30	1.08	0.82
	40	1.41	1.10
	50	1.73	1.37
2,000	10	0.09	0.06
	20	0.15	0.11
	30	0.22	0.16
	40	0.28	0.22
	50	0.34	0.27

\*Production rate, based on 100% cyclopropane capture efficiency and final gelant concentration of 0.5 mole%.

The tabulated data indicate the relationship of the LH<sub>2</sub> flow rate and the gas flow rate required to produce LH<sub>2</sub> containing 0.5 mole% cyclopropane. If the LH<sub>2</sub> flow rate is increased to a value in excess of that shown in the table for a given gas mixture flow rate and concentration, then the LH<sub>2</sub> produced will contain less than 0.5 mole% cyclopropane. Also, if the cyclopropane capture efficiency is less than 100%, due to particle entrainment in the gaseous effluent, then the gelled LH<sub>2</sub> will contain less than 0.5 mole% cyclopropane. Thus, the table provides the requisite guidelines for the selection of appropriate experimental conditions of gas mixture and LH<sub>2</sub> flows.

### III, A, Preparation of Hydrocarbon Particles (cont.)

#### c. Flow Measurement and Control

The gas mixture flow rates, as noted above, were established to be in the range 2,000-10,000 cc/min. Flow rates of this order of magnitude are readily controlled by means of a micrometer needle valve. Flow measurement is achieved conveniently by means of small diameter rotometers calibrated for hydrogen/hydrocarbon mixtures.

Control of the flow rate of  $\text{LH}_2$  is also accomplished by means of a micrometer needle valve. The metal components of the valve and the gas/liquid mixer act as large heat reservoirs and require a period of  $\text{LH}_2$  flow to dissipate the heat and achieve thermal equilibrium. Therefore, the flow of  $\text{LH}_2$  through the needle valve at various positions is best calibrated after assembly of the entire system.

#### d. Gas Mixture Heater and Mixer Design

Experience with the formation of small particles in cryogenic fuels has shown that the condensable material (gelant) tends to collect on the inside surfaces of the gas injection tube unless the gas mixture is heated. Rapid heat exchange from the metal injection tube to the cryogenic fluid is responsible for this effect. Therefore, it was considered desirable to incorporate a gas mixture heater just upstream of the injection orifice. A bayonet heater, employing a nichrome resistance heating element mounted in an alumina sleeve, was inserted in the gas mixture inlet tube. The heater was constructed and installed so that the end of the heater was about 1/8-in. from the injection orifice.

### III, A, Preparation of Hydrocarbon Particles (cont.)

The mixer consisted of a standard 3/8-in. stainless steel tubing tee fitted with a gas injection orifice and an  $\text{LH}_2$  injection port. These ports were situated so as to form a 90-degree impingement angle at an impingement point about 1/8-in. from the face of the gas injector orifice plate. The purpose of this arrangement was to accomplish the mixing of the two streams as rapidly and thoroughly as possible with minimum contact of the  $\text{LH}_2$  with the gas injector orifice. The gas injector orifice initially installed was 0.010 in. in diameter; this size was selected so that the gas through the orifice would be at or near sonic velocity. The tube section at and downstream of the mixing zone was of considerably larger diameter than the pre-mixing-zone passages to accommodate the large volumes of gaseous hydrogen produced in the mixing process. A sketch of the mixing chamber and injection ports is shown in Figure 8. A photograph of the fabricated assembly is shown in Figure 9. An external Dewar was placed around the apparatus during operation. The product fuel was directed toward the bottom of the flask to prevent the accumulation of hydrocarbon particles on the wall of the flask. The experimental results are discussed in Section IV.

### B. CHEMICAL ANALYSIS OF THE PRODUCT FUEL

After the hydrocarbon particles had been prepared, samples of the liquid hydrogen fuel were withdrawn by applying a vacuum to the sampling tube which was immersed to a fixed level in the fuel preparation flask (see Figure 3). Upon withdrawal, the liquid vaporized into an evacuated stainless steel cylinder which served as the sample collector. The gases in the sample collector were analyzed by gas chromatography for hydrogen, helium and hydrocarbons.

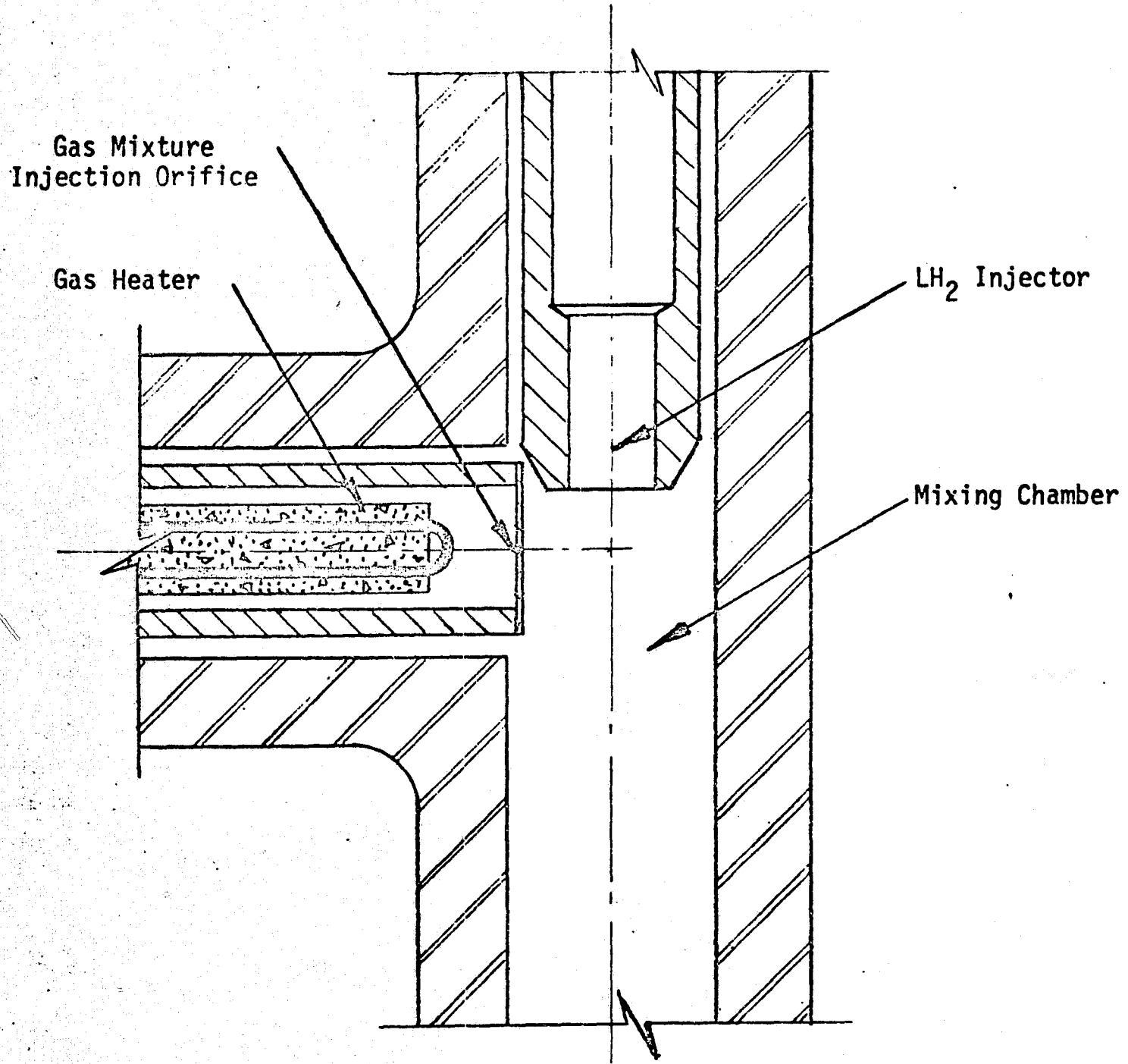


Figure 8. ENLARGED SECTION VIEW OF MIXING CHAMBER



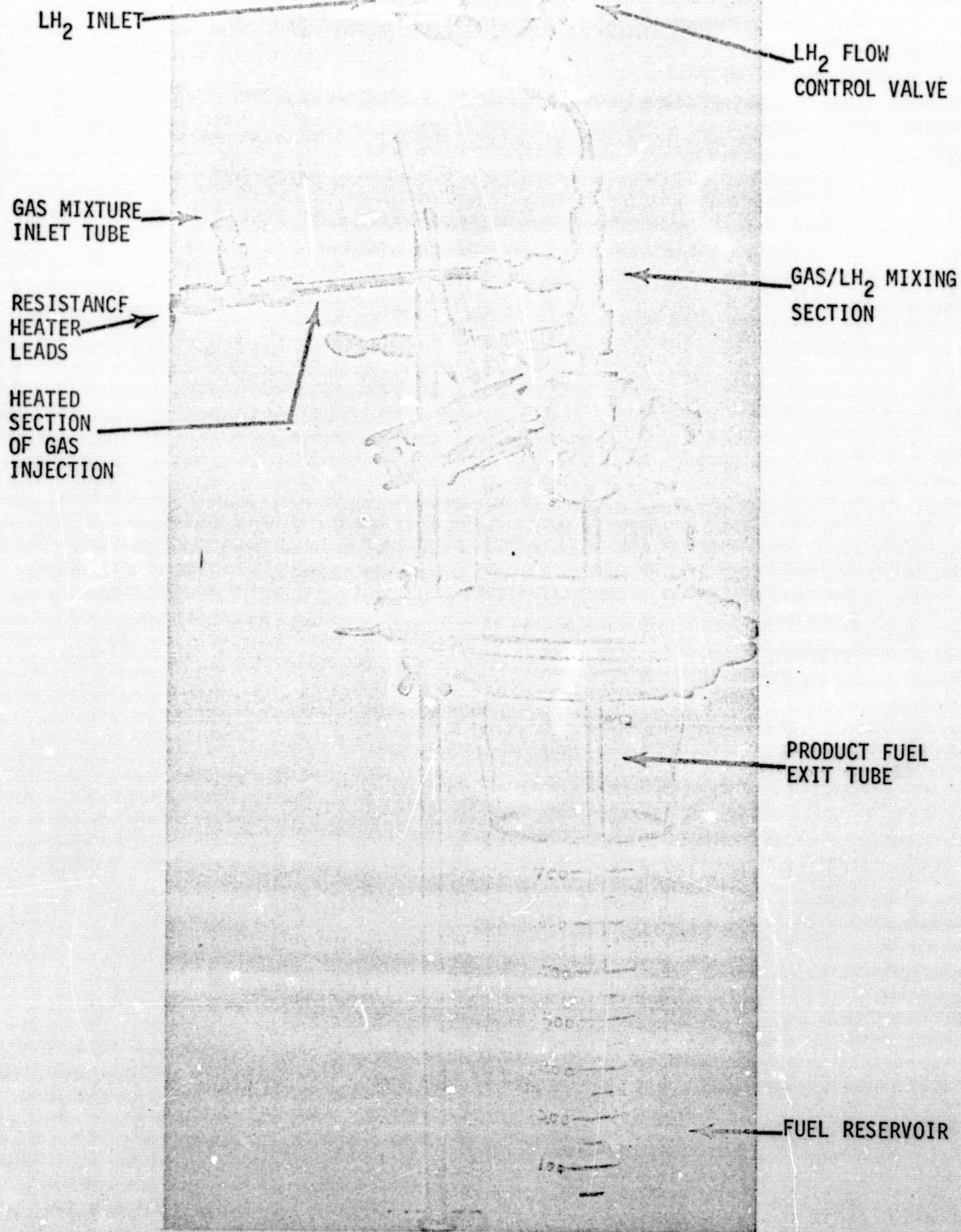


Figure 9. FLOWING LIQUID HYDROGEN SYSTEM FOR PREPARATION OF SMALL HYDROCARBON PARTICLES

### III, B, Chemical Analysis of the Product Fuel (cont.)

Initially, a Fisher Gas Partitioner was used to determine the methane concentration in liquid hydrogen. The partitioner had a threshold sensitivity limit of 2000 ppm methane in hydrogen using the thermal conductivity cellas as the detector elements. Because it soon became apparent that a more sensitive method was required to measure the hydrocarbon content in the liquid hydrogen, a Perkin-Elmer Vapor Fractometer, Model 154D with a flame ionization detector which was capable of detecting hydrocarbon concentration down to less than one volume part-per-million level was used for the analyses. Subsequently, this instrument was used throughout the program and the majority of the chemical analyses were obtained using this instrument.

In practice, liquid samples were periodically withdrawn during an experiment and stored in the sample collector for a period of a few hours before analysis. The storage period before analysis allowed sufficient time for thorough mixing of the sample which may have undergone some fractionation initially. In order to establish the reliability of the sampling procedure, two sampling tubes were used in some of the experiments to obtain consecutive samples. The results of the chemical analysis are incorporated in the discussion in Section IV.

#### C. PRODUCT CHARACTERIZATION

The product fuels prepared in this investigation were of two distinct types: (1) liquid hydrogen gels, and (2) suspensions of colloidal-size hydrocarbon particles in liquid hydrogen. The characterization of the liquid hydrogen gels involved chemical analysis as a function of time, measurement of the yield stress of the gel, and measurement of the viscosity of the gels. The characterization of the colloidal suspension of hydrocarbons involved only the chemical analysis of the product as a function of time because there is no apparent change in the viscosity of the product. The discussion in this section is devoted to the measurement of the yield stress and viscosity.

### III, C, Product Characterization (cont.)

#### 1. Yield Stress

Yield stress is a measure of the force required per unit area to strain a material beyond its elastic limit and, therefore, it is used as a relative indication of the degree of structure that a gel possesses. The method of measurement used in this investigation is basically a modification of the normal penetrometer method.

A series of glass spheres of constant dia were fabricated and weighted with varying amounts of mercury. The spheres are gradually lowered onto the surface of the gel so that the initial shear stresses on the gel were minimal. From observation of the depth to which the sphere sinks into the gel and the known weight of the sphere, the yield stress value for the gel can be calculated. The spheres used in the current investigation provided a range of available values from 135 dynes/cm<sup>2</sup> to greater than 3,000 dynes/cm<sup>2</sup>. The data obtained from the measurements are presented in the discussion of the experimental results.

#### 2. Viscosity

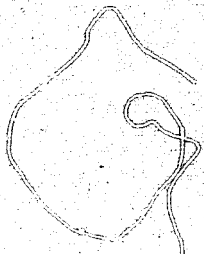
The flow properties of gelled propellants are defined by the viscosity values. Two principal methods for the determination of the viscosity values of gelled cryogenic propellants have been used, rotational and flow methods. The first reproducible values for the viscosity of gelled cryogenic propellants were obtained with rotational viscometers. Technidyne measured the viscosity of liquid hydrogen gelled with a particulate gelling agent using a Rotoviscometer (Reference 2). Earlier, Aerojet measured the viscosity of liquid oxygen gels at various shear rates with a Brookfield viscometer with excellent reproducibility (Reference 3). The principal difficulty encountered with the rotational viscometer data is that the values are relative

### III, C, Product Characterization (cont.)

and, therefore, cannot be used to predict accurate pressure drop values in the hardware system in which the propellants are to be used. An improved flow viscometer was successfully used by Aerojet to measure the flow properties of gelled  $OF_2$  (Reference 1). Because the flow-type viscometer is much more likely to provide useful data for the engineering design of hardware than the rotating-type viscometer, the flow-type viscometer was used to obtain viscosity data for the hydrocarbon/hydrogen fuels.

The first viscometer is basically a 3/8-in. copper tube coiled to fit inside the Pyrex gelling vessel. The dia of the coil is approximately 4 in. and the total length of tubing, including the straight inlet and outlet portions, is 70.7 in. The coil is immersed in the gelled liquid at the beginning of the flow measurement. The inlet section is in the form of an inverted-J with the entrance near the bottom of the Pyrex vessel. This positioning of the entrance allows utilization of a major portion of the gel for the measurement and is intended to minimize coring. A small vertical tube is installed approximately 1 in. above the entrance to permit injection of helium into the copper tubing. The helium is cooled by passing through the 1/8-in. tubing coil above the copper coil which is also immersed in the gel. The injection of helium prevents the liquid from flowing through the tubing and eliminates the need for a valve in the flow system.

The inverted-J section of tubing is followed by the coiled section and the coiled section is followed by the straight outlet section. The outlet section extends through the bottom of the Pyrex vessel by means of a ball-socket joint (glass/stainless steel). The assembled apparatus is shown in Figure 10. The exit of the tubing is immersed in a bath of liquid hydrogen. After passage through the copper tubing, the gel is discharged into the liquid hydrogen bath. The effluent will raise the level of the liquid hydrogen bath immediately external to the Pyrex gelling vessel, and the volume of the effluent is determined quantitatively by measuring this change in level.



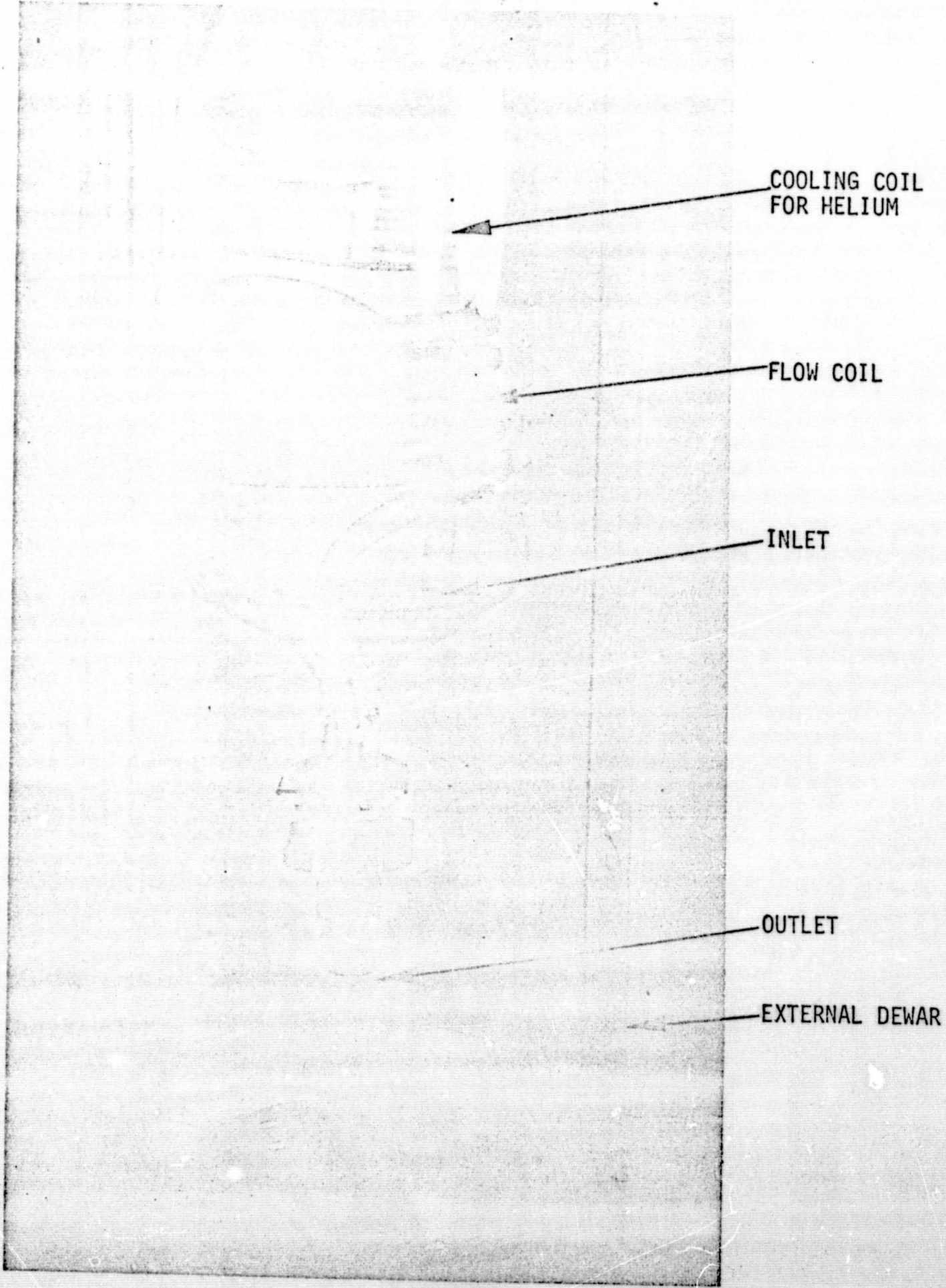


Figure 10. FLOW COIL FOR VISCOSITY MEASUREMENTS

### III, C, Product Characterization (cont.)

The measurement of the flow properties of the gel is accomplished in the following manner. During preparation of the gel, helium, at liquid hydrogen temperature, is injected through the small tube into the copper tubing to prevent gel from entering the coil. After the gel is prepared, the helium flow is stopped, and the Pyrex gelling vessel is pressurized to a preselected value and flow through the tubing begins. The volume of gel flowing through the tubing is detected by means of fiducial marks and is recorded as a function of time. Flow can be stopped at will anytime by injecting helium into the copper tubing.

Two parameters are measured during the flow experiment, the pressure drop across the copper tubing and the flowrate. These two parameters are plotted in the form of  $\frac{D\Delta P}{4L}$  versus  $\frac{8V}{D}$ , where D is the dia of the tubing, L is the effective length of the tubing,  $\Delta P$  is the pressure drop across the tubing, and V is the flow velocity. Because the tubing is coiled rather than straight, the equivalent length of the tubing was calculated using conventional relationships (Reference 4).

The second viscometer was constructed similar to the first except that 1/4-in. copper tubing was coiled in three layers. The dia of the coil averaged 3 in. and the total length of tubing was approximately 40 ft. An equivalent length of the coil was calculated on the basis of Reference 4 and found to be 43.4 ft. The assembled apparatus is shown in Figure 11. The experimental results of the measurements are presented in Section IV.

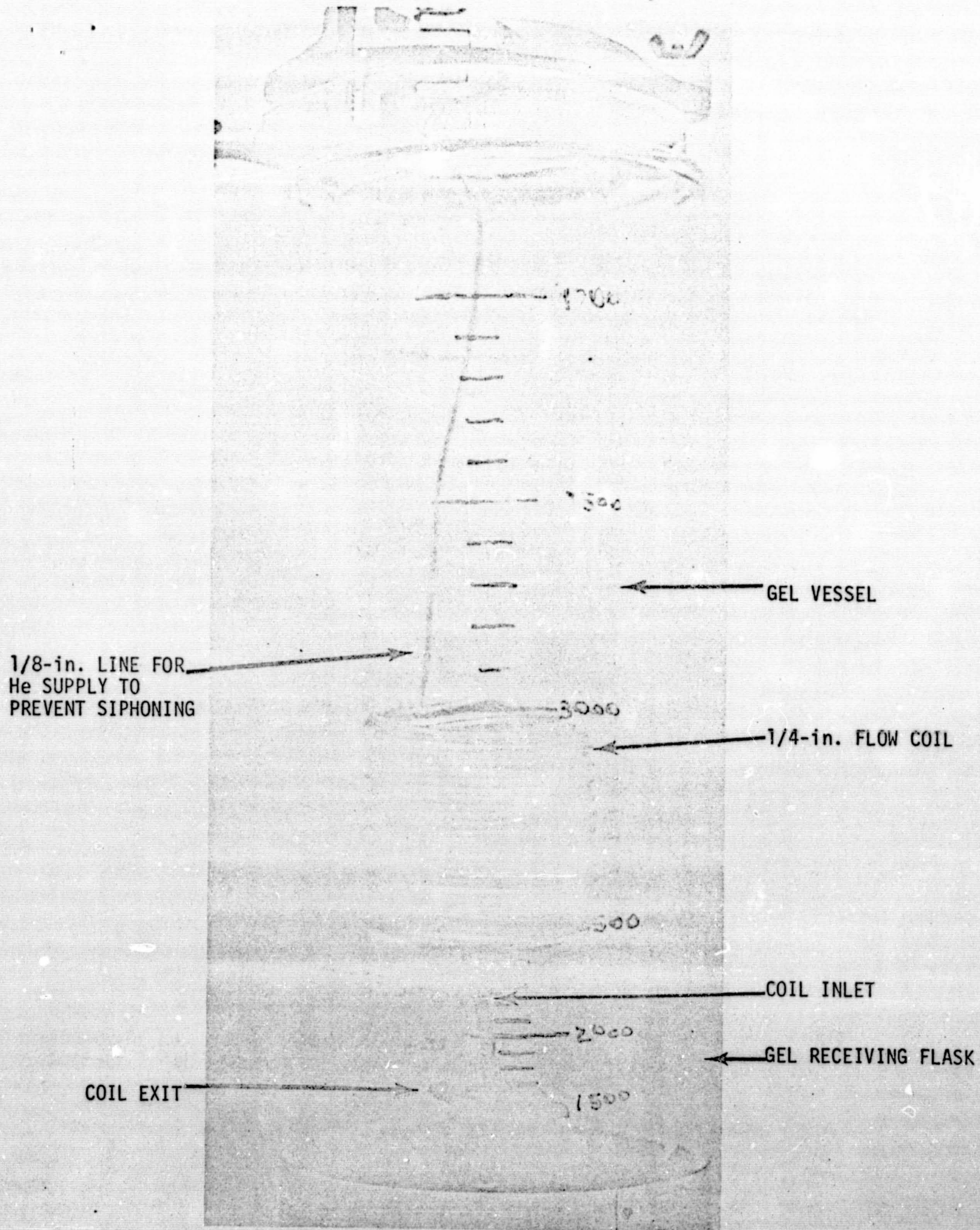


Figure 11. ASSEMBLED FLOW APPARATUS WITH 1/4-in. COIL

#### IV. EXPERIMENTAL RESULTS AND DISCUSSION

The ultimate objective of this research program was to prepare stable, uniform suspensions of ultrafine hydrocarbon particles in liquid hydrogen. Phase I of the program was devoted to identifying the more suitable hydrocarbon candidates for use in the preparation of colloidal hydrocarbon suspensions and for use in the preparation of liquid hydrogen gels. The results from Phase I were summarized in a Technical Report (Reference 11). Phase II of the program was devoted to (1) optimizing the conditions for preparing ethane particles for use as gelants for liquid hydrogen, (2) improving the procedure for preparing colloidal size particles of cyclopropane for use as a suspension of hydrocarbon in liquid hydrogen, (3) characterizing gelled liquid hydrogen, and (4) determining the stability of liquid hydrogen gelled with ethane and suspensions of cyclopropane in liquid hydrogen. Because the data from Phase I provides a basis for the work conducted in Phase II, typical results from Phase I are included in the following discussion in order to provide a comprehensive compilation of the data. The discussion of the results is organized under two headings: (1) Suspensions of Hydrocarbon Particles in Liquid Hydrogen, (2) Gelation of Liquid Hydrogen, and (3) Implications of the Experimental Results.



## IV, Experimental Results and Discussion (cont.)

### A. SUSPENSIONS OF HYDROCARBON PARTICLES IN LIQUID HYDROGEN

The investigation was initiated with methane as the candidate hydrocarbon and the various parameters affecting the particle size were initially evaluated using methane. The subsequent experiments were conducted with alternative hydrocarbons. The particles during Phase I of the program were prepared in the static liquid hydrogen system described in Section III, A, 1, the Phase II investigation was conducted using both a static liquid hydrogen system and a flowing liquid hydrogen system described in Section III, A, 2. Because of this the discussion is organized under three headings: (1) Preparation of Methane Suspensions in Liquid Hydrogen, (2) Preparation of Alternative Hydrocarbon Suspensions in Liquid Hydrogen, and (3) Preparation of Cyclopropane Suspensions in a Flowing Liquid Hydrogen System.

#### 1. Preparation of Methane Suspensions in Liquid Hydrogen

Because the ultimate objective of the program is to prepare a dilute, uniform suspension of a hydrocarbon in liquid hydrogen, the initial effort was directed towards forming the smallest methane particles possible using the condensation method described in Section III, A, 1. If sufficiently small particles can be produced and if they do not agglomerate, the kinetic energy of the particles themselves will maintain an adequately uniform dispersion.

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

Based on the hypothesis that the condensable contents of each bubble of gas formed during the injection of gas into liquid hydrogen leads to the formation of an individual solid particle, there are two approaches available for preparing small particles of methane. The first approach is to maintain a high dilution ratio of carrier gas to methane; the second approach is to inject the gaseous mixture through very small orifices. The dilution approach has practical limitations. The particle size reduction that occurs by this procedure is proportional to the cubic root of the concentration of the hydrocarbon, i.e., an eight-fold reduction in the concentration of methane in the carrier gas reduces the radius of the methane particle by one-half. One soon reaches the point of diminishing returns in such an approach, but some reduction in particle size is theoretically possible.

The second approach to producing small particles of methane is to reduce the size of the injection orifice. The size of a gas bubble produced by injection of gas into a liquid is dependent, within limits, on the size of the injection orifice (Reference 5). If the liquid wets the tube material, the bubble will form from the inner wall of the tube and the minimum bubble size produced in the configuration used will be the same radius as that of the inner tube surface. If the liquid does not wet the tube material, the bubble will form from the outer wall of the tube and the minimum bubble radius will be governed by the outer radius of the tube. One can estimate the approximate minimum size of a gas bubble that is stable in liquid hydrogen by the following calculation, using the pressure inside the bubble as the criterion for stability.

The pressure inside a gas bubble surrounded by a liquid medium is expressed by Equation (3), as discussed in Reference 6.

$$P = hg_p + 2 \alpha / r \quad (3)$$

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

where

- $h$  = height (cm) of the liquid column above the bubble
- $g$  =  $980.6 \text{ cm sec}^{-2}$
- $\rho$  = density in  $\text{g/cm}^{-3}$
- $\alpha$  = surface tension in  $\text{dynes/cm}^{-1}$
- $r$  = radius (cm) of the bubble
- $P$  = pressure in  $\text{dynes/cm}^{-2}$

The first term on the righthand side of Equation (3) is the pressure due to the hydrostatic head; the second term is due to the excess pressure required on the concave side of a surface to maintain stability. For liquid hydrogen, the density at  $20.4^\circ\text{K}$  is  $0.0710$  and the surface tension at  $20.4^\circ\text{K}$  is  $2.25 \text{ dynes/cm}$  (Reference 7). Based on these values, one can calculate the pressure inside gas bubbles of various radii in liquid hydrogen. The calculated data are presented in Table V.

TABLE V

VARIATION OF PRESSURE INSIDE GAS BUBBLES IN LIQUID HYDROGEN AS A FUNCTION OF BUBBLE SIZE

Bubble Size (radius in cm)	Pressure Inside Bubble	
	Required To Maintain Concave Radius ( $\text{dynes/cm}^2$ )	Total Pressure in a 1 Atm Environment (psia)
$1 \times 10^{-7}$	$4.5 \times 10^7$	666.7
$1 \times 10^{-6}$	$4.5 \times 10^6$	79.7
$1 \times 10^{-5}$	$4.5 \times 10^5$	21.2
$1 \times 10^{-4}$	$4.5 \times 10^4$	15.3
$1 \times 10^{-3}$	$4.5 \times 10^3$	14.77
$1 \times 10^{-2}$	$4.5 \times 10^2$	14.71
$1 \times 10^{-1}$	$4.5 \times 10$	14.7
1	4.5	14.7

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

From the data one can deduce that (1) the bubbles with a minimum radius of 10 to 100 $\mu$  ( $\mu = 10^{-4}$  cm) will be stable in liquid hydrogen because the pressure required to maintain the concave radius is negligible and (2) it is unlikely that gas bubbles with a radius of 1 $\mu$  or less will exist because of the appreciable pressure required to maintain the concave radius. The significant item to be noted from the preceding data is that, because of the pressure required, there is no theoretical advantage in attempting to prepare gas bubbles less than approximately 10 $\mu$  in radius.

After establishing that gas bubbles in liquid hydrogen are most likely to have a minimum radius somewhere between 10 and 100 $\mu$ , one can calculate the final size of a solid particle that is produced by the collapse of one bubble. For the sake of calculation, let us assume that

bubble radius = 25 $\mu$ ,

gas composition = 5 volume percent methane in helium,

temperature of the injected gas = 145°K, and

density of methane at 20°K = 0.52 g/cc,

then one gas bubble will contain  $4.4 \times 10^{-2}$  g of methane. This will produce a solid particle with a radius of 1.26 $\mu$ . For comparison purposes, a similar calculation with a bubble radius of 700 $\mu$  (which would be produced by the injection tube shown in Figure 3) shows that the radius of the solid particle is 35.5 $\mu$ . This 28-fold reduction in radius of the particles is apparently attainable by reducing the dia of the injection tube orifice from 0.140 cm to 0.005 cm. A metal porous plug was used as the outlet of the injection tube to maintain the flow rate at a practical level.

Based on the foregoing calculations, the preparation of methane particles in liquid hydrogen was initiated passing methane-hydrogen and methane-helium mixtures through an injection tube fitted with porous metal frits which contained 10 $\mu$  dia orifices. Four concentration levels of methane in hydrogen

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

and one concentration level of methane in helium were used as sources of methane for the formation of particles. The injection velocities were not varied appreciably because of the manner in which the injection tube functioned. The nominal quantity of liquid hydrogen used in the experiments was 600 ml.

The first set of experiments was conducted with 7.63 mole% methane in hydrogen being injected into liquid hydrogen through the metal frit. The pressure drop across the injector was a nominal 50 psi. Initially, the electrical power supplied to the injector-tube heater was inadequate and methane froze in the frit, terminating the experiment. However, with increased electrical power, the tube was operated for five min and the liquid hydrogen became opaque due to the presence of fine particles. The particles agglomerated within fifteen min and settled to the bottom of the flask with a large, fluffy appearance. Several additional experiments were conducted in which the methane concentration was determined by analysis of the slurry. The data are presented in Table VI.

None of the experiments produced an apparent stable collidal suspension of methane in liquid hydrogen. The particles that are initially produced give the appearance of a colloid but after a period of approximately 15 min, the solid material settles as large flocculent particles. The samples of the resulting liquids were obtained by agitating the solution with a helium sparge. The lower limit of detection of methane in the analytical procedure used in these experiments is approximately 2000 ppm.

Two of the experiments, Numbers 5 and 6, were conducted with helium as the carrier gas rather than hydrogen. The liquid hydrogen remained transparent during the experiments and methane was evidently swept out with the helium. On this basis, and because hydrogen is already present in the final system, the use of hydrogen appeared to be the preferable carrier gas.

IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

TABLE VI

DATA OBTAINED FROM THE INJECTION OF DILUTE METHANE THROUGH A 10 $\mu$  FRIT INTO LIQUID HYDROGEN

Exp. No.	CH <sub>4</sub> Conc. mole %	Time Interval min	Gas Flow Rate l/min	Pressure Drop Across Orifice psig	CH <sub>4</sub> Analysis ppm
1	2.81	3	0.9	41	<2000
		12	0.5	47	
		15	0.4	47	
2	2.81	5	0.9	52.5	<2000
		11	0.8	53	
		16	0.4	58	
		19	0.2	58.5	
3	1.53	5	1.4	63	<2000
		10	1.2	65	
		16	0.5	67	
		20	0.5	68	
4	1.53	2	1.2	72	trace CH <sub>4</sub>
		6	0.9	73	
		10	0.9	72	
		16	0.5	73	
5	0.92 (in helium)	2	0.9	44	trace CH <sub>4</sub>
		4	0.7	44	
		6	0.9	43	
		8	0.7	44.5	
		12	0.5	51.5	
6	0.92 (in helium)	2	2.4	54	no visible solid particles, CH <sub>4</sub> analysis showed none present.
		4	2.4	54	
		7	2.1	53.5	
		8	1.9	54	
		12	1.7	54	
		16	1.4	54	
7	13.6	1	1.4	18.5	<2000, injector plugged
		3	0.5	24	
8	13.6	2	1.4	43	6800
		4	0.7	45.5	
9	13.6	2	1.4	64	24600
		5	1.4	67	

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

Unfortunately, the pressure drop across the orifice required to maintain a steady flow of gas into the liquid hydrogen also caused the expected small bubble pattern exiting from the frit to degrade into a large gas bubble at the tip of the tube. Experiment 7, which produced a small pattern of bubbles at a pressure drop of nominally 20 psi, could be continued for only 3 min before clogging occurred. The other experiments were conducted with the higher pressure drop values across the orifice; because the large bubble formed at the tip, there was no advantage to conducting the experiments with significantly higher values than the nominal 50 psi range.

Of further interest is the fact that, in Experiment 9, the methane particles were allowed to settle until they occupied a constant volume. In the first 30 min, the particles settled from a 500 ml volume to a 200 ml volume. After 60 min, the volume occupied by the particles was reduced to 100 ml. During the next 3 hr, the volume remained constant. The inference of the data is that an initial gel structure may occur with 12.8 weight percent methane using the  $10\mu$  orifice. This is a significantly lower concentration level of methane than had been reported previously as required for gelation of liquid hydrogen.

The next series of experiments was conducted using a single 0.025 in. orifice for the injection port rather than the  $10\mu$  metal frit. Based on the experience of the previous set of experiments, hydrogen was used as the carrier gas. The results are presented in Table VII. The majority of the experiments were terminated because the methane froze in the injection orifice; a problem which can be overcome by increasing the heat-input into the gas stream. Nevertheless, the results obtained from the experiments are adequate to establish trends.

TABLE VII

DATA OBTAINED FROM THE INJECTION OF DILUTE METHANE  
INTO LIQUID HYDROGEN USING A 0.025 IN. ORIFICE

Exp. No.	CH <sub>4</sub> Conc. mole %	Time Interval min	Gas Flow Rate l/min	Pressure Drop Across Orifice psi	Final CH <sub>4</sub> Analysis and Remarks
1N	1.46	3	0.28	45.5	Trace CH <sub>4</sub>
		5	0.23	49.0	
		6*	0.01	49.0	
2N	1.46	2	0.47	72.0	Trace CH <sub>4</sub>
		5	0.12	73.0	
		8	0.06	74.0	
		10*	0.01	79.0	
3N	5.31	2	0.94	50.6	<2000 ppm CH <sub>4</sub>
		4	0.28	53.1	
		4.5	0.28	----	
		4.75*	----	57.0	
4N	5.31	1	0.42	75.3	<2000 ppm CH <sub>4</sub>
		3	0.09	75.5	
		5	0.08	76.0	
		6.5*	0	76.3	
5N	5.31	1	0.94	89.9	<2000 ppm CH <sub>4</sub> , large flocculent precipitate of CH <sub>4</sub> settled out during the experiment.
		2	0.47	88.8	
		4	0.16	88.8	
		6	0.08	90.6	
		10	0.05	83.6	
		16	0.05	79.4	
6N	15.06	1	0.79	87.5	11,000 ppm CH <sub>4</sub> in 580 cc of LH <sub>2</sub> , flocculent particles settled to occupy a volume of 130 ml.
		2	0.13	89.1	
		3	0.08	89.1	
		4*	0	89.5	
7N	15.06	1	0.34	58.5	33,600 ppm CH <sub>4</sub> in 450 cc of LH <sub>2</sub> , flocculent particles settled to fill a volume of 300 ml.
		8	0.34	58.1	
		10	0.34	58.1	
		15	0.34	58.0	
8N	15.06	1	0.71	31.1	Injector clogged within a minute.

\*Injector clogged.



#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

The use of the 0.025 in. dia orifice failed to produce a stable colloidal solution of methane in liquid H<sub>2</sub>. Within one min after injection, the solid methane agglomerated and settled as large flocculent particles. The flocculent particles appeared similar regardless of the dilution ratio used in the gas mixture or the rate at which the gas stream was injected. The significant result from use of this injection tube is that it appears that the initiation of gel structure in liquid hydrogen can occur with approximately 5 weight percent methane as the gelant. This value is inferred from the results of Experiments 6 and 7 concerning the volume of the settled particles. The value of 5 weight percent should be compared to the value of 12.8 weight percent obtained with the use of the 10 $\mu$  orifice injection tube.

In addition to the experiments with the 0.025 in. orifice injection tube, three experiments were conducted with an injection tube which had a frit with 10 $\mu$  orifices which faced upward in the liquid hydrogen rather than downward as the original tube with the 10 $\mu$  orifices. The new tube was used to avoid the accumulation of a large gas bubble at the surface of the metal frit as reported in the initial experiments. The results of the experiments are presented in Table VIII.

TABLE VIII

DATA OBTAINED FROM THE INJECTION OF DILUTE METHANE INTO LIQUID HYDROGEN USING 10 $\mu$  ORIFICES FACING UPWARD

Exp. No.	CH <sub>4</sub> Conc. in H <sub>2</sub> mole %	Time Interval min	Gas Flow Rate l/min	Pressure Drop Across Orifice psi	Remarks
9N	9.2	3	1.26	76.0	
		6	1.26	75.8	Large particles settled after two minutes.
		9	1.26	75.1	
		12	1.00	74.5	
10N	9.2	2	0.75	60.4	
		3	0.50	60.4	
		6	0.50	60.0	
		9	0.23	60.6	
		10*	9	60.6	
11N	9.2	1	1.3	60.2	Colloidal appearance disappeared after 40 seconds.

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

In Experiment 9N, the solution appeared opaque because of the dispersion of very small particles. After approximately two min of operation, the particles agglomerated to form larger particles that rapidly settled. The particles were not as flocculent as those produced using the single 0.025 in. (635 $\mu$ ) dia orifice.

In Experiment 10N, the particles within the first two min of operation were small and made the solution opaque. These particles agglomerated into a more flocculent precipitate than described for Experiment 9N. The particles lost some of the original flocculent character as they settled.

In Experiment 11N, an opaque solution formed immediately, but after 40 sec of operation small nuclei were observed on the walls of the flask. The flow of gas mixture was stopped at the end of one min and the solution became clear after approximately 40 sec. The small particles agglomerated to form a fluffy precipitate. In summation, the colloidal solutions of methane particles produced using the upward facing 10 $\mu$  frit exhibited less stability than those produced with the original injection tube which had the downward facing frit.

The preceding experimental data demonstrated that a uniform suspension of methane particles at a concentration level of 5000 ppm would have a transitory existence in liquid hydrogen. Within a period of minutes, the majority of the particles agglomerate and settle out of the suspension. The particle preparation method appeared to form a wide range of sizes and it was possible that some particles were so small (<1 $\mu$ ) that they were not detectable by visual observation. The next series of experiments with methane was conducted to determine the concentration level of methane particles that would persist for several min in liquid hydrogen. In order to do this, a different analytical procedure was used. The detection unit for the gas

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

chromatography method was changed from a thermal conductivity cell system to a flame ionization detector (the details are presented in Section III, B) and the limit of detection changed from 2000 ppm to 20 ppm by weight methane in hydrogen.

The particles were prepared as in the earlier experiments and the agglomerated particles were allowed to settle to the bottom of the flask. At selected times, a small liquid sample, approximately 1 ml, was withdrawn through the sampling tube as shown in Figure 4 and analyzed for methane content. The point of sampling in the liquid was approximately two in. above the settled particles to avoid entrainment of the solids during the withdrawal of the sample. The results of the experiments are presented in Table IX. During the experiments, the liquid hydrogen slowly evaporated from the fuel preparation flask because the outer Dewar contained liquid nitrogen as the cooling bath. The total volume of the liquid hydrogen in the fuel preparation flask at the time of sample is presented in the table along with the time at which the sample was withdrawn.

TABLE IX

DATA OBTAINED FROM THE EVALUATION OF METHANE  
PARTICLE SUSPENSIONS IN LIQUID HYDROGEN

Exp. No.	Injection Orifice Size	Average $\Delta P$ Across Orifice psi	Methane Concentration ppm	Total Volume At Sampling Time ml	Elapsed Time min
1J	0.025 in.	47.3	503	750	5
			640	480	20
			128	400	30
3J	10 $\mu$	5.8	328	750	5
			440	550	20
16J	10 $\mu$	3.5	920	400	10
			720	325	57
17J	10 $\mu$	12.5	560	600	10
			344	425	63

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

The trend to be noted from the data in Table IX is that the methane concentration in the liquid hydrogen continues to decrease with elapsing time. The data in Experiment 3J indicate a slight increase in concentration, but the total actual number of particles present has not increased if one takes the decrease in volume of the liquid hydrogen into account. The data from the other experiments which were conducted for longer time periods all indicate a significant decrease in the methane concentration. Agglomeration of the methane particles continued for at least one hr after preparation of the particles. The significance of the data is that the methane suspensions which can be prepared in liquid hydrogen should be used immediately after preparation. The storage of the colloidal-size particles of methane in liquid hydrogen as stable suspensions is not possible.

##### 2. Preparation of Alternative Hydrocarbon Suspensions in Liquid Hydrogen

Trimethylamine and several hydrocarbons were evaluated as potential alternatives to methane in the preparation of carbon-containing suspensions in liquid hydrogen. The results are discussed under two headings: (1) Trimethylamine, and (2) Alternative Hydrocarbons.

###### a. Trimethylamine

Previous experimental work in liquid  $N_2$  indicated that trimethylamine particles did not agglomerate to form flocculent particles but remained in a very finely divided state for prolonged periods (Reference 8). Because of this behavior, trimethylamine appeared to be an excellent candidate for the preparation of a colloidal suspension of a carbon-containing compound in liquid  $H_2$ .

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

Three experiments were conducted with the injection tube with the 0.025 in. orifice, the results are presented in Table X. Hydrogen was used as the diluent gas for the trimethylamine.

TABLE X

DATA OBTAINED FROM THE INJECTION OF DILUTE TRIMETHYLAMINE INTO LIQUID HYDROGEN USING A 0.025 IN. ORIFICE

Exp. No.	(CH <sub>3</sub> ) <sub>3</sub> N Conc. mole %	Time Interval min	Gas Flow Rate l/min	Pressure Drop Across Orifice psi	Remarks
1TN	7.0	2	0.31	54.1	Granular particles formed and quickly settled, not flocculent like the CH <sub>4</sub> particles.
		5	0.31	54.1	
		8	0.31	54.3	
		12	0.31	54.6	
		15	0.31	54.7	
2TN	7.0	1	0.20	54.6	Small granular particles formed along with a trace of colloidal size particles.
		2	0.20	55.0	
		4	0.20	55.5	

The data in Experiment 1TN failed to confirm the anticipated result that trimethylamine would be better than methane for the formation of suitable colloidal particles. In Experiment 2TN, the addition of the dilute methylamine stream was stopped so that the behavior of the particles in suspension could be observed. The bulk of the solid particles were small, dense, and settled rapidly. The supernatant liquid contained some very small particles that slowly settled as they agglomerated. The very small particles disappeared within 3 min after terminating the experiment. Experiment 2TN was then repeated; the results were identical.

Four additional experiments were conducted using the metal frit with the 10 $\mu$  orifices which faced upward in the liquid H<sub>2</sub>.

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

Experiment 4TN utilized a gas mixture of 6.1 mole percent trimethylamine in hydrogen and a pressure drop of 74 psi was used across the orifice; this resulted in a gas flow rate of 0.66 l/min. The orifices clogged after two min operation; 0.151 mole of trimethylamine had been added to the liquid H<sub>2</sub>. Very little solid material remained in the flask. Experiment 5TN was conducted in a similar manner except that the pressure drop across the orifice was reduced to 59.4 psi. The orifice clogged after 45 sec operation, the final solution appeared similar to that of the previous experiment.

Experiments 6TN and 7TN were conducted with a mixture of 6.4 mole percent trimethylamine in helium. The experimental conditions were the same as those in Experiment 4TN and the orifices clogged after 45 sec operation with only traces of solid material appearing in the liquid H<sub>2</sub>. The low vapor pressure of trimethylamine compared to that of methane led to premature termination of the experiments. However, the material that was injected did agglomerate to form dense particles.

On the basis of the foregoing experiments, it is apparent that trimethylamine will agglomerate in liquid H<sub>2</sub> and this negates the possibility of producing a stable colloidal suspension. The characteristics of solid trimethylamine are not conducive to the formation of liquid H<sub>2</sub> gels with low concentrations of the hydrocarbon.

##### b. Alternative Hydrocarbons

The hydrocarbons which were evaluated as potential candidates for suspension in liquid hydrogen were: ethylene, ethane, propylene, cyclopropane, isobutane, and butene-1. In the initial series of experiments, the particles were prepared by injecting a 10 volume percent hydrocarbon/90 volume percent hydrogen gas mixture through a 0.025 in. dia orifice into liquid

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

hydrogen for 1 min. The particles were allowed to settle to the bottom of the flask and liquid samples were withdrawn periodically at a point 2 in. above the settled particles. The liquid hydrogen evaporated slowly during the experiments and the total volume of liquid remaining at the time of sampling was noted. Typical data obtained from these experiments are presented in Table X.

The data in Table XI show that some cyclopropane particles remain suspended for at least 46 min. There is a notable degree of agglomeration of the cyclopropane particles during the first minutes during and immediately following preparation. In Experiment 9D, the cyclopropane concentration is still in the 5000 ppm range after seven min. However, it should also be noted that the solution was rapidly evaporating, 250 ml lost during 5 min, and the turbulence in the liquid undoubtedly contributed to the high concentration level at the sampling point. In the subsequent Experiments 10D and 11D, the evaporation rate was significantly less and the system appeared quiescent. The data indicate that no significant agglomeration is occurring after approximately 10 min. The concentration values increase with time because the evaporation of the hydrogen is occurring, but the total quantity of cyclopropane suspended remains constant. The concentration level which persisted is approximately one order of magnitude less than the goal of the program.

Experiments 13D through 17D, involving the preparation of ethylene particles in liquid hydrogen, demonstrate that there is a gradual agglomeration of the particles with progressing time. After 34 min, the concentration of ethylene has decreased to 300 ppm from an initial value of greater than 11,000 ppm. The fact that ethylene particles remained suspended at the 5000 ppm level for approximately 15 min indicates that the suspension does have a measurable metastable existence.

TABLE XI

DATA INDICATIVE OF THE STABILITY OF COLLOIDAL-SIZE  
HYDROCARBON PARTICLES IN LIQUID HYDROGEN

Exp. No.	Hydrocarbon Candidate	$\Delta P$ Across Orifice psi	Hydrocarbon Concentration at Fixed Sampling Point, ppm	Total Volume At Sampling Time, cc	Elapsed Time min
9D	Cyclopropane	53	5,040	550	2
			4,730	300	7
10D	Cyclopropane	44	210	600	10
			400	310	37
11D	Cyclopropane	44	210	650	16
			504	310	46
13D	Ethylene	50	6,580	300	5
14D	Ethylene	52	11,750	500	2
			3,010	450	12
15D	Ethylene	50	6,300	700	12
16D	Ethylene	50	4,200	450	15
17D	Ethylene	48	308	360	34
20D	Ethane	49	525	450	3
			615	300	10
21D	Butene-1	51	4,770	800	2
			420	550	10

Ethane particles evidently continue to agglomerate slowly after an initial rapid agglomeration. Within 15 sec after the first particles were prepared, large flocculent particles of ethane began to form. Butene-1 particles also exhibited agglomeration in liquid hydrogen, isobutane particles settled out immediately after preparation.

Based on the results from the initial series of experiments, additional experiments were conducted with cyclopropane, ethylene, and



IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

ethane with increased storage duration. The gaseous mixture, 10 volume per- cent hydrocarbon/90 volume percent hydrogen, was injected into the liquid hydrogen for 1 min. The major portion of the hydrocarbon particles settled quickly due to agglomeration and the remaining clear liquid hydrogen solution was sampled periodically. Typical results obtained with cyclopropane are presented in Table XII.

TABLE XII

DATA INDICATIVE OF THE STABILITY OF COLLOIDAL-SIZE PARTICLES OF CYCLOPROPANE IN LIQUID HYDROGEN

Exp. No.	Injection Orifice Size	$\Delta P$ Across Orifice psi	Hydrocarbon Concentration at Fixed Sampling Point, ppm	Total Volume At Sampling Time, cc	Elapsed Time min
95	0.025 in.	14	273	580	10
			462	400	65
105	0.025 in.	16	1050	590	6
			483	350	120
11J	0.025 in.	27	420	700	3
			630	410	120
13J	0.025 in.	43	378	750	7
			609	350	187
10M	0.025 in.	13.5	546	640	30
			882	340	145
15F	0.025 in.	4.0	672	610	30
			567	570	35
			1155	375	140
			1575	370	145
16F	0.025 in.	3.1	1365	360	171
1F	10 $\mu$ frit	2.8	2667	750	5
			798	340	120
3F	10 $\mu$ frit	6.4	1281	325	93
3M	10 $\mu$ screen	8.3	315	680	3
			294	550	48
			714	325	182

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

The significant item to be noted from the data is that the cyclopropane concentration generally increases with increasing storage time. Because the hydrogen evaporates gradually, the explanation for this behavior is that a significant number of cyclopropane particles of very small size form and do not agglomerate. After the large particles have settled out, the total number of the small particles in solution remains essentially constant. Therefore, if the volume of the liquid decreases by one-half, the concentration of the hydrocarbon is doubled.

The data reported for Experiment 15F give an indication of the reproducibility of the analyses. The scatter in the data is appreciable, but this was expected at these low concentration levels. For example, for cyclopropane, 100 ppm by weight corresponds to approximately 5 ppm by volume; the limit of sensitivity of the analytical method is 1/2 ppm by volume.

The pressure drop data in the scoping experiments indicate that the number of small particles formed is not directly related to the velocity at which the gas mixture is injected into the liquid hydrogen. The effect of orifice size in the range utilized in these experiments does not appear to be significant. The effect may become apparent if a larger range of sizes is employed.

In Experiment 10M, helium was used as the carrier gas for the cyclopropane rather than the hydrogen normally used. Comparison of the results from Experiment 10M with the other experiments in the table confirms that the use of a non-collapsing gas, such as helium in liquid hydrogen, offers no advantage over hydrogen itself.

The results of this series of experiments are very encouraging in regard to preparing uniform suspensions of colloidal-size hydrocarbon particles in liquid hydrogen. The fact that significant quantities of

IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

cyclopropane remain in suspension for at least three hr implies that a prolonged existence of such a suspension is possible. Cyclopropane is the most promising candidate for such suspensions.

Similar experiments were conducted with ethylene, ethane, and a cyclopropane/ethane mixture. The results are presented in Table XIII.

TABLE XIII

DATA ON THE PREPARATION OF COLLOIDAL-SIZE PARTICLES OF HYDROCARBONS IN LIQUID HYDROGEN AND INDICATIVE OF THEIR STABILITY

Exp. No.	Injection Orifice Size	Average $\Delta P$ Across Orifice psi	Hydrocarbon Candidate	Hydrocarbon Concentration at Fixed Sampling Point ppm	Total Volume At Sampling Time, cc	Elapsed Time min
55	10 $\mu$	1.4	Ethylene	868	750	7
				504	400	27
7J	0.025 in.	1.4	Ethylene	168	800	3
				28	550	57
5M	0.025 in.	3.0	Ethylene	560	700	3
				742	360	148
12M	0.025 in.	2.7	Ethylene	714	590	30
				938	330	150
13M	0.025 in.	2.5	Ethylene	224	610	30
				196	305	150
11F	0.025 in.	5.3	Ethane	45	720	10
				45	370	296
18F	10 $\mu$	9.7	Ethane	210	470	5
				105	300	95
8M	0.025 in.	2.8	Ethane/ Cyclopropane 1/1	112	615	30
				44	380	145

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

The data in the table indicate that ethylene behaves similarly to cyclopropane, but that agglomeration continues during the storage period. Although the ethylene concentration increases in a few cases, the total number of ethylene particles decreases in all cases. Ethane particles continue to agglomerate as evidenced by the data. However, note that the flocculent nature of the agglomerated ethane particles is attractive for gelation of the hydrogen. Experiment 8M was conducted with a 1:1 ethane/cyclopropane mixture to determine if a hydrocarbon mixture would result in less particle agglomeration than a pure hydrocarbon. The decreasing concentration of hydrocarbons in the liquid hydrogen with time indicates that the particles continue to settle.

In summation, cyclopropane is apparently the most suitable hydrocarbon candidate of those evaluated for the preparation of suspensions of colloidal-size hydrocarbon particles in liquid hydrogen. Repeatedly, the total number of suspended particles remains constant while the volume of the solution decreases.

#### 3. Preparation of Cyclopropane Suspensions In A Flowing Liquid Hydrogen System

The preparative procedure used in the previous scoping experiments led to the formation of primarily large hydrocarbon particles which settled in liquid hydrogen. Because the hydrocarbon particles formed initially in the liquid hydrogen reservoir can function as condensation sites for the gaseous hydrocarbon injected into the reservoir, this process can lead to the formation of larger hydrocarbon particles after the system is in operation than the particles formed initially. In an effort to produce smaller hydrocarbon particles and to minimize the number of large particles formed by the preparative procedure, the static liquid hydrogen reservoir was replaced by

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

a flowing liquid hydrogen stream. In this system fresh liquid was continuously sweeping the gaseous injection orifice and the freshly formed particles would not provide condensation sites for the injected hydrocarbon.

Because cyclopropane appeared to be the most suitable hydrocarbon candidate for use as a suspension of colloidal-size particles in liquid hydrogen, the experiments with flowing liquid hydrogen were conducted with cyclopropane as the hydrocarbon. The apparatus used for the experiments is shown in Figure 8. The injection orifice for the gaseous mixture was 0.010 in. in dia and the internal heating element was operated at the 85 watt level. The system was operated until approximately 700 cc of product was collected in the reservoir. The reservoir contents were sampled periodically at two levels; one sample tube was used to withdraw liquid from near the liquid surface and the other tube was used to withdraw a sample from the bottom of the flask. The bottom contained the settled volume of cyclopropane particles while the supernatant liquid contained the small particles of cyclopropane in suspension. The cyclopropane concentration in the injected gas mixture was varied, 1, 3, and 10 volume percent were used. The product was stored for periods up to 80 minutes to obtain an indication of the stability of the suspensions.

Typical results are presented in Table XIV. The concentration level of cyclopropane in the supernatant liquid is given along with the concentration level of cyclopropane in the settled volume of particles. The supernatant appeared to be transparent during the storage periods. A distribution ratio of suspended cyclopropane to cyclopropane settled at the bottom of the flask was calculated from the chemical analysis and the values are presented in the last column of the table. Data from two experiments using the static liquid hydrogen system employed in the scoping experiments are included in the table and designated as Experiments 9AA and 10AA. Based on

TABLE XIV

## DATA CONCERNING THE INJECTION OF GASEOUS CYCLOPROPANE/HYDROGEN MIXTURES

Exp. No.	Composition of Injected Gas Volume Percent Cyclopropane	Concentration of Cyclopropane In Liquid Hydrogen				Time of Sampling After Preparation min.	$\Delta P$ Across Injection Orifice psi	Period of Gas Injection min.	Distribution Ratio of Cyclopropane Suspended/ Settled
		Supernatant Liquid Volume (cc)	ppm (wt)	Settled Particles Volume (cc)	ppm (wt)				
15AA	1	670	105			5	78.8	4	$5.2 \times 10^{-2}$
		470	168	50	$2.73 \times 10^4$	7			
16AA	1			40	$2.73 \times 10^4$	80	72.1	10	$7.2 \times 10^{-2}$
		645	210	85	$5.46 \times 10^4$	5			
		455	525			7			
12AA	3			50	$6.51 \times 10^4$	78	73.5	10	$7.2 \times 10^{-2}$
		445	1365			80			
		320	1281	230	$1.30 \times 10^5$	15			
13AA	3			210	$1.49 \times 10^5$	17	76.8	7	$2.0 \times 10^{-2}$
		580	2100			72			
		360	1218	160	$1.07 \times 10^5$	74			
14AA	3			150	$1.39 \times 10^5$	75	73.5	7	$2.2 \times 10^{-2}$
		535	1008			5			
		380	1890	170	$1.05 \times 10^5$	7			
3S	10			135	$1.26 \times 10^5$	69	72.0	3	$4.2 \times 10^{-2}$
		305	4137	215	$1.47 \times 10^5$	71			
4S	10			200	$1.26 \times 10^5$	45	74.0	3	$4.0 \times 10^{-2}$
		260	987			48			
9AA	3	510	357			49	67.5	2	$1.0 \times 10^{-2}$
				110	$3.78 \times 10^4$	52			
10AA	3	285	630			30	58.4	10	$4.4 \times 10^{-2}$
				460	$7.56 \times 10^4$	31			
						32			$5.2 \times 10^{-3}$

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

flow measurements and the pressure drop values in the gas mixture tank, not all the cyclopropane was trapped in the liquid hydrogen. The data indicate that from 50 to 100 percent of the hydrocarbon was captured.

The significant items to be noted from the data in Table XV are that (1) only from 1 to 7 percent of the cyclopropane particles remain suspended after five minutes following preparation of the particles, (2) the cyclopropane concentration used in the injected gas mixture does not affect the distribution ratio significantly, but increasing cyclopropane concentration in the injected gas mixture does increase the concentration of cyclopropane which remains in suspension initially, and (3) the flowing liquid hydrogen system does produce a greater concentration of cyclopropane particles in suspension than the static liquid hydrogen system, compare Experiment 12AA with 10AA. The fact that less than 7 percent of the cyclopropane particles are in suspension five minutes after preparation in the flowing liquid hydrogen system indicates that considerable agglomeration of particles does occur.

In an attempt to obtain an indication of the particle-size of the cyclopropane which remained in suspension, the 6 mm I.D. sampling tube was replaced with sample tubes having glass frit filters. The results are presented in Table XV.

IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

TABLE XV

DATA OBTAINED IN ATTEMPT TO DETERMINE THE SIZE  
OF CYCLOPROPANE PARTICLES SUSPENDED IN LIQUID HYDROGEN

Exp. No.	Composition of Injected Gas Volume Percent Cyclopropane	$\Delta P$ Across Injection Orifice psi	Period of Gas Injection min.	Concentration of Cyclopropane in Liquid Hydrogen Sample Withdrawn ppm (wt)	Sampling Time min.	Conditions Tube I.D.
18AA	1	72.0	2	100	90	6 mm
19AA	1	74.5	3	<10 <10	5 85	fine porosity frit, 4-5.5 $\mu$
1S	1	73.2	3	20	5	medium porosity frit, 10-15 $\mu$
4S	10	74.0	3	987	52	6 mm, subcooled
5S	10	73.1	3	40	49	coarse porosity frit, 40-60 $\mu$ , subcooled

The concentration of cyclopropane in the liquid hydrogen filtered through the frits was negligible compared to the concentration obtained with the unfiltered samples. At first glance, one might assume that the cyclopropane particles in suspension are greater than 50 $\mu$  in dia. However, particles of this size should readily settle in liquid hydrogen. It may be assumed that convection in the flask could maintain some large particles in suspension, but in Experiments 4S and 5S the liquid was subcooled and then pressurized to reduce convection due to boiling.

The rate of liquid sampling through the frit was slow compared to the liquid flow through 6 mm tubes and this may lead to fractionation of the mixture as it progresses to the sample bomb. In addition, there is



#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

some tendency for the small particles to adhere to the glass surface initially and it is conceivable that the cyclopropane particles adhered to the glass frits. Because of these factors, it is felt that the filtration of the liquid samples is not a valid means of determining the size of the cyclopropane particles in suspension.

In summation, the use of the flowing hydrogen system did lead to a increase in the concentration of cyclopropane particles in suspension as compared to that obtained with the use of the static liquid hydrogen system. However, the majority of the cyclopropane particles do agglomerate within a matter of minutes after preparation of the initial particles. The determination of the storability of the cyclopropane particles in suspension as a function of time is discussed in the next section.

#### 4. Storage of Cyclopropane Suspensions in Liquid Hydrogen

During the initial scoping experiments, suspensions of cyclopropane particles were stored as long as three hours while the concentration level remained at the 500 ppm level. The tests were conducted with an external liquid nitrogen bath and the gradual evaporation of liquid hydrogen from the inner storage flask limited the period of storage.

To provide a system in which the cyclopropane suspension in liquid hydrogen could be stored indefinitely, an apparatus was built as shown in Figure 12. A large double-walled flask was partially silvered so that view slots remained and then evacuated. This liquid hydrogen storage Dewar served as an external liquid hydrogen bath. The sample storage flask was fabricated so that after preparation of the suspension, the entire flask could be submerged in the liquid hydrogen bath. A sampling tube was installed in the sample storage flask so that liquid samples could be periodically withdrawn.

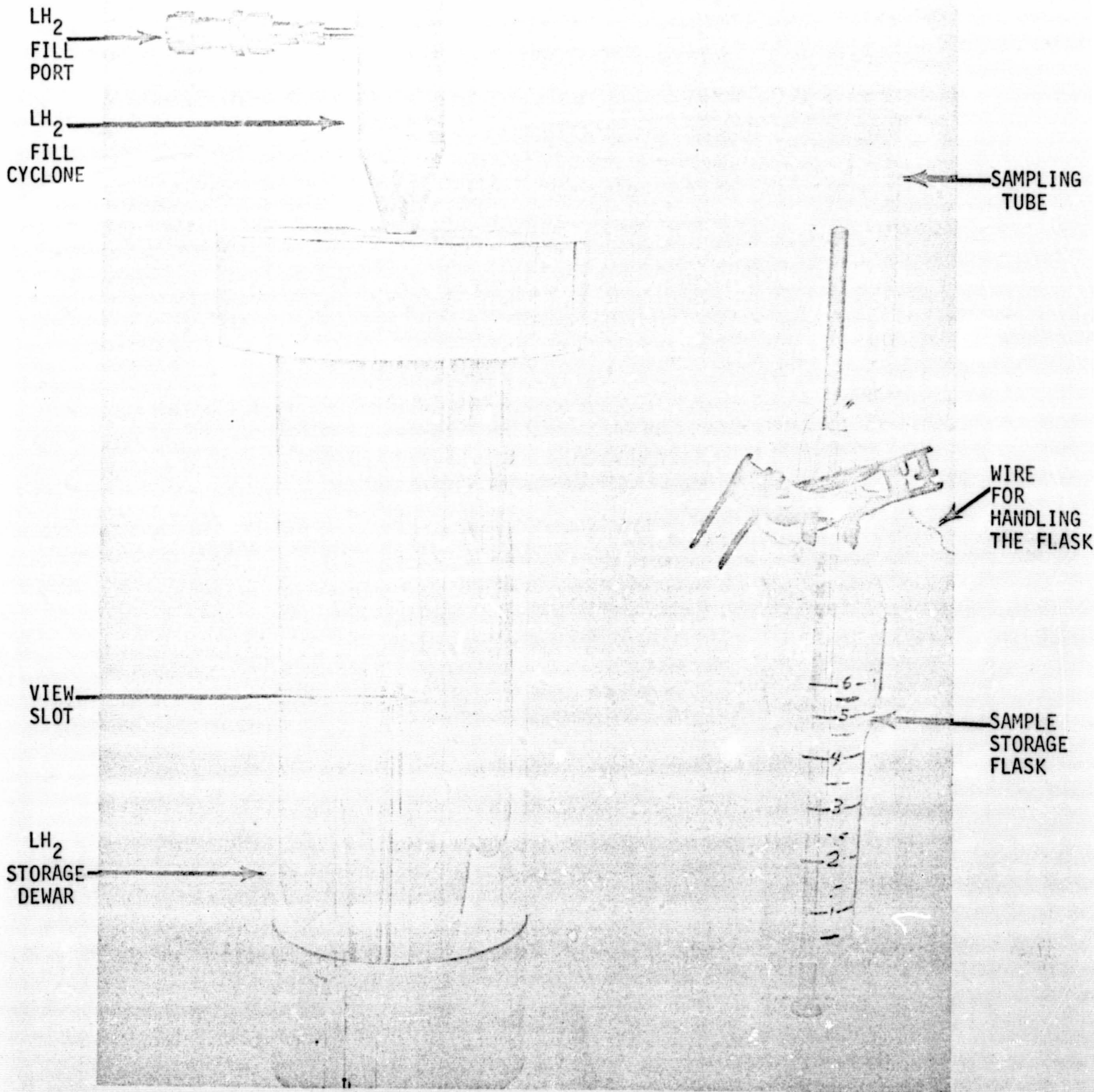


Figure 12. COMPONENTS FOR STORAGE TEST OF COLLOIDAL-SIZE PARTICLES IN LIQUID HYDROGEN

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

The assembled apparatus is shown in Figure 13. A tygon tube with appropriate valves was attached to the sample tube in order to provide controls for sampling. After withdrawal of a liquid sample, the ullage of the storage flask was repressurized with helium to immediately repress boiling due to the partial vacuum created by sampling.

The suspension of cyclopropane particles was prepared by injecting a 10 percent cyclopropane in hydrogen gaseous mixture through a 0.025 in. dia orifice into the liquid hydrogen in the sample storage flask for one minute. Liquid hydrogen was added as necessary to maintain a 600 cc liquid level during the preparation procedure. The pressure drop across the orifice was 2.7 psi. Based on previous experiments, this procedure should produce a suspension of cyclopropane in liquid hydrogen of approximately 1000 ppm by weight. The total liquid volume was 500 cc and the settled volume of cyclopropane particles was 40 cc. The sample tube inlet was located at the 300 cc level. The apparatus was assembled as shown in Figure 13 and the samples were withdrawn at one day intervals. The results of the storage test are presented in Table XVI.

TABLE XVI

DATA OBTAINED DURING THE STORAGE OF A  
CYCLOPROPANE SUSPENSION IN LIQUID HYDROGEN

<u>Time Elapsed Since Preparation of Particles, hr</u>	<u>Concentration of Cyclopropane Suspended in Liquid Hydrogen ppm (wt)</u>
19.3	100
44.4	80
65.9	16

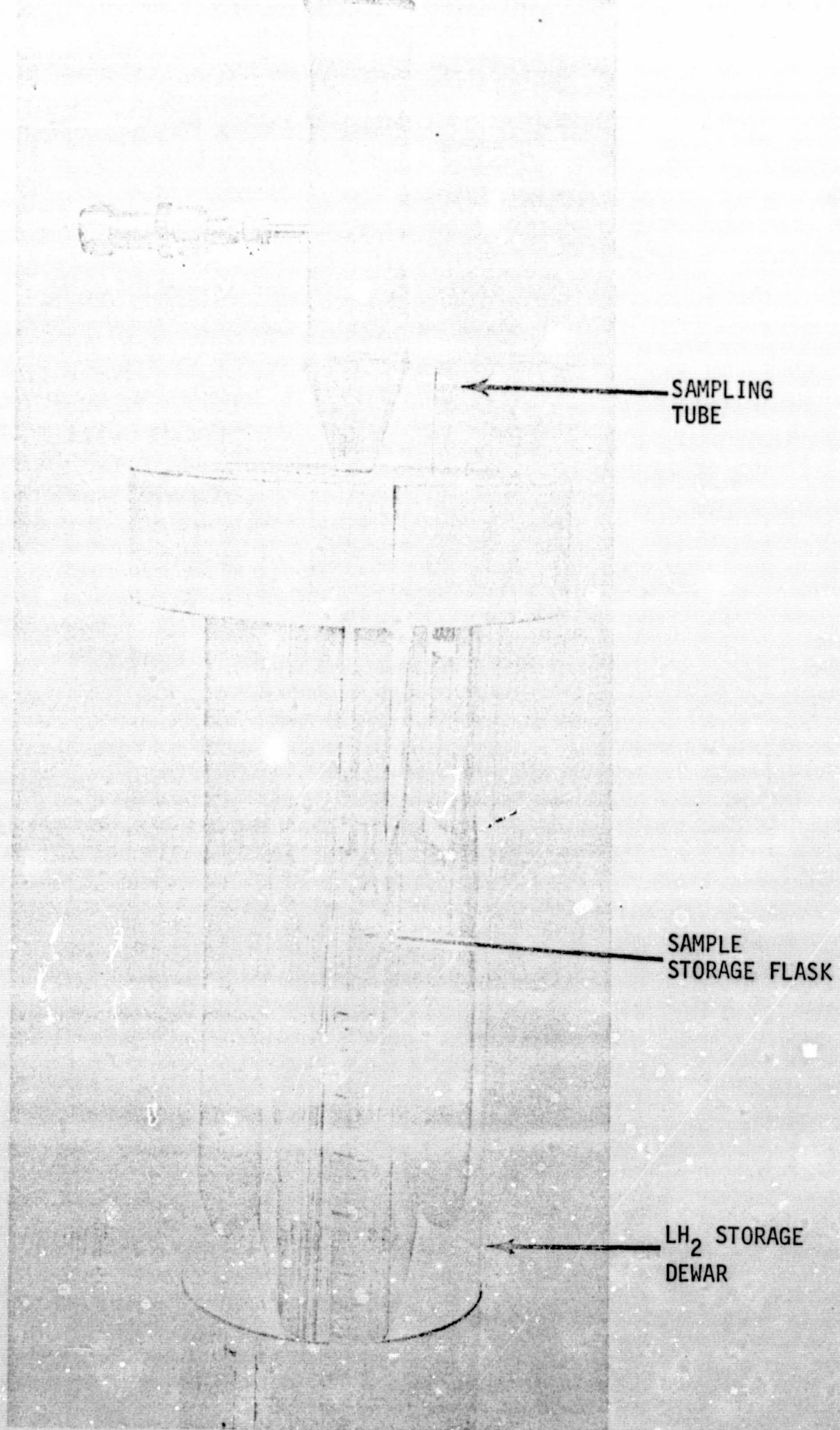


Figure 13. ASSEMBLED APPARATUS FOR STORAGE TEST OF COOLIDAL-SIZE PARTICLES IN LIQUID HYDROGEN

#### IV, A, Suspensions of Hydrocarbon Particles in Liquid Hydrogen (cont.)

At the end of 66 hours of storage the test was terminated because the concentration level of 16 ppm corresponds to approximately the limit of detection of the analytical procedure. The fact that the concentration level had dropped down to 100 ppm after 19 hours indicates that the cyclopropane particles continue to agglomerate and consequently settle out of suspension. The significance of the storage test results is that it does not appear to be feasible to prepare suspensions of colloidal-size particles of hydrocarbons in liquid hydrogen which have an unlimited life time. Suspensions can be prepared with life times on the order of minutes, but a stable colloidal suspension which is storable for days or years does not appear to be available for use in the nuclear rocket engine.

#### B. GELATION OF LIQUID HYDROGEN

The gelation of liquids with particulate gelants is generally dependent on the specific surface area of the particles, i.e., the smaller the particle size, the greater surface energy per mass available for gelation. In addition to the interparticle attractive forces, liquid surface attractive forces can also contribute to the gel formation. In this program in which hydrocarbons are to be used as the gelants for liquid hydrogen, it is essential that the hydrocarbon particles be completely insoluble in the liquid hydrogen. Otherwise, the smaller particles will dissolve and the larger particles will increase in size to some equilibrium value. If this occurs, then one observes, on the macroscopic scale, that the gelling capacity of the particles will decrease gradually until the gel structure disappears. The discussion of results is divided into the following sections: (1) Scoping Experiments, (2) Optimization of Conditions to Prepare Ethane Gelant Particles, (3) Storage Tests of Liquid Hydrogen Gelled with Ethane Particles, (4) Preparation of a Gelled Hydrogen Slush, and (5) Characterization of Gelled Liquid Hydrogen.

## IV, B, Gelation of Liquid Hydrogen (cont.)

### 1. Scoping Experiments

In order to survey the relative effectiveness of candidate hydrocarbon particles for gelation of liquid hydrogen, an initial series of experiments was conducted in which candidate gas mixtures were injected for periods of time ranging from 6 to 10 min and the volume of the settled particles was measured and analyzed. To obtain a relative measurement of gelling capacity, the apparent constant volume of settled particles was selected as a criterion for the minimum quantity of hydrocarbon required for imparting gel structure to liquid hydrogen. The actual concentration required to impart gel structure to liquid hydrogen is appreciably greater than this minimum value. Initial experiments conducted with methane indicated that less dense particles were obtained using the 0.025 in. dia orifice instead of the 10 $\mu$  metal frit. Consequently, the hydrocarbon particles were prepared by injecting a nominal 10 volume percent hydrocarbon/90 volume percent hydrogen gas mixture into liquid hydrogen through a 0.025 in. dia orifice. The results from this series of experiments are presented in Table XVII.

Of the hydrocarbons considered in this series of experiments, ethane appears to have the greatest gelling capacity for liquid hydrogen; the settled volume of particles being less than 4 weight percent in each experiment. Methane appears to be the second choice for a gelant, with a 5 weight percent value when prepared with the same injection orifice as the other hydrocarbon particles. Propene, ethylene, and cyclopropane exhibited values in the 10 weight percent category, and evaluation of the isobutane and butene-1 particles indicate that greater than 20 weight percent is required for gelation of liquid hydrogen; values in this regime are prohibitive with regards to performance degradation in a nuclear engine. The trend of the data indicates that the use of higher molecular weight hydrocarbons than those evaluated would result in still higher concentrations of particles required for gelation.

TABLE XVII

DATA ON THE MINIMUM QUANTITY OF HYDROCARBON  
REQUIRED TO GEL LIQUID HYDROGEN

Exp. No.	Hydrocarbon Candidate	Minimum Weight Percent Required For Gelation	Time Required To Attain Constant Vol min	Remarks
9	Methane	12.8	60	Used 10 $\mu$ frit, volume of particles remained constant for 3 hrs after initial hr of settling.
6N	Methane	4.9	30	Used 0.025 in. orifice.
7N	Methane	5.0	30	Used 0.025 in. orifice.
1D	Isobutane	22.2	35	Small, compact particles.
3D	Isobutane	20.8	25	Relatively dense, settled rapidly.
4D	Propene	10.5	30	Small, flocculent particles.
5D	Propene	10.5	22	
8D	Cyclopropane	12.8	30	Relatively flocculent particles formed which tended to compact further on standing.
12D	Ethylene	8.9	30	Small particles which did not agglomerate readily, settled slowly.
18D	Ethane	2.8	15	Particles settled very gradually, no visible particles remain in the supernatant liquid after 15 min.
19D	Ethane	3.8	15	
20D	Ethane	2.6	15	
22D	Butene-1	45.0	--	Large, dense particles appeared almost immediately and began to settle.

IV, B, Gelation of Liquid Hydrogen (cont.)

Based on the foregoing, additional experiments were conducted with methane and ethane as gelants for liquid hydrogen. The additional data obtained with methane is presented in Table XVIII.

TABLE XVIII

DATA INDICATIVE OF THE MINIMUM QUANTITY OF METHANE REQUIRED FOR GELATION OF LIQUID HYDROGEN

Exp. No.	Injection Orifice Size in.	Average $\Delta P$ Across Orifice psi	Volume of Settled Particles cc	Concentration of Methane in Gels wt%	Elapsed Time min.
23D	0.025	47	270	11.0	36
14J	0.025	40	50	12.4	180
15J	0.025	60	400	6.4	1
			300	8.6	10
			200	12.9	35
			200	12.9	70
			180	14.3	110
			150	17.2	150
			150	17.2	230

The data indicate that the particles continue to grow for at least two hr after which the volume of particles remains constant. The significant item to be derived from the data is that the methane concentration required to produce a gel in liquid hydrogen is at least 12 weight percent and may be greater than 17 weight percent. These values are considerably greater than the minimum values reported in Table XVII. The data in Table XVII are based only on the volume of settled particles without any apparent gel structure present; the values in Table XVIII were obtained with the gel structure apparent in the liquid hydrogen.



#### IV, B, Gelation of Liquid Hydrogen (cont.)

A gaseous mixture of 10 volume percent ethane/90 volume percent hydrogen was used to prepare the ethane gelant particles. The injection tube orifice was 0.025 in. dia and the gaseous mixture was injected for periods of approximately ten min. A small layer of liquid hydrogen was maintained on the surface of the gelled liquid to prevent a crust of particles from forming on the surface. The yield stress values of the gels were measured by the weighted sphere method described in Section III, C. The weighted spheres were prechilled and then gently lowered onto the gel surface. Based on the dia and weight of the sphere, a yield stress value was calculated. The data obtained from these experiments are presented in Table XIX. The data indicate that a minimum of 10 weight percent ethane is required to impart significant gel structure in liquid hydrogen as indicated by a yield stress of greater than 135 dynes/cm<sup>2</sup>. All of the gels reported in Table XIX supported the sphere which exerted 135 dynes/cm<sup>2</sup> on the surface, but would not support the sphere which exerted 500 dynes/cm<sup>2</sup>. Withdrawal of the heavier sphere from the gel left a hole which maintained its structure, further demonstrating that the gel is self-supporting.

Two prolonged storage tests were conducted for a period of eight hr. The first, designated as Experiment 12F, was conducted with liquid nitrogen in the outer bath. The evaporation rate of hydrogen from the gelation flask was such that small quantities of liquid hydrogen had to be added periodically. This addition of liquid hydrogen disturbed the gel, a measurable loss in gel volume was noted following each addition. Experiment 2M was subsequently conducted with liquid hydrogen in the outer Dewar to avoid the necessity of adding liquid hydrogen to the gelation flask. After 8 hr of storage, the ethane concentration in the gel increased from an initial 11.3 weight percent to a value of 13.8 weight percent. Again these values are considerably greater than the data values obtained during the scoping experiments reported in Table XVII. The data reported in Table XIX is for mixtures which possess measurable gel structure, while no gel structure was apparent in the experiments described by the data in Table XVII.

IV, B, Gelation of Liquid Hydrogen (cont.)

TABLE XIX

DATA INDICATIVE OF THE QUANTITY OF ETHANE  
REQUIRED FOR GELATION OF LIQUID HYDROGEN

<u>Exp. No.</u>	<u>Average <math>\Delta P</math> Across Orifice psi</u>	<u>Volume Of Gel cc</u>	<u>Concentration Of Ethane In Gel wt%</u>	<u>Yield Stress dynes/cm<sup>2</sup></u>	<u>Elapsed Time min.</u>
5F	65	420	9.2	>135 <500	80
6F	63	200	8.4	>135 <500	120
8F	3.4	430	10.3	>135 <500	81
10F	2.6	380	10.0	>135 <500	140
12F	3.0	750	11.1	>135 <500	72
		440	18.9	>135 <500	480
2M*	1.8	550	11.3	>135 <500	8
		495	13.8	>135 <500	484

\*Liquid hydrogen was substituted for liquid nitrogen in the outer Dewar to reduce evaporation from the gel vessel.

#### IV, B, Gelation of Liquid Hydrogen (cont.)

At this point, it should be borne in mind that the preparation of the particles for gelation had not been optimized. The effect of dilution ratio with the carrier gas had not been evaluated, and the effect of the orifice size had received only cursory investigation. However, the particles of the various candidate hydrocarbons had been prepared under similar conditions and a comparison of the relative gelling capacities of the particles of the candidates should be valid. Based on the foregoing results it was apparent that ethane particles were the most suitable of the candidates evaluated for the gelation of liquid hydrogen.

##### 2. Optimization of Conditions to Prepare Ethane Gelant Particles

On the basis of the experimental results from the scoping experiments, ethane was selected as the prime hydrocarbon candidate to use as a gelant for liquid hydrogen. The experimental effort was directed toward the definition of the optimum conditions for preparing ethane gelant particles. The effects of injector orifice size, composition of the ethane-hydrogen mixture which is injected into the liquid hydrogen, and the velocity at which the gas mixture is injected into liquid hydrogen were evaluated.

In these experiments, the concentration of ethane in the settled particle volume in liquid hydrogen served as an indication of the relative size of the ethane particles. As the gelant particle size decreases, the gelling capacity of the particle increases and the weight of gelant required for gelation decreases. Minimizing the ethane concentration in the settled volume of particles is the desired result and the conditions which lead to minimizing the ethane particle size are to be considered as optimum for preparing gelant particles.

#### IV, B, Gelation of Liquid Hydrogen (cont.)

Three orifice sizes, 0.010, 0.025, and 0.052 in. dia, were used in the experiments. The ethane concentrations in the gas mixture which was injected into the liquid hydrogen to form ethane particles were 100, 50, 10, 5, 3, and 1 mole percent in hydrogen. The velocity of the injected stream is represented by the value of the pressure drop across the orifice. The particles were allowed to settle and age for 45 min after preparation in order to insure that a constant volume was attained. The data obtained from the experiments are presented in Table XXI and are also plotted in Figure 14.

The significant items to be noted from the data are as follows. First, as the ethane concentration in the injected gas mixture decreases from 100 to 1 mole percent, the particle size decreases as evidenced by the decreasing concentration of ethane in the settled volume of particles. Below the 10 mole percent ethane level, the concentration effect is less pronounced. Second, as the orifice size decreases, the size of the particles also decrease significantly. At the 1 mole percent level however, the capture efficiency with the largest orifice was extremely low so that no significant quantity of gelant particles was accumulated in the liquid hydrogen. Third, the velocity of the injected stream is a secondary effect; comparing Experiments 7JJ and 8JJ with 9JJ and 10JJ indicates that the average ethane concentration increases from 6.2 to 6.8 weight percent in the settled particles, but the difference in the values lies within the limits of experimental error. The trends to be noted from the data are that as the orifice size is decreased and the ethane concentration in the injected gas reduced, the ethane particles become more effective for gelling liquid hydrogen. The data are indicative of the minimum quantity of ethane required for gelation, however, the ethane concentration required for a long-term storage of gelled hydrogen may be appreciably greater than the minimum values presented in Table XX.

IV, B, Gelation of Liquid Hydrogen (cont.)

TABLE XX

DATA INDICATIVE OF CONDITIONS REQUIRED FOR PREPARATION OF  
SMALL PARTICLES OF ETHANE FOR GELLING LIQUID HYDROGEN

Exp. No.	Ethane Concentration In Injected Gas Mixture mole percent	Pressure Drop Across Orifice psi	Orifice Size diameter, inch	Ethane Concentration in Settled Volume of Particles in Liquid Hydrogen weight percent
15MM	100	7.0	0.052	52.5
16MM	100	5.9	0.052	52.5
5JJ	100	0.5	0.025	35.4
6JJ	100	1.0	0.025	37.5
17MM	100	73	0.010	18.0
18MM	100	75	0.010	16.5
13MM	50	5.6	0.052	25.5
14MM	50	6.8	0.052	34.5
9MM	50	3.6	0.025	13.5
10MM	50	3.0	0.025	14.8
11MM	50	78	0.010	12.4
12MM	50	80	0.010	11.7
5MM	10	3.0	0.025	7.4
6MM	10	66	0.010	5.7
7JJ	5	20	0.025	6.4
8JJ	5	18	0.025	6.0
9JJ	5	5.0	0.025	6.0
10JJ	5	3.5	0.025	7.5
11JJ	5	60	0.010	5.8
12JJ	5	58	0.010	4.2
13JJ	5	60	0.010	4.8
3JU	3	68	0.010	3.8
5JU	3	63	0.010	4.7
4JJ	1	1.1	0.025	6.4
2JJ	1	67	0.010	4.0
3JJ	1	64	0.010	4.0
19MM	1	72	0.010	4.3

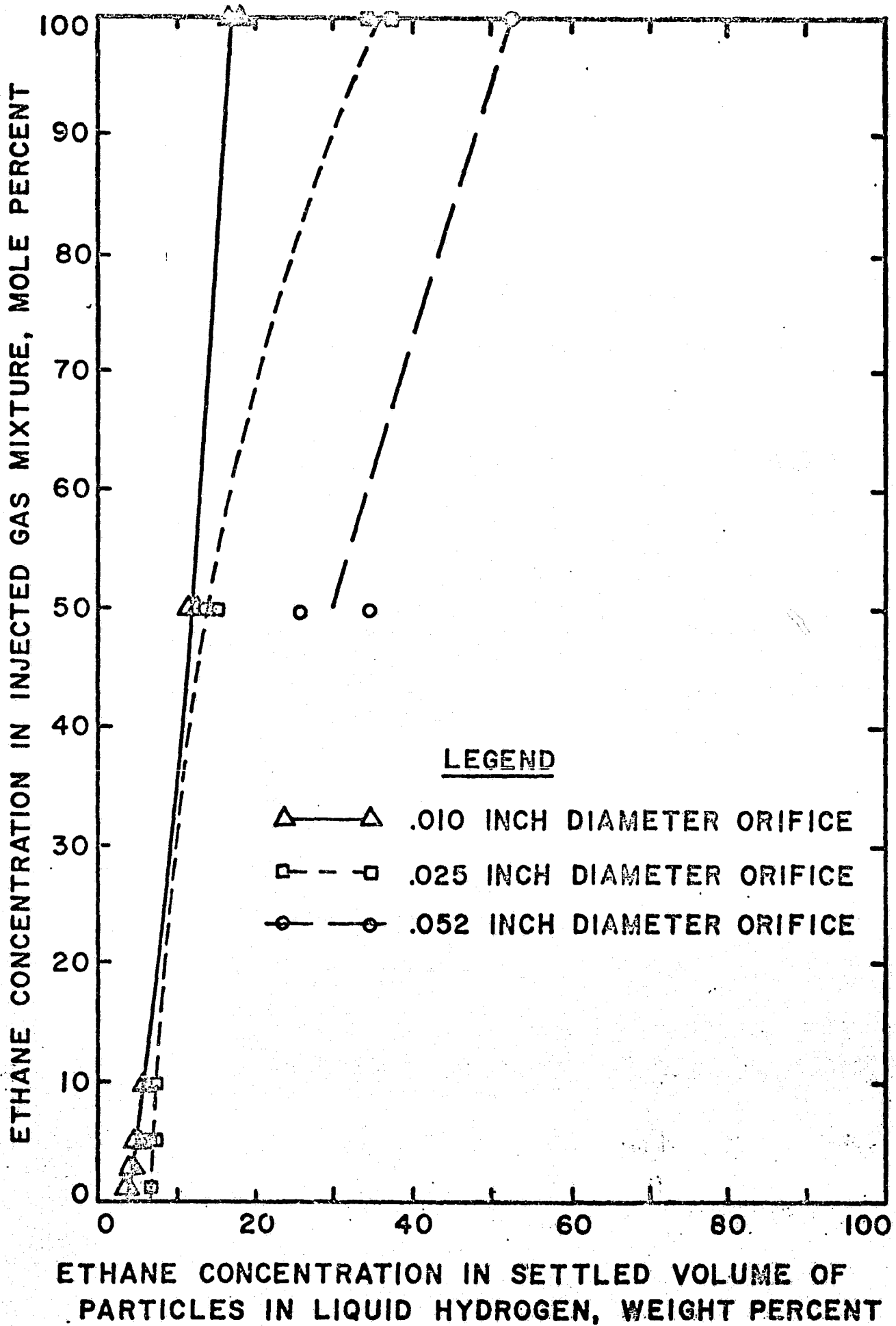


Figure 14. EFFECT OF ETHANE CONCENTRATION IN INJECTED GAS AND ORIFICE SIZE ON THE CONCENTRATION OF SOLID ETHANE PARTICLES REQUIRED FOR GELATION OF LIQUID HYDROGEN

#### IV, B, Gelation of Liquid Hydrogen (cont.)

##### 3. Storage Tests of Liquid Hydrogen Gelled with Ethane Particles

The data obtained from the optimization of the procedure for preparation of gelant particles gave a preliminary indication of the minimum quantity of ethane required to produce gel structure in liquid hydrogen. The data indicate that the use of the smallest orifice (0.010 in. dia) enhances the formation of the smaller solid ethane particles as evidenced by the small values of the ethane concentration in the settled volume of particles. The data also indicate that the low concentration of ethane in the injected gas mixture favors the formation of smaller particles. In order to determine the minimum quantity of ethane that is required for gelation of liquid hydrogen, two gel storage experiments were conducted for periods of approximately 400 minutes.

The first gel was prepared using the 0.010 in. dia orifice and 5 volume percent ethane in hydrogen as the injection gas mixture. The gel was stored for 397 minutes; the gel structure index was found to exceed 200 dynes/cm<sup>2</sup>; and chemical analysis showed that 9.0 weight percent ethane was present in the gel. The second gel was prepared using the 0.010 in. dia orifice and 1 volume percent ethane in hydrogen as the injection gas mixture. The gel was stored for 407 minutes; the gel structure index was found to be less than 200 dynes/cm<sup>2</sup> and the chemical analysis showed that 6.3 weight percent ethane was present in the gel. Based on these data, it was apparent that the gelled liquid hydrogen for a five-day storage test should be prepared using the 0.010 in. dia injection orifice and the 1 volume percent ethane in hydrogen as the injection gas for preparing the ethane particles.

Initially, the gel particles for the five-day storage test of gelled liquid hydrogen were prepared using a 1 volume percent ethane in hydrogen as the gas mixture which is injected into the liquid hydrogen.

#### IV, B, Gelation of Liquid Hydrogen (cont.)

But the use of a smaller preparation flask allowed the gelant particles to be carried out of the flask as a fluidized bed and an adequate quantity of gelant particles for the gel storage test could not be attained. This situation was avoided by using a 3 volume percent ethane in hydrogen as the mixture for injection into the liquid hydrogen. After the gelled hydrogen was prepared, the gel was sampled, the flask was capped, and the entire flask immersed in a liquid hydrogen storage Dewar. The apparatus used is shown in Figure 15.

Liquid hydrogen was added periodically through the cyclone to the liquid hydrogen storage Dewar. The storage Dewar was silvered with only two view slots left for observation. The gel volume was monitored by visual observation during the storage period.

The gel volume decreased from an initial value of 320 cc to a value of 300 cc after 40 hours and there was no further change in volume during the remaining 81 hours of this storage test. The chemical analysis showed that the initial ethane concentration in the gel volume was  $8.8 \pm 0.2$  weight percent. A sample withdrawn at the termination of the storage test was analyzed and found to contain  $11.6 \pm 0.2$  weight percent ethane. However, during the final sample procedure some of the gel was compacted as the tube was lowered, so the analysis is considered to represent an upper limit value. Based on volume change, the gel should have contained 9.7 weight percent ethane at the end of the test.

The storage test demonstrated that the gelant particles remain essentially unchanged during the five days and that prolonged storage of gelled liquid hydrogen should be possible as far as the gelant-liquid hydrogen interactions are concerned. The test further demonstrated that 10 weight percent ethane in liquid hydrogen is quite adequate for gelation of the liquid hydrogen for use in the nuclear engine system.



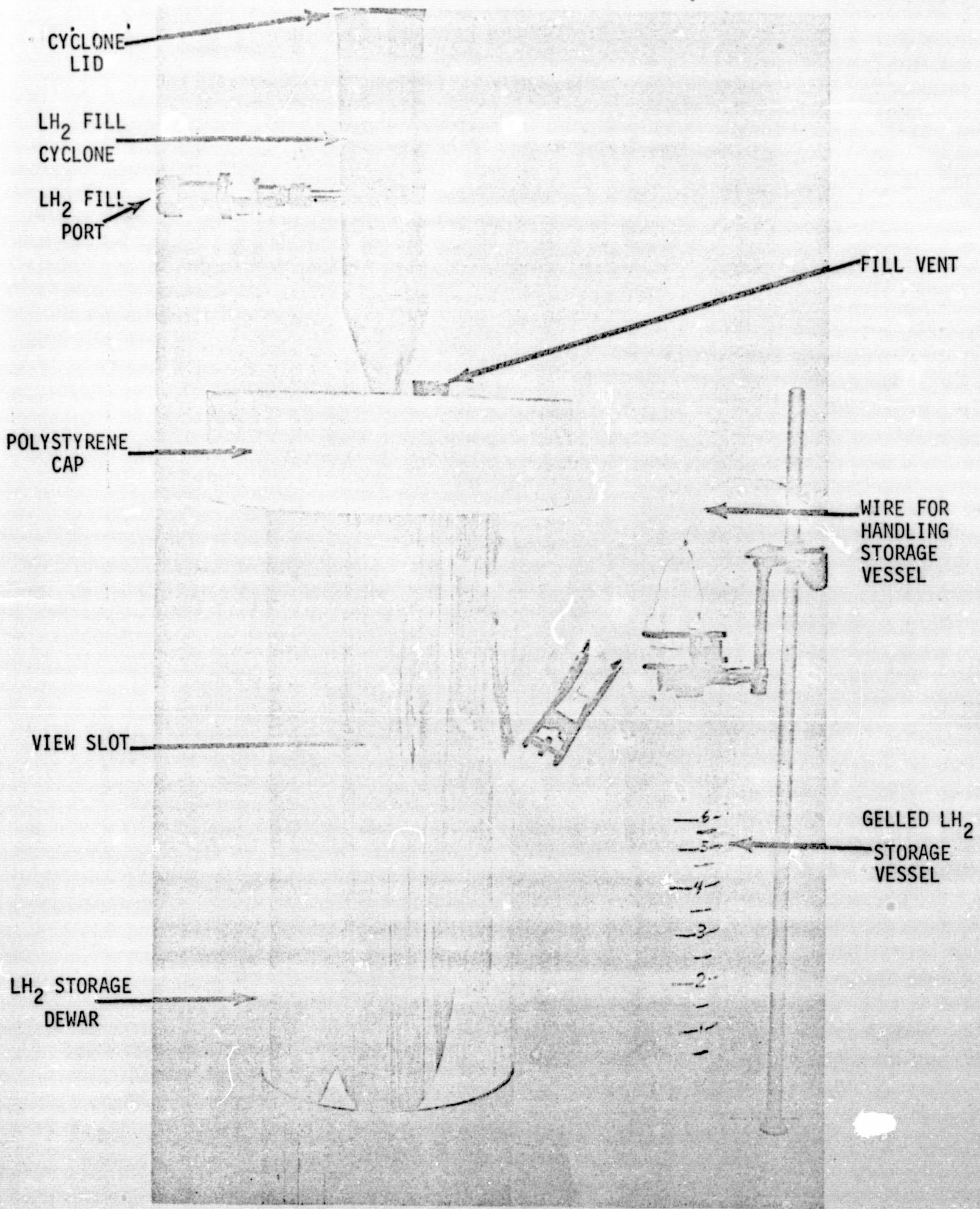


Figure 15. APPARATUS FOR STORAGE OF GELLED LIQUID HYDROGEN

## IV, B, Gelation of Liquid Hydrogen (cont.)

### 4. Preparation Of A Gelled Hydrogen Slush

As slush hydrogen ages there is a gradual growth in the size of the solid hydrogen particles and the solid hydrogen particles settle out. Although it is not possible to prevent this growth of crystals, the hydrogen crystals can be maintained in suspension uniformly by gelation of the liquid hydrogen.

A gelled hydrogen slush was prepared and stored for fifteen minutes. The extremely short storage period was determined by the heat-soak rate into the apparatus that was used. The ethane gelant particles were prepared by injecting a 3 volume percent ethane-in-hydrogen mixture through a 0.010 in. dia orifice into liquid hydrogen. After preparing the particles, the injection tube was replaced by a stirring rod and the liquid hydrogen was evaporated by applying a vacuum until the slush formed. The mixture was stirred during the evaporation step to maintain uniformity. The resulting slush was firmly gelled with 4 weight percent ethane. Volumetric measurements indicated that the slush contained 50% solid hydrogen. There was no apparent degradation of mixture during the brief observation period.

From visual inspection of the gelled mixture, the gelant concentration apparently was higher than required to maintain a uniform slush. The lack of suitable apparatus to maintain the slush for prolonged periods, negates any effort at this time to determine the minimum concentration of gelant necessary to maintain uniformity in the slush.

#### IV, B, Gelation of Liquid Hydrogen (cont.)

##### 5. Characterization of Gelled Liquid Hydrogen

The gelled liquid hydrogen was characterized with respect to viscosity over a range of shear rates and the yield stress measured by a modified penetrometer method. The methods and procedures have been described in Section III.C.

The flowability of the gelled liquid hydrogen through a nominal 1/4-in. dia tubing was demonstrated at several gelant concentrations. The apparatus used for these experiments is shown in Figure 11. Sufficient ethane was used to impart slight gel structure to the liquid hydrogen. Liquid hydrogen was then flowed through the same coil to obtain comparative data. The data are presented in Table XXI; the apparent viscosity values were calculated using conventional relationships for coiled tubes (Reference 4).

The data indicate that the gelation of the liquid hydrogen at the ethane concentration levels reported causes approximately two to three fold increase in the apparent viscosity at the shear rates encountered in the experiments. Based on the Reynolds number values, the flow in these experiments was in the turbulent regime. The data are plotted in Figure 16 in the form of shear stress versus shear rate. The ratio of these values is the apparent viscosity. For comparison purposes a dotted line designated as "theoretical LH<sub>2</sub>" is included in the figure to represent the viscosity of liquid hydrogen in the laminar flow regime. The viscosity value of  $1.34 \times 10^{-4}$  poise at 20°K (Reference 10) was used to generate the line.

The scatter in the data is due to the fact that the measurements are being made at the normal boiling point of the liquid and due to errors in pressure readings because relatively low pressures are required to initiate and maintain flow. The apparent fact that the gel with 6% ethane

TABLE XXI

DATA INDICATIVE OF THE APPARENT VISCOSITY OF GELLED LIQUID  
HYDROGEN FLOWING THROUGH 0.19 INCH DIAMETER TUBING

<u>Gelant Concentration wt%</u>	<u>ΔP Across Coil psi</u>	<u>Flow Rate cc/sec</u>	<u>Calculated Apparent Viscosity cp</u>
9.6	0.40	12.1	0.23
9.6	0.50	14.3	0.24
9.6	0.55	14.2	0.27
8.1	0.16	10.5	0.11
8.1	0.18	9.5	0.13
8.1	0.25	11.5	0.15
8.1	0.25	13.5	0.13
8.1	0.30	16.4	0.13
8.1	0.45	15.6	0.20
6	0.44	13.2	0.23
6	0.65	21.0	0.21
6	0.68	18.0	0.26
6	0.90	20.7	0.30
6	0.90	23.3	0.27
6	1.35	27.3	0.34
6	1.40	27.6	0.35
6	2.75	50.0	0.38
None	0.05	5.6	0.061
"	0.06	6.4	0.064
"	0.11	10.0	0.076
"	0.11	10.7	0.071
"	0.12	9.9	0.088
"	0.13	10.3	0.088
"	0.16	11.2	0.098
"	0.20	14.1	0.098
"	0.50	22.7	0.15

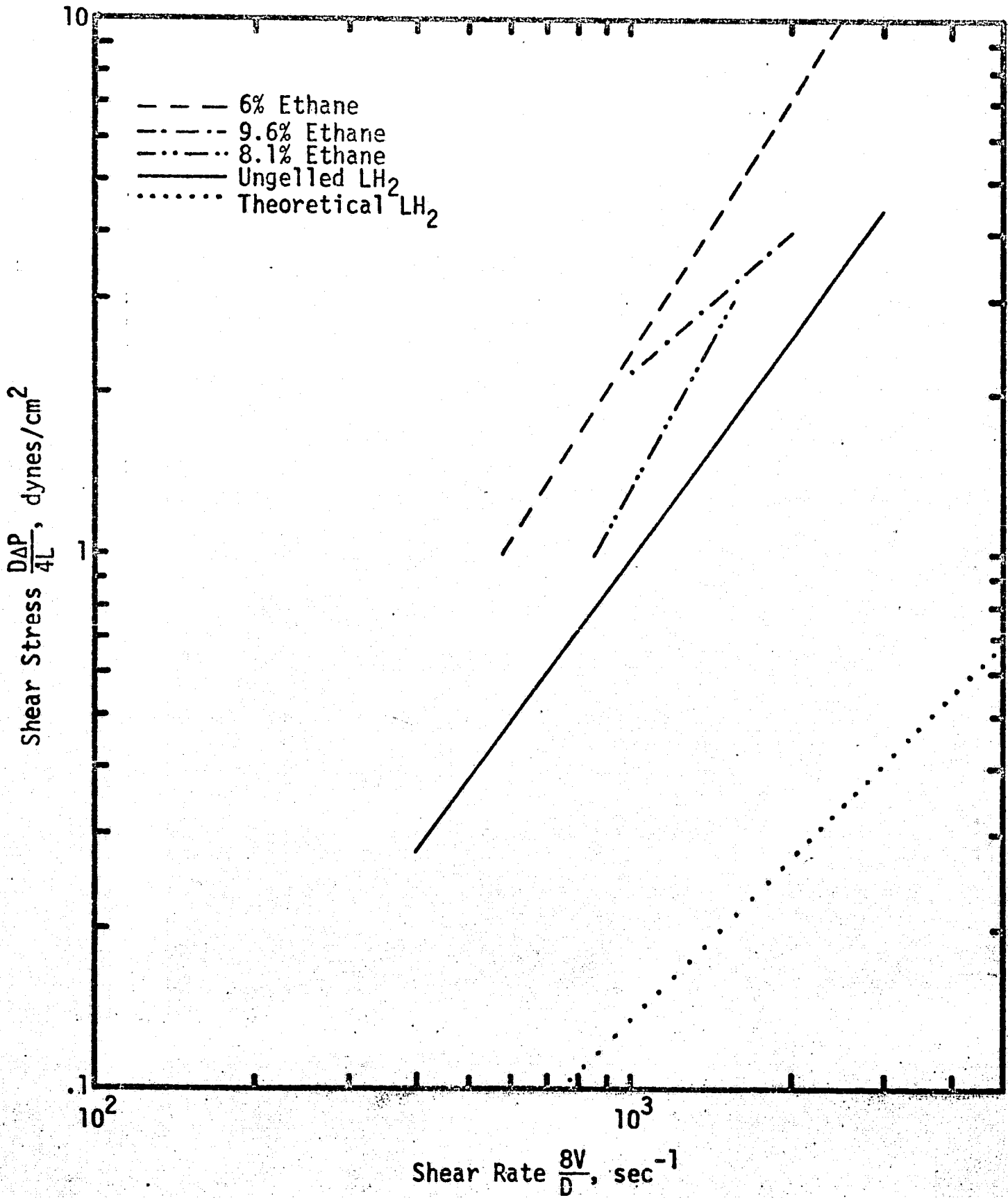


Figure 16. CHARACTERISTIC FLOW CURVES FOR GELLED AND UNGELLED LIQUID HYDROGEN USING A COIL OF 1/4 INCH TUBING

#### IV, B, Gelation of Liquid Hydrogen (cont.)

present is more viscous than gels with additional ethane present may be partially attributed to the fact that the value of 6% was deduced from previous experiments and was not measured due to loss of the sample. This behavior also indicates that the gel shear thins rapidly and viscosity values are not strongly dependent on the gelant concentration.

The gelled liquid hydrogen was also flowed through nominal 3/8-in. tubing to evaluate further the flow behavior. The apparatus used for these experiments is shown in Figure 10. Typical data from the experiments is presented in Table XXII; the apparent viscosity values were calculated as previously denoted.

The data indicate that the gelation of liquid hydrogen at the ethane concentration levels reported causes approximately two to four fold increase in the apparent viscosity at the shear rates encountered in the experiments. The measurements were made in the turbulent flow regime as with the 1/4-in. tubing. The data are plotted in Figure 17 in the form of shear stress versus shear rate. The gel containing 7.35% ethane is apparently more viscous than the gel containing 9.15% ethane. The chemical analyses of both gels are considered valid and the reversal is attributed to the viscosity values being relatively independent of the gelant concentration because of the "shear thinning" which occurs during flow.

In summary, the flow data demonstrate that the gelled liquid hydrogen can be transferred readily through lines with pressure drop values approximately three fold greater than the values required for liquid hydrogen itself.

TABLE XXII

DATA INDICATIVE OF THE APPARENT VISCOSITY OF GELLED LIQUID  
HYDROGEN FLOWING THROUGH 0.315 INCH DIAMETER TUBING

<u>Gelant Concentration wt%</u>	<u>ΔP Across Coil psi</u>	<u>Flow Rate cc/sec</u>	<u>Calculated Apparent Viscosity cp</u>
7.35	0.09	26.5	0.94
7.35	0.20	46.9	1.18
7.35	0.40	167	0.66
7.35	0.40	147	0.75
9.15	0.05	18.9	0.73
9.15	0.05	18.0	0.77
9.15	0.10	40.7	0.68
9.15	0.10	49.2	0.56
9.15	0.20	80.0	0.69
9.15	0.23	131	0.49
5.40	0.10	139	0.39
5.40	0.15	209	0.39
None	0.05	32.3	0.29
None	0.075	67.9	0.21
None	0.10	78.4	0.24
None	0.125	112	0.21
None	0.125	110	0.22
None	0.125	121	0.20

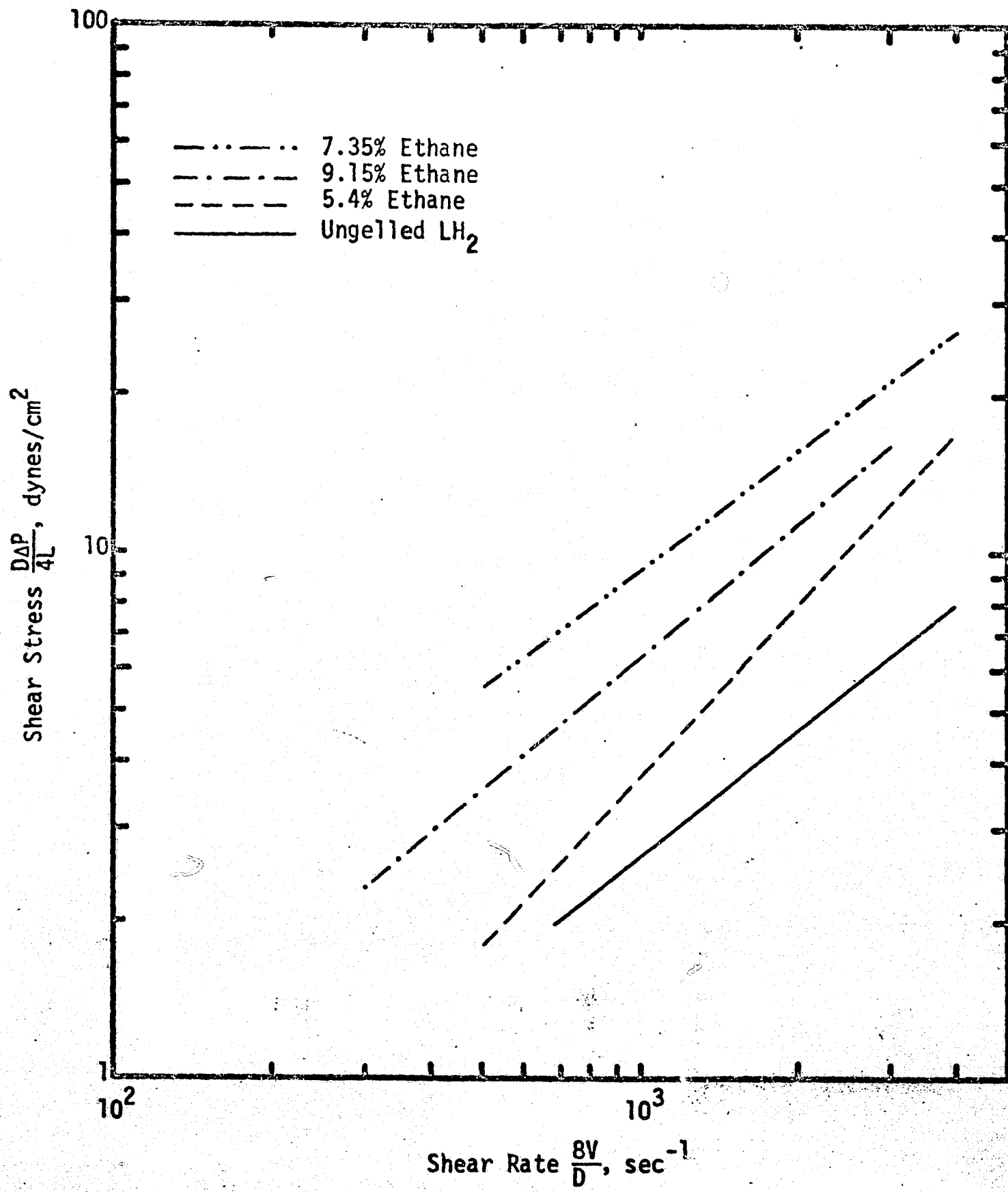


Figure 17. CHARACTERISTIC FLOW CURVES FOR GELLED AND UNGELLED LIQUID HYDROGEN USING A COIL OF 3/8 INCH TUBING



#### IV, B, Gelation of Liquid Hydrogen (cont.)

The yield stress values were obtained by using the weighted sphere method described in Section III.C. The values obtained in this manner are not actual yield values, but provide a good approximation. Typical values as a function of gelant concentration are presented in Table XXIII.

TABLE XXIII

#### YIELD STRESS VALUES FOR LIQUID HYDROGEN GELLED WITH ETHANE

<u>Experiment Number</u>	<u>Concentration of Ethane in Gel wt%</u>	<u>Yield Stress Value dynes/cm<sup>2</sup></u>	
5F	9.2	>135	<500
6F	8.4	>135	<500
8F	10.3	>135	<500
10F	10.0	>135	<500
12F	11.1	>135	<500
2M	11.3	>135	<500
13S	9.0		200
14S	10.7		200
15S	12.7		200

The significance of the data shown in the table is that gel structure can be imparted to liquid hydrogen by the use of 10 weight percent ethane, and a uniform distribution of hydrocarbon particles can be maintained in suspension by the gelation process.

## IV, Experimental Results and Discussion (cont.)

### C. IMPLICATIONS OF THE EXPERIMENTAL RESULTS

The use of hydrocarbon/liquid hydrogen fuels in nuclear propulsion systems with carbon-containing reactor cores can reduce the corrosion problem in the core and increase engine longevity. For utilizing the propellants there are three basic approaches.

The first approach involves the use of one fuel tank in which a suspension of hydrocarbon particles is stored indefinitely at the concentration necessary to inhibit the corrosion reaction. The nominal concentration level required to do this is equivalent to 5,000 ppm of methane. This concept requires a storable suspension of colloidal-size particles.

The second approach involves the use of the liquid hydrogen fuel tank plus a supply of gaseous hydrocarbon which can be injected into the liquid hydrogen stream during operation of the engine. This requires additional hardware and power to heat the gaseous mixture and can result in two-phase flow in the feed system. The hydrocarbon particles do not have to be formulated into a storable blend.

The third approach involves the use of two concentric liquid hydrogen tanks, one containing the ungelled liquid hydrogen and the other one containing gelled liquid hydrogen. The gelled and ungelled liquid hydrogen can be blended during engine operation to produce the desired concentration of hydrocarbon in the propellant and the flow of the fuel should keep the particles in suspension. Many variations can be used in connection with these approaches and mechanical devices can also be used to maintain the suspensions.

#### IV, C, Implications of the Experimental Results (cont.)

The experimental results from the program demonstrate that the first approach is not feasible. Suspensions of colloidal-size particles of hydrocarbons cannot be stored for prolonged periods of time. All the hydrocarbons evaluated in the program eventually agglomerated and settled. Mechanical agitation would be required to maintain the particles in suspension.

The second approach, in-situ preparation appears to be feasible. The hydrocarbon particles will remain in suspension at useful concentration levels for periods varying from seconds to minutes, depending on the hydrocarbon.

The third approach is also feasible based on the fact that storable liquid hydrogen gels can be prepared using 10 or more weight percent of hydrocarbon particles. This allows a great deal of flexibility in selection of the gel composition to be used in the system. Based on the experimental data, a storable gel can be prepared containing as little as 10 weight percent ethane while considerably more than 50 weight percent butene-1 could be incorporated in liquid hydrogen gel.

The direct utilization of gelled liquid hydrogen in the nuclear engine system results in a significant performance decrease. The effect of ethane concentration on the theoretical performance is shown graphically in Figure 18. Assuming that 10 weight percent ethane is used to gel the hydrogen, the specific impulse performance degradation is 2.5% compared to liquid hydrogen itself at 450 psia chamber pressure, 4500°R, and with an expansion ratio of 100. The use of ethane to gel 50% slush hydrogen can be accomplished with 4 weight percent ethane and this would result in a performance loss of 1.1 percent.

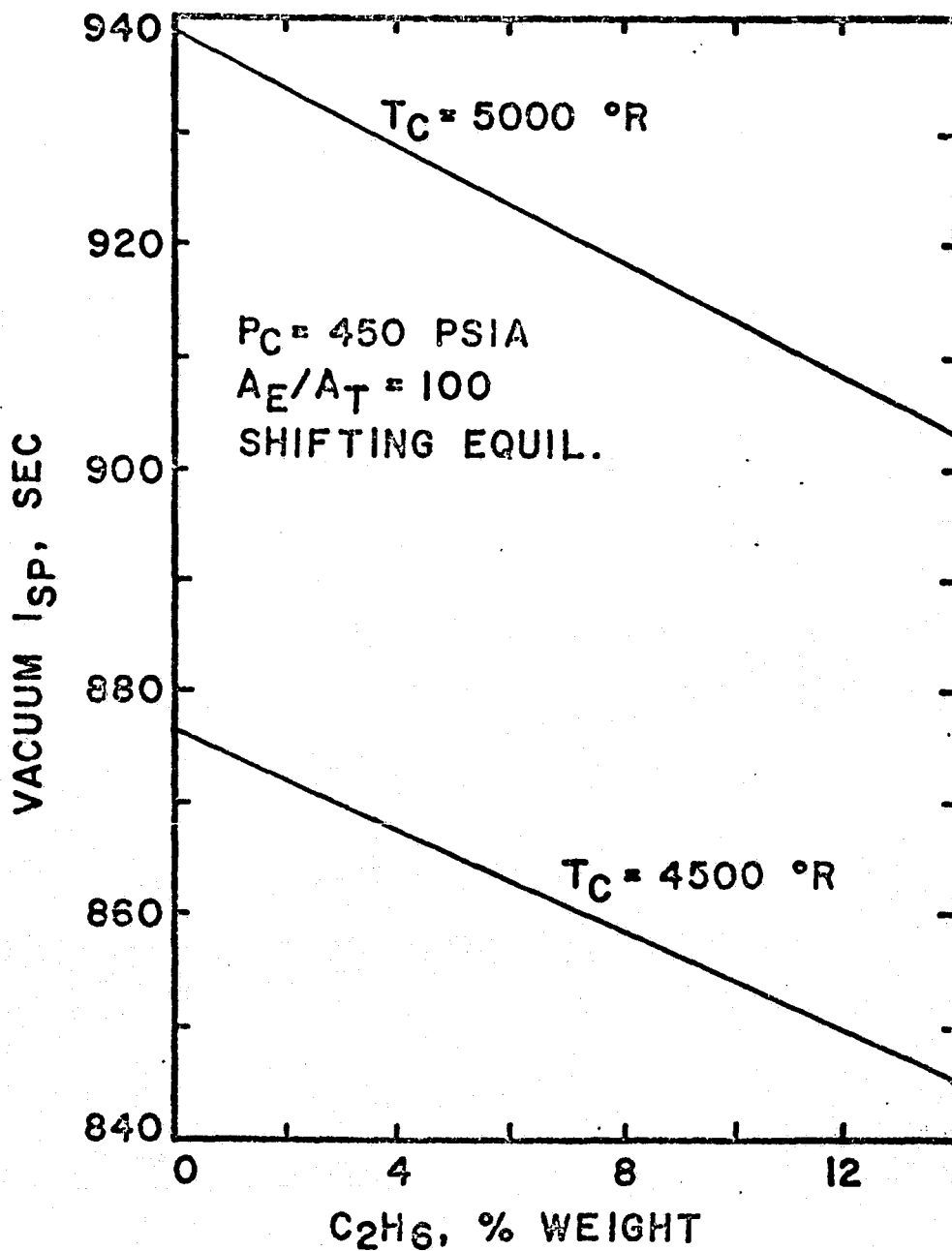


Figure 18.. EFFECT OF ETHANE CONCENTRATION IN LIQUID HYDROGEN ON THE THEORETICAL VACUUM SPECIFIC IMPULSE VALUES

Chamber Pressure = 450 psia  
 $\epsilon = 100$   
 Shifting Equilibrium

#### IV, C, Implications of the Experimental Results (cont.)

In summation, the experimental results have demonstrated that a stable liquid hydrogen gel can be prepared with as little as 10 weight percent ethane. This gelant concentration can be reduced to 4 weight percent if slush hydrogen is used. Suspensions of hydrocarbons can be prepared at the 5000 ppm level which have a life-time of minutes before agglomeration becomes excessive, but preparation of a storable suspension of colloidal-size hydrocarbon particles is not feasible. Fuel acquisition systems can be designed to utilize the fuels prepared during the course of this program.

## V. CONCLUSIONS AND RECOMMENDATIONS

### A. CONCLUSIONS

The following conclusions are drawn from the data obtained during the program:

1. Ultrafine hydrocarbon particles can be prepared which remain suspended in liquid hydrogen for periods ranging from minutes to hours. However, all suspensions do agglomerate eventually and no suspension appears storable for a matter of days at a concentration level greater than 100 ppm. Cyclopropane appears to be the best candidate for suspensions with ethylene as a possible alternate.
2. Liquid hydrogen can be gelled with 10 weight percent ethane particles to produce a gel which is storable. The storability has been demonstrated for a period of five days. Slush hydrogen can be gelled with 4 weight percent ethane particles. Ethane particles possess the greatest gelant capacity for hydrogen of the hydrocarbons evaluated in this program.
3. The viscosity values of gelled hydrogen at shear rates of  $10^3 \text{ sec}^{-1}$  are approximately three fold greater than that of the liquid hydrogen itself.
4. The yield stress value of gelled hydrogen is approximately  $200 \text{ dynes/cm}^2$  at a gelant concentration of 10 weight percent ethane.
5. The feasibility of using hydrocarbon/liquid hydrogen fuels for nuclear engines has been demonstrated by the preparation of hydrocarbon suspensions and the flowability of gels containing the hydrocarbon as gelant.
6. A method for preparing hydrocarbon particles in a flowing liquid hydrogen system was developed and demonstrated.

## V, Conclusions and Recommendations (cont.)

### B. RECOMMENDATIONS

The following recommendations are made on the basis of the experimental results.

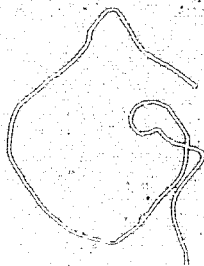
1. The results merit the scale-up of the procedure for preparation of the hydrocarbon particles.

2. The effect of boil-off, gel-structure, stratification, vibration on gel structure, and sloshing characteristics of the gelled hydrogen should be investigated.

3. The heat transfer characteristics of the gelled hydrogen should be investigated.

4. The surface properties of the gels, such as surface tension, wetting characteristics, and capillary behavior require investigation.

5. The stability of suspensions with regard to settling during transfer should be investigated.



## REFERENCES

1. R. H. Globus, et al., System Analysis of Gelled Space-Storable Propellants, Summary Report T038-02S, Aerojet-General Corp., Contract NAS 7-473, SA-1, July 1968
2. H. Kartluke, C. D. McKinney, R. Pheasant, and W. B. Tarpley, Gelling of Liquid Hydrogen, Final Report NASA CR-54055, Technidyne Incorporated, Contract NAS 3-2568, 31 July 1964
3. Feasibility of a Tripropellant Feed System, Report AFRPL TR-65-29, Aerojet-General Corp., Contract AF 04(611)-957, September 1964  
[CONFIDENTIAL]
4. Flow of Fluids Through Valves, Fittings, and Pipe, Technical Paper No. 410, Crane Company, Chicago, Illinois
5. A. W. Adamson, Physical Chemistry of Surfaces, Second Edition, Interscience Publishers, Inc. (1967)
6. S. Glasstone, Textbook of Physical Chemistry, Second Edition, Van Nostrand Company, Inc. (1959)
7. D. B. Chelton and D. B. Mann, "Cryogenic Data Book," University of Calif., Radiation Laboratory, UCRL-3421, May 1956
8. R. H. Globus, et al., System Analysis of Gelled Space-Storable Propellants, Summary Report T038-03S, Aerojet-General Corp., Contract NAS 7-473, SA-2, July 1969
9. E. M. Vander Wall and J. J. Bost, The Gelation of LH<sub>2</sub> and Preparation of Uniform LH<sub>2</sub> Slush, Final Report 8717-01-1, Aerojet-General Corp., Independent Research and Development 8717-01, May 1968 [AEROJET OFFICIAL USE ONLY]
10. Woolley, H. W., Scott, R. B., Brickwedde, S. G., "Compilation of Thermal Properties of Hydrogen in Various Isotopic and Ortho-Para Modifications," J. Research, National Bureau of Standards, 41, 379 (1948) (R.P. 1932)
11. E. M. Vander Wall, Carbon Compounds/Liquid Hydrogen Fuels, Phase I Report, Technical Report FR01-W396, Aerojet Liquid Rocket Company, May 1970