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THEORETICAL, EXPERIMENTAL, AND ANALYTICAL EXAMINATION OF SUBCOOLED AND SOLID HYDROGEN

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Abstract:

(U) Methods were investigated, both theoretically and experimentally, for production of liquid-solid mixtures of hydrogen ('hydrogen slush'). Small scale experiments were conducted to determine the feasibility of a number of techniques; the practicability and costs for these methods were determined theoretically. The theoretical analyses showed that techniques for producing hydrogen slush by vacuum pumping appeared most practical in view of capital investment and operating costs. Injection of cold helium gas was determined to be the most promising method for upgrading the solid content of slush mixtures after transfer to flight vehicle tankage. The theoretical analyses were verified within expectable error by large scale experiments in a low heat leak apparatus that permitted visual observation of experiments through a periscopic device. Liquid-solid hydrogen mixtures were produced having solid contents ranging from 20 percent to 55 percent. A number of characteristics were noted which varied with the production techniques used and with attempts to upgrade the quality of the slush produced. Some mixtures were flowable, and others were not. (Author)

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FOREWORD

This is the final report of research performed by Union Carbide Corporation, Linde Division under Contract No. AF 33(657)-10248. This contract was initiated under Project No. 8169, Task No. 816901. The contract work was performed under the direction of the Air Force Aero Propulsion Laboratory, Research and Technology Division. Mr. C. W. Elrod, Jr. was the project engineer for RTD.

The major contract activities were performed during the period from November 15, 1962 to December 15, 1963 under the supervision of Mr. R. R. Carney and Mr. R. F. Dwyer. They were assisted by Mr. L. R. Niendorf, Mr. J. L. Coppen, Mr. E. P. Eardley, and Mr. J. R. Hamilton, Jr. Additional assistance and contributions were rendered by Dr. G. A. Cook, Dr. H. M. Long, and other Linde Division consultants. Mr. J. Wary was the Contract Administrator for this project.

ABSTRACT

Methods were investigated, both theoretically and experimentally, for production of liquid-solid mixtures of hydrogen ("hydrogen slush"). Small scale experiments were conducted to determine the feasibility of a number of techniques; the practicability and costs for these methods were determined theoretically. The theoretical analyses showed that techniques for producing hydrogen slush by vacuum pumping appeared most practical in view of capital investment and operating costs. Injection of cold helium gas was determined to be the most promising method for upgrading the solid content of slush mixtures after transfer to flight vehicle tankage. The theoretical analyses were verified within expectable error by large scale experiments in a low heat leak apparatus that permitted visual observation of experiments through a periscopic device.

Liquid-solid hydrogen mixtures were produced having solid contents ranging from 20 percent to 55 percent. A number of characteristics were noted which varied with the production techniques used and with attempts to upgrade the quality of the slush produced. Some mixtures were flowable, and others were not.

This technical documentary report has been reviewed and is approved.

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SECTION 1

INTRODUCTION

Linde Division's initial interest in liquid-solid hydrogen mixtures stems from research performed by Linde's Low Temperature Measurements Group at Tonawanda, New York. This group on many occasions prepared mixtures of solid and liquid hydrogen for use in calibrating low temperature measuring devices at the triple point of hydrogen. The mixture was given the name, "Hydrogen Slush." Observations of the properties of this mixture led to the realization that liquid-solid hydrogen mixtures might provide the means for increasing the density of this otherwise superior fuel. A small apparatus was constructed by Linde Division to investigate the mixture further, and the results looked increasingly attractive. Further investigations were carried out under Air Force contract.

Under the terms of the contract with RTD, certain objectives were established. They were:

1. to investigate theoretically several methods for the large scale production of liquid-solid mixtures of hydrogen, identifying the most promising methods.
2. to experimentally verify the most attractive of those methods.
3. to learn as much as possible about the characteristics of liquid-solid hydrogen mixtures in conjunction with the experimental work.
4. to perform a literature survey of work performed earlier on liquid-solid hydrogen in order to establish the state-of-the-art.

The contract work performed in pursuit of these objectives and the results of this work are recorded in this document.

Manuscript released by the authors 24 March, 1964 for publication as an RTD Technical Documentary Report.

SECTION 2

SUMMARY

The theoretical investigation of hydrogen slush production techniques showed that the vacuum pumping methods were the most practical and offered the lowest costs. Of the vacuum pumping methods, cascaded and branched flow vacuum pumping appeared more attractive than the straight vacuum pumping or semi-flow vacuum pumping methods. This was primarily because of the smaller tankage requirements of the earlier methods. The use of helium gas refrigerators or liquid helium for slush production indicated, respectively, extremely high capital costs and high operating costs. Joule-Thomson cooling of helium-hydrogen mixtures, compression and expansion of liquid hydrogen, and Venturi cooling of liquid hydrogen were investigated until insurmountable difficulties became apparent. These investigations were then terminated. Helium gas injection cooling was found to be too costly to consider for production of hydrogen slush, but appeared to be the only reasonable method of upgrading the slush after it was on board a non-evacuable space vehicle tank.

Concurrently with the theoretical investigation, a small scale experimental examination of hydrogen slush was conducted. Qualitative observations of the characteristics of the hydrogen slush were made along with quantitative analyses. Techniques were developed for determining the solid content in hydrogen slush, and they were used to measure the solid content of various qualities of slush in further experiments. The handling characteristics of the various qualities of slush were identified; some of these qualities could be mixed and transferred,and others could not. There were indications that partial melting was a key to both high solid content and flowability. Storage experiments were conducted which showed no deleterious effect on the slush except, of course, the expected melting of some of the solid due to heat leak. The maximum flowable slush was found to be about 55 percent solid by weight.

Based on the partially completed theoretical and small scale experimental work, a larger apparatus was designed for experimental examination of hydrogen slush on a larger scale by all of the vacuum pumping methods. This apparatus consisted essentially of a small, cascaded, branched flow production plant made of glass to facilitate interior observation with a periscope and enclosed in a metal guard chamber kept at liquid hydrogen temperature. The theoretical work on vacuum pumping was experimentally verified well within expectable error, the small scale analyses were verified on a larger scale, and information was obtained on the characteristic differences

of slush produced by different methods. The need for partial melting to achieve high (50 percent) solid fractions in settled slush was established. Various solid formations were produced by the cascaded branched flow vacuum pumping method including stalactite-type formations of hydrogen which appeared to be nonporous, particle-formed hydrogen that appeared to be packable into denser masses, and loosely-fragmented hydrogen which was dry and nonsticking.

The literature survey, which is discussed in Appendix I of this report, was conducted early in the contract performance period. No significant state-of-the-art advances or techniques were discovered in the literature surveyed.

Considerable additional development work is recommended to achieve higher solid contents in hydrogen slush and to more firmly establish the production and handling techniques where problem areas are apparent.

SECTION 3

THEORETICAL INVESTIGATION OF HYDROGEN SLUSH PRODUCTION TECHNIQUES

An investigation was undertaken to establish theoretical operating conditions for several hydrogen slush production techniques and to determine the relative merits of each. The techniques investigated included: vacuum pumping, helium gas refrigeration, liquid helium cooling, Joule-Thomson cooling, compression and expansion of liquid hydrogen, venturi cooling, and helium gas injection. Each of these techniques is analyzed in the following discussions.

3.1 VACUUM PUMPING PRODUCTION TECHNIQUES

3.1.1 Straight Vacuum Pumping

In the straight vacuum pumping process, the evaporation of some of the liquid from a storage tank provides the refrigeration to reduce the temperature of the remaining liquid to the freezing point (triple point) and then, by continued evaporation, to produce mixtures of solid and liquid or to completely freeze the remaining hydrogen. The process can be followed thermodynamically on the temperature entropy diagram in Figure 1. During pump down, the liquid hydrogen follows the saturated liquid line from o to t while the evaporated gas follows the saturated vapor line from o' to t'. The triple point liquid at t is pumped to produce solid at s.

The process of cooling by evaporation may be evaluated by solving the heat balance equation between an initial mass, x, and a vaporized mass, dx,

$$x c_{sat}\, dT = \lambda dx \qquad (1)^*$$

while employing continuous functions for the saturation specific heat, c_{sat}, and for the latent heat of vaporization, λ, over the desired temperature range. Alternatively, the process may be evaluated by considering a series of discrete isentropic expansions for which the change in entropy of the process must be zero

$$\Delta S_{process} = 0 \qquad (2)$$

These stepsize expansions are shown in Figure 1.

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* All symbols and their definitions are listed in Appendix II.

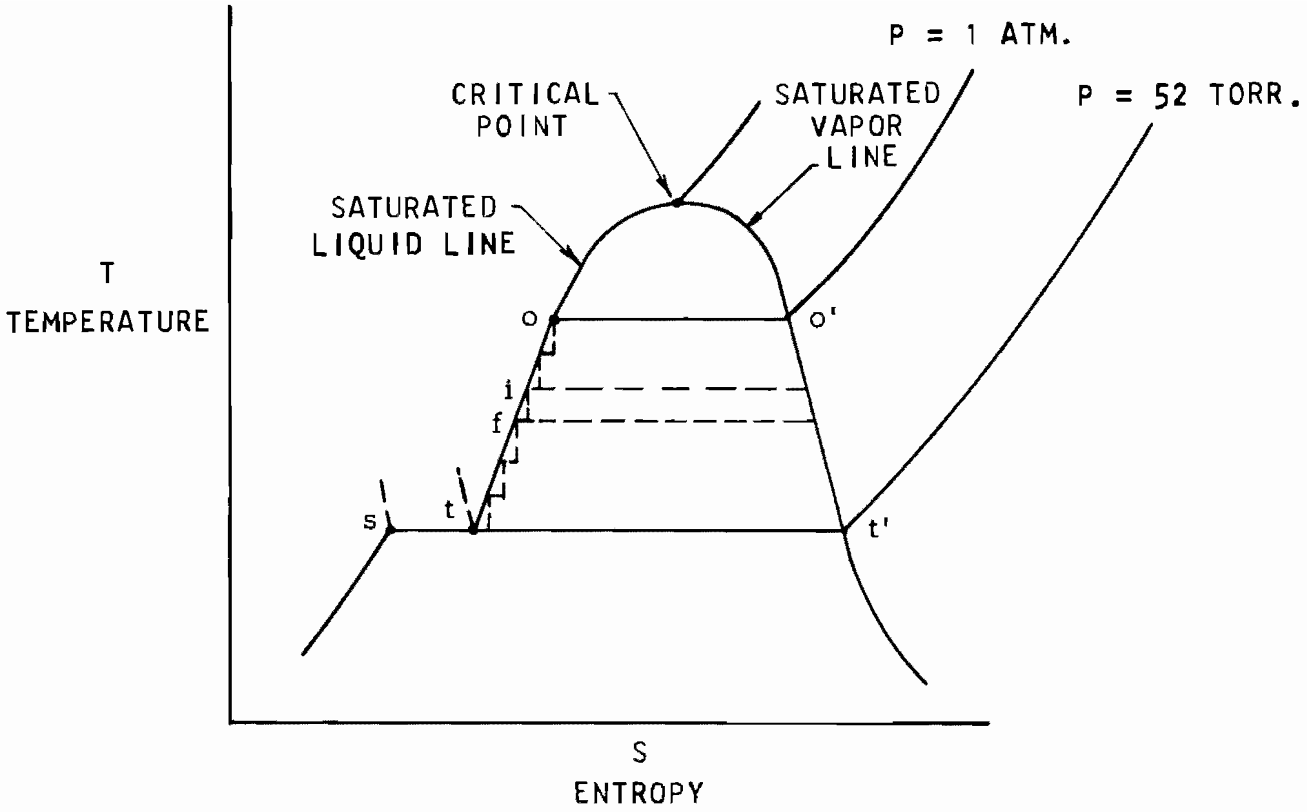

Figure 1. The Straight Vacuum Pumping Thermodynamic Process

For this work, the calculation of the series of isentropic expansions was employed to evaluate the straight vacuum pumping process. Since the refrigeration is provided by vaporization of liquid, the evaluation of the straight vacuum pumping process involves calculation of the amount of liquid which must be vaporized to achieve the desired end product. Furthermore, since the process is considered to be a simple batch process, wherein vapor is pumped directly from a storage tank as in Figure 2, the calculation of evaporated mass should be in terms of the initial liquid mass required to reach the desired terminal conditions. The ratio of the initial mass to the final mass is the mass required to produce a unit quantity of final material and is the parameter to be calculated. This parameter is termed the specific mass requirement and designated SMR. For the interval over which x changes from x_i to x_f

$$SMR_{if} = x_i/x_f \ . \tag{3}$$

To calculate the specific mass requirement one must obtain solutions for equation (2) which employ the measured thermodynamic properties.

Equation (2) may be rewritten in terms of the changes in the liquid and vapor phases present as

$$\Delta S_L = \Delta S_V \ .$$

Introducing the initial and final liquid masses, x_i and x_f , and the vaporized mass, y_{if} , into equation (2) gives

$$x_i s_{Li} - x_f s_{Lf} = y_{if} s_{v\ avg} \tag{2a}$$

where s_{Li} and s_{Lf} are the saturated liquid entropies at temperatures T_i and T_f and $s_{v\ avg}$ is the average entropy of the vapor between the temperatures T_i and T_f . The vaporized mass, y_{if} , is the difference between the initial and final liquid masses

$$y_{if} = x_i - x_f \tag{4}$$

so that upon substitution in equation (2a)

$$x_i s_{Li} = x_f s_{Lf} + (x_i - x_f)\ s_{v\ avg}$$

$$x_i\ (s_{Li} - s_{v\ avg}) = x_f\ (s_{Lf} - s_{v\ avg})$$

and the ratio of the initial to final mass of liquid is

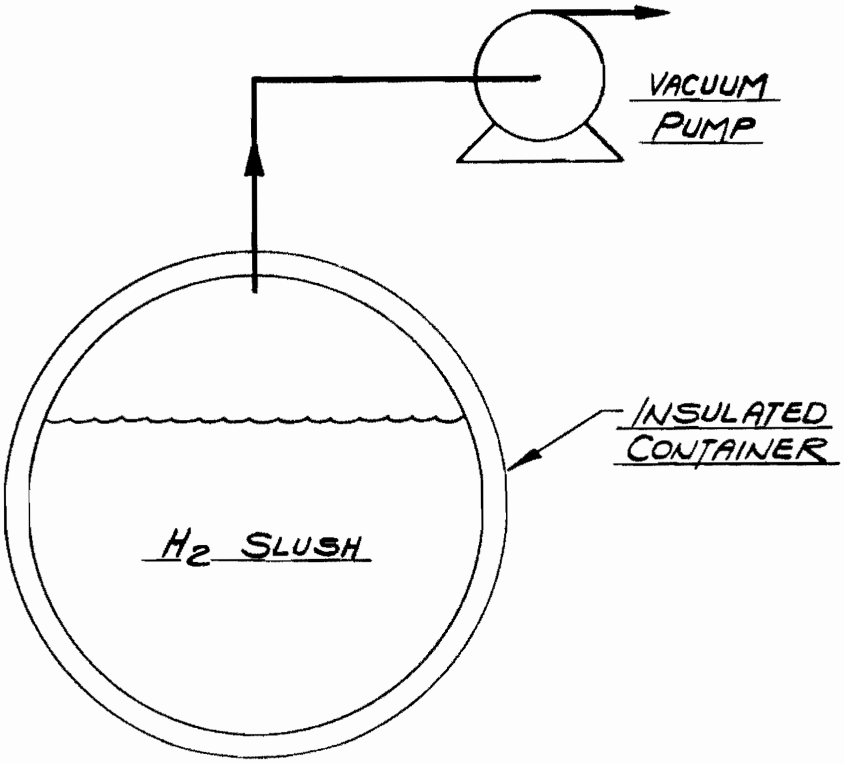

Figure 2. Straight Vacuum Pumping Process Equipment

$$SMR_{if} = x_i/x_f = \frac{s_{Lf} - s_{v\ avg}}{s_{Li} - s_{v\ avg}} = \frac{s_{v\ avg} - s_{Lf}}{s_{v\ avg} - s_{Li}} \ . \tag{3a}$$

Since the numerical value of this ratio gives the initial mass required at T_i to produce a unit quantity of liquid at T_f it is the specific mass requirement, SMR_{if}, for the temperature interval T_i to T_f. For the average vapor entropy in equation (3a) the simple arithmetic average

$$s_{v\ avg} = (s_{vi} + s_{vf})/2 \tag{5}$$

of the vapor entropies at temperatures T_i and T_f are used.

The SMR_{if} calculated by equation (3a) are incremental values for the specified temperature intervals T_i to T_f, and they give the mass required at the initiation of the interval in order that a unit mass remain at the termination of the interval. For the evaluation of a production process, the specific mass requirement needed is that which is calculated for the whole series of steps leading to the final temperature of the process.

The total specific mass requirement between temperatures T_o and T_t is defined as

$$SMR_{ot} = x_o/x_t \tag{6}$$

where x_o is the mass at the beginning of the process, and x_t is the mass at the conclusion. However, since the process is not linear in temperature nor entropy, this equation cannot be solved by direct substitution of entropies as was done in equation (3a) for the incremental values. For a process between T_o and T_t with an incremental step at temperature T_i we have

$$SMR_{ot} = (x_o/x_i)\,(x_i/x_t) \tag{7}$$

which by substitution of equation (3) becomes

$$SMR_{ot} = (SMR_{oi})\,(SMR_{it}) \ . \tag{7a}$$

For additional steps during the process, the incremental SMR_{if} for these steps are multiplied as in equation (7a) in order to obtain the total SMR_{ot}. Thus, the series of steps are accounted for in the product from o to t

$$SMR_{ot} = \prod_{o}^{t} SMR_{if} \ . \tag{8}$$

Equation (8) is used to calculate the initial mass required at any starting saturated condition, o , to yield a unit mass of liquid at condition t. For slush production, the condition t is the triple point.

The freezing process, in which triple point liquid is pumped to produce solid-liquid mixtures, occurs at a constant pressure and constant temperature rather than over a range of pressures and temperatures. The process is still isentropic so that the entropy of the initial liquid equals that of the final mixture plus the entropy of the vaporized mass

$$x_i s_{L'} = (x_f s_{L'} + z s_{s'}) + y_{if} s_{v'} \tag{9}$$

where x_i and x_f are initial and final liquid mass; z the solid mass; y_{if} the vaporized mass; and s_L , s_s , and s_v the entropies of the liquid, solid, and vapor at the triple point pressure and temperature. Again, the vaporized mass is equal to the difference between the initial and final condensed phase masses

$$y_{if} = x_i - (x_f + z) \tag{10}$$

so that

$$x_i s_L = x_f s_L + z s_s + (x_i - x_f - z)\, s_v$$

$$x_i\,(s_L - s_v) = x_f\,(s_L - s_v) + z\,(s_s - s_v)$$

$$x_i = x_f + z\,(s_s - s_v)/(s_L - s_v) \tag{11}$$

The specific mass requirement to go from triple point liquid, x_i , to a liquid-solid mixture, $(x_f + z)$, is

$$SMR_{if} = x_i/(x_f + z) = [x_f + z\,(s_s - s_v)/(s_L - s_v)]/(x_f + z)\,. \tag{12}$$

When the mass is completely frozen $x_f = o$, and

$$SMR_{solid} = (s_s - s_v)/(s_L - s_v)\,. \tag{13}$$

For solid concentrations between 0 and 100 percent the quality q as percent solids is

$$q = 100z/(x_f + z)\,. \tag{14}$$

From this equation the liquid fraction, x_f , is

$$x_f = z\,(100 - q)/q \,. \tag{14a}$$

Substituting (13) and (14a) in (12) gives the specific mass requirement in terms of the quality q and the SMR_{solid}

$$SMR_q = 1 + (q/100)\,(SMR_{solid} - 1)\,. \tag{15}$$

This expression for SMR_q is linear in q as is required by the freezing process. For q = o , $SMR_{q\,=\,o} = 1$; for q = 100 , $SMR_{q\,=\,100} = SMR_{solid}$ as given by equation (13). The SMR_q for the desired quality is used as the final entry in the product equation (8) since it represents an additional expansion step equivalent to the T_i to T_f steps. Thus

$$\begin{aligned} SMR_{oq} &= (\prod_{o}^{t} SMR_{if})\,(SMR_q) \\ &= (\prod_{o}^{t} SMR_{if})\,[\,1 + (q/100)\,(SMR_{solid} - 1)] \end{aligned} \tag{16}$$

where again o represents a starting saturated liquid condition and q the final slush quality, the total specific mass requirement SMR_{ot} (equation (8)), and, SMR_{oq} (equation (16)), are used to determine the size of the vessel needed for the initial charge of liquid hydrogen to yield a final required amount of colder liquid or slush of various qualities, q .

Having determined the vessel size, the capacity of the vacuum pumps must next be determined. The vacuum pumps must remove the vaporized mass, y_{if} , in order to produce the required refrigeration. To size the pumps, these vaporized masses must be calculated. From equations (3) and (4) we have that the vaporized mass is

$$y_{if} = x_f[(x_i/x_f) - 1] = x_f\,(SMR_{if} - 1) \tag{17}$$

or, in terms of the initial mass x_i ,

$$y_{if} = x_i\,(SMR_{if} - 1)/SMR_{if}\,. \tag{18}$$

This allows calculation of the mass at temperature T which must be pumped from an initial mass, x_i , in order to change the temperature of the remaining material from T_i to T_f .

For a process involving a series of steps from o to t , the total mass required for the whole series of steps must be introduced as the initial mass x_i in equation (18) since we wish to obtain the incremental masses pumped to produce a final unit mass. Therefore, the mass pumped during the initial step to produce a unit mass of liquid at condition t is

$$Y_{if} = SMR_{ot}\,(SMR_{if} - 1)/SMR_{if} \tag{19}$$

and for the pumped mass during the initial step in the process to produce unit mass of slush of quality q

$$Y_{if} = SMR_{oq}\,(SMR_{if} - 1)/SMR_{if} \tag{20}$$

Thus, to obtain the pumped mass for the incremental steps in the production process, the SMR_{if} , SMR_{ot} , and SMR_{oq} for each of the incremental steps of the process are first calculated from equations (3a), (8), and (16). The final SMR_{ot} or SMR_{oq} for the overall process is then introduced into equation (18) as x_i for the first interval and, together with the SMR_{if} for that interval, is used to calculate the mass pumped.

For the second step in the process, the initial mass is calculated by substracting the mass pumped during the first interval from the starting mass for the first interval. Thus

$$X_2 = SMR_{ot} - Y_{12} = X_i - Y_{12}$$

or in general form

$$X_{i+1} = X_i - Y_{if} \,. \tag{21}$$

These calculations are repeated to cover the whole series of incremental expansions in the process. When each of the steps in the process has been calculated, the total mass requirement is obtained by summation.

$$Y_{ot} = \sum_{o}^{t} Y_{if} \tag{22}$$

or

$$Y_{oq} = \sum_{o}^{q} Y_{if} \,. \tag{23}$$

The vaporized mass, Y_{if}, is used to calculate the volume vaporized and thus to size the vacuum pumps required for the production process, once the temperature of the pumps is fixed. The volume of the vaporized mass associated with each of the incremental steps must be calculated separately since the pressure changes along the saturation line as the process progresses. For a given increment, the volume is calculated by the equation

$$V_{Tif} = Y_{if} v_{Tif\ avg} = Y_{if}/\rho_{Tif\ avg} \tag{24}$$

where $v_{Tif\ avg}$ and $\rho_{Tif\ avg}$ are the average of the specific volume and density at the temperature T of the vacuum pump and at pressures P_i and P_f given by

$$v_{Tif\ avg} = (v_{Ti} + v_{Tf})/2 \tag{25}$$

and

$$\rho_{Tif\ avg} = (\rho T_i + \rho T_f)/2 \tag{26}$$

As for the vaporized masses, the total volume for the series of steps is obtained by summing the incremental volumes

$$V_{Tot} = \sum_{o}^{t} V_{Tif} \tag{27}$$

and

$$V_{Toq} = \sum_{o}^{q} V_{Tif} . \tag{28}$$

By analogy with the incremental equation (4) we have for the overall process

$$Y_{ot} = X_o - X_t \tag{29}$$

and by equation (6)

$$SMR_{ot} = X_o/X_t$$

so that

$$Y_{ot} = SMR_{ot} - 1 . \tag{30}$$

Equation (30) can be used to check the correctness of the calculations for the pumped mass and the SMR_{ot} by comparison with equation (22). A similar check equation can be written for the o to q process.

If the vacuum pump is allowed to run cold, and thus to effectively accept vapor at the saturation temperature, then the temperature as well as the pressure of the vapor at the pump will correspond to the saturation values. For this case, equations (22) through (28) are still valid although the saturated specific volumes and densities are employed rather that the specific volumes and densities at temperature T.

The necessary set of equations have now been developed to allow the calculation of the process requirements for the straight vacuum pumping method of slush production. The numerical values calculated, using these equations, are given in Tables 1 and 2.

TABLE 1

STRAIGHT VACUUM PUMPING

SPECIFIC MASS REQUIREMENTS

Temperature Interval, T_i to T_f °K	SMR_{if} for Temperature Interval	SMR_{ot} for process From 20.278°K @ 1 atm. to 13.8°K @52 Torr
20.278 20.00	1.0060102	1.0060102
20.00 19.00	1.02057819	1.02671207
19.00 18.00	1.01939081	1.04662084
18.00 17.00	1.01818769	1.06565644
17.00 16.00	1.01728981	1.08408144
16.00 15.00	1.01646856	1.10193469

TABLE 1 (CONTINUED)

STRAIGHT VACUUM PUMPING

SPECIFIC MASS REQUIREMENTS

Temperature Interval, T_i to T_f °K	SMR_{if} for Temperature Interval	SMR_{ot} for process From 20.278°K @ 1 atm. to 13.8°K @ 52 Torr
15.00 14.00	1.01584052	1.11938990
14.00 13.813 (triple point liquid)	1.00295259	1.12269499
SMR_{tq} (q = 100%)	1.12922744	
SMR_{oq} (q = 100%)		1.26777797

Table 1 presents the calculated values of SMR_{if} from equation (3a) and SMR_{ot} from equation (8) for integral temperature intervals from the normal boiling point of para-hydrogen, 20.278°K, to the triple point, 13.813°K*. Also included in this table is the value of SMR_{oq} (q = 100%) for the interval and total process. The entropy values for these calculations were obtained from Mullins, Ziegler, and Kirk (1)** in a National Bureau of Standards tabulation of thermodynamic functions of para-hydrogen. Representative numerical calculations of the entries in Table 1 are given in Appendix 2.

As shown in Table 1, the production of one pound of triple point liquid will require 1.12269499 pounds of liquid saturated at 1 atmosphere. For one pound of solid hydrogen the requirement will be 1.26777797 pounds of saturated liquid at 1 atmophere. The volume of the initial liquid per pound of product is obtained for the two cases by dividing the SMR_{ot} by the liquid density at the

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* Note that on the 1956 temperature scale, the triple point of hydrogen is at 13.803°K. The tables in (1), however, are on the older temperature scale, and because they are an integral part of the calculations, it was more convenient to use the older temperature scale throughout the calculations. To obtain 1956 temperatures, subtract 0.01 from all temperatures reported in these calculation.

** The list of references starts on page 158.

initial saturated condition or by multiplying by the saturated specific volume. Thus, the tankage for any production quantity can be calculated from Table 1.

For initial conditions other than one atmosphere saturation the SMR_{ot} must be recalculated. The values of SMR_{if} from the middle column of Table 1, starting at the new initial temperature, are used in equation (8) to calculate the new SMR_{ot}. If the initial conditions are for saturation pressures higher than one atmosphere, additional tabular SMR_{if} must be calculated from equation (3a) for use in equation (8).

Table 2 presents the calculated values for the temperature range from 20.278°K to 13.813°K for the pumped mass to produce one pound of triple point liquid and to produce one pound of solid hydrogen. Also presented are the saturated vapor densities and the pumped volumes for the case of saturated vapor inlet to the pumps. The NBS thermodynamic tables of Mullins, Ziegler, and Kirk (1) were used as in Table 1 for the calculations. Sample numerical calculations for Table 2 are given in Appendix 2.

The volumes given in Table 2 are divided by pumping time to determine the capacity of the vacuum pump, or pumps, needed for the process. For example, if each step of the oq process were to take 1 minute, the last column shows that a pump for the 20°K to 9°K step should have a pumping capacity of 0.376 cfm, while the pump capacity for the final freezing step should be 16.6 cfm. In this case, several size pumps may be used and the total pumping capacity increased as the steps progress. Nevertheless, the overall process would require approximate 8 minutes, and the final 1 minute step would require a total capacity of 16.6 cfm. If, however, this same 16.6 cfm capacity pump were used throughout the process, the total pumping time would be approximately 1.3 minutes, which is a considerable reduction in time. Alternatively, the original 8 minute production time can be accomplished by a 3 cfm pump operating continously with increasing time periods per step, as the volume per step increases. By similar reasoning, the information in Table 2 can be utilized to size the vacuum pumps for any desired quantity and time period for slush production.

A test of the numerical values in Table 2 by the application of equation (30) shows that the calculations have a very small error. For example, in the case of the production of triple point liquid, the difference between equations (30) and (22) is

$$0.2269505 - 0.2269499 = 0.0000006$$

and for the production of triple point solid, the difference between equations (30) and (23) is

$$0.26778544 - 0.26777797 \approx 0.00000767 \ .$$

Both of these errors are well within the error of the tabular values upon which the calculations are based.

TABLE 2

STRAIGHT VACUUM PUMPING

PUMPED VOLUME REQUIREMENT

Interval °K	$\rho_{sat\ if\ avg}$ Average Saturated Vapor Density for Interval Lb./Ft.^{3}	Y_{if} Mass Pumped to Produce 1 Lb. of Triple Point Liquid (Lb.)	$V_{sat\ if}$ Volume Pumped to Produce 1 Lb. of Triple Point Liquid (Ft.^{3})	Y_{if} Mass Pumped to Produce 1 Lb. of Solid (Lb.)	$V_{sat\ if}$ Volume Pumped to Produce 1 Lb. of Solid (Ft.^{3})
20.278 20.00	0.081	0.00670731	0.083	0.00757408	0.094
20.00 19.00	0.0675	0.02250196	0.333	0.02540983	0.376
19.00 18.00	0.0500	0.02080024	0.416	0.02348820	0.470
18.00 17.00	0.036	0.01916117	0.532	0.02163732	0.601
17.00 16.00	0.0255	0.01790565	0.702	0.02021955	0.793
16.00 15.00	0.0175	0.01677883	0.959	0.01894711	1.083
15.00 14.00	0.011	0.01588729	1.443	0.01794036	1.629
14.00 13.813	0.0082	0.00295260	0.360	0.00334157	0.407
Triple Point Liquid to Solid Hydrogen	0.0078			0.12922742	16.568

TABLE 2 (CONTINUED)

STRAIGHT VACUUM PUMPING

PUMPED VOLUME REQUIREMENT

Interval °K	$P_{sat\ if\ avg}$	Y_{if}	$V_{sat\ if}$	Y_{if}	$V_{sat\ if}$
$Y_{ot} = \sum_{o}^{t} Y_{if}$		0.12269505			
$V_{ot} = \sum_{o}^{t} V_{sat\ if}$			4.828		
$Y_{oq} = \sum_{o}^{q} Y_{if}$				0.26778544	
$V_{oq} = \sum_{o}^{q} V_{sat\ if}$					22.021

The straight vacuum pumping system entails high capital investment since it must provide tank capacity for all of the liquid hydrogen initially required to produce the desired amount of slush. The hydrogen losses are high since the hydrogen itself provides the necessary refrigeration through evaporation.

The vacuum pump required is much smaller in capacity if it is designed for low temperature operation as assumed for Table 2 , rather than for room temperature operation. Also, a room temperature vacuum pump requires heat exchangers to warm the suction gas. For the use of a multiple stage reciprocating pump, a saving is possible by manifolding the stages in parallel during higher pressure operation and in series during lower pressure operation.

The capital and operating costs to produce 75,000 lb. of 50 percent slush in seven days have been calculated, and are presented in Appendix IV.

3.1.2 Semiflow Vacuum Pumping

In this method, saturated liquid hydrogen at one atmosphere, supplied from a transport vessel, is first expanded through a Joule-Thomson valve into an evacuable tank held at a pressure slightly above the triple point and then vacuum pumped in that tank until the desired slush quality is obtained. The isenthalpic, Joule-Thomson expansion from one atmosphere to the triple point is quite efficient; however, it will be shown that the specific mass requirement is higher for semiflow vacuum pumping than straight vacuum pumping.

The process is shown on the thermodynamic diagram in Figure 3. Saturated liquid at point i is expanded at constant enthalpy to point f at the triple point pressure and temperature, yielding a liquid fraction fa and a vapor fraction fb. The liquid fraction is vacuum pumped to yield a solid liquid mixture along the fusion line bc.

The process equipment shown in Figure 4 includes the use of transport equipment to provide a continuous supply of hydrogen to the expansion valve (J.T. valve) which discharges directly to the production tank. As before, a vacuum pump maintains subatmospheric process pressure in the production tank.

As in the straight vacuum pumping process, the refrigeration for the semiflow vacuum pumping process is derived from the liquid hydrogen supplied to the process. The ratio of the initial liquid mass to the final mass is therefore used in the process evaluation. Again as before, this ratio is termed the specific mass requirement, and as given by equation 3 is

$$SMR_{if} = x_i/x_f \quad .$$

The subscripts again refer to the initial and final conditions of the expansion.

For an isenthalpic expansion process

$$\Delta H = o \tag{31}$$

or, in terms of the liquid and vapor enthalpies, the enthalpy of the initial liquid must equal the enthalpy of the final liquid plus that of the vaporized mass

$$x_i h_{Li} = x_f h_{Lf} + y_{if} h_{vf} \tag{32}$$

where h_{Li} is the specific enthalpy of the initial liquid, h_{Lf} the specific enthalpy of the final liquid, and y_{if} and h_{vf} the mass and specific enthalpy of the vapor phase.

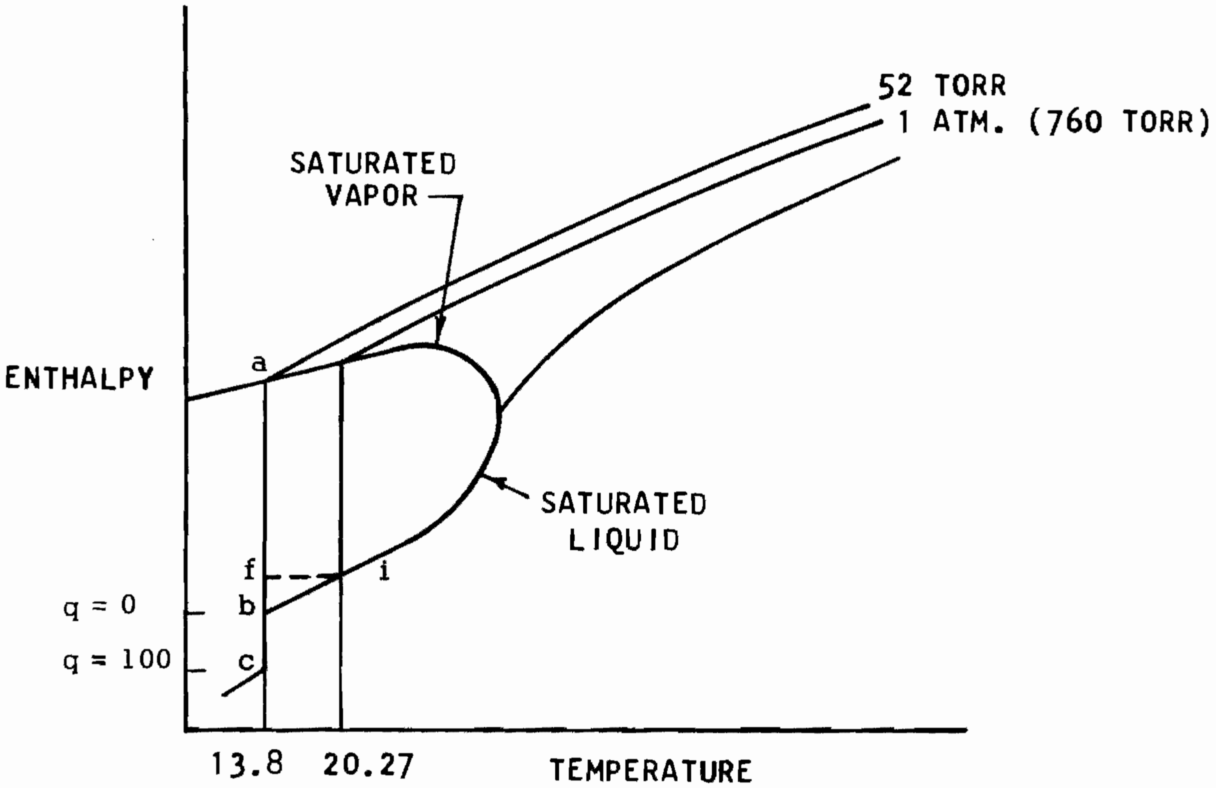

Figure 3. Semiflow Vacuum Pumping Thermodynamic Process

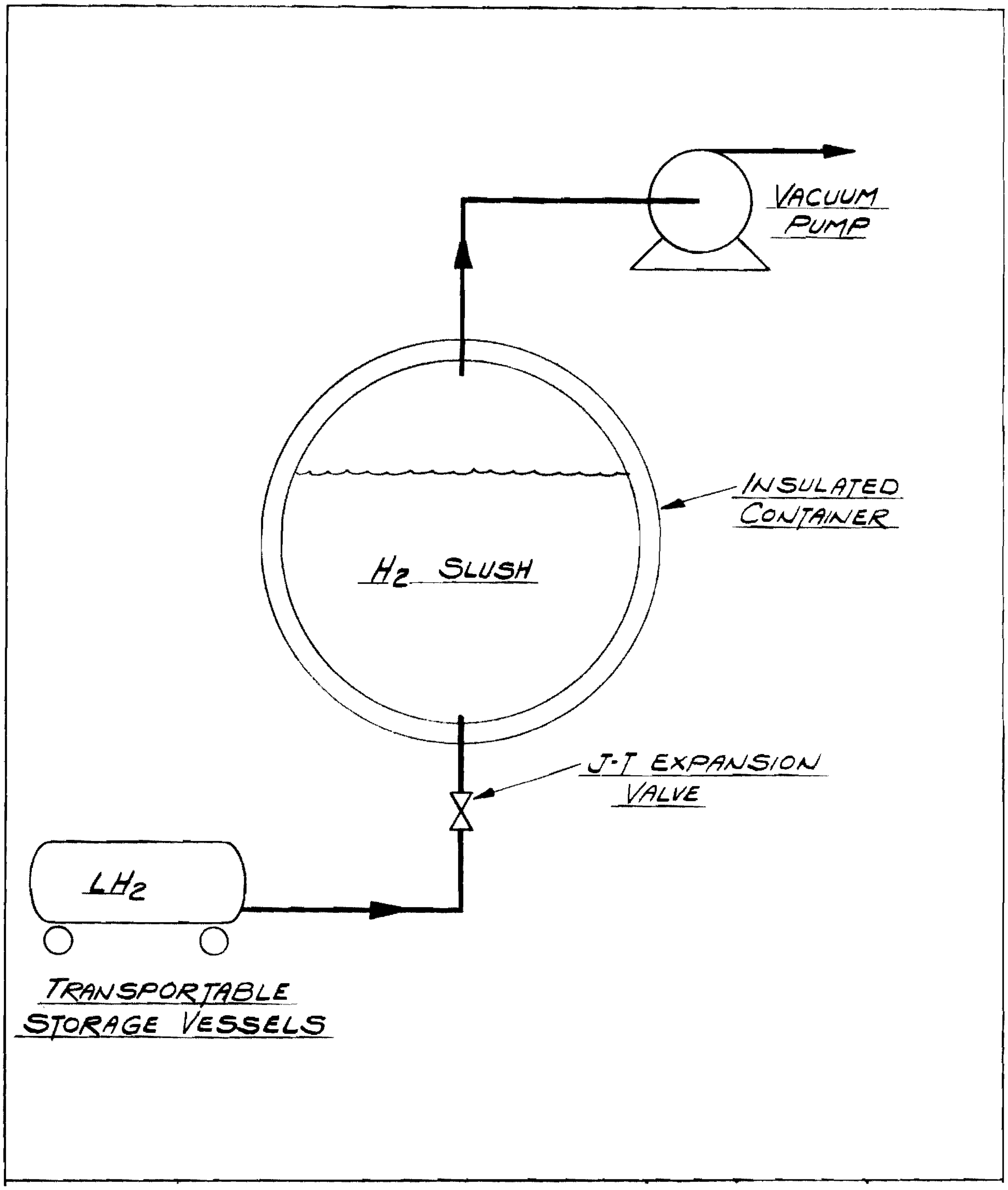

Figure 4. Semiflow Vacuum Pumping Process Equipment

Since by equation (4)

$$y_{if} = x_i - x_f$$

equation (32) becomes

$$x_i h_{Li} = x_f h_{Lf} + (x_i - x_f)\, h_{vf}$$

and solving for the specific mass requirement

$$SMR^*_{if} = x_i / x_f = (h_{Lf} - h_{vf})/(h_{Li} - h_{vf}) \qquad (33)$$

where the asterisk denotes an isenthalpic specific mass requirement. Following the convention adopted for the previous analysis, the specific mass requirement for the overall process to produce cold liquid is designated SMR^*_{ot} . Since we consider only a single step isenthalpic expansion from one atmosphere pressure to the triple point pressure, we have that

$$SMR^*_{ot} = SMR^*_{if} = (h_{Lt} - h_{vt})/(h_{Lo} - h_{vt}) \qquad (34)$$

where the o subscript refers to the conditions at the origin of the process and t to the terminal liquid conditions.

The specific mass requirement to produce solid-liquid mixtures of various qualities from triple point liquid is the same for this process as for the straight vacuum pumping, so equation (15) is again employed.

$$SMR_q = 1 + (q/100)\,(SMR_{solid} - 1)$$

The general equation (8)

$$SMR_{ot} = \prod_{o}^{t} SMR_{if}$$

for the specific mass requirement of a stepwise process is applicable to this two-step process of producing solid-liquid mixtures from a liquid. Thus the SMR is obtained from the product of the SMR^*_{ot} (equation (34)) and the SMR_q (equation (15))

$$SMR^*_{oq} = SMR^*_{ot} \left[1 + (q/100)(SMR_{solid} - 1)\right] . \qquad (35)$$

The calculation of the pumped mass and volume is carried out by using equations (17) through (28) as developed for the straight vacuum pumping process but with the SMR^* for this isenthalpic process. Sample numerical calculations for the semiflow vacuum process are given in Appendix 2. Table 3 lists the results of the various calculations.

TABLE 3

SPECIFIC MASS REQUIREMENT AND PUMPED VOLUMES FOR THE SEMIFLOW VACUUM PUMPING PROCESS

Temperature Interval $T_i - T_f$ °K	SMR^*_{ot} = SMR_{if} Lbs./Lb. Product	SMR_{solid} Lbs./Lb. Product	SMR^*_{os} = $(SMR_{ot})(SMR_{solid})$ Lbs./Lb. Product	$V_{sat\ ot}$ ft.^{3}/Lb. Product	$V_{sat\ os}$ ft.^{3}/Lb. Product
20.278 13.813	1.1349696			17.30379	
liquid to solid @ 13.813		1.12922744			
20.278 to solid @ 13.813			1.28168306		36.11321

In the operation of this process, the production tank is filled with triple point liquid with the vacuum pump maintaining the pressure; then by continued pumping, the desired quality slush is produced. Thus, while the vacuum pump must handle the entire volume ($V_{sat\ os}$ = 36.11321 ft.^{3} per pound of produced solid (Table 3)), the production tank volume need be only the size required for the SMR^*_q since the mass vaporized during the isenthalpic expansion is removed during the Joule-Thomson fill operation.

The advantage of this method over the straight vacuum pumping method is that the storage capacity need only be provided for the denser liquid at the triple point from which some vapors have already been removed. Some capital investment saving can therefore be obtained by installing a smaller tank.

Since the vapors formed from the expansion must be removed at the low pressure, the volume removed is considerably higher than in straight vacuum pumping, thus requiring a larger capacity pump. Compare the volumes in Tables 2 and 3. The relative cost of storage and pumping will determine which of these two methods is more economical. The pumping costs will be affected directly by the time available to accomplish slush formation.

The capital investment and operating cost were obtained as before for the given conditions of 75,000 lb. of 50 percent slush to be produced in seven days and are presented in Appendix IV.

3.1.3 Branched-Flow Vacuum Pumping

The branched-flow vacuum pumping production method employs two isenthalpic expansions into the production vessel. One of the Joule-Thomson expansion valves discharges into the vapor space of the tank while the other discharges into the bottom of the tank. Both valves are supplied from transport vessels as shown by the diagram in Figure 5. As in the previous methods, a vacuum pump maintains the required sub-atmospheric pressure in the production vessel.

The thermodynamic process is shown in Figure 6 where liquid at condition i expands at constant enthalpy to conditions f and f' which represent the vapor-liquid and vapor-solid mixtures at temperatures and pressures just above and just below the triple point, 13.8°K. For the vapor-liquid expansion the specific mass requirement is given by equation (33)

$$SMR^*_{if} = x_i/x_f = (h_{Lf} - h_{vf})/(h_{Li} - h_{vf})$$

as derived for the semiflow process.

For the vapor-solid expansion the heat balance equation is

$$x_i h_{Li} = z_{f'} h_{sf'} + y_{if'} h_{vf'} \tag{36}$$

where $z_{f'}$ and $h_{sf'}$ are mass and specific enthalpy of the solid produced, and the other symbols are for liquid and vapor as previously defined. Again

$$y_{if'} = x_i - z_{f'}$$

and the specific mass requirement to expand from liquid at condition i to vapor-solid mixture f' is

$$SMR^*_{if'} = x_i/z_{f'} = (h_{sf'} - h_{vf'})/(h_{Li} - h_{vf'}) \ . \tag{37}$$

We consider that the static head of the product in the production tank is sufficient to provide the slight pressure difference between the discharges of the two valves so that both expansions may occur into the same tank. The specific mass required to produce a mixture of solid and liquid by these simultaneous processes is the sum of the two SMR's weighed by the amount of the solid and liquid respectively

$$SMR^*_{oz} = (x \, SMR^*_{if} + z \, SMR^*_{if'})/(x + z) \tag{38}$$

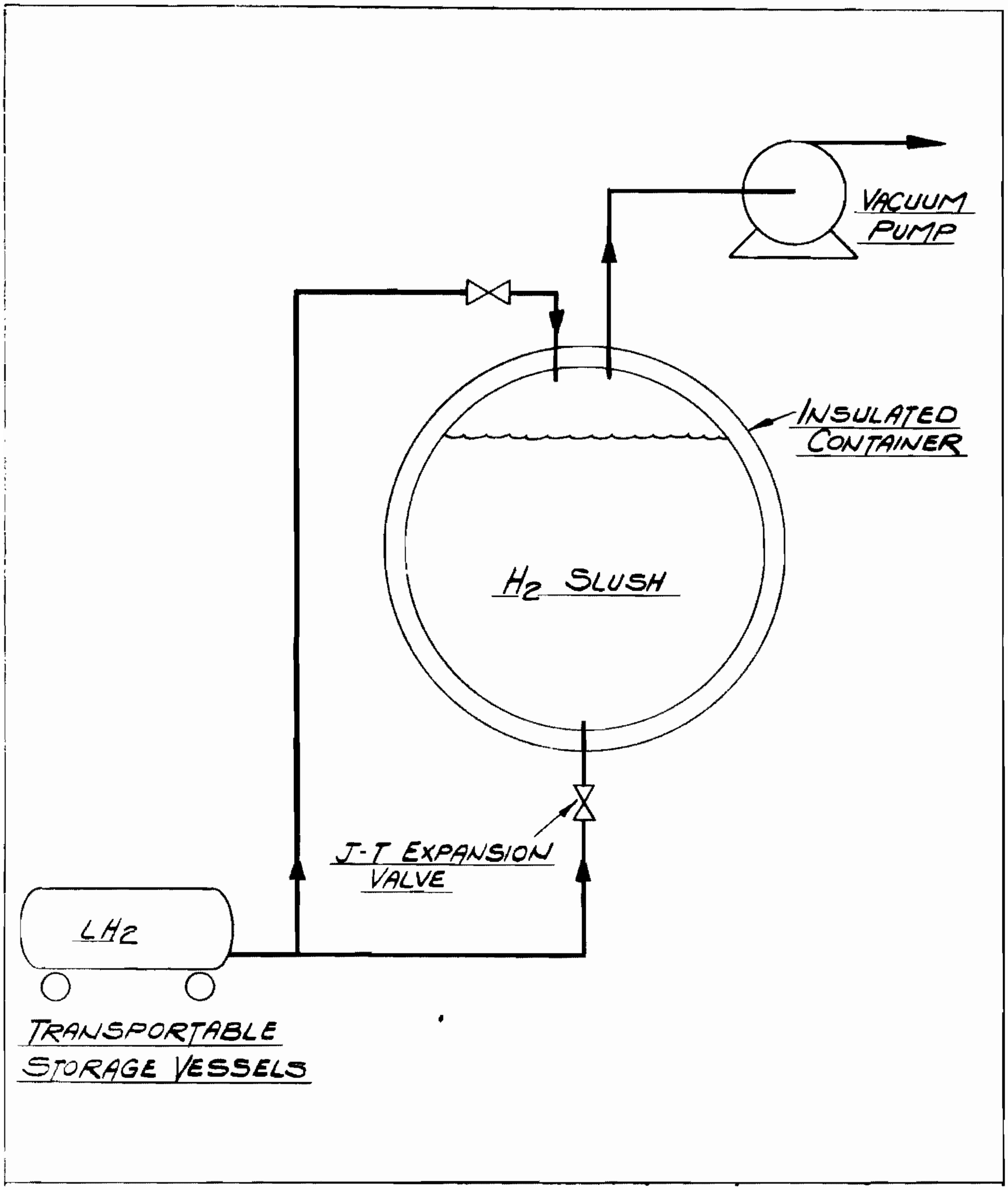

Figure 5. Branched Flow Vacuum Pumping Process Equipment

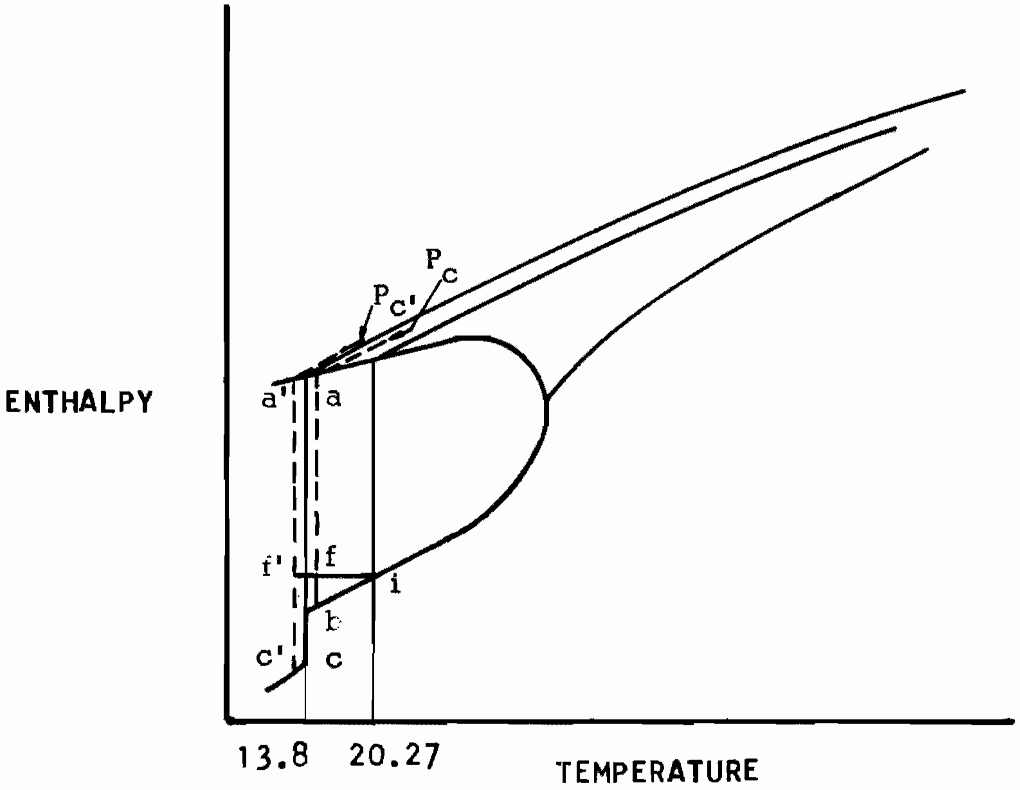

Figure 6. Branched Flow Vacuum Pumping Process

The quality of the resultant solid-liquid mixture is given, in percent solids, by a modified equation (14)

$$q = 100z\ (x + z)$$

The total specific mass requirement in terms of the quality of the final product mixture is obtained by substituting (14) in (38)

$$\begin{aligned} \mathrm{SMR}^*_{oq} &= (1 - q/100)\ \mathrm{SMR}^*_{if} + (q/100)\ \mathrm{SMR}^*_{if'} \\ &= \mathrm{SMR}^*_{ot} + (q/100)\ (\mathrm{SMR}^*_{os} - \mathrm{SMR}^*_{ot}) \qquad (39) \end{aligned}$$

where, as before, the interval conditions i and f are replaced by the one step terminal conditions o and t for the vapor-liquid process and by o and s for the vapor-solid process. Equation (39) is linear in q and equals SMR^*_{ot} and SMR^*_{os} respectively at qualities of 0 and 100 percent.

For comparison with previous processes, it is instructive to reduce equation (39) by factoring SMR^*_{ot} to obtain the form

$$\mathrm{SMR}^*_{oq} = \mathrm{SMR}^*_{ot}\ (1 + (q/100)\ [(\mathrm{SMR}^*_{os}/\mathrm{SMR}^*_{ot}) - 1]) . \qquad (39a)$$

Now $\qquad \mathrm{SMR}^*_{os} = (h_{sf'} - h_{vf'})/(h_{Li} - h_{vf'}) \qquad (37)$

and $\qquad \mathrm{SMR}^*_{ot} = (h_{Lf} - h_{vf})/(h_{Li} - h_{vf}) \qquad (33)$

so that for the circumstance where conditions f and f' are very near the triple point conditions, they may be considered equal and we have

$$\mathrm{SMR}^*_{os}/\mathrm{SMR}^*_{ot} = (h_{s'} - h_{v'})/(h_{L'} - h_{v'}) \qquad (40)$$

where the enthalpy values are all at the triple point conditions as indicated by the accents. For a process which is at both constant pressure and constant temperature, as in this triple point process,

$$\Delta h = T\Delta s$$

so that equation (40) may be rewritten

$$(h_{s'} - h_{v'})/(h_{L'} - h_{v'}) = (s_{s'} - s_{v'})/(s_{L'} - s_{v'})$$

we have from equation (13) that

$$SMR_{solid} = (s_{s'} - s_{v'})/(s_{L'} - s_{v'})$$

so that upon substitution in equation (39a)

$$SMR^*_{oq} = SMR^*_{ot} \; (1 + (q/100) \; [SMR_{solid} - 1] \;)$$

which is equation (35) derived for the semiflow vacuum process. Thus, the specific mass requirement for these two processes are identical under the assumed conditions, (i.e.) that the two expansion processes have the same feed pressures and nearly identical discharge pressures at the triple point.

The advantage of this method over the previous methods is that it reduces the required slush tank capacity to a minimum since only slush of the desired density need be introduced into the production tank. Thus, the tank volume is of unit value as given by the slush density with no allowance for pumped mass. The pumped mass and volume are identical to those for the semiflow process as listed in Table 3.

The capital investment and operating cost for the production of 75,000 lbs. of 50 percent slush is seven days by this method in Appendix IV.

3.1.4 Cascaded Vacuum Pumping Method

The various methods of producing slush hydrogen are actually methods of refrigeration; and, as in other refrigeration applications, greater efficiency is achieved if the process can be divided into small steps. With small steps covering only a part of the temperature range, the losses associated with a step can be absorbed at a higher temperature than would be the case for a single process step covering the whole required range. The provision of intermediate steps for the vapor-liquid isenthalpic expansion of the branched flow process leads to a method termed the cascaded vacuum pumping method. In this method, a series of chambers with expansion valves are introduced between the liquid supply and the expansion valves which discharge directly into the production tank. A vacuum pump maintains progressively lower pressures in the chambers. As shown in Figure 7, these chambers are actually separators which direct the

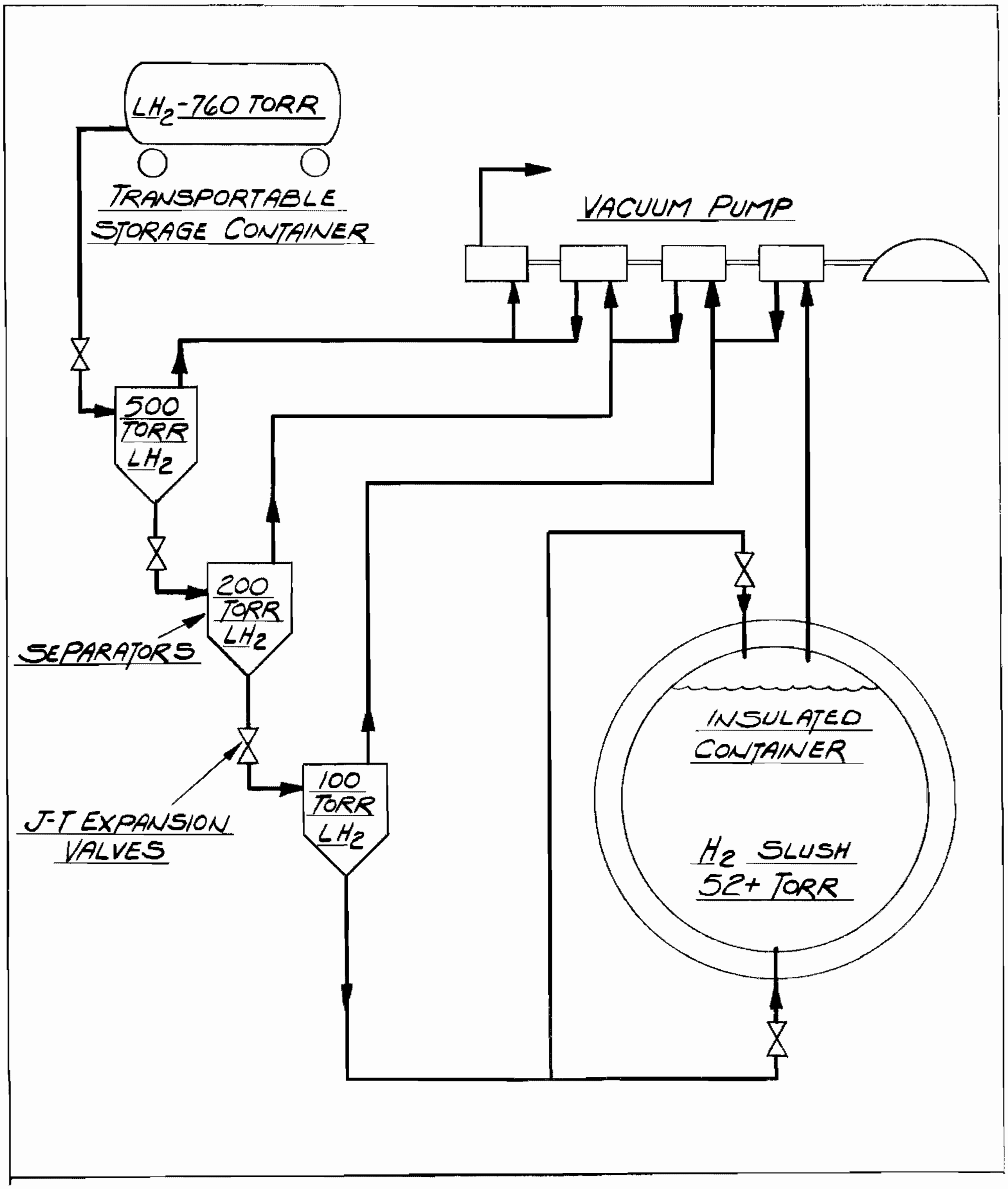

Figure 7. Cascade Vacuum Pumping Process Equipment

vapors to the vacuum pump and the liquid to the next lower pressure expansion chamber, ending with the branched flow into the production tank.

The stepwise process with three intermediate pressures is shown on the thermodynamic diagram in Figure 8. In a step, liquid is expanded from initial condition i to final condition f, the several steps beginning at o and ending at t and t' adjacent to the triple point line. The specific mass requirement for an interval expansion is given by the previously derived equation (33)

$$SMR^{*}_{if} = x_i/x_f = (h_{Lf} - h_{vf})/(h_{Li} - h_{vf}) .$$

Since the feed liquid to the n_{th} step is the product liquid from the $(n - 1)_{th}$ step, the SMR for a process made up of several steps is the product of the individual SMR_{if}, as in the following modification of equation (8)

$$SMR^{*}_{ot} = \prod_{o}^{t} SMR^{*}_{if}$$

In this cascaded isenthalpic expansion process, the SMR_{if} are calculated by equation (33) employing enthalpies. The final production step involving the expansions to solid-vapor and liquid vapor have been discussed for the branched flow process. The final equation for the cascaded vacuum pumping process for slush of quality q is equation (35) with the SMR_{ot} replaced by its value from equation (8)

$$SMR^{*}_{oq} = \prod_{o}^{t} SMR^{*}_{if} [1 + (q/100)(SMR_{solid} - 1)] \tag{41}$$

This equation is of the same form as equation (16) derived for the multiple step straight vacuum pumping analysis. Again, one should note that although the SMR_{solid} for the triple point process is the same for the isenthalpic and isentropic analysis, the SMR_{if} are calculated using entropies and the SMR^{*}_{if} are calculated using enthalpies, and the results are accordingly different as the isentropic and isenthalpic processes have different losses.

The masses and volumes which must be pumped at each of the expansion steps are calculated using the equations previously derived. Thus, the mass to be pumped for an interval i to f is determined by a modified equation (18)

$$y_{if} = x_i (SMR^{*}_{if} - 1)/SMR^{*}_{if} \tag{18a}$$

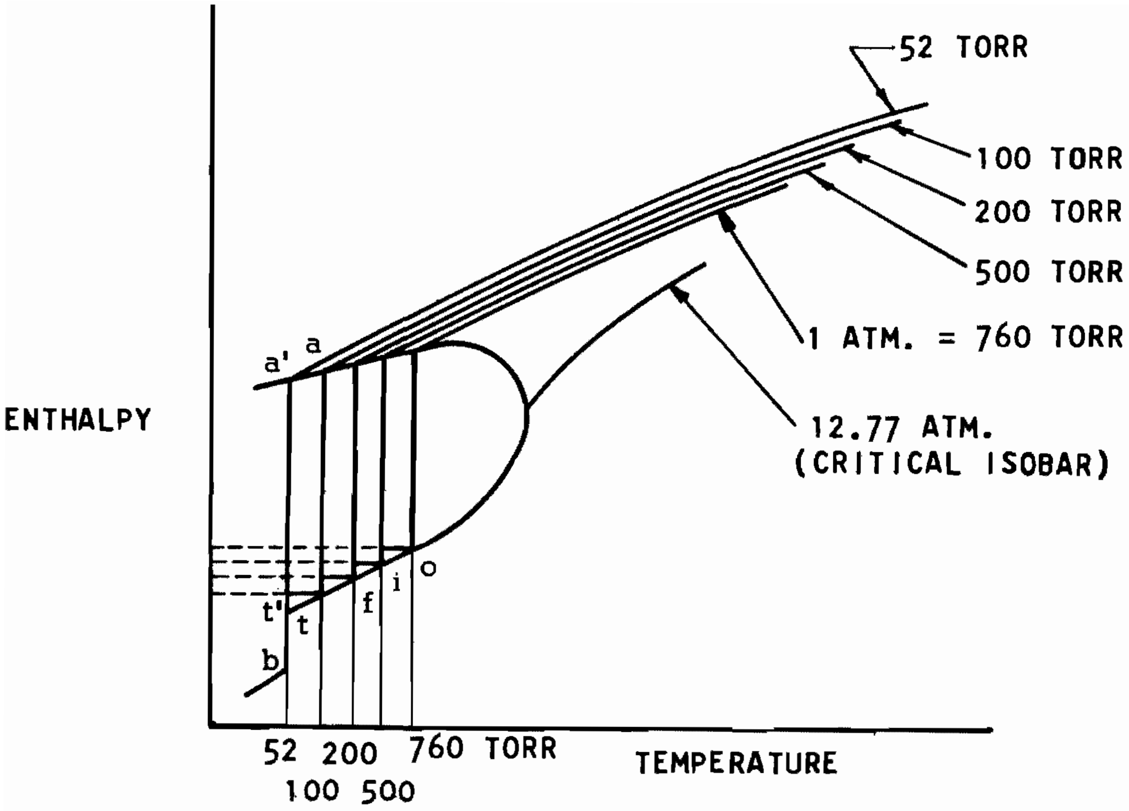

Figure 8. Cascaded Vacuum Pumping Process

while the volume is given by an equation similar to (24)

$$V_{Tif} = Y_{if} v_{Tf} = Y_{if} / \rho_{Tf} \tag{42}$$

where the specific volume, v_{Tf}, and densities, ρ_{Tf}, at the downstream pressure of the Joule-Thomson expansion replace the average values.

The total pumped mass requirements are obtained by summation of Y_{if} and Y_{oq} using equations (22) and (23)

$$Y_{ot} = \sum_{o}^{t} Y_{if}$$

$$Y_{oq} = \sum_{o}^{q} Y_{if}$$

the pumped volumes are obtained by the summation equations (27) and (28)

$$V_{Tot} = \sum_{o}^{t} V_{Tif}$$

$$V_{Toq} = \sum_{o}^{q} V_{Tif} .$$

Calculated values of the SMR^*_{if} and SMR^*_{ot} for the cascade pumping process are given in Table 4. The values for the pumped mass and volume are given in Table 5. Sample numerical calculations of the entries in these tables are given in Appendix 2.

The pressure increments for Tables 4 and 5 were chosen to correspond to the tabulated thermodynamic properties given by Mullins, Ziegler, and Kirk (1). In an actual process the pressure levels would most likely be chosen to give equal compression ratios for each step or to give some specified volume through-put for each pump. The pressure increments in Tables 4 and 5 give nearly equal compression ratios and thus serve to demonstrate the operational characteristics of the equal compression ratio process. The SMR^*_{if} per step, down to triple point liquid, given in the second column, are nearly equal so that each pump stage handles about the same mass load. The expansion from 100 Torr to 52+ Torr is carried out through two parallel valves as described in the process discussion, and the two specific mass entries for this expansion

TABLE 4

CASCADED VACUUM PUMPING

SPECIFIC MASS REQUIREMENT

$P_i \rightarrow P_f$ Torr	SMR_{if}^* Lbs./Lb. Product	SMR_{ot}^* Lbs./Lb. Product
760 500	1.029202	1.029202
500 200	1.048059	1.078664
200 100	1.026084	1.106800
100 52+ (Triple Point Liquid) (q = 0)	1.019125	1.127967
(100 Percent Solid) (q = 100)	1.150864	1.273776

TABLE 5

CASCADED VACUUM PUMPING

PUMPED MASS AND VOLUME REQUIREMENT

$P_i \rightarrow P_f$ Expansion Torr	$\rho_{T'f}$ Vapor Density at Pump Inlet (lb./ft.^{3})	Y_{ot} Mass Pumped to Produce 1 lb. of Triple Point Liquid (lb.)	$V_{T'f}$ Vol. Pumped to Produce 1 lb. of Triple Point Liquid (lb.)	Y_{oq} Mass Pumped to Produce 1 lb. of Solid (lb.)	$V_{T'oq}$ Vol. Pumped to Produce 1 lb. of Solid (ft.^{3})
760 to 500	0.057	0.032004	0.561474	0.036141	0.634054
500 to 200	0.0255	0.050256	1.970823	0.055931	2.225585
200 to 100	0.0139	0.026583	1.912446	0.030019	2.159666
100 to 52+	0.0078	0.019125	2.451923	0.150864	19.024620

step show the requirement to produce triple point liquid and solid hydrogen. The SMR_{if}^{*} for the solid is much higher than that for the liquid due to the extra refrigeration needed to freeze the product. The last column lists the total mass required per step, for each expansion step, in going to triple point liquid, $q = 0$, and to solid hydrogen, $q = 100$, as calculated by equation (41).

These SMR_{ot}^{*} are used to determine the quantity of hydrogen needed to produce a unit quantity of cold liquid or slush of quality q. As in the other flow vacuum processes, the production vessel is sized by the final product volume and not by the terminal SMR_{ot}^{*}, as is done for the straight vacuum process. The SMR_{ot}^{*} are used, however, to determine the amount of transport volume needed to supply liquid to the process. The SMR_{if}^{*} and SMR_{ot}^{*} of Table 4 are used in equations (18), (22), (23), (27), (28), and (42) to obtain the incremental and total mass pumped and volume pumped for the cascaded vacuum pumping method. These masses and volumes are listed in Table 5. The mass pumped entries in Table 5 give the mass of hydrogen which must be pumped from the lowest pressure of each expansion step to atmospheric pressure. In order that this process may proceed in a continuous manner these masses must be pumped during the same time period. The mass flow rate through the individual pumps for each stage can be obtained by dividing the mass by the time allotted for production of the required quantity of product. A multistage pump can be employed with the lowest pressure masses being pumped through the higher pressure stages. The mass flow through the stages would then be calculated by summing the mass from the lower pressure stages.

The volumetric through-put of the individual pumps or the stages of the multistage pumps are calculated by dividing the mass flow rates by the density at the stage suction pressure. The volumetric entires in Table 5 are computed for the case of saturated vapor inlet to the pump as was done in Tables 2 and 3 for the other vacuum production methods. The large volumetric requirement in the production of solid as compared to triple point liquid indicates that for the production of slushes of high quality, this pump stage will be the determining factor for the pump size and cost. The cascaded process combines the low tankage requirement of the branched flow vacuum pumping method with the low pump capacity requirement of the straight vacuum pumping process.

The capital investment and operating costs for this system to produce 75,000 pounds of 50 percent slush in seven days are shown in Appendix IV.

3.1.5 Summary of Vacuum Pumping Methods

The results of the analysis of the various vacuum pumping methods of slush production are collectively presented in graphical form in Figures 9 and 10. The specific mass requirement to produce various slush qualities are given in

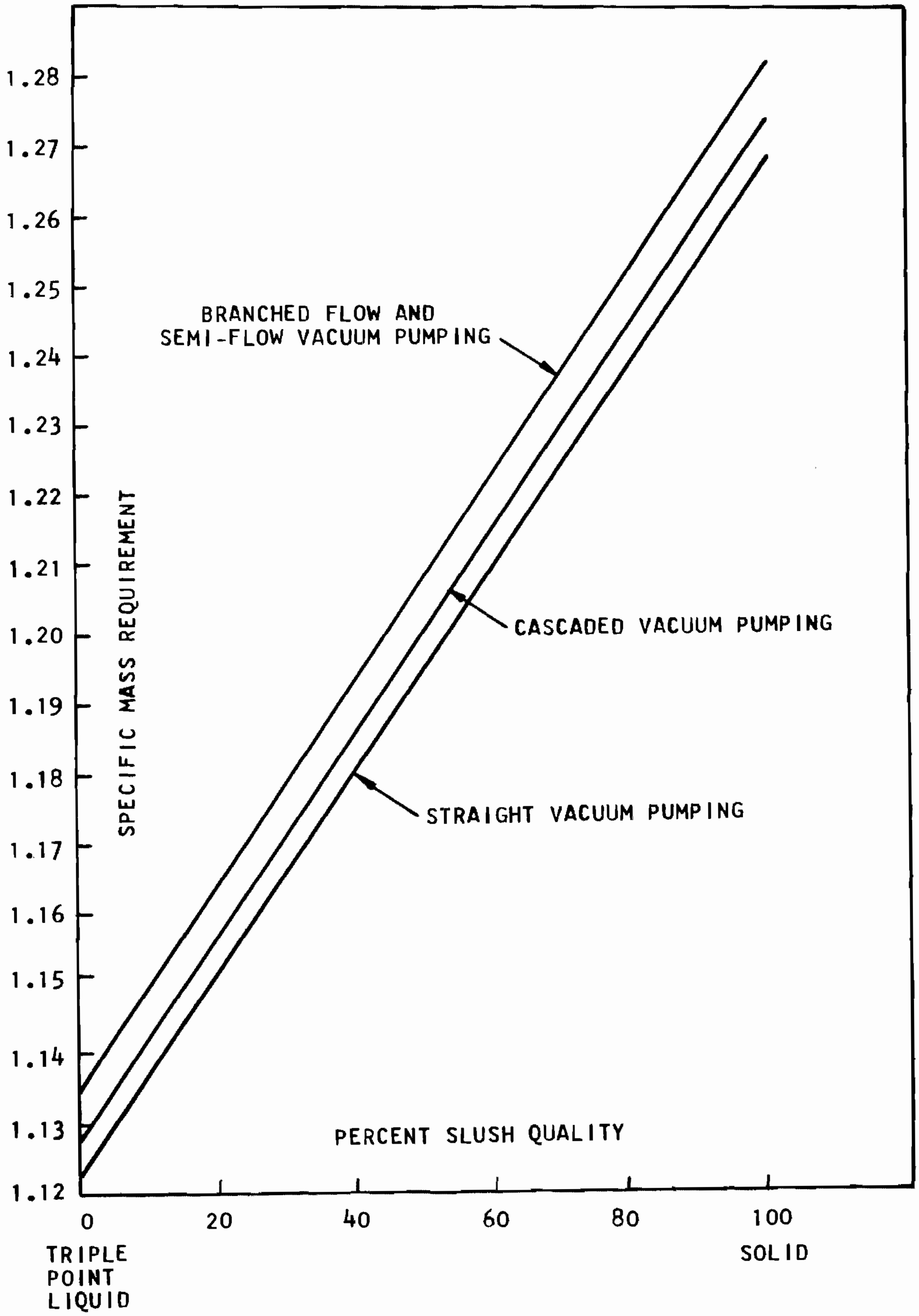

Figure 9. Specific Mass Requirement for Vacuum Pumping Methods

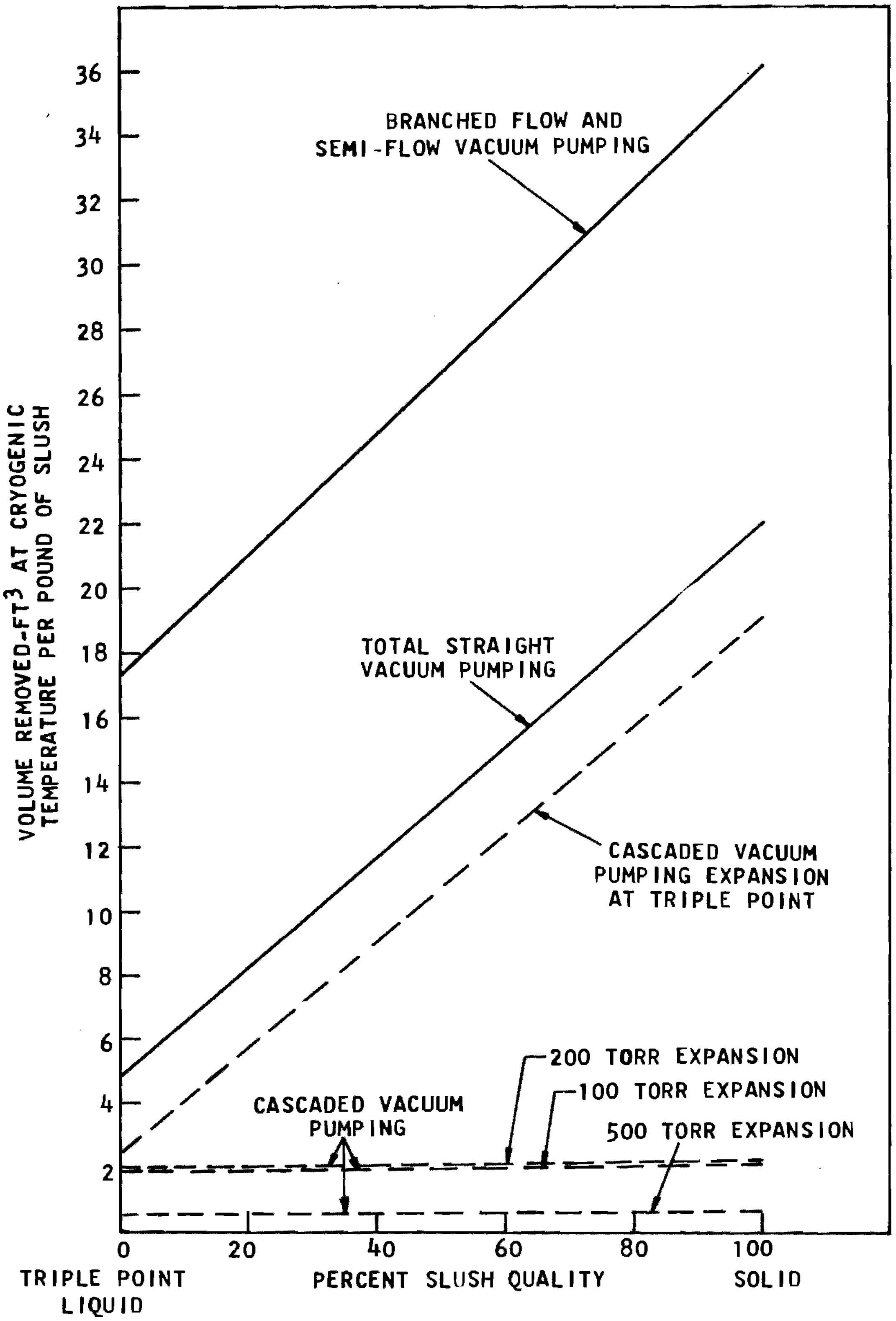

Figure 10. Vapor Volume Removed Versus Slush Quality for Various Vacuum Pumping Production Methods

Figure 9. The initial values for 0 percent quality are the SMR_{ot} needed to produce triple point liquid while the terminal values for 100 percent quality are the SMR_{oq} for solid. Both SMR_{ot} and SMR_{oq} are from Tables 1, 3 and 4. The SMR_{oq} intermediate qualities fall on a straight line between these terminal points as was shown by the equations developed in this process analyses. These curves clearly show the lower SMR requirement of the straight vacuum pumping method. The slopes of the lines for the semiflow and cascaded flow processes are slightly greater than the one for the straight vacuum pumping process. The higher SMR in these methods is due to the higher SMR required to produce liquid by these more irreversible processes.

Figure 10 shows the vapor volumes removed in producing various quality slush by the vacuum pumping methods. The numerical values in these graphs are from Tables 2, 3 and 5 and consider saturated vapor at the pump inlet. The branched and semiflow processes require pumping the largest volume of vapor because all the vapor for these processes is pumped at the triple point pressure. The straight vacuum and cascaded processes have lower pumped volumes because some of the vaporization occurs at higher pressures, and these methods have lower total masses to be pumped per unit product. The cascaded process requires simultaneous pumping on the several expansion steps so that the volume requirement for each expansion step is shown separately. The volumes for the higher pressure expansion steps for the cascaded system have a slight slope since the mass through-put of each stage is proportional to the slush quality to be produced in the final expansion.

3.2 HELIUM GAS REFRIGERATOR COOLING PRODUCTION TECHNIQUES

Cooling of liquid hydrogen to produce hydrogen slush by means of a helium gas refrigerator can be performed in either a batch or a flow process. In both processes the cold helium gas is heat exchanged with the hydrogen to effect cooling. The production of hydrogen slush by the helium gas refrigerator cooling method has an advantage over the vacuum pumping methods in that no hydrogen is lost during production. However, this method does require more extensive equipment installation including special production tanks.

3.2.1 Helium Gas Refrigeration Batch Process

The helium gas refrigeration batch process requires that a heat exchange surface be installed in the production tank as shown in Figure 11. The cold helium gas from one or more refrigerators is piped through the exchanger to cool and freeze the hydrogen. If only one refrigerator is employed, its operating temperatures must be lower than 13.8°K during the freezing process in order that heat be transferred to the helium. During the cooldown, the temperature of the refrigerating helium need be only a few degrees below the tank contents at any instant to ensure continuation of the process. Refrigeration is thus required at temperatures varying from just below the initial saturation temperature to just below the triple point temperature.

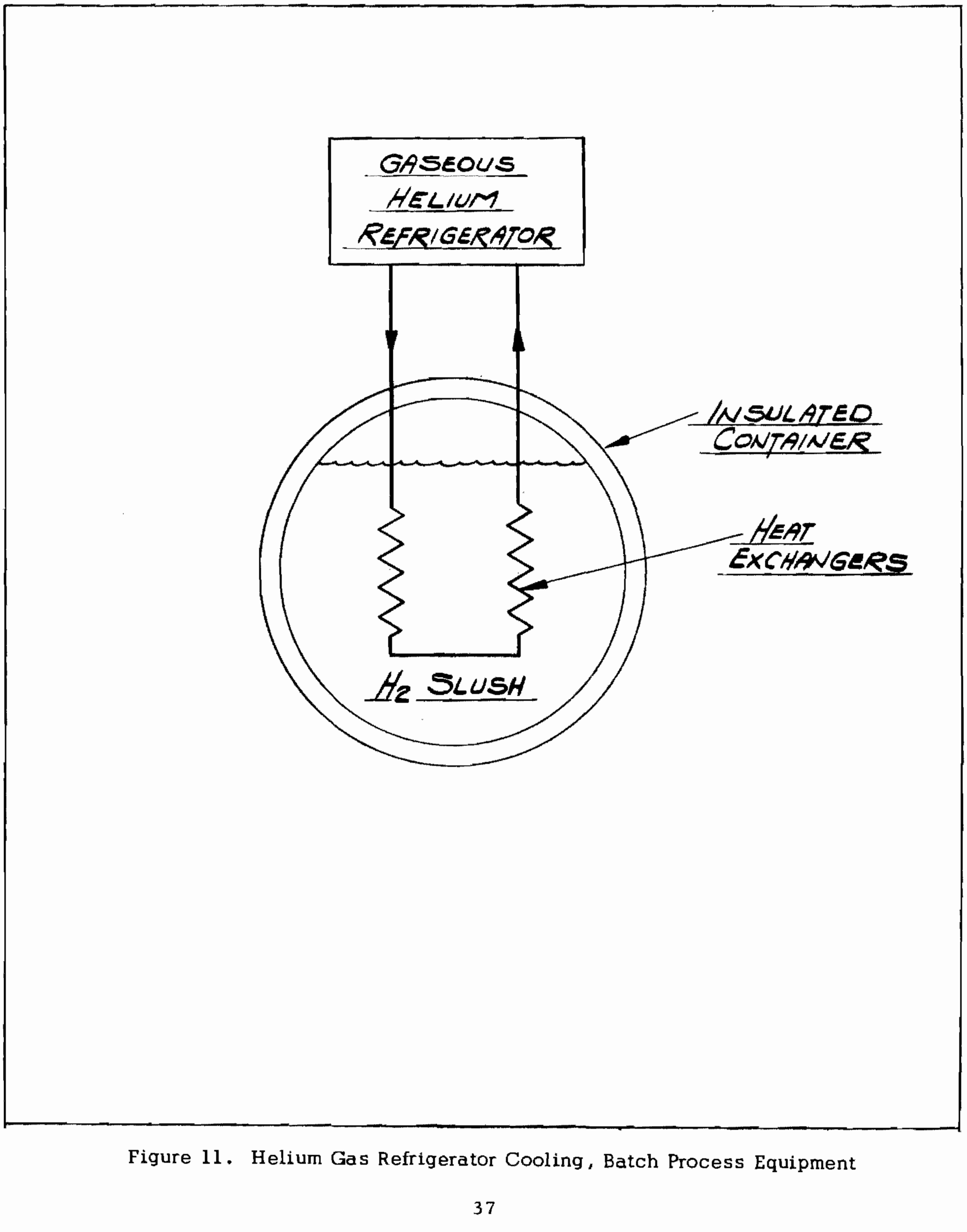

Figure 11. Helium Gas Refrigerator Cooling, Batch Process Equipment

The heat to be removed in reducing the temperature of the liquid hydrogen along the saturation line is

$$Q_{if} = x_i \int_{T_i}^{T_f} c_{sat} dT = x_i (h_{sat\ i} - h_{sat\ f}) \tag{43}$$

where x_i is the mass of hydrogen cooled, T_i and T_f the initial and final temperatures, c_{sat} the saturated specific heat, dT the differential temperature, and h_{sat} i and h_{sat} f the saturated enthalpies at temperatures T_i and T_f. At the triple point, the heat required to freeze liquid to produce a slush of quality q is,

$$Q_q = q x_i (h_{tL} - h_{ts}) \tag{44}$$

where h_{tL} and h_{ts} are the enthalpies of the triple point liquid and solid respectively. These enthalpies are constants, their difference being the latent heat of fusion at the triple point, so that the heat to be removed in freezing is linear in the quality q as is expected.

For a stepwise cooling process, the heat removed in each step is calculated by equations (43) and (44) and summed to give the total heat to be removed

$$Q_{oq} = \sum_{o}^{t} Q_{if} + Q_q \ . \tag{45}$$

The refrigerator capacity, W, needed for cooling and freezing is obtained by dividing the heat to be removed, given by equations (43) thru (45), by the time allowed for the process.

$$W_{if} = Q_{if} / \tau_{if} \tag{46}$$

$$W_q = Q_q / \tau_q \tag{47}$$

$$W_{oq} = \sum_{o}^{t} (Q_{if} / \tau_{if}) + Q_q / \tau_q \tag{48}$$

$$= \sum_{o}^{t} W_{if} + W_q$$

In equation (48) the time interval for the individual process step is divided into the heat for that step, and, in the general case, the heats and times will differ from step to step, giving a different capacity for the refrigerator for each step. For the case of a fixed capacity refrigerator operating over the total temperature range, the time interval for each temperature step is obtained by dividing the heat removed during the step by the refrigerator capacity

$$\tau_{if} = Q_{if}/W_{if} \tag{46a}$$

$$\tau_q = Q_q/W_q \tag{47a}$$

and the total time is obtained by the summation

$$\tau_{oq} = \sum_{o}^{t} (Q_{if}/W_{if}) + Q_q/W_q \tag{48a}$$

If a single refrigerator of constant capacity is used for all of the liquid cooling and freezing steps, $W_{if} = W_q$, and

$$\tau_{oq} = (\sum_{o}^{t} Q_{if} + Q_q)/W_q \ . \tag{48b}$$

The heat to be removed in each process step must be transferred in the time τ_{if} or τ_q by the heat exchanger immersed in the production tank. The heat exchanger is sized by the relation

$$W_{if} = U_{gL} A \theta_{gL} \tag{49}$$

where U_{gL} is the average rate of heat transfer from the liquid hydrogen to the gaseous helium during the interval i to f , A the area over which this heat transfer occurs, and θ_{gL} the average temperature difference between the liquid hydrogen and gaseous helium during the interval i to f. By introducing equation (46) into (49) the heat transferred is given by

$$Q_{if} = U_{gL} A \theta_{gL} \ \tau_{if} \tag{50}$$

which shows that for a fixed installation in which Q_{if} , U_{gL} , and A are constant, the temperature and time differences, θ_{gL} and τ_{if} , vary inversely with each other. Thus, for quick cooling, a large θ_{gL} must be provided. For a low θ_{gL} , a long time must be provided. An economic upper limit exists for θ_{gL} .

The economic limit is determined by the fact that the cost of refrigeration varies as an inverse function of the average temperature at which the refrigeration is supplied. The average temperature of the refrigerating gas for the temperature interval i to f is

$$T_{rif} = [(T_i - \theta_{gL}) + (T_f - \theta_{gL})]/2$$

$$= (T_i + T_f)/2 - \theta_{gL} \tag{51}$$

provided that $\theta_{gL} > (T_i - T_f)$ so that the cold surface is always colder than the liquid. θ_{gL} must be kept small to keep the average temperature up. There is also a natural upper limit to θ_{gs} for the freezing process since the thermal conductivity of solid hydrogen is no doubt low and most probably decreases with temperature resulting in a diminishing return on reducing the lower temperature much below the triple point.

The heat transfer coefficient, U_{gL}, in equation (49) is dependent upon both the hydrogen liquid and helium gas heat transfer properties. This overall heat transfer coefficient between the gas and liquid is the resultant of two coefficients; that for the gas to the wall confining the gas, u_g, and that due to the heat from the wall to the liquid, u_L. Since the liquid and solid hydrogen are confined to the production vessel and can be stirred only moderately, if at all, the properties of the liquid and solid hydrogen are expected to be the determining limit on the value of U_{gL}. The area A in the heat transfer equation obviously has some practical maximum value since the heat exchanger is considered to be installed within the production vessel.

For a general insight into process equipment requirement, the heat transfer coefficient, u_L, is used alone since it makes the problem reasonably tractable without detailed design. If no stirring mechanism is provided in the production tank, the heat transfer must be achieved through free convection of the liquid. Consider that the heat exchanger immersed in the liquid is constructed of a series of vertical plates; then the free convection heat transfer coefficient is given by the expression

$$u_L = 0.071\ (k/D)\ (N_{Ra})^{1/3}\ (H/D)^{-1/9} \tag{52}$$

where N_{Ra} is the Rayleigh number, H the plate height, D the distance between the plates, and k the thermal conductivity of the liquid. The Rayleigh number is given by

$$N_{Ra} = \rho^2 c_p g \beta \theta_L D^3 / \eta k \tag{53}$$

where ρ is liquid density, c_p the specific heat, g the acceleration due to gravity, β the cubic expansion coefficient, θ the temperature difference between the plate and liquid, and η the viscosity of the liquid. Substituting equation (53) in (52)

$$u_L = 0.071\ k\ (\rho^2 c_p g \beta \theta_L/\eta k)^{1/3}\ (H/D)^{-1/9}\ \text{watts/cm}\ ^\circ\text{C}$$

$$= 0.071\ k\ (\alpha\theta_L)^{1/3}\ (H/D)^{-1/9} \qquad (54)$$

where the quantity α is dependent on the fluid properties only, and is called the convection modulus. These equations have been substantiated for heating and cooling fluids over a range of temperatures, but no results are available for cryogenic fluids. The following discussion will nevertheless employ these equations for analysis of the heat exchange to liquid hydrogen.

If the heat exchangers are constructed so that the helium gas flows between two surfaces which are in contact with the liquid hydrogen, the volume of liquid to be cooled by the heat transferred across the area A_L is $A_L D/2$ and its mass is

$$x = \rho_{avg} A_L D/2\ . \qquad (55)$$

The heat to be removed to cool this mass from T_i to T_f is

$$Q_{if} = x\ (h_i - h_f) = (\rho_{avg} A_L D/2)\ (h_i - h_f)\ . \qquad (56)$$

If this cooling is to occur in the time τ_{if}, the cooling rate for the temperature increment T_i to T_f is

$$W_{if} = Q_{if}/\ \tau_{if} = (\rho_{avg} A_L D/2)\ (h_i - h_f)/\ \tau_{if}\ . \qquad (57)$$

The heat transfer from a plate of area A_L is given by the equation

$$W_L = u_L A_L \theta_L\ . \qquad (58)$$

Substituting (54) into (58) gives

$$W_L = 0.071\ k\ A_L \alpha^{1/3}\ \theta_L^{4/3}\ (H/D)^{-1/9}\ \text{watts.,} \qquad (59)$$

Since θ_L is raised to the 4/3 power, the heat transfer is improved considerably by increasing the temperature difference θ_L. Thus, from this expression, there is a requirement to increase θ_L to improve convective heat transfer while there is a need to reduce θ_L to keep the average refrigerator temperature from being too low.

It is convenient to neglect the H/D term in equation (59) since its value depends upon the final detailed tank and heat exchanger design. For spheres or horizontal cylindrical tanks, H is the diameter of the tank. For spheres, H will most likely be less than 70 ft. and for cylinders less than 50 ft. Since the spacing, D, will probably be several feet, the ratio H/D is not likely to be much greater than 10. When $H/D < 10$, $(H/D)^{1/9} < 1.25$ so that neglecting H/D for these cases will represent an error of less than 25 percent in τ_{if} or D and even less in θ_L. Eliminating H/D then gives the working formula for the heat transfer rate to liquid hydrogen as

$$W_L = 0.071\, k A_L \alpha^{1/3} \theta^{4/3} \text{ watts.} \tag{59a}$$

Upon substitution of (55) for A_L in (59a), the heat transfer rate is given by

$$W_L = 0.142\, k x \alpha^{1/3} \theta^{4/3} / \rho_{avg} D. \tag{59b}$$

The cooling rate of the liquid, W_{if}, must be equal to the heat transfer rate, W_L, so that equating (57) and (59a) and solving for the time interval yields

$$\tau_{if} = 7.04\, \rho_{avg} D\, (h_i - h_f)/k\alpha^{1/3} \theta_L^{4/3}. \tag{60}$$

This equation can be rewritten to give D or θ_L directly

$$D = 0.14\, k\alpha^{1/3} \theta_L^{4/3}\, \tau_{if} / \rho_{avg} (h_i - h_f) \tag{61}$$

$$\theta_L = 4.32\, [\rho_{avg} D\, (h_i - h_f)/k\alpha^{1/3}\, \tau_{if}]^{3/4}. \tag{62}$$

These expressions can be employed to determine the process and equipment parameters for the liquid cooling portion of the process. The equations for the freezing process must include the thermal resistance resulting from the frozen solid on the heat exchanger surface in addition to the thermal convection just discussed. A detailed review of this heat transfer was not undertaken because of the lack of sufficient characterization of the solid produced at the surface, particularly the thermal conductivity of the solid.

As an example of the use of the equations developed so far, consider the refrigeration rate and the time required to cool liquid hydrogen through one degree at 20°K, near the normal boiling point, and at 14°K, near the triple point, using a refrigerator which produces an average temperature of 11°K at the plate surfaces. Table 6 shows numerical results of the calculations which are given in Appendix 2. It should be understood that the refrigerator temperature level is lower than 11°K by the temperature difference, θ_g , needed for heat transfer from the gas to the heat exchanger.

TABLE 6

HELIUM GAS REFRIGERATION BATCH PROCESS

HEAT REMOVED, COOLING TIMES, AND HEAT TRANSFER RATES

FOR LIQUID HYDROGEN COOLED BY AN 11°K REFRIGERATOR

Hydrogen Temperature T°K	Q_{if} Btu/lb.°K	τ_{if} sec./°K	W_L watts/lb.
20	4.24	39.1D	115/D
14	3.05	226D	14.3/D

Thus, in this system with a fixed heat exchanger area and spacing and a constant refrigerator temperature, it takes 5 times longer to cool through one degree at 14°K than at 20°K. The refrigerator capacity required at 20°K is seven times larger than the capacity required for 14°K. For intermediate temperatures, the times and refrigerator capacities are intermediate between the values listed. The calculated values of W_L are the maximum heat transfer rates from the heat exchanger plates due to free convection. If less refrigeration than W_L is supplied, the total time required must be increased. The converse is not true, however, and to decrease the time interval, the plate spacing must be reduced or the heat transfer temperature difference must be increased.

If a refrigerator sized for the 14°K interval were used at 20°K, the time for cooling through one degree would have to be increased seven fold

However, by comparison with the 14 °K interval, this would represent only a 35 percent increase in the cooling time interval as determined by dividing $W_{L(14\,°K)}$ into $Q_{if(20\,°K)}$ according to equation (46a).

Table 7 lists the magnitudes of Q_{if} (from Mullins, Ziegler, and Kirk (1) and equation (43)) for each temperature interval from the boiling point down to the triple point along with the ratio of each Q_{if} to the Q_{if} for 14 °K. This ratio gives the relative operating time required at each temperature interval by a refrigerator sized to cover the 14 °K temperature interval in a specified length of time as determined from equation (46a). The sum of these ratios gives the ratio of the total cooling time over the temperature range to the cooling time for the low temperature interval.

Table 8 presents the Q_q for freezing slush in quality increments of 25 percent along with the freezing time intervals based on the 14 °K incremental refrigerator capacity. The freezing time increments are added to those of Table 7 to obtain the total process time, with the last column in Table 8 being the total time to reach q quality slush relative to the time required to cool from 15 °K to 14 °K. The assumption is made that the required heat transfer through the solid is accomplished with the same heat transfer rate as the 14 °K liquid. This assumption is by no means on firm foundation and may prove to be a very poor one, leading to much longer freezing times.

The problem of fouling the heat exchanger surface by solid deposits can be remedied by scraping the solids from the surfaces as they are formed. Such scraped surface exchangers are used in many thermal processes, but they have not, to date, been employed in cryogenic equipment. The development of the attendent mechanism to actuate the scrapers may prove to be difficult, but the addition of scrapers would allow virtually the same heat transfer during freezing as for the liquid cooling at the lower temperatures.

The equation and tabular information developed can be used to determine the refrigerator size and operating time to produce slush of a desired quality in a production tank outfitted with vertical heat exchange surfaces. The minimum plate spacing can also be determined from this analysis. The plate spacing is large enough that only a small fraction of the tank volume need be occupied by the heat exchanger. As a result, the production tank requirement for this process is simply a tank large enough to contain the required mass of saturated liquid hydrogen.

The refrigerator size and capital investment for the production of 75,000 pounds of 50 percent slush in seven days by this batch process is presented in Appendix IV.

TABLE 7

HELIUM GAS REFRIGERATION BATCH PROCESS HEAT REMOVAL REQUIREMENT FOR INTEGRAL TEMPERATURES FROM THE BOILING POINT TO THE TRIPLE POINT

T °K	Q_{if} Btu/lb. $= (h_i - h_f)/x$	Q_{if}/Q_{15-14} $= \tau_{if}/\tau_{15-14}$
20.278 -20	1.19	0.38
20 - 19	4.09	1.32
19 - 18	3.85	1.24
18 - 17	3.61	1.16
17 - 16	3.40	1.10
16 - 15	3.23	1.04
15 - 14	3.10	1.00
14 - 13.813	0.56	0.18
ΣQ_{if}	23.03	
$\Sigma Q_{if}/Q_{15-14} = \tau_{20.278-13.813}/\tau_{15-14}$		7.42

TABLE 8

HELIUM GAS REFRIGERATION BATCH PROCESS HEAT REMOVAL AND FREEZING TIMES FROM THE TRIPLE POINT FOR VARIOUS QUALITY SLUSH

q Slush Quality %	Q_q Btu/lb.	Q_q/W_{15-14} $= \tau_q/\tau_{15-14}$	$\Sigma Q_{oq}/Q_{15-14}$
0	0	0	7.42
25	6.26	2.02	9.44
50	12.52	4.04	11.47
75	18.78	6.08	13.48
100	25.03	8.10	15.50

3.2.2 Helium Gas Refrigeration Flow Process

A schematic of a helium gas refrigerator flow system is shown in Figure 12. Liquid hydrogen from a transportable storage reservoir is first passed through an external helium gas-cooled heat exchanger where its temperature is reduced to 13.8°K. This liquid then flows into the storage tank where a second helium gas-cooled heat exchanger removes the additional heat required to produce various qualities of hydrogen slush. This process is a flow process because the hydrogen slush is being produced while the triple point liquid hydrogen is flowing into the vessel. It differs from the batch process in that, for the batch process, the vessel is first filled with saturated liquid hydrogen at one atmosphere, and then slush production is started.

In the flow process, the liquid hydrogen is cooled at constant pressure from an initial P_o and T_o to P_o and $T \sim 13.8°K$ with no freezing. This near triple point liquid is then introduced into the production vessel where it is frozen to the desired quality slush in a manner quite similar to that discussed for the batch process. The pressure of the production vessel is maintained at the liquid hydrogen supply pressure by gaseous helium pressurization so that there is no throttling at the inlet to the vessel.

The refrigeration for the process is required at variable temperatures to cool the liquid and at a fixed temperature to freeze the liquid to the desired quality. The heat load on the refrigerator to cool x units of liquid to near the triple point is

$$Q_{ot} = x(h_o - h_{ot}) \tag{63}$$

where h_o is the enthalpy of saturated hydrogen at the inlet pressure and h_{ot} is the enthalpy of liquid hydrogen at the inlet pressure and at near the triple point temperature. Since the melting curve is a strong function of temperature ($dp/dT \sim 35$ atm./°K), the temperature of the liquid will be only a few hundreths of a degree above the triple point, and the triple point temperature may be used as the outlet temperature of the liquid cooling exchanger.

The heat load on the refrigerator to produce slush of quality q from triple point liquid is

$$Q_{tq} = xq\,(h_{ot} - h_{os}) \tag{64}$$

where h_{ot} and h_{os} are the enthalpies of the liquid and solid at the pressure and temperature of the production vessel heat exchanger.

The total heat load on the refrigerator is the sum of the loads

$$Q_{oq} = Q_{ot} + Q_{tq}. \tag{65}$$

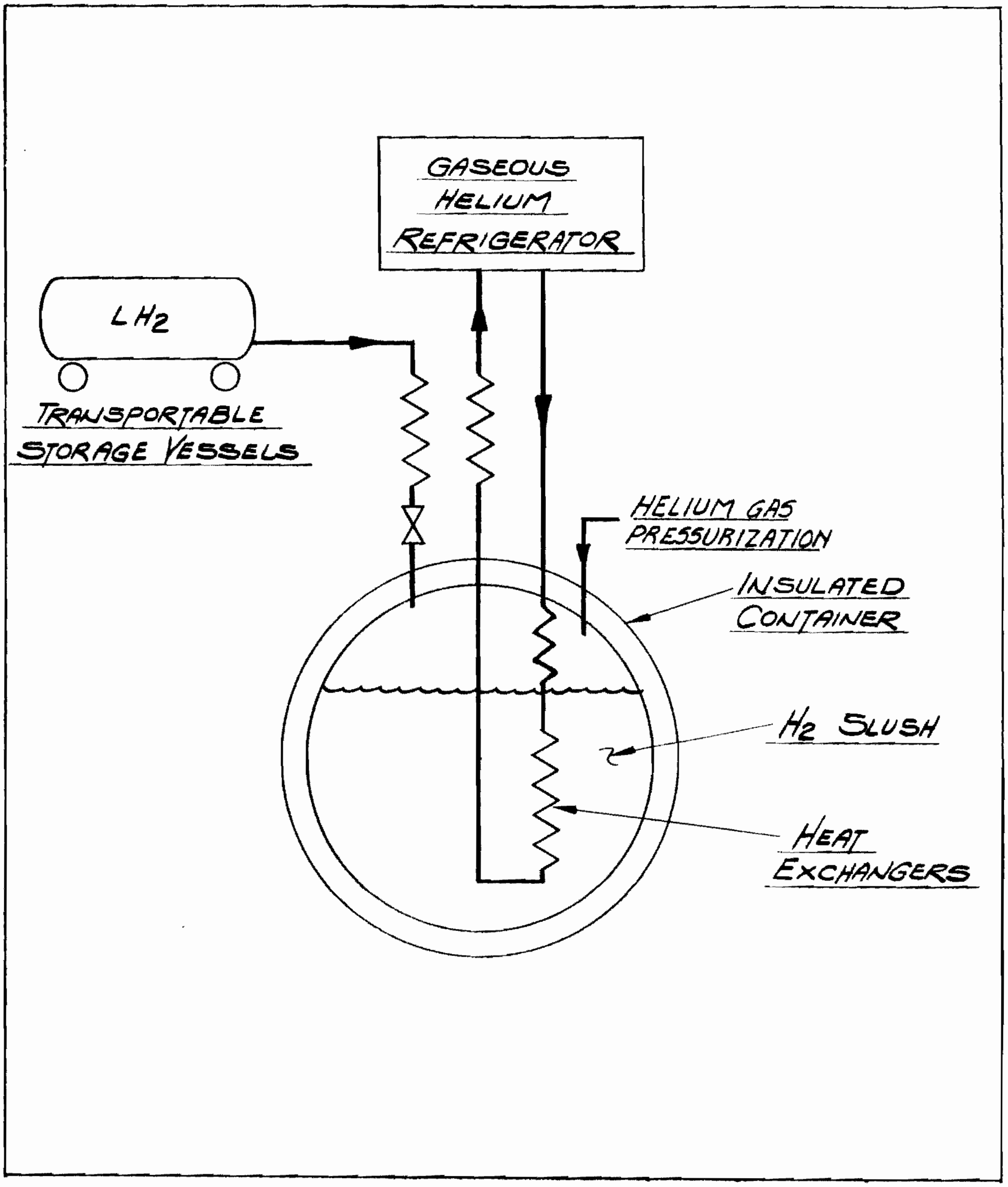

Figure 12. Helium Gas Refrigerator Cooling, Flow Process Equipment

The first heat load occurs over a temperature range of T_o to T_t while the last occurs at a fixed temperature, the triple point temperature. The refrigeration can be supplied by separate refrigerators for these two regions. However, since the gaseous helium refrigerator is not an isothermal refrigerator, but instead requires the helium gas to be warmed over a temperature range, there is some logic in employing a single refrigerator to cover both regions, allowing a single helium stream to be warmed from a temperature below the hydrogen triple point to near the boiling point.

In this flow process, the heat exchange problem is fundamentally different from that of the batch process since the flowing hydrogen can be conducted through heat exchange passages to affect the desired heat transfer by forced convection rather than free convection. The assumption is therefore made that these heat exchangers can indeed be designed, and no detailed heat transfer discussion will be undertaken. The refrigerator is sized by dividing the total heat load given by equation (65) by the time allowed for the refrigeration

$$W_{oq} = Q_{oq}/\tau_{oq} \quad . \tag{66}$$

The refrigerator must produce a cold gas stream whose temperature is far enough below the hydrogen triple point to provide heat transfer to the isothermal process, and it must accept a return gas stream whose temperature is near the normal boiling point of liquid hydrogen. Since the heat capacity of the helium gas stream is expected to be less than the heat capacity of the hydrogen liquid stream, the helium is expected to warm up to very near the inlet hydrogen temperature. A temperature difference must exist along the helium stream in the freezing exchanger as the warming of this stream is the source of refrigeration. With a constant helium mass, m, and specific heat, cp, the refrigeration available over the temperature range T_i to T_f is

$$Q_{if} = mc_p (T_i - T_f) \, . \tag{67}$$

For the liquid cooling process step

$$\begin{aligned} Q_{ot} &= mc_p[(T_o - \theta_o) - (T_t - \theta_L)] \\ &= mc_p [T_{o\theta} - (T_t - \theta_L)] \end{aligned} \tag{68}$$

where $T_{o\theta}$ is the temperature of the helium which is very near the temperature of the inlet hydrogen T_o, and θ_L is the temperature difference at the triple point.

For the freezing process step

$$Q_{tq} = mc_p[(T_t - \theta_L) - (T_t - \theta_q)]$$

$$= mc_p(\theta_q - \theta_L) \tag{69}$$

where θ_L and θ_q are the warm and cold end temperature differences. Summing equations (67) and (68) gives

$$Q_{oq} = mc_p[T_{oe} - (T_t - \theta_q)] \tag{70}$$

where $(T_t - \theta_q)$ is the temperature of gas coming from the refrigerator

$$T_{ro} = T_t - \theta_q \tag{71}$$

Equating the refrigeration to the heat removal requirements of the two portions of the process gives

$$x(h_o - h_{ot}) = mc_p[T_{oe} - (T_t - \theta_L)] \tag{72}$$

$$qx(h_{ot} - h_{os}) = mc_p(\theta_q - \theta_L) . \tag{73}$$

Solving these equations simultaneously for θ_q yields

$$\theta_q = \theta_L + q[T_{oe} - (T_t - \theta_L)](h_{ot}-h_{os})/(h_o-h_{ot}). \tag{74}$$

The refrigeration outlet temperature is therefore

$$T_{ro} = T_t - \theta_L - q[T_{oe} - (T_t-\theta_L)](h_{ot}-h_{os})/(h_o-h_{ot}) \tag{75}$$

where equation(74) has been introduced into equation (71).

The refrigerator must be specified by its operating temperatures and refrigeration capacity. The applicable temperature is the logarithmic mean of the temperature range over which the helium is warmed

$$T_{mean} = [T_{oe} - T_{ro}]/\ln(T_{oe}/T_{ro}) \tag{76}$$

Assuming that it is practical to design the liquid cooling exchanger for a one degree cold end temperature difference, $\theta = 1.0°C$, and choosing $T_{oe} = 20°K$, the set of equations (73), (75), and (76) yield the refrigeration mean and outlet temperatures given in Table 9 for various slush qualities.

TABLE 9

HELIUM GAS REFRIGERATION FLOW PROCESS
REFRIGERATOR MEAN AND OUTLET TEMPERATURES

q Slush Quality %	T_{ro} Outlet Temp. °K	T_{mean} Mean Temp. °K
0	12.8	16.2
25	10.8	15.0
50	8.9	13.7
75	6.9	12.3
100	5.0	10.8

Sample numerical calculations are given in Appendix II. The lowest outlet temperature is required by q = 100 percent as is expected. The very low mean temperature indicates that a two refrigerator process may be more economical for the production of high quality slush, but no analysis has been made for multi-refrigerator processes.

The production vessel size for this flow process is less than that for the batch process since it need be sized only for the volume of slush of desired quality. The allowance in the heat exchangers should be about the same as in the batch process if the same production rate is required since the heat load is equal for equal production rates.

The capital and operating costs to produce 75,000 pounds of 50 percent slush in seven days by the flow process is given in Appendix IV.

3.3 LIQUID HELIUM COOLING PRODUCTION TECHNIQUES

Cooling liquid hydrogen with the refrigeration available from liquid helium is of interest since it eliminates the hydrogen loss inherent in the vacuum pumping methods and avoids the high capital investment of the helium gas refrigerator cooling method. However, operating costs will be very high since the refrigeration must be supplied from 4.2°K. As with the helium gas refrigerator, slush production can be accomplished in either a batch or a flow type system.

3.3.1 Batch Process

The process equipment for a typical batch liquid helium cooling system is shown in Figure 13. The insulated container is first filled with liquid hydrogen at atmospheric pressure, and then the internal liquid helium container is filled and closed. The latent heat of vaporization of the helium is transferred through the walls of the internal liquid helium container while the sensible cooling available is transferred to the liquid hydrogen by use of a heat exchanger. This heat exhanger could possible be eliminated by passing the helium vapors directly through the hydrogen. The sensible heat would then be recovered by the direct contact between the helium and

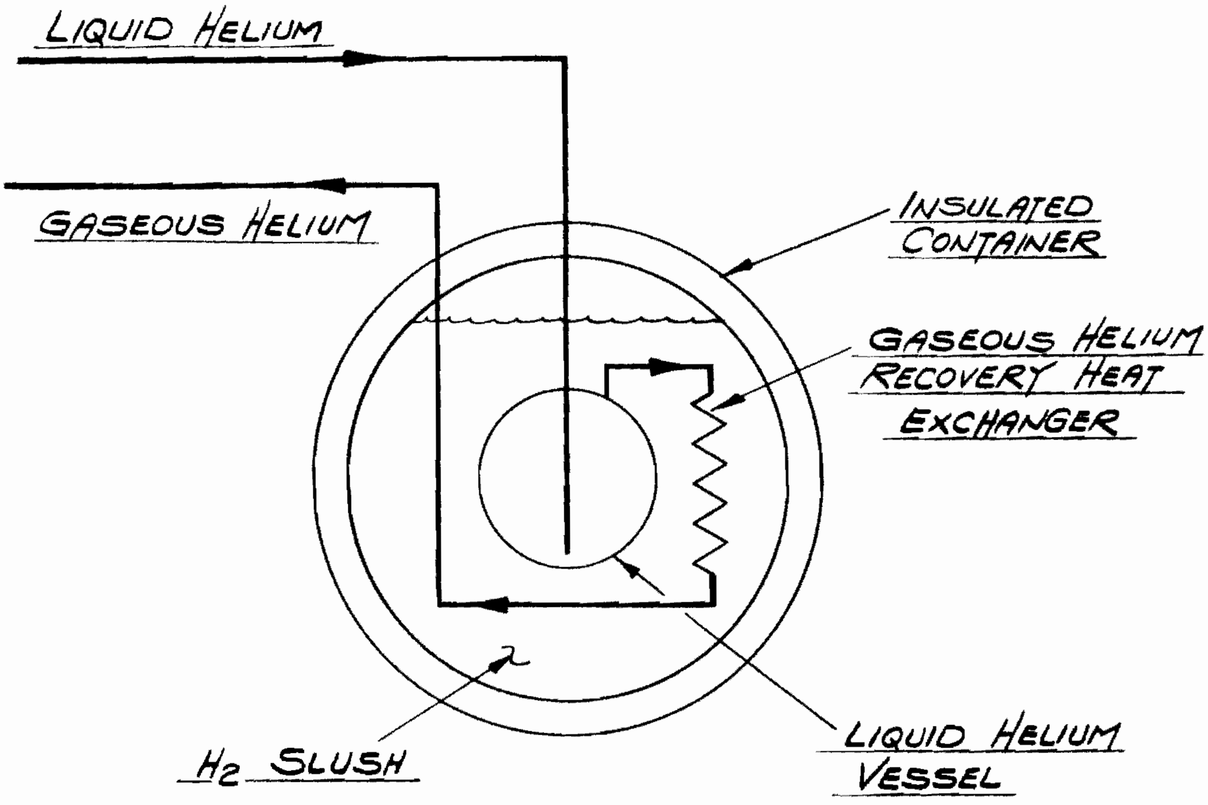

Figure 13. Liquid Helium Cooling, Batch Process Equipment

hydrogen, and additional cooling would accrue from the evaporation of hydrogen into the helium bubbles.

The heat must be removed from the hydrogen in two steps given by equations (63) and (64)

$$Q_{ot} = x(h_o - h_t)$$

$$Q_{tq} = xq(h_{tq} - h_s)$$

The cooling available from the liquid helium is the latent heat of vaporization, λ , plus the sensible heat required to warm the helium mass, m, to a temperature, T_e, near the temperature of the hydrogen product.

$$Q_{He} = \int_o^m [\, \lambda + \int_{4.2}^{T_e} c_p dT] \; dm \quad . \tag{77}$$

At the beginning of the cooling phase of the process, the temperature T_e is near the normal boiling point of liquid hydrogen, whereas at the conclusion of the cooling phase, the temperature T_e is near the triple point of hydrogen. If the specific heat of helium gas is constant from its boiling point (4.2°K) up to the higher process temperatures, equation (77) simplifies to

$$Q_{He} = m(\lambda + c_p \, [\, (T_o + T_t)/2 - 4.2 \;)\,] \, . \tag{78}$$

The helium gas is warmed to the average temperature between the triple point and boiling point of hydrogen. The amount of helium needed to produce a unit quantity of triple point liquid is determined by equating the heat to be removed from the hydrogen, equation (63), to the cooling available from the helium equation (78), and solving for m/x

$$(m/x)_q = (h_o - h_t) \,/\, (\, \lambda + c_p \, [\, (T_o + T_t)/2 - 4.2 \;)\,] . \tag{79}$$

During the freezing of this liquid the temperature of the helium cannot be warned to move than the triple point temperature of hydrogen, 13.8 K as that for this phase of the process the cooling available from the helium is

$$Q_{He} = m(\lambda + c_p \, [\, T_t - 4.2] \;) \tag{78a}$$

The amount of helium needed to produce a unit quantity of slush of quality q from the triple point liquid is determined by equating the heat to be removed from the hydrogen, equation (64), to the cooling available (from the helium, equation (78a) and solving for m/x)

$$(m/x)_{tq} = q(h_t - h_s)/[\lambda + c_p (T_t - 4.2)] \tag{80}$$

The total amount of helium to produce the desired quality slush from normal boiling hydrogen is determined by summing the requirement for the two phases,

$$(m/x)_{oq} = (m/x)_{ot} + (m/x)_{tq} \tag{81}$$

The heat exchange within the vessel will take place by free convection as in the gaseous helium batch process. The time and geometrical limitations developed in the analysis of that process are applicable here and would provide the limiting rate at which the helium could be passed through the system. It is assumed that the heat transfer rate is low enough to allow the helium vessel to be filled initially. A possible mode of operation is to continue filling helium during the process so that a semiflow process occurs. This would reduce the volume of the helium vessel to that value needed for process control. In either case, supplemental heat exchange area may be required to augment the surface of the helium vessel. In fact, the helium vessel may be a long cylinder rather the sphere shown, in order to increase the surface to volume ratio.

The helium specific mass requirement for the production of slush of various qualities by this batch liquid helium process are given in Table 10. Sample calculations are given in Appendix II.

TABLE 10

LIQUID HELIUM COOLING BATCH PROCESS

SPECIFIC HELIUM MASS REQUIREMENT

q	(m/x) lbs. He/lb.H_2
0	0.581
25	0.775
50	0.968
75	1.162
100	1.356

The capital costs and operating costs to produce 75,000 lbs. of 50 percent slush in seven days by this method are presented in Appendix IV.

3.3.2 Flow Process

The process equipment for a typical flow liquid helium cooling system is shown in Figure 14. Liquid helium is maintained in the internal vessel during production. The latent heat is transferred through the walls of the liquid helium vessel, while the sensible heat is transferred both in the internal heat exchanger and in the external heat exchanger which exchanges directly with the liquid hydrogen being transferred to the insulated container. This process will require a smaller tank than the batch process, and it is also more efficient since the sensible heat of the cold helium gas can be utilized to near 20.3°K during almost the entire production period.

The total heat removal required is given by equation (65) as the sum of the heat to be removed in cooling to the triple point and that to be removed in freezing to the desired slush quality q.

$$Q_{oq} = x(h_o - h_{ot}) + xq\,(h_{ot} - h_{os})$$

The subscript o indicates that the production vessel is pressurized to P_o, the feed pressure of the supply hydrogen.

As in the batch process, the total refrigeration available from a mass, m, of liquid helium in warming from 4.2°K liquid to a temperature, $T_{o\theta}$, near the boiling temperature is derived from equation (77). Here, however, the average temperature is not employed since helium exit temperature does not change with time. The refrigeration available is

$$Q_{He} = m\,[\,\lambda + c_p\,(T_{o\theta} - 4.2)\,] \tag{82}$$

The mass of helium required to produce a unit quantity of slush of quality q is obtained from equations (65) and (82) and is

$$(m/x)_q = [\,(h_o - h_t) + q\,(h_t - h_s)]\,/[\lambda + c_p\,(T_{o\theta} - 4.2)] \tag{83}$$

Obviously the helium must be colder than the hydrogen at all times during the process. To be sure that this is the case, an enthalpy balance is made at various locations along the heat exchanger and the temperature of the hydrogen and helium streams compared. When the hydrogen enthalpy changes from h_i to h_f, the helium enthalpy must change a like amount

$$x\,(h_i - h_f) = mc_p\,(\Delta T_{He})_{if} \tag{84}$$

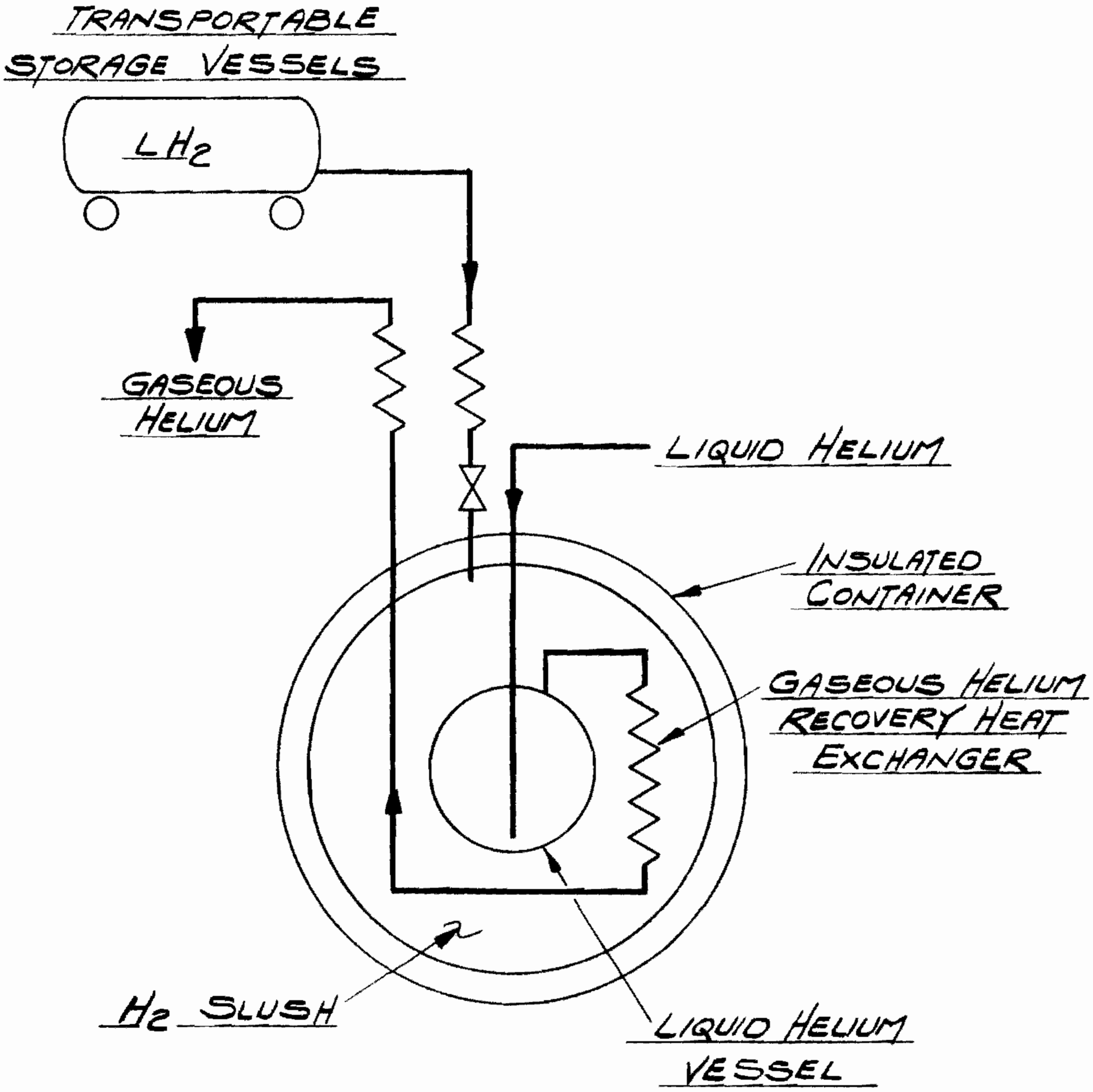

Figure 14. Liquid Helium Cooling, Flow Process Equipment

where $(\Delta T_{He})_{if}$ is the temperature change of the helium mass m during interval if. At the location along the exchanger where the hydrogen enthalpy is h_f, the helium temperature must be

$$T_{f\theta} = T_f - (\Delta T_{He})_{if} \tag{85}$$

Introducing equation (84) in (85) gives

$$T_{\theta} = T_f - (x/mc_p)\,(h_i - h_f)\ . \tag{86}$$

$T_{f\theta}$ is the temperature of the helium stream at the location where the hydrogen stream has the temperature T_f corresponding to h_f. Finally, the local temperature difference between the helium and hydrogen streams is

$$\begin{aligned} \theta_f &= T_f - T_{f\theta} \\ &= T_f - T_{f\theta} + (x/mc_p)\,(h_i - h_f) \end{aligned} \tag{87}$$

The (m/x) for equation (87) are obtained from equation (83) for various qualities of slush. The value of θ_f at the triple point gives the temperature of the helium entering the heat exchanger that feeds the production vessel during the production of slush of various qualities. Table 11 presents values of (m/x) and $\theta_f = \theta_t$ at the triple point for slush of several qualities with $T_{o\theta}$ taken to be 20°K so that the warm end temperature difference of the exchanger is 0.278°K.

TABLE 11

LIQUID HELIUM COOLING FLOW PROCESS SPECIFIC HELIUM MASS REQUIREMENT AND HEAT EXCHANGER ENTRY TEMPERATURE DIFFERENCES

q Slush Quality Percent	(m/x)q lbs. He per lb. H_2	θ_t °K Temperature Difference at Exchanger Cold End
0	0.497	9.6
25	0.633	9.2
50	0.767	6.5
75	0.902	4.6
100	1.038	3.2

Sample numerical calculations are given in Appendix II. θ_f has been calculated for each one degree temperature change in the liquid hydrogen for several slush qualities to be certain that it does not go to zero or become negative.

The production vessel for this process is sized to contain slush of the desired quality and is thus smaller than that for the batch process. As in the batch process, a helium vessel is contained inside the hydrogen tank, but its size is much reduced since the helium is continually flowing into the system. The final production vessel size should not be much larger than that required for the flow vacuum processes since the helium vessel need be only a small fraction, possibly 10 percent, of the hydrogen volume.

The capital and operating costs for producing 75,000 lbs. of 50 percent slush in seven days by the liquid helium flow process are presented in Appendix IV.

3.4 JOULE-THOMSON PRODUCTION TECHNIQUE

The production of hydrogen slush can be accomplished by Joule-Thomson cooling of a helium-hydrogen gas mixture. In this process, the gas mixture is precooled by a regenerative heat exchanger and then passed through a Joule-Thomson expansion valve to achieve the desired quality slush hydrogen as the condensed phase with a helium-hydrogen vapor phase. The slush is withdrawn from the production vessel, and the helium-hydrogen vapor is recirculated. Hydrogen is added to the process stream at an approximate temperature to make up the hydrogen withdrawn as slush.

A schematic of the Joule-Thomson system considered in this analysis is shown in Figure 15. The incoming helium-hydrogen stream at 25 atmospheres total pressure (chosen for optimum Joule-Thomson coefficient) is cooled by heat exchange with both the cold hydrogen gas efflux from the liquid hydrogen precooler and the return helium-hydrogen (96 percent helium) gas stream (E1). The liquid hydrogen precooler operates at one atmosphere, part of its vapor being returned to make up the product stream. The latent heat of the liquid hydrogen in the precooler is exchanged with the warm helium-hydrogen stream through heat exchanger (E2). Joule-Thomson heat exchanger (E3) further cools the incoming stream for expansion to one atmosphere total pressure through the Joule-Thomson valve. Product hydrogen slush is removed by slight pressurization of the make pot. This process would require a storage tank of the same size as that used in branch flow vacuum pumping. The hydrogen slush formed is expected to have the same physical characteristics as that formed by any of the "flow" vacuum pumping systems (e.g., cascaded vacuum pumping).

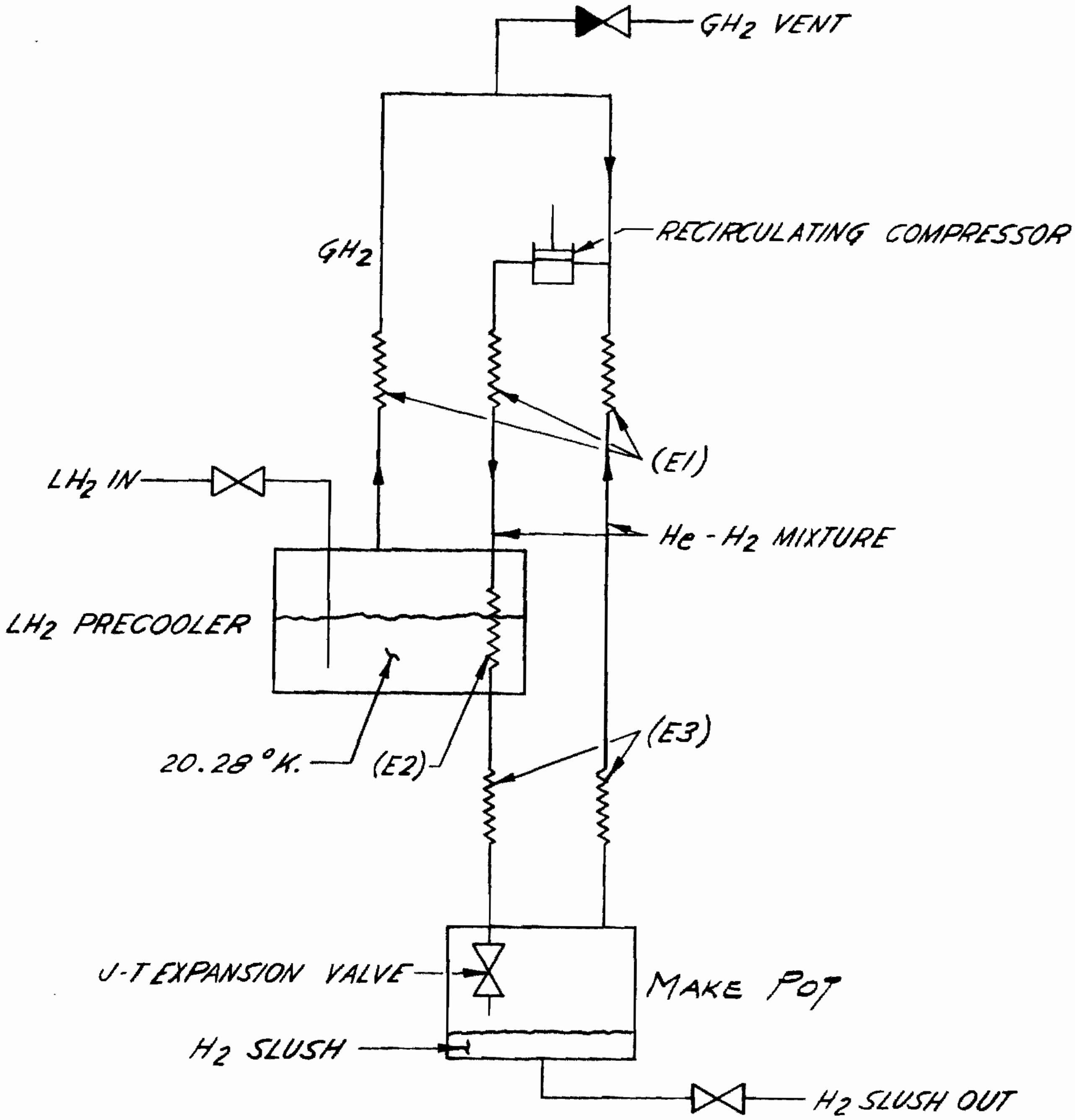

Figure 15. Joule-Thomson Cooling of a Helium-Hydrogen Mixture

The primary reason for investigating Joule-Thomson cooling of a helium-hydrogen mixture is that it can be operated at or above atmospheric pressure with the attendant elimination of the need for evacuable storage vessels and vacuum pumps. The helium component would be used to keep the expansion vessel at one atmosphere or greater total pressure. This advantage, however, must be weighed against certain disadvantages of the system. The main disadvantage is that it accomplishes essentially the same results as vacuum pumping, but with added capital and operating costs.

Various systems employing helium-hydrogen Joule-Thomson cooling and all using liquid hydrogen (20°K) precooling have been investigated. Liquid nitrogen precooling (even if vacuum pumped) without liquid hydrogen is not sufficient; liquid nitrogen in addition to liquid hydrogen was considered, but was found unnecessary. In all cases, the hydrogen vapor from the liquid hydrogen precooler was considered for recovery to make up the hydrogen component of the helium-hydrogen mixture. This means that para-hydrogen would be used in the product stream, eliminating the need for catalytic ortho-para conversion of the product stream hydrogen.

The thermodynamics of this helium-hydrogen mixture requires cooling to a low temperature before realizing appreciable Joule-Thomson cooling; the low inversion temperature (50°K) of the helium component is the determining factor. Pure helium must be cooled below 20°K before much is gained by Joule-Thomson cooling; this is not the case with hydrogen which has a much higher inversion temperature (140°K). In a system using 20°K precooling of a helium-hydrogen stream, therefore, one would expect little isenthalpic cooling from the helium component; the bulk of the cooling would be effected by the hydrogen component. In the system analysis discussed herein, it was found that the helium component functioned primarily as a pressurant and supplied very little refrigeration. To prevent a net loss due to the helium, its sensible heat is utilized in cooling the incoming helium-hydrogen stream.

In the absence of sufficient data on helium-hydrogen mixtures at low temperatures, a first approximation of the helium-hydrogen system was made wherein it was assumed that the system followed a direct weight proportioning of their specific enthalpies. This was done knowing that various investigations (Prausnitz and Myers (3); Beenakker, Varekamp, and Itterbeck (4)) have indicated that quantum effects are quite significant at these low temperatures, producing mixing effects. A complete analysis of these "mixing effects" was beyond the scope of this program, indicating the need for further experimental and/or theoretical investigation in this area for precise analysis of the Joule-Thomson cooling system. It is not expected that precise analysis would alter the conclusions reached.

The capital and operating costs for producing 75,000 lbs. of 50 percent slush in 7 days by this process, which are quite high in comparison to the costs of the vacuum pumping processes, are presented in Appendix IV.

3.5 COMPRESSION AND EXPANSION PRODUCTION TECHNIQUE

The basic concept behind compression and expansion of liquid hydrogen to produce slush hydrogen is that the thermodynamic efficiency of slush production might be improved by starting the expansion at some pressure higher than atmospheric, such as point (3) of Figure 16, rather than point (1).

Isenthalpic expansion from high pressures such as point (3) to points (5A) and (5B) results in a higher specific mass requirement than isenthalpic expansion from atmospheric pressure point (1) to point (6). This follows from the thermodynamic data for hydrogen by Roder and Goodwin (5) and Mullins, Ziegler, and Kirk (1) (portions of which are shown schematically in Figure 16) and from the SMR equation

$$SMR = \frac{1}{(1 - X_S)}$$

where X_S is the fraction of gas produced during the expansion.

The reason for the increase in SMR in this case is that the inversion point of isenthalps in this region lies on or close to the saturated liquid line, and an increase in temperature instead of the desired decrease is the initial result during expansion from pressures higher than the saturation pressure. Therefore, the most efficient process in terms of SMR will occur with expansion of saturated liquid from the lowest practicable temperature and pressure. Such a system, proceeding from saturated atmospheric pressure liquid hydrogen to slush hydrogen in one stage, was previously discussed as branched flow vacuum pumping.

Isentropic expansion of liquid hydrogen from point (3) of Figure 16 would produce a lower SMR as shown by the expansion from point (3) to point (4), but the SMR is not much less than for an isentropic expansion from atmospheric pressure from point (1) to point (7) (discussed earlier as straight vacuum pumping) or isenthalpic expansion from point (1) to point (6) (previously discussed as branched flow vacuum pumping). Because the expansion engine or turbine would have to handle liquid and solid hydrogen, continuous expansion will not be practicable within existing state-of-the-art, and it would be necessary to use a batch system such as that illustrated in Figure 17 to achieve isentropic expansion.

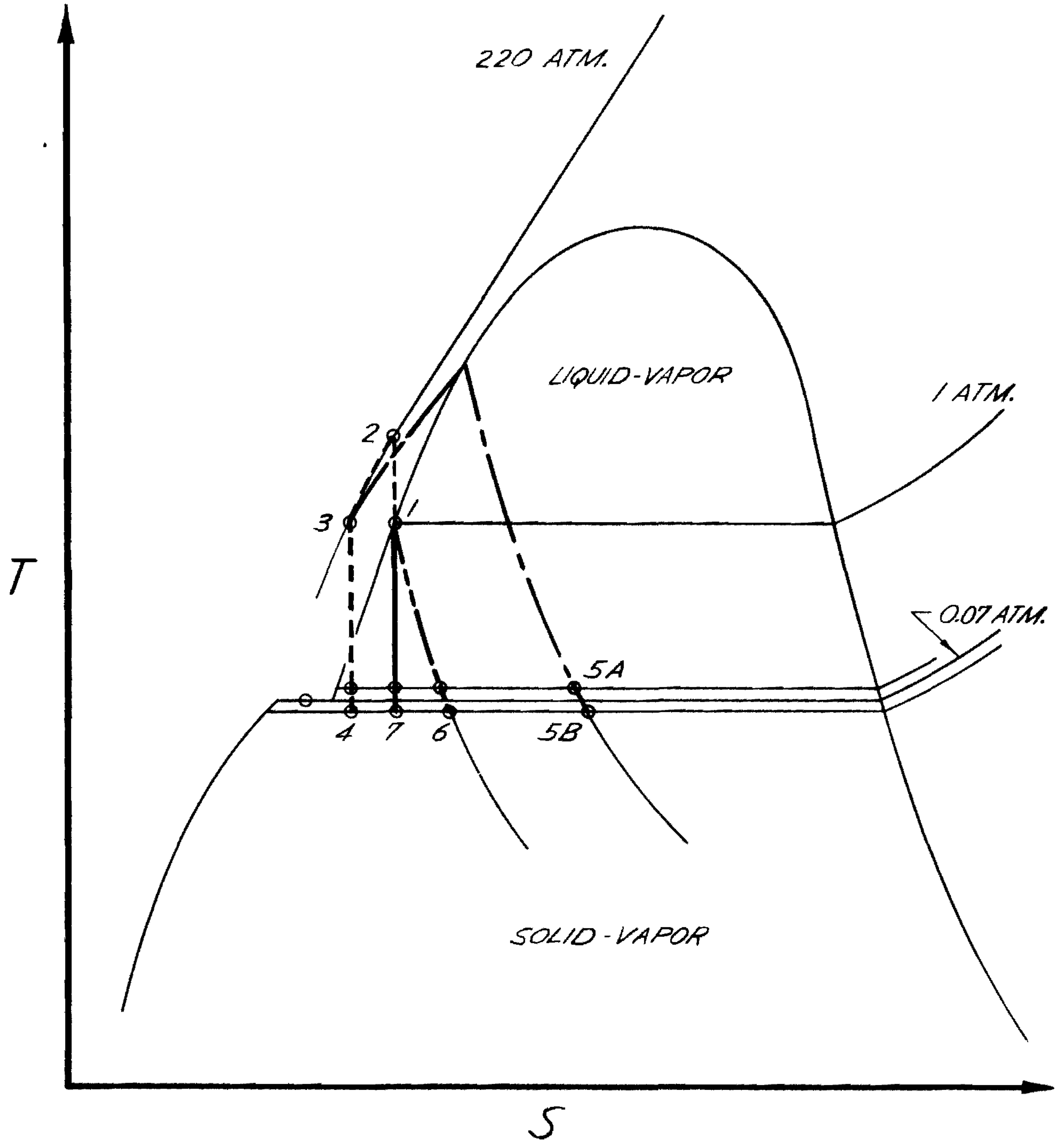

Figure 16. Schematic Temperature-Entropy Diagram of Para-Hydrogen

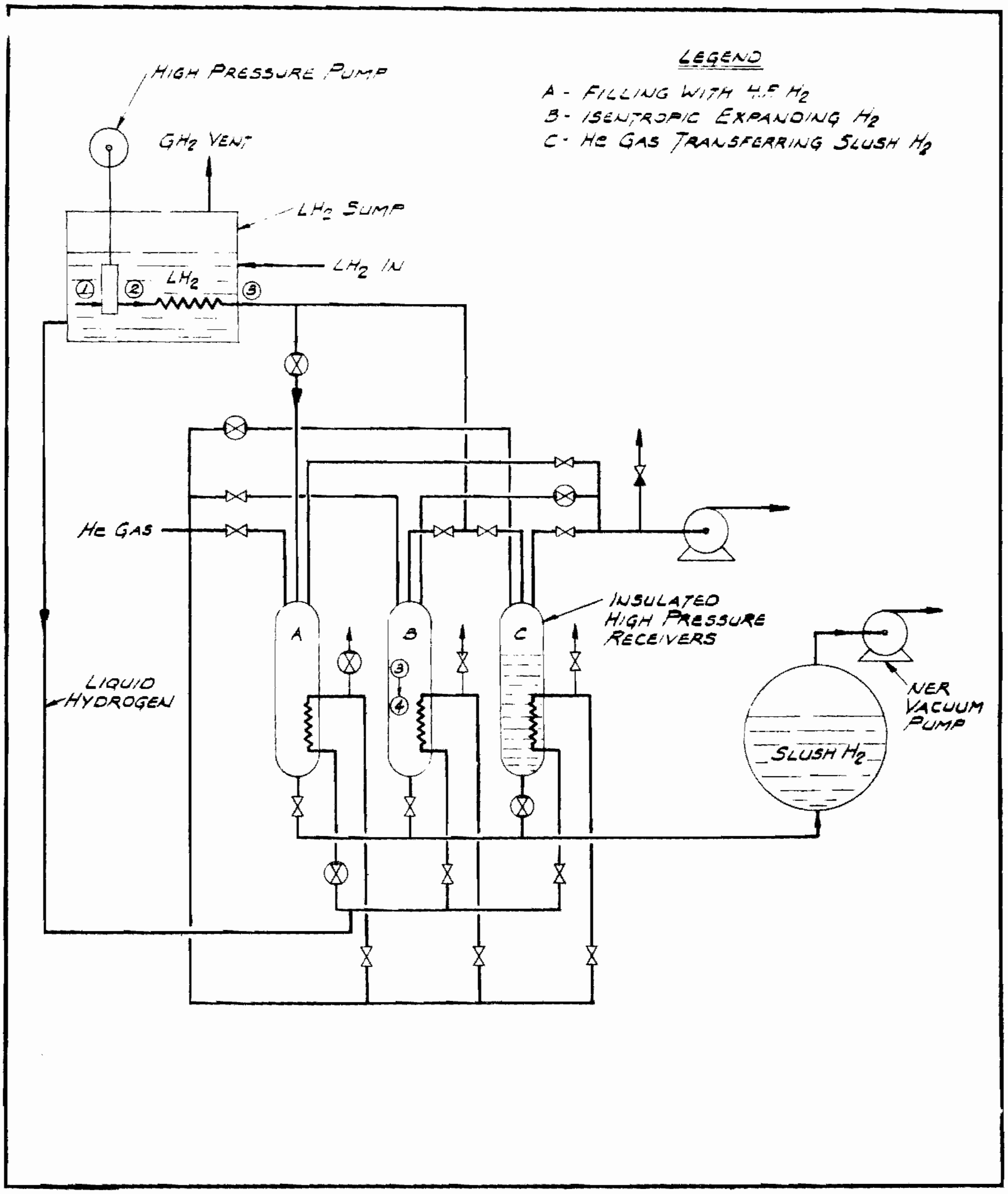

Figure 17. High Pressure Isentropic Expansion System

There are four cycles considered in this discussion. The first two cycles have been described in paragraphs 3.1.1 and 3.1.3; the other two are covered here.

The third cycle, isentropic expansion of hydrogen from 220 atmospheres, is a three-stage batch process wherein each stage alternately undergoes:

1. charging with high pressure hydrogen
2. isentropic expansion
3. slush transfer to the storage tank

Figure 17 depicts this process at the state when Receiver A is at charging, Receiver B is undergoing expansion and Receiver C is undergoing slush transfer. The circled valves indicate the open valves at the time of this state of the process; all other valves are closed.

Equipment for the isenthalpic expansion of hydrogen from 220 atmospheres (Figure 18), which is the fourth cycle, is essentially identical to that for the branched flow vacuum pumping process (Figure 5) except that since the hydrogen undergoing expansion is at 220 atmospheres, it is necessary to provide a vent to remove the heat of compression. The numbering in Figure 18 corresponds to that in the T-S diagram (Figure 16).

Because of the greatly increased complexity and cost of equipment for isentropic expansion of high pressure fluid weighed against the relatively small increase in yield over isenthalpic expansion of liquid hydrogen at atmospheric pressure,isentropic expansion of high pressure fluid hydrogen is not a desirable method of slush production. Isenthalpic expansion of high pressure liquid hydrogen is less efficient than isenthalpic expansion of atmospheric liquid hydrogen.

3.6 VENTURI COOLING PRODUCTION TECHNIQUE

When a liquid is passed through a venturi, the expansion to a low pressure and high velocity at the throat is an isentropic expansion with the associated highly efficient isentropic cooling. However, when the stream is slowed down for collection in a storage tank, the kinetic energy appears as heat, and the stream is warmed back to near the original temperature. If it were possible to effect heat exchange between the supersonic stream in the nozzle and a second stream, it would be possible to produce cooling in the second stream. The lower portion of Figure 19 illustrates the equipment required for this process to produce hydrogen slush. The numbering on the nozzle-heat-exchanger corresponds to the numbering on the T-S diagram given in the upper portion of the same figure. The T-S diagram depicts the thermodynamic steps of the process. This mechanism of refrigeration has been

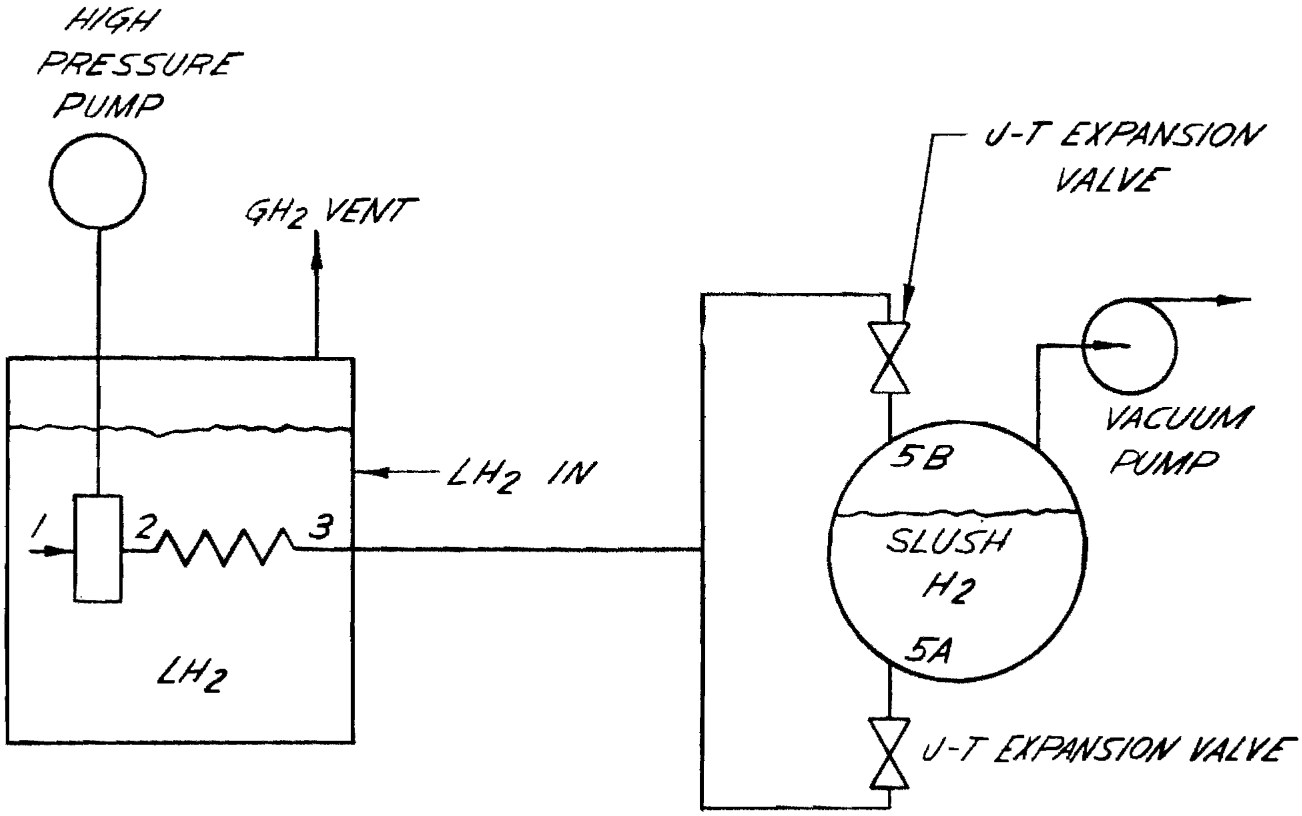

Figure 18. High Pressure Isenthalpic Expansion Process Equipment

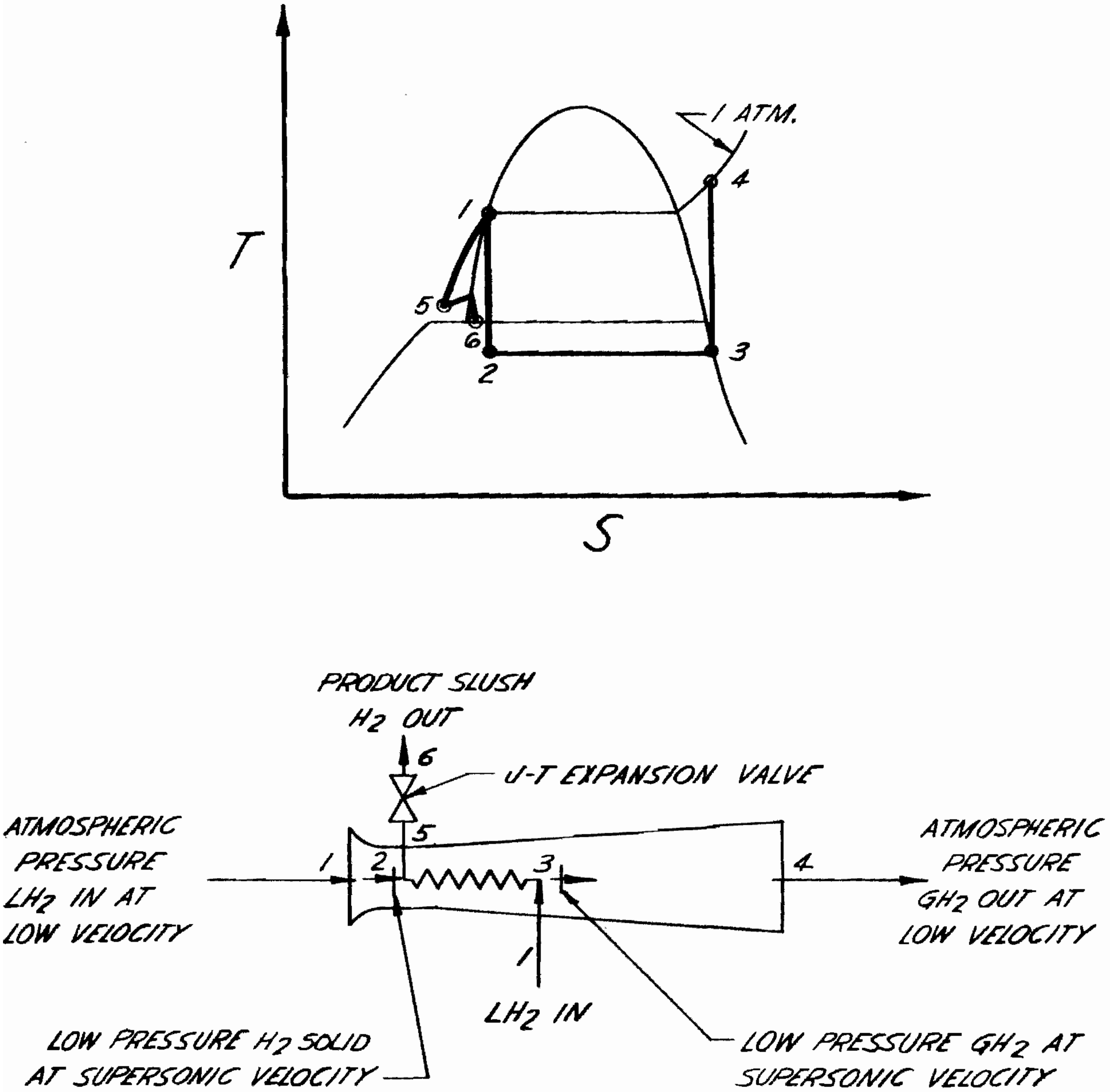

Figure 19. Venturi Cooling

investigated previously by this laboratory for other cryogenic fluids with the conclusion that efficient heat exchange with fluids at sonic volocity is a formidable problem because of friction heating. At such time as efficient sonic heat exchangers are developed, venturi cooling could be an efficient means of producing hydrogen slush, as well as for producing refrigeration in general. Within the present state-of-the-art, venturi cooling of liquid hydrogen does not appear to be practical as a method for producing hydrogen slush.

3.7 HELIUM GAS INJECTION COOLING PRODUCTION TECHNIQUE

When a non-condensing gas is injected into a liquid bath the temperature of the liquid is lowered as a result of the vaporization of a portion of the liquid into the bubbles of gas as they rise through the liquid. The cooling achieved by this process is dependent upon the amount of liquid which is vaporized and carried from the bath by the flow of the injected gas. Since the cooling is produced by vaporization of the initial liquid, this process is quite similar to the straight vacuum pumping process already discussed. The equipment for the process, shown in Figure 20, consists of a production vessel fitted with an array of nozzles to distribute the injected helium over the bottom of the tank and a heat exchanger to cool the incoming helium gas by the effluent helium-hydrogen mixture.

The amount of liquid which can be vaporized, and thus the amount of cooling which can be achieved, is dependent upon the concentration of vapor in the gas-vapor mixture that can exist in equilibrium with the liquid which forms the bubble surface. The liquid at the surface may dissolve some of the injected gas, thereby affecting the gas vapor equilibrium mixture. Thus, a complete analysis, such as the one performed by Larsen, Randolph, Vaninam, and Clark (6), requires a consideration of the effect of the gas solubility. For the present discussion, however, the effect of solubility can be neglected since the solubility of helium in liquid hydrogen has been shown by Street (8) to be very low. If this solubility is neglected, the amount of liquid vaporized is that required to raise the partial pressure of vapor in the bubble up to the vapor pressure of the saturated liquid at the temperature produced at the bubble surface by evaporation. The mass which is evaporated into the bubbles in order to cool the liquid through a temperature interval is dependent only on the latent heat of vaporization of the liquid and its saturated specific heat. Thus, the mass evaporated is the same as in the straight vacuum pumping method, and the SMR_{if} of Equation (3) can be used. The total pressure in the bubble is equal to the pressure above the liquid bath, and for this analysis it is taken to be one atmosphere. The difference between the saturation vapor pressure of hydrogen for the temperature interval T_i to T_f and the total pressure is the pressure of the injected helium gas, P_m,

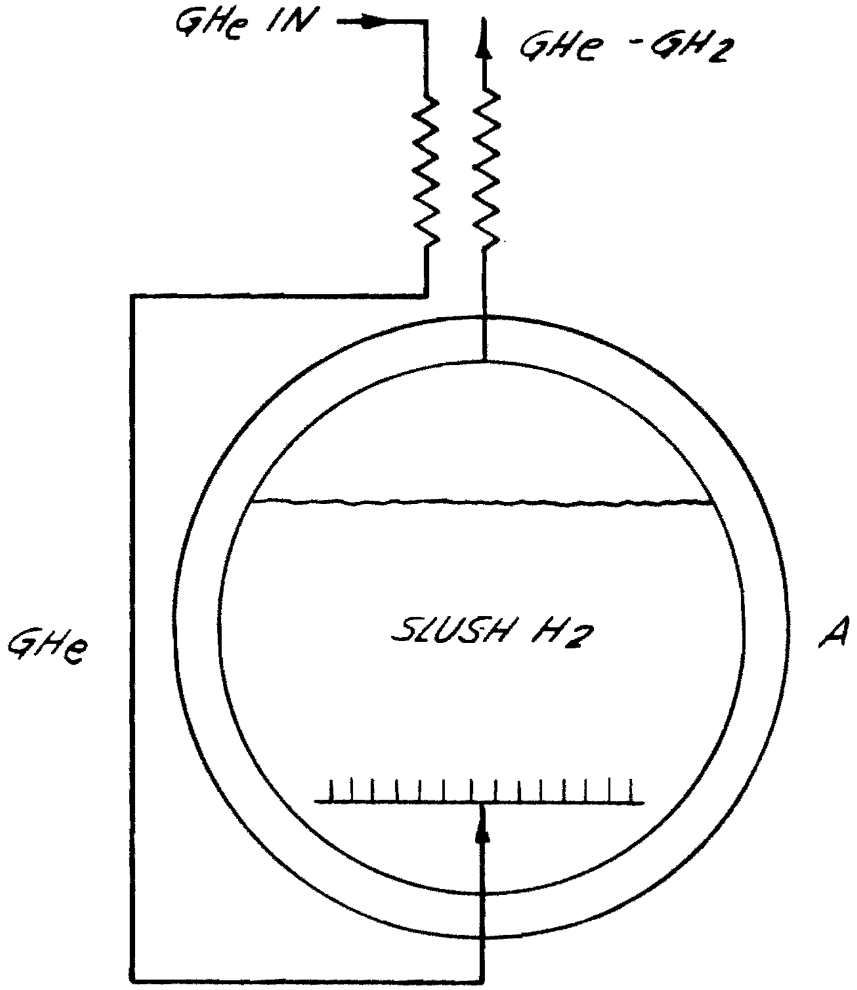

Figure 20. Helium Gas Injection Cooling Process Equipment

$$P_m = P_o - P_{y(if)} \tag{88}$$

By Dalton's law, the volume is the same for all components and

$$P_m V = (P_o - P_{y(if)})V \ . \tag{89}$$

However,

$$\begin{aligned} V &= m v_{He(if)} \\ &= y v_{H_2(if)} \end{aligned} \tag{90}$$

where m and y are the mass of helium and hydrogen in the volume, and $v_{He(if)}$ and $v_{H_2(if)}$ are the specific volumes of helium and hydrogen at the temperature and their respective partial pressures in the bubble. Therefore

$$P_m m v_{He(if)} = (P_o - P_{y(if)})\, y v_{H_2(if)} \tag{91}$$

If the volume of helium at the temperature and pressure of the process which must be injected to vaporize a unit mass of hydrogen is $v^*_{He(if)}$, then

$$\begin{aligned} v^*_{He(if)} &= (m/y) v_{He(if)} \\ &= v_{H_2(if)} \left(P_o - P_{y(if)}\right) \Big/ P_m \end{aligned} \tag{92}$$

The volume of helium at one atmosphere and normal temperature which must be injected to evaporate a unit mass is

$$v^*_{He(if)n} = v^*_{He(if)} \left(P_m \big/ P_{atm}\right) \left(T_{norm} \big/ T_{if}\right) \tag{93}$$

when combined with Equation (92) this gives

$$v^*_{He(if)n} = v_{H_2(if)} \left[\left(P_o - P_{y(if)}\right) \Big/ P_{atm} \right] \left(T_{norm} \big/ T_{if}\right) \tag{94}$$

In the vacuum pumping process, the initial total mass to be pumped and cooled through the interval T_i to T_f and leave a unit mass of product was determined and designated SMR_{if}. The evaporated mass was given as $Y_{if} = x_f(SMR_{if} - 1)$ in Equation (17). In the present process, the helium volume to be injected to leave a unit mass of final product is

$$V_{He(if)n} = v^*_{He(if)n} (1 - SMR_{if}) \tag{95}$$

Substituting (94) in (95) gives

$$V_{He(if)n} = v_{H_2(if)} \left[(1-SMR_{if}) \; (P_o - P_{y\ if}) / P_{atm} \right] (T_{norm}/T_{if})$$

$$= V_{sat(if)} \left[(P_o - P_{y(if)}) / P_{atm} \right] (T_{norm}/T_{if}) \qquad (96)$$

The $V_{sat(if)}$ is the volume pumped in the straight vacuum pumping process as given in Table 2. The pressure, $P_{y(if)}$, and temperature, T_{if}, are the average values for the intervals obtained from Mullins, Ziegler, and Kirk (1).

As in the vacuum pumping process, the total mass required for several steps is obtained by summing the individual steps. Thus the helium required to go from atmospheric boiling hydrogen to triple point hydrogen is given by

$$V_{He(ot)n} = \sum_{o}^{t} V_{He(if)n} \qquad (97)$$

and the helium needed to go to slush of quality q is

$$V_{He(oq)n} = \sum_{o}^{q} V_{He(if)n} \; . \qquad (98)$$

Calculated values of these helium volumes are given in Table 12. Sample calculations are in Appendix II. The second column of Table 12 gives the volume injected to produce triple point liquid, while the third gives that required to produce all solid. The volume of helium needed for a one degree interval increases as the temperature is lowered because of the reduced saturation vapor pressure of the hydrogen. The helium volume required to freeze the hydrogen is extremely large as the latent heat of fusion must be removed at the very low triple point pressure. These large helium volume requirements cause the helium injection method to have a very high operating cost as is shown in the analysis of operating and capital cost for producing 75,000 pounds of 50 percent slush in seven days given in Appendix IV.

The volume of the production vessel required for this method is the same as that for the straight vacuum pumping method since boiling hydrogen is the starting material.

TABLE 12

HELIUM GAS INJECTION COOLING

TABULATED GASEOUS HELIUM REQUIREMENT

Temperature Increment °K	$V_{He(if)n}$ Volume of Helium ft.^{3} NTP required to produce cooling through the given temperature increment per pound of triple point liquid produced	$V_{He(of)n}$ Volume of Helium ft.^{3} NTP required to produce cooling through the given temperature increment per pound of solid produced
20.278 20.00	0.0398	0.0449
20.00 19.00	0.9923	1.1205
19.00 18.00	2.8732	3.2445
18.00 17.00	5.4735	6.1808
17.00 16.00	9.2252	10.4173
16.00 15.00	15.0926	17.0430
15.00 14.00	26.2592	29.6526
14.00 13.813	7.0573	7.9693
$V_{He(ot)n} = \sum_{o}^{t} V_{He(if)n}$	67.0131	75.6730
$V_{He(tq)n}$	-	328.4942
$V_{He(oq)n} = \sum_{o}^{q} V_{He(if)n}$	-	404.1672

3.8 UPGRADING HYDROGEN SLUSH BY HELIUM GAS INJECTION COOLING

Despite the unattractively high cost of producing hydrogen slush by helium gas injection cooling as presented in Appendix IV, further investigation of helium gas injection is desirable because this may be the only possible method of upgrading the slush hydrogen after it is on board the space vehicle tankage. Upgrading is desirable to counteract the melting that is caused by heat leak during ground hold and/or to increase the solid weight percent above that which is flowable.

Two examples presented in Appendix V illustrate the use of gaseous helium injection cooling to maintain and upgrade 50 percent hydrogen slush:

1. To maintain 75,000 pounds of 50 percent slush by balancing the system heat leak for one hour of ground hold

2. To upgrade 75,000 pounds of 50 percent slush to 60 percent after loading on board the vehicle.

In either case, it has been assumed that the gaseous helium will be precooled to 13.8°K in a separate precooler. Figure 21 shows a proposed system for upgrading hydrogen slush. The precooled gaseous helium would pass through the hydrogen slush, carrying the vaporized hydrogen out with it through the vent. The portion of hydrogen removed as vapor would then be replaced by slush through the fill line.

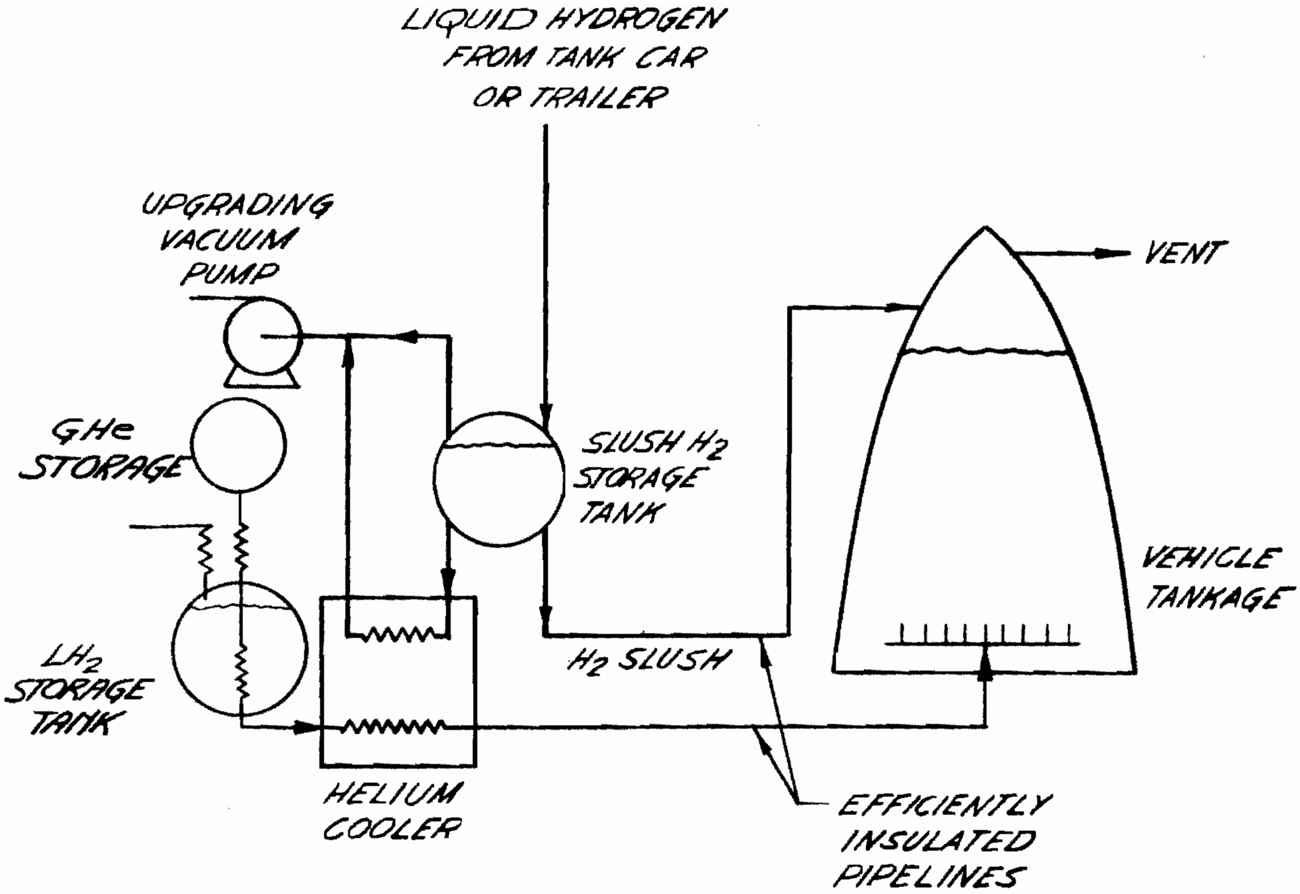

Figure 21. Upgrading of Hydrogen Slush by Helium Gas Injection Cooling

SECTION 4

SMALL-SCALE EXPERIMENTAL EXAMINATION OF HYDROGEN SLUSH

These experiments were designed to obtain information on handling and storage characteristics of freshly prepared hydrogen slush on a small scale basis. The program was divided into two parts to facilitate both qualitative and quantitative analysis of the slush.

4.1 QUALITATIVE EXPERIMENTATION

4.1.1 Apparatus

Three simple experimental configurations were used in these preliminary studies. Each is discussed separately. However, all the work was performed in an unsilvered cryostat that had internal dimensions on the inner Dewar of 760 mm length by 75 mm internal diameter. Figure 22 is a simplified drawing of the cryostat. All hydrogen used was at, or near, the equilibrium ortho-para ratio at 20°K, which is essentially 100 percent para.

4.1.2 Qualitative Experiment Number I

In this first experiment, an attempt was made to establish an adiabatic system in which the transfer capability of slush could be tested both immediately after formation and after storage.

Figure 23 is a full scale drawing of the experimental vessel. The all-glass vessel is sealed to the head closure of the cryostat by means of rubber sleeves. The tubing passes through the closure to the external plumbing. Figure 24 is a schematic of this plumbing. The plumbing was arranged to deliver helium, hydrogen, and vacuum where necessary. The vessel was suspended inside the cryostat and surrounded by a bath of liquid-solid hydrogen of low solid content. After precooling in the hydrogen bath, the experimental vessel was filled to two-thirds of its capacity with liquid hydrogen condensed from gaseous hydrogen. The gaseous hydrogen was drawn from the head space of a liquid hydrogen container. Since this gas was in equilibrium with liquid hydrogen in the container, its ortho-para ratio was at equilibrium for 20°K.

A crust of solid hydrogen was formed over the liquid hydrogen in the experimental vessel (Figure 23) by vacuum pumping the hydrogen gas in the vessel through Tube (1). Small amounts of gaseous hydrogen were then bubbled

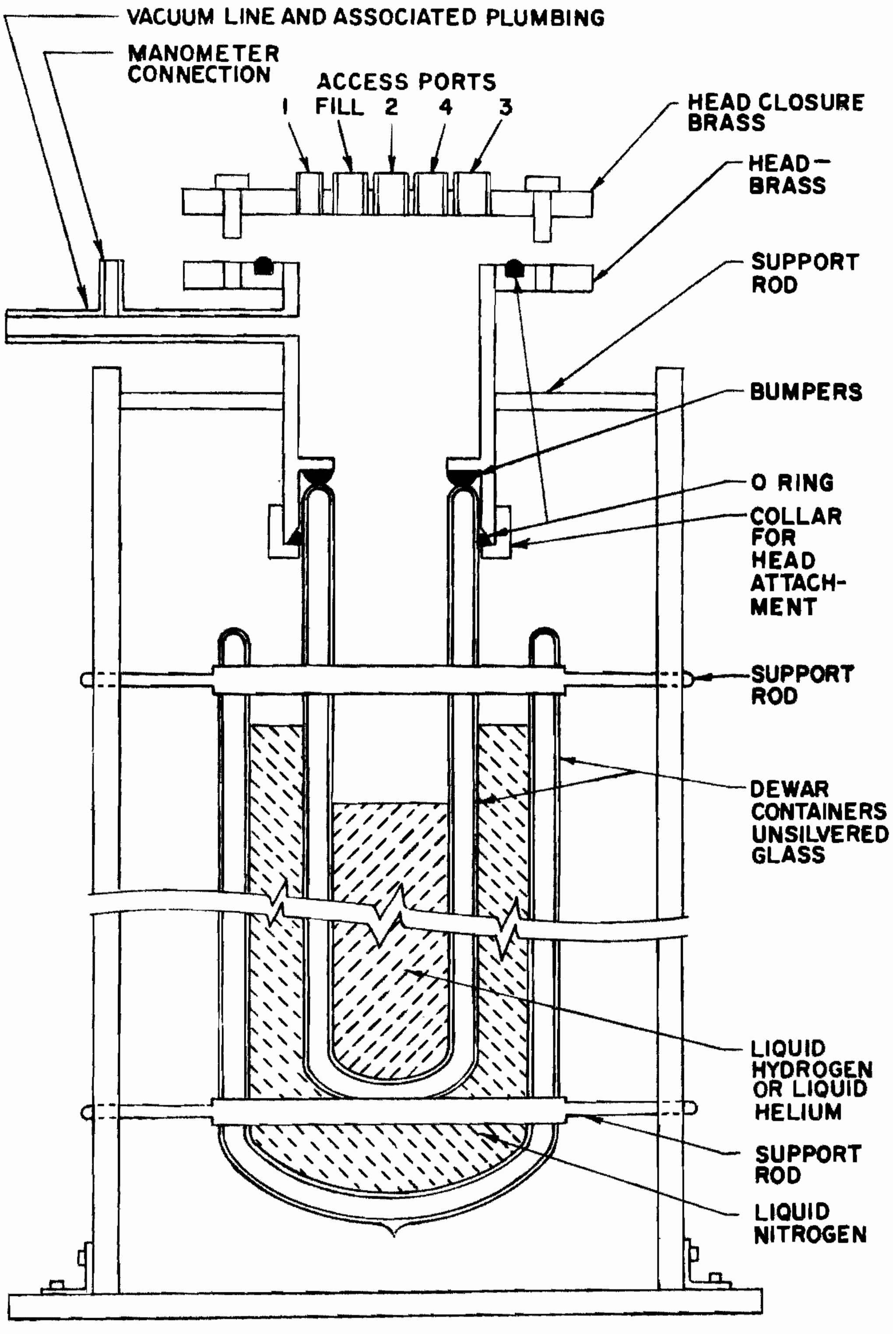

Figure 22. Cryostat

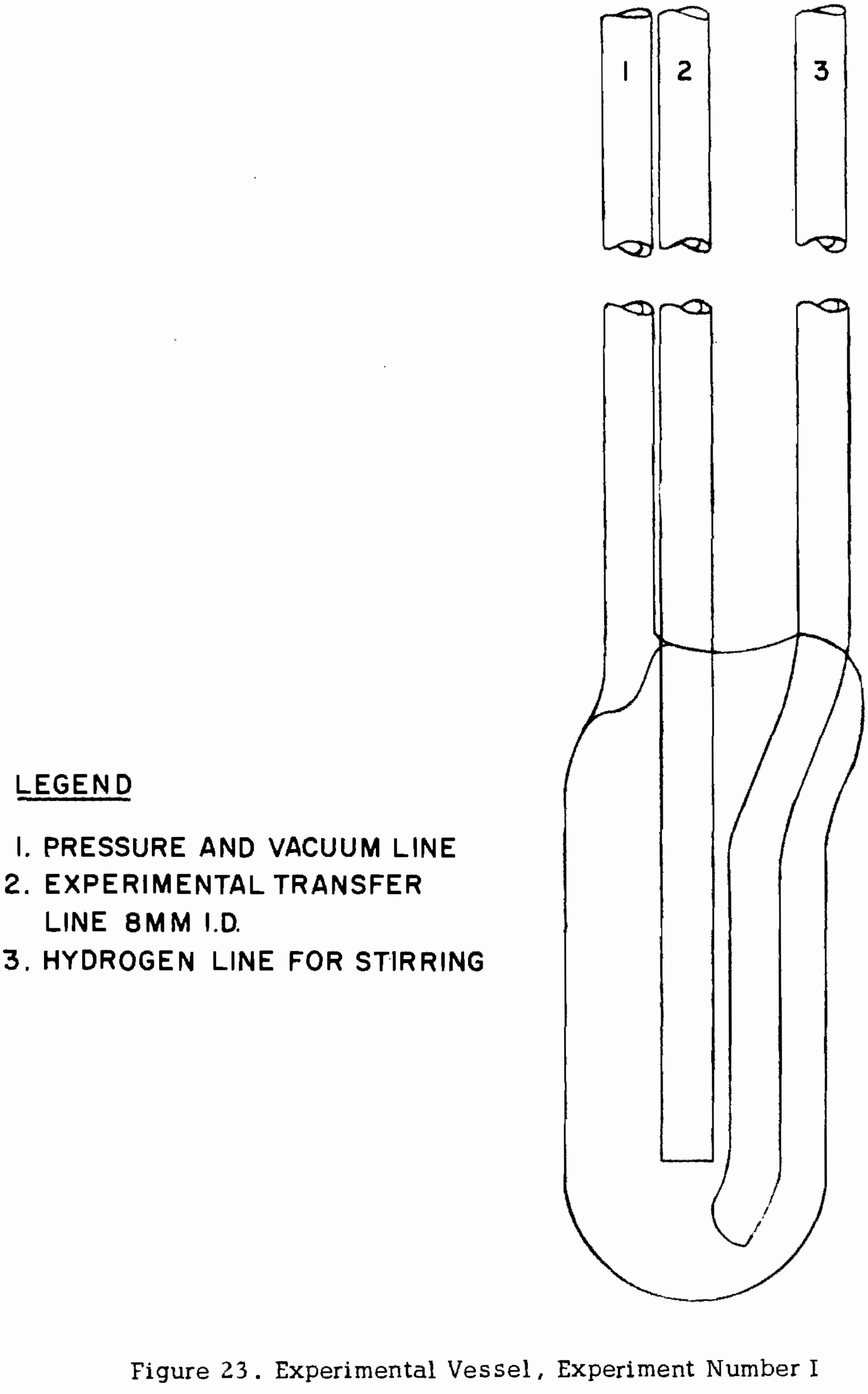

Figure 23. Experimental Vessel, Experiment Number I

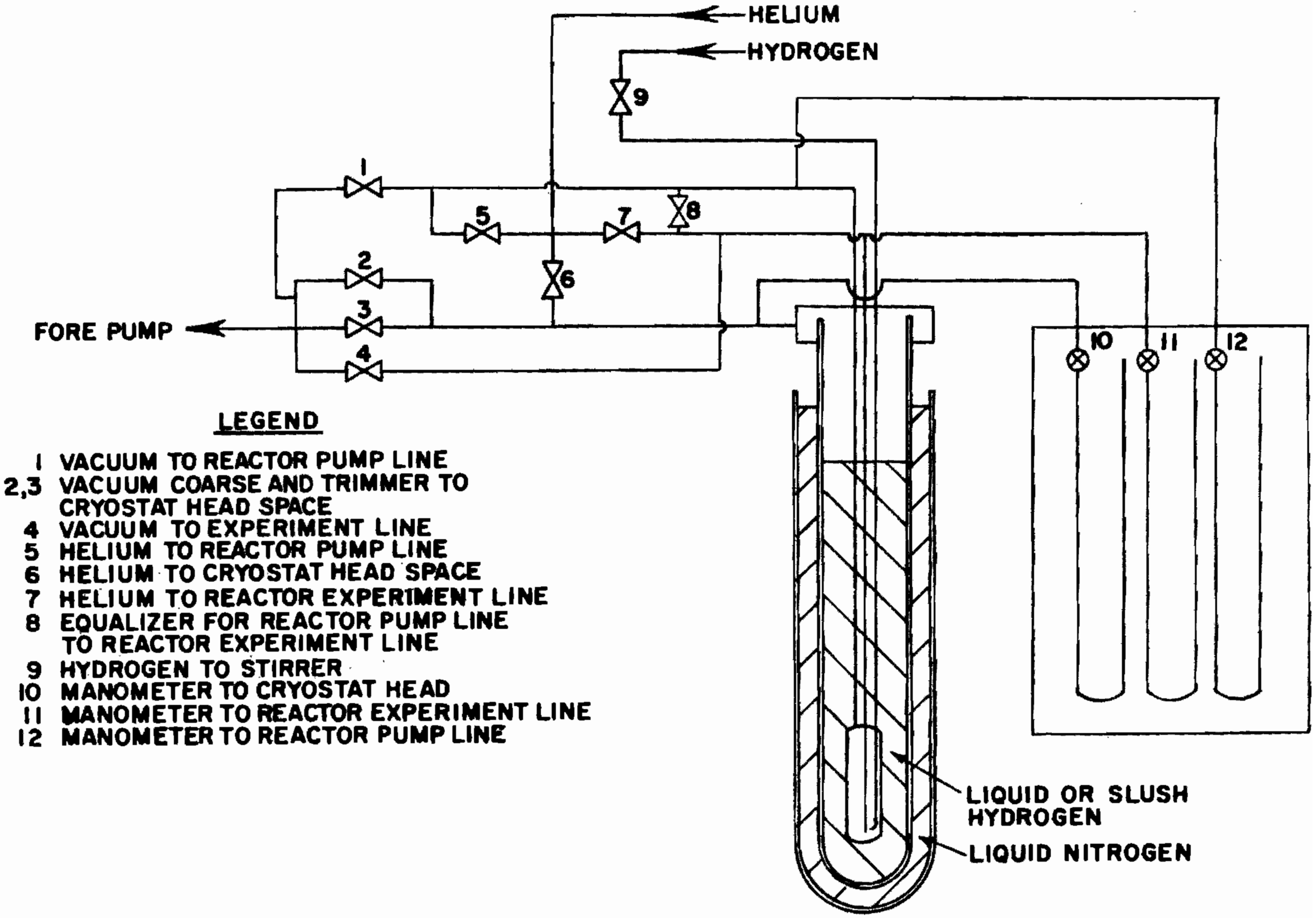

Figure 24. Plumbing on Cryostat and Experimental Vessel

through Tube (3) in an attempt to mix the solid and liquid hydrogen. The hydrogen crust was strong enough so that the agitated liquid was not capable of dislodging the crust from the walls of the vessel. Even when a "burst" of hydrogen gas was introduced through Tube (3) while still pumping through Tube (1), the crust was not broken, although the liquid was lifted above the solid. The liquid merely drained back through the porous crust. Gas stirring, at least in the experimental vessel described, was not sufficient for mixing the newly formed solid with the remaining liquid hydrogen. In a later configuration, the hydrogen gas used for stirring introduced too much heat to be practical.

The vessel (Figure 23) was designed so that slush could be pushed up Tube (2) by pressurizing the head space of the vessel with a few Torr of helium. The helium was introduced down Tube (1) after interrupting the vacuum pumping. Even though the gaseous hydrogen had failed to stir the solid crust into the liquid, an attempt was made to push liquid hydrogen up the experimental Tube (2) by using helium pressurization just to test the mechanics of the system. Immediately after introducing a small amount of helium down Tube (1), liquid hydrogen began to pulse violently in Tubes (2) and (3). With the experimental vessel isolated from the attached plumbing by means of valves above the cryostat head closure, this pulsing continued for fifteen minutes without abating. A possible explanation of this phenomenon is that the helium may have been oscillating in Tube (1) and, therefore, pumping heat into the vessel. The changing pressure is capable of pumping liquid up Tubes (2) and (3). Initially, when there was some solid in the experimental vessel, this pumping action rapidly melted it. The liquid was not completely vaporized because of the solid-liquid hydrogen surrounding the vessel.

When all the liquid in the experimental vessel was converted to solid, no differential helium pressure could be established between Tubes (1) and (2). The solid appeared to be very porous.

4.1.3 Qualitative Experiment Number II

Concurrent with the design and fabrication of a new vessel capable of storing and transferring slush under adiabatic conditions and equipped with a mechanical stirrer for preliminary mixing, two simple systems were used for short preliminary studies of hydrogen slush.

The vessel from experiment I was removed from the cryostat, and an 8 mm I.D. glass tube was inserted through access port (1) of the cryostat head closure. Access ports (2) and (3) were closed off. A wooden rod was inserted through access port (4) of the head closure and extended to the bottom of the cryostat. It was sealed to the head closure with a rubber sleeve. By manually moving the part of the wooden rod extending above the head closure, the lower end of the rod which was in the cryostat could be made to stir any material in the cryostat.

Liquid hydrogen was placed in the inner Dewar of the cryostat, and a solid crust was formed on it by vacuum pumping the gaseous hydrogen from above the liquid. This was the same method used to produce the liquid-solid hydrogen bath for Experiment Number I. The solid crust was then broken with the wooden rod. By this means, small particles of solid hydrogen were dispersed in the liquid hydrogen. Although the crust was rather strong, it felt soft when stirred with the rod. When the stirring was stopped, the small particles slowly settled to the bottom of the liquid hydrogen and two layers were produced. The top layer was liquid hydrogen and the bottom layer was liquid-solid mixture with a rather low solid content. If a slight pressure was exerted upon the surface of the liquid by admitting helium gas to the cryostat, liquid hydrogen with some solid dispersed in it was forced up the 8 mm glass tube whose end was buried in the solid-liquid mixture. However, thermal unbalances immediately forced the liquid back, and it was very difficult to assess whether or not the material transported in the glass tube had the same percent solid as the pool from which it was drawn.

A solid-liquid mixture was also drawn up the 8 mm tube by vacuum pumping at the top of the tube rather than pressurizing above the pool.

The solid-liquid lower phase was very easily stirred with the wooden rod, even after standing for 20 minutes. The small particles of solid hydrogen did not appear to adhere to each other or to the glass Dewar walls.

4.1.4 Qualitative Experiment Number III

In Experimental Configuration Number II it was demonstrated that a liquid-solid mixture could be pushed up an 8 mm glass tube. However, the velocity in the tube was so high that it was impossible to observe whether or not the material in the tube had the same solid content as the pool from which it was drawn. To overcome this disadvantage, experiment III utilized a trap built into the tube to collect the transferred material (see Figure 25). Except for the addition of the trap, the configuration was the same as that used for Experiment Number II. Transfer of the slush from the pool to the trap would demonstrate the movement from one vessel to another.

The experiment failed because of the development of the same type of helium pulsing as noted in the earlier experiments. Also, as the cryostat

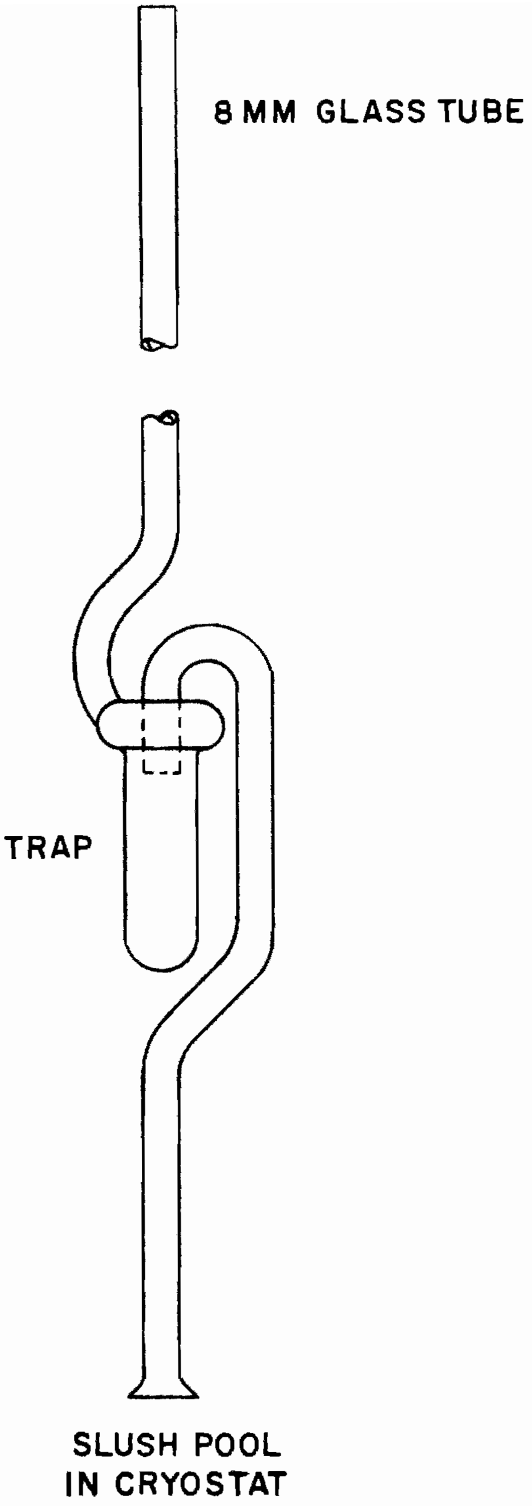

Figure 25. Experimental Vessel, Experiment Number III

was filled with liquid hydrogen, it was noted that the liquid was rising in the center tube past the level of the trap. This was expected.

4.1.5 Conclusions and Observations

Many of the observations made during the qualitative study are perhaps obvious, but all have been included for the sake of completeness. General conclusions in preliminary hydrogen slush experiments were:

1. When cooling was effected by pumping on the liquid, the solid formed at the surface of the liquid.

2. The solid crust formed on the surface of the liquid was very porous but had considerable structural strength.
    a. The crust could not be stirred into the liquid by injecting hydrogen gas into the liquid for agitation.
    b. Both gaseous and liquid hydrogen passed through the crust without disturbing the structure.
    c. A differential gas pressure (helium) could not be developed across the solid crust.

3. The crust contained very little liquid, but felt "soft" when probed with a wooden rod.

4. When formed, the crust adhered to the walls of the vessel quite strongly.

5. The solid crust could be mechanically stirred into the liquid. It dispersed as small crystalline-formed particles and settled to the bottom when stirring was stopped. Two separate layers were observed. The lower layer was a solid-liquid mixture, and the upper layer was liquid.

6. The solid-liquid layer formed by the settling of the small particles of solid hydrogen was quite fluid. It appeared to be easily pushed or pulled in an 8 mm I.D. tube with only a few Torr differential pressure. Even after standing for twenty minutes, the material was still very fluid. There was no tendency for the small particles of solid hydrogen to adhere to the glass Dewar walls or to each other.

7. If a small vessel containing liquid hydrogen was inserted into the cryostat containing liquid hydrogen, and this small vessel had small-diameter straight tubing attached to it and leading to the outside of the cryostat, helium pulsated in the tubing and pumped heat into the vessel when the small vessel was pressurized with a few Torr of helium. When slush was present, the heat was sufficient to rapidly melt all the solid. This phenomenon was probably a thermal oscillation.

4.2 QUANTITATIVE EXPERIMENTATION

In the previous experimentation, the production of hydrogen slush and its mixing and transfer properties were discussed in a preliminary and qualitative manner. The next experimentation extended this work in a more quantitative manner through the measurement of the solid content of the hydrogen slush. As before, all experiments were carried out in glass vessels, and solid hydrogen was produced only by vacuum pumping. Only freshly prepared slush was considered, i.e., slush which had not aged more than about ten minutes.

4.2.1 Apparatus

The apparatus used for the qualitative experimentation (Figure 22) was also used for the first two quantitative methods of determining the percentage of solids in hydrogen slush. A third quantitative method utilized Vessel A (Figure 23) inserted into the Dewar (Figure 22).

4.2.2 Settled Slush

Included in the list of conclusions in the qualitative experimentation was the statement: "The solid-liquid layer formed by the settling of the small particles of solid hydrogen was quite fluid." When sufficiently low concentrations of solid hydrogen dispersed in liquid hydrogen, two layers were found to develop upon standing. While the small particles of solid hydrogen settled to the bottom, they were still interspersed with liquid. The upper layer contained no solid. The lower layer is referred to as "settled slush," and the concentration of solid in this layer is referred to as the "settled slush concentration."

Settled slush appeared almost as fluid as liquid hydrogen. Any slush in which the over-all concentration (i.e., the concentration in the stirred liquid) of solid hydrogen was below the settled slush concentration, apparently can be easily transferred.

When there were two layers (upper, liquid; lower, settled slush) and some of the material was withdrawn from the bottom of the vessel, the over-all solid content of the remaining portion was reduced, since settled slush was being withdrawn and clear liquid remained in the vessel.

Two methods were used to produce settled slush in the inner Dewar of the cryostat pictured in Figure 22. In the first method, referred to as the partial melting method, liquid hydrogen was placed in the Dewar and solid was produced by vacuum pumping and stirring until all the liquid was converted to solid. The Dewar was then isolated and the heat leak of the system was allowed to slowly melt the slush. The slush was stirred, by means of a wooden rod introduced through the head closure, for as much of the time during production and melting as possible. There was a short time in this process when there was so much solid that stirring was impossible. Stirring was occasionally interrupted during the melting phase so that the first appearance of a clear liquid upper layer could be observed. At the first appearance of a small amount of clear liquid, the Dewar could be considered, for practical purposes, to contain only settled slush; that is, the over-all solid composition of the contents was essentially equal to that of settled slush.

In the second method used to produce settled slush in the Dewar, referred to as the freezing method, liquid hydrogen was placed in the Dewar and solid was produced by vacuum pumping. The mixture was stirred; but the stirring was interrupted from time to time, and the solid was allowed to settle. Pumping was stopped as soon as no liquid upper layer could be seen when stirring was interrupted.

4.2.3 Determination of Percent Solid Hydrogen in Settled Slush

The solid concentration in settled slush was determined by two methods described below.

4.2.3.1 Volume Change Method The first method involved the difference in density between the liquid and the solid at the triple point. A calibration curve for the volume of the inner Dewar versus the height as measured with a cathetometer was first constructed. Settled slush was produced by the partial melting method described above, and the volume (V_1) of the mixture was determined by measuring the height of the slush at the moment the first amount of clear liquid appeared above the slush. Mixing was then resumed and continued until the solid melted completely. Just as the last trace of solid melted, the volume (V_2) was determined. Similarly, if the slush had been produced by the freezing method, V_1 would be the volume of the slush and V_2 that of the liquid after all the solid in the slush had melted.

The percent solid (x) in the settled slush was then calculated from the formula:

$$x = \frac{1 - V_1/V_2}{1 - 0.07703/0.08664} \times 100 = \frac{1 - V_1/V_2}{0.11092} \times 100 \text{ wt-\%} \tag{99}$$

where 0.07703 and 0.08664 are, respectively, the densities of liquid and solid para-hydrogen at the triple point, as calculated from Tables 31 and 34 in Wooley, Scott, and Brickwedde (9) with the assumption that the density of solid para-hydrogen is the same as that of solid normal-hydrogen. (No data are available on the density of solid para-hydrogen, but it is assumed that the para-hydrogen value is very close to that of normal-hydrogen.)

4.2.3.2 Melting-Time Method A second method of measuring the percent solid in settled slush was employed to check the results of the volume change method described above. This second method involved a comparison of the length of time it takes to melt settled slush with the time necessary to melt an equal weight of 100 percent solid hydrogen.

A batch of 100 percent solid hydrogen was first produced by pumping. The time (t_1) was noted, and the solid was allowed to gradually melt. At first the solid was hard to stir, but as soon as it was possible, stirring was begun. The stirring was occasionally interrupted and the solid allowed to settle. At the first sign of the formation of a clear upper liquid layer, the time (t_2) was noted. This was the "settled slush" stage. Stirring was then started again and was continued until the last particle of solid hydrogen melted, at which point the time (t_3) was noted.

Let D_1 = duration from t_1 to t_2

D_2 = duration from t_2 to t_3

then the percent solid (x) in settled slush is given by the formula

$$x = \frac{D_2}{D_1 + D_2} \times 100 \qquad (100)$$

This method depends upon the assumption that heat leaks into the system at a constant rate. Actually, the heat leak into the 100 percent solid was probably slightly lower than that into the system after a continuous liquid phase was formed, because of the poor physical contact of the solid with the vessel wall. This poor contact occurred only during the first few minutes of melting and was not considered to be a source of large error; it made D_1 a little high and (x) a little low.

4.2.3.3 Results Obtained With the Two Methods The melting-time and volume-change methods of determining the solid content in settled slush were applied simultaneously in four experiments using slush produced by the partial-melting method. The results are listed in the first two columns of Table 13. It can be seen that the agreement in results obtained by these two methods is excellent and that settled slush can contain as high as 57 to 59 percent solid.

The results obtained on four batches of settled slush produced by the freezing method are given in the third column of Table 13. It can be seen that these values were considerably lower than those for the slush produced by the partial-melting method. Visual observation leads us to think that the percent solid in slush produced by the freezing method actually was lower, as shown

TABLE 13

PERCENT SOLID IN SETTLED SLUSH

	Production by Partial Melting Method		Production by Freezing Method
Run No.	Assay by Volume Change	Assay by Melting Time	Assay by Volume Change
1	53	49	
2	57	55	
3	59	55	
4	61	57	
5	-	-	36
6	-	-	49
7	-	-	49
8	-	-	47
Average	57	57	45

Note: Percentage figures are in weight-% = mole-%

by the analyses, because the particles produced were more porous and bulky than the dense, closely packed particles produced by the partial melting method.

4.2.4 Vapor-Volume Method for Determining Percent Solid in Slush

This method was developed to determine the solid content of a batch of slush without having to melt the solid. A new experimental vessel (Figure 26) was designed for use with this method.

With the vapor-volume method, the volume of hydrogen gas pumped from a batch of liquid during slush production was measured, and the percent solid calculated from the following: the measured volume of starting liquid hydrogen, the volume of hydrogen gas pumped off, the heat of vaporization of hydrogen, the heat of solidification (same as the heat of fusion of hydrogen), and the heat leak into the vessel.

Before any measurements by this method were made, a calibration curve for the volume of Vessel A (Figure 26) as a function of height was constructed with the height being measured with a cathetometer.

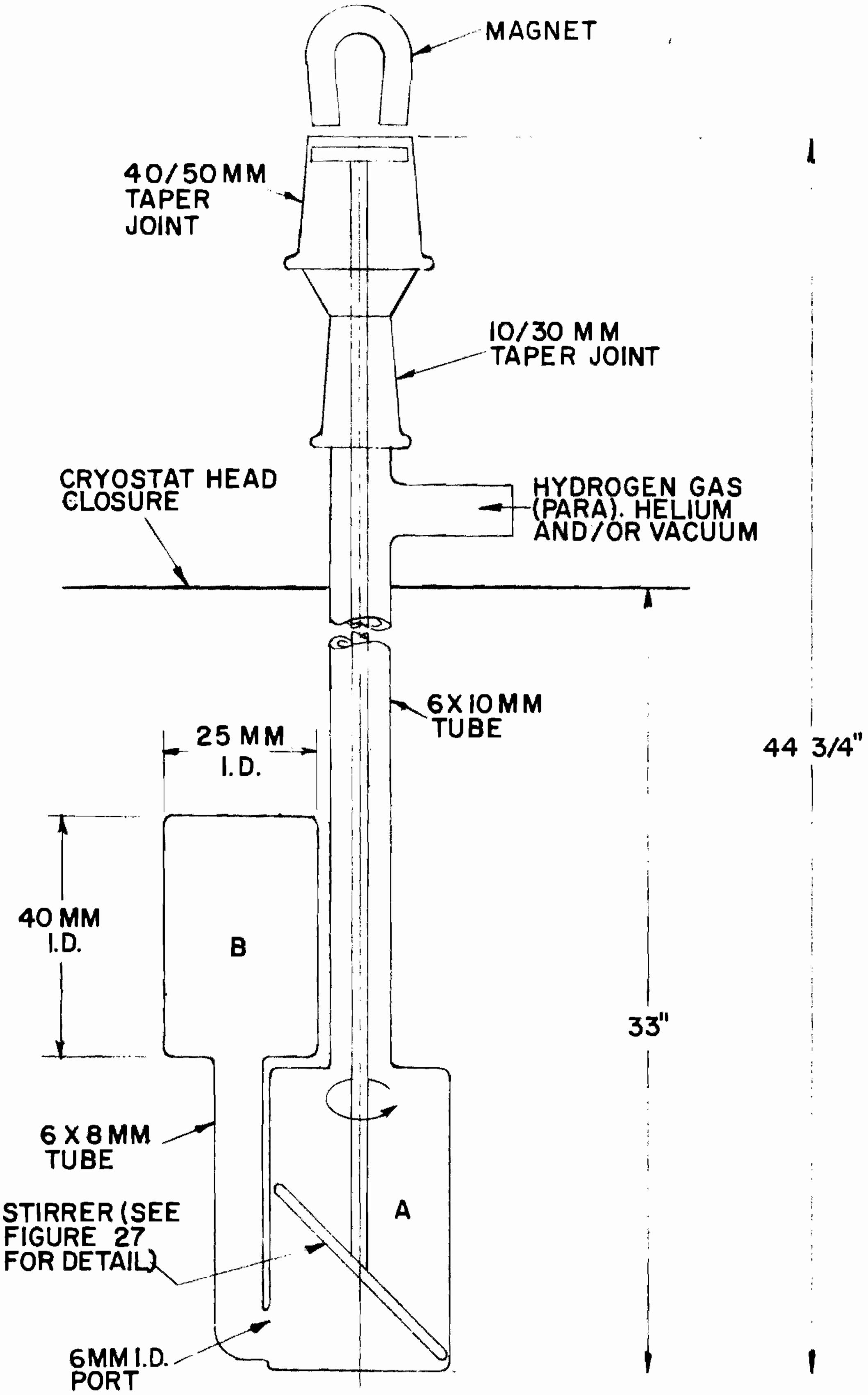

Figure 26. Experimental Hydrogen Slush Vessel

To make a determination of the percent solid in a sample of slush, the following steps were carried out:

1. The Dewar surrounding Vessel A (Figure 26) was filled with liquid para-hydrogen.

2. Para-hydrogen gas from the head space of a liquid hydrogen container was condensed into Vessel A.

3. The temperature of the liquid hydrogen bath surrounding Vessel A was adjusted by pumping on it until the temperature fell to the desired value, which was usually the triple point temperature.

4. The vacuum pump was turned on, and hydrogen gas was pumped off the liquid, with stirring, until the triple point was just reached, as evidenced by the first appearance of particles of solid hydrogen. To produce liquid at the triple point, these particles were just barely allowed to melt. When the last particle disappeared, the time was recorded as t_3, and pumping was started again, as described below.

5. The total rate of heat flow, hereinafter called the "heat leak," into Vessel A was measured. This was the sum of the rate of heat flow from the bath to Vessel A and any heat leaking down the tube and stirrer connecting rod. To measure the heat leak, a small amount of solid was produced inside Vessel A by pumping, and the volume of hydrogen that was pumped off to produce this solid was measured by means of a wet drum meter placed downstream from the vacuum pump. The material in Vessel A was stirred continuously. When a convenient quantity of solid had been produced, the vacuum valve was closed and the time (t_4) noted. (The time elapsed between t_3 and t_4 was called D_3 and was usually only about five seconds.) The solid was allowed to melt, the stirring being continued all the while. When the last particle of solid hydrogen disappeared, the time (t_5) was noted. (The time elapsed between t_4 and t_5 was called D_4.) The heat leak was then calculated by the method given after Step 8 below.

6. The liquid in the vessel was now at the triple point temperature. Its volume, V_5, was measured by use of the cathetometer and the calibration curve for Vessel A. Stirring was discontinued during this measurement.

7. Stirring was resumed, and the vacuum valve was turned on. Solid hydrogen formed in Vessel A. When the desired quantity of solid had been produced, the vacuum valve was shut off, and the time (t_6) was recorded. The hydrogen pumped off was metered, and its volume was recorded as G_5.

8. From the recorded data, the percent (by weight) solid in the slush produced between t_5 and t_6 was calculated as follows:

Calculation of Heat Leak

To calculate the heat leak, Q, (calories per minute) a heat balance is first made for duration D_3:

Heat loss = heat gain + heat released by formation of solid hydrogen

$$G_3 L_v = QD_3 + M_3 L_f \tag{101}$$

and a separate heat balance for duration D_4:

Heat gain = heat absorbed by melting of solid hydrogen

$$QD_4 = M_3 L_f \tag{102}$$

Combining Equations (101) and (102):

$$Q = \frac{G_3 L_v}{D_3 + D_4} = HL_v = \text{heat leak in calories per minute} \tag{103}$$

In the above equations:

D_3 = duration from t_3 to t_4, minutes

D_4 = duration from t_4 to t_5, minutes

G_3 = volume of hydrogen gas metered from t_3 to t_4, cu.ft. corrected to dry gas at STP (0 C. and 1 atm.)

L_f = heat of fusion (heat of solidification) of hydrogen, 28.03 calories/mole

L_v = heat of vaporization of hydrogen at the triple point, 273.81 calories/cu. ft.

M_3 = moles of solid hydrogen produced between t_3 and t_4

H = $\dfrac{G_3}{D_3 + D_4}$ = heat leak into Vessel A expressed in cu. ft. hydrogen/minute

Q = heat leak into Vessel A, calories per minute

Calculation of Moles of Solid Hydrogen Formed

For duration D_5, the heat balance is:

$$G_5 L_v = QD_5 + M_5 L_f \tag{104}$$

from which:

$$M_5 = \frac{G_5 L_v - QD_5}{L_f} \tag{105}$$

In this equation:

M_5 = quantity of solid hydrogen formed between t_5 and t_6, moles

G_5 = volume of hydrogen gas pumped off between t_5 and t_6, cu. ft. corrected to dry gas at STP

D_5 = duration from t_5 to t_6, minutes

Calculation of Percent Solid in Slush

$$x = \text{percent solid} = \frac{\text{Moles of solid formed}}{\begin{pmatrix}\text{moles of } H_2 \text{ present}\\ \text{initially}\end{pmatrix} - \begin{pmatrix}\text{moles } H_2\\ \text{pumped off}\end{pmatrix}} \cdot 100 \tag{106}$$

$$x = \frac{M_5}{\dfrac{V_5}{26.176} - 1.2625\, G_5} \cdot 100 = \frac{G_5 L_v - QD_5}{L_f \left(\dfrac{V_5}{26.176} - 1.2625\, G_5\right)} \cdot 100 \tag{107}$$

Here 26.176 is the molar volume (cc/mole) of liquid hydrogen, and 1.2625 is:

$$\frac{28.31625 \text{ liters/cu.ft.}}{22.4279 \text{ liters/mole}} = 1.26254 \text{ moles per cu.ft. of hydrogen at STP}$$

Using the following:

L_f = 28.03 calories per mole at the triple point

L_v = $\frac{28.31625}{22.4279}\ \underset{\text{(STP)}}{(216.87)}$ = 273.81 calories per cu.ft.

M_o = quantity of liquid hydrogen at the beginning of a run, moles = $\frac{V_5}{26.176}$

Q = HL_v from equation ( )

V_5 = Volume of liquid hydrogen at the triple point

H = $\frac{G_3}{D_3 + D_4}$ = heat leak into vessel A expressed in cu.ft. hydrogen/minute

$$x = \frac{9.7685\ (G_5 - HD_5)}{M_o - 1.2625\ G_5} \cdot 100 = \frac{255.70\ (G_5 - HD_5)}{V_5 - 33.046\ G_5} \cdot 100 \qquad (108)$$

Either form of this equation, depending upon convenience, may be used to calculate x.

Example:

In this example both heat leak test and an actual run were made. During the heat leak test the total time elapsed for both parts ($D_3 + D_4$) was 2.46 minutes, and the volume of hydrogen gas, corrected to dry gas at STP, was 0.12 cu.ft. The volume of liquid hydrogen at the start of the actual run was 30.60 cc. The duration (D_5) of the actual run was 2.33 minutes and the volume (G_5) at STP of hydrogen gas pumped off was 0.053 cu.ft.

From Equation (108):

$$x = \frac{255.70\ \frac{0.053 - 0.012 \times 2.33}{2.46}}{30.60 - 33.046 \times 0.053}\quad 100 \quad = 37.0\%\ \text{solid in the slush}$$

The expression x may be thought of as being in either weight-percent or mole-percent or both, since for a one-component system these are the same.

Sources of Values for Physical Constants in Equations

Molar Volume for Para-hydrogen No molar value for para-hydrogen has been found in the literature. This value is believed, however, to be very close to that for normal-hydrogen, which is given in Wooley, Scott, and Brickwedde (9, page 396) as 22.4279 liters at 0 C, 760 mm. Hg.

Molar Volume of Liquid Para-hydrogen This is given in Table 31 of Wooley, Scott, and Brickwedde (9) as 26.176 cm.^{3}/mole.

Heat of Fusion, L_f, of Solid Hydrogen The value of 28.03 cal/mole at the triple point is taken from p. 3 of Mullins, Ziegler, and Kirk, "The Thermodynamic Properties of Para-hydrogen from 1 to 22 K," Engineering Experiment Station, Georgia Institute of Technology, November, 1961 (1).

Heat of Vaporization, L_v, of Para-hydrogen The value of 216.87 calories/mole at the triple point is taken from Mullins, Ziegler, and Kirk (1, pp. 10;25).

4.2.4.1 Accuracy of the Vapor-Volume Method for Determining Percent Solid in Slush

The gas metering system was calibrated so that the flow of gas measured was known to be accurate within approximately ± 1 percent. The volume of gas metered from a cylinder of known volume was the same when it passed through the vacuum pump and when, in another test, it was allowed to flow directly from the cylinder to the meter. The metered flow was, within the metering error, independent of either pumping speed or pressure.

In calibrating the liquid volume of the vessel, a quantity of liquid hydrogen was placed in the vessel and the height of the liquid was measured. All the liquid was then pumped through the gas metering system to determine the quantity of liquid in the vessel. This procedure was repeated with more than ten different volumes of liquid hydrogen, and was found to be reproducible within ± 2 percent.

As a further check, a quantity of liquid hydrogen was converted to 100 percent solid at the triple point temperature, and the percent solid determined by the vapor-volume method described above. The answer obtained was 98 percent. This is evidence that the vapor-volume method is accurate within a few percent.

4.2.5 Conclusions

Three methods were developed for the measurement of the solid content in hydrogen slush. The first was based on the change in density, and the second was based on the time it takes to melt the solid. Both of these methods required the destruction of the slush. A third method, based upon the heat of solidification and the heat of vaporization of hydrogen, was a dynamic method and was capable of measuring the solid content of slush over the entire composition range without destruction of the slush. Starting with a known quantity of liquid hydrogen at its triple point temperature, solid was produced by vacuum pumping. The gaseous hydrogen removed was quantitatively metered. From this gas volume and the heats of solidification and vaporization, the quantity of solid produced were calculated.

4.3 STUDY OF MIXING AND TRANSFER CHARACTERISTICS OF HYDROGEN SLUSH

Studies were performed on the mixing and transfer characteristics of hydrogen slush. Performed primarily as experiments, these studies provided a wide range of data for quantitative evaluation.

4.3.1 Apparatus

The equipment used for the quantitative evaluation of the transfer properties of hydrogen slush is illustrated in Figure 26 . The slush was prepared and mixed in the lower vessel (A) and then transferred to the upper vessel (B). The entire system was suspended from the head of the cryostat in liquid hydrogen or slush kept at a controlled temperature inside the cryostat's inner Dewar.

4.3.2 Slush Mixing Experiments

Several types of stirrers were tried in attempts to adequately mix slush produced by vacuum pumping. Helium and hydrogen gases were tried as stirrers (described in 4.1.2) in Qualitative Experiment Number I, but neither gas succeded in breaking the porous crust of solid hydrogen formed above the liquid hydrogen. In Qualitative Experiment Number II, a wooden rod (described in 4.1.3) was used as a stirrer with some success. Additional mechanical stirrers (described below) were employed in slush mixing experiments utilizing Vessel A (Figure 26).

The first mechanical stirrer tried in Vessel A was a horizontal, screen-like system of bars spaced so that there were 1/16 inch squares of open space between the bars. The rim of this system of bars was circular and of just slightly smaller diameter than the vessel. The stroke of the stirrer was vertical. The stirrer was actuated by means of a magnetically driven linkage located above the cryostat. This vertical stirring action was not effective in mixing hydrogen slush. Even though the stirrer was fabricated with an open lattice, slush still tended to be packed in the vessel above and below the limits of the stroke. Since the packing began even at rather low solid concentrations, this type of stirrer was soon abandoned.

The most useful stirrer tried in Vessel A is shown in Figure 27. Figure 26 shows the position of this stirrer in the vessel. The stirrer was operated in a circular motion through a magnetically driven linkage located above the cryostat. The rod leading down to the stirrer was inside the 6 x 10 mm tube which also was used to admit and pump off gas from Vessel A. At low and medium concentrations of solid, this stirrer mixed the slush very well. The crust of solid formed above the liquid during pumping was easily broken, and the individual particles of solid produced in the stirring were small and well dispersed in the liquid. As the solid content rose above about 60 percent, however, the stirrer tended to cut a hole in the mixture rather than to mix it. This is because the slush no longer moved adequately from points that the stirrer did not reach mechanically. Also, the slush at this percent tended to build up on the walls of the vessel and on the shaft of the stirrer.

The stirrer shown in Figures 26 and 27 proved to be quite satisfactory for the small-scale experimental work.

4.3.3 Transfer of Hydrogen Slush Through a Small-Diameter Tube

Transfer of slush from Vessel A to Vessel B in Figure 26 was accomplished by pressurizing the slush in Vessel A with helium gas introduced down the center tube. This forced the slush in Vessel A to flow through the 6 mm. I.D. glass tube connecting the two vessels and into Vessel B. Six mm. was the minimum tube diameter considered practical for these experiments, as this diameter was about three times the maximum dimensions of the solid hydrogen particles. If smaller diameter tubing had been used, it would be difficult to apply small-vessel data to larger equipment in making engineering calculations. A minimum diameter tube was utilized so that potential transfer failures could be observed.

4.3.3.1 Description of Table 14 Data for the transfer experiments are given in both Table 14 and the notes that go with it. The appropriate symbol used in equation (108), which may be used to calculate the percent solid, is given under each heading of the table, where applicable. In all cases the percent solid hydrogen was determined by the vapor-volume method.

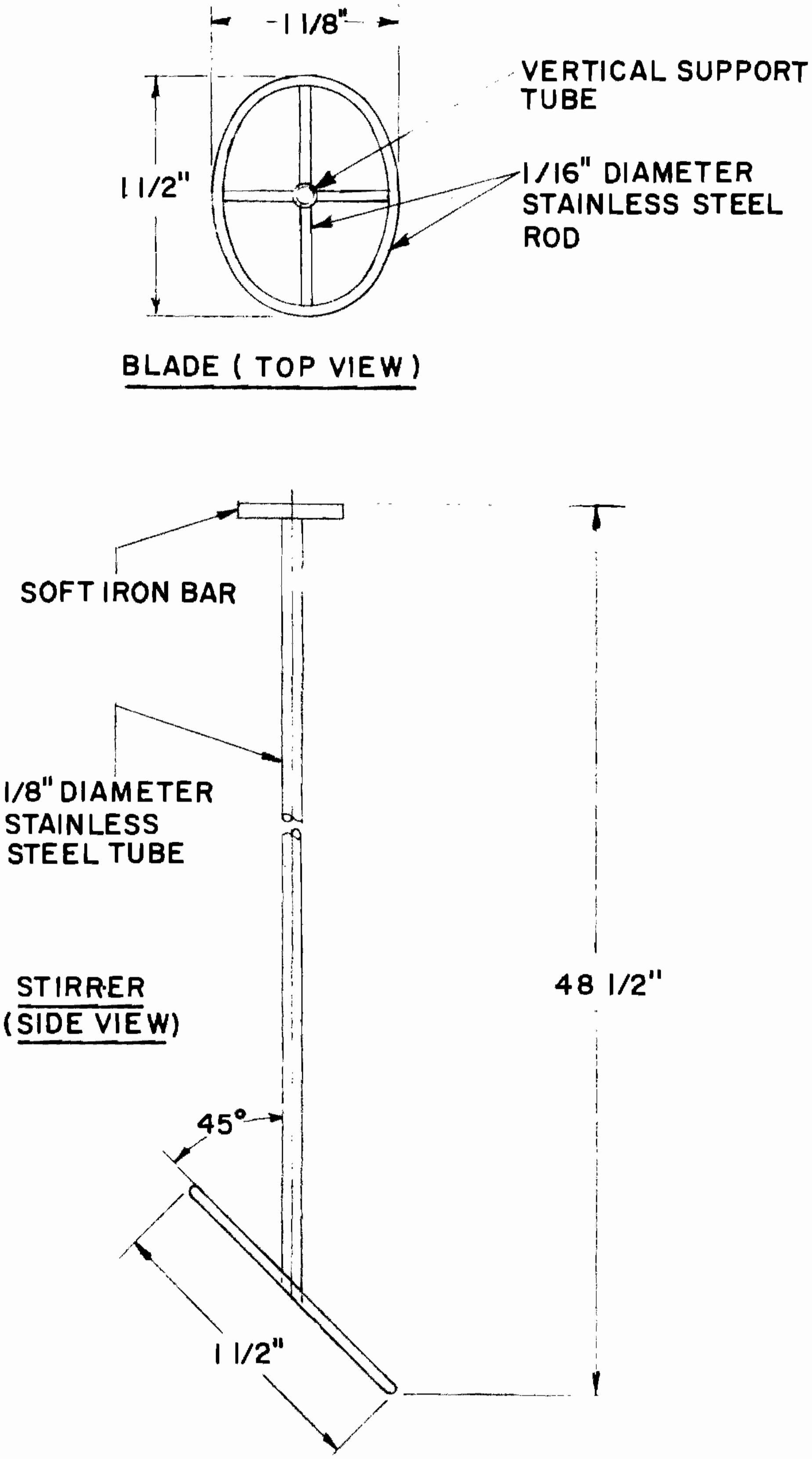

Figure 27. Detail of Most Useful Slush Stirrer

TABLE 14

STUDY OF MIXING AND TRANSFER CHARACTERISTICS OF HYDROGEN SLUSH

Source	Run No.	Quantity of Starting Liquid, Moles	Gas Evac., Cu. ft. STP	Heat Leak Rate, Cu. ft. STP per min.	Production Time, min.	% Solid
		M_o	G_5	H	D_5	x
			Calibration Runs			
9750-5-16	1	0.844	0.080	0.0054	1.12	98
9216-96-6	2	0.981	0.020	0.0045	0.85	16
			Production Conditions - High Heat Leak Rate and Long Production Time			
9750-15-1	3	1.12	0.085	0.025	1.60	46
9750-13-1	4	1.09	0.098	0.025	2.0	50
9750-4-17	5	1.08	0.037	0.015	1.04	24
9750-4-1	6	1.11	0.054	0.013	1.46	33
9216-96-4	7	1.024	0.071	0.011	1.95	54
9216-94-8	8	1.016	0.064	0.011	1.6	52
9750-12-1	9	1.20	0.071	0.010	2.62	41
9216-96-3	10	1.297	0.070	0.009	1.0	50
			Production Conditions - Low Heat Leak Rate and/or Short Production Time			
9750-5-1	11	1.024	0.022	0.009	0.52	18
9750-6-1	12	0.955	0.038	0.0055	1.19	34
9750-7-1	13	1.23	0.054	0.0045	1.9	38
9750-12-13	14	1.17	0.053	0.0045	2.33	38
9216-96-5	15	0.981	0.040	0.0045	1.85	35
9216-95-15	16	1.327	0.067	0.0036	2.3	46
9216-95-14	17	1.165	0.043	0.0036	1.8	31
9750-6-18	18	0.982	0.041	0.0036	1.43	46
9750-14-1	19	1.11	0.072	0.0036	3.67	57
9750-16-1	20	1.12	0.051	0.0027	1.25	44

Runs 1 and 2 were performed to check the "vapor-volume" method of determining the value of (x), the percent solid in the slush. The product in Runs 1 and 2 was not transferred.

Notes for Table 14

Run 1. As well as could be determined visually, the hydrogen was completely solidified. The value of (x) should therefore be close to 100 percent.

Run 2. The value of (x) was simultaneously determined by the "volume change" method; by this method, (x) was 19 percent, in fair agreement with the value of 16 percent measured by the vapor-volume method.

Runs 3-20. In all of these runs, the slush was transferred from Vessel A to Vessel B (Figure 26) by applying helium gas pressure to the slush in Vessel A.

Runs 3-10. "High heat-leak rate" means that the value of H is equal to or greater than 0.09 cu. ft./min. "Long production time" means that the value of D_5 is equal to or greater than 1.0 minute.

Run 4. After half the slush was transferred, channeling through the solid took place and only liquid was transferred thereafter.

Run 5. The stirrer was not in operation during the transfer.

Run 11. Note the very short production time.

Run 19. Note the exceptionally long production time. The solid channeled before all the slush was transferred.

Runs 3 to 10 and 11 to 20 are listed in order of decreasing heat-leak rates to show how (x) varies with the magnitude of the heat leak. The values of (x) in these runs are considered to represent slush having approximately the maximum percent solid that could be mixed and transferred. It can be seen (Runs 3 to 10) that under conditions of relatively high heat leak, slush containing 40 to 50 percent solid could usually be mixed and transferred, whereas at relatively low heat leak (Runs 11 to 20), only 35-46 percent solid could be readily mixed and transferred.

Run 11 shows the effect of abnormally short production time. Run 19 shows the effect of abnormally long production time. It should be understood that in most of the experiments summarized in Table 14 the slush was not "settled slush" as defined in 4.2.2.

4.3.3.2 Discussion of Transfer Experiments Generally, transfer of the slush was a less serious problem than mixing. When the slush was well mixed and had a solid content of less than 50 percent, transfer usually took place readily.

Several interesting phenomena were noted in the transfer experiments. It became apparent that the transfer must be made at relatively high linear velocities through the transfer tube, or else the slush in the receiver will have a lower solid content than the slush in the production vessel. When attempts were made to transfer slush of 30-60 percent solid content at low speeds, the solid tended to bridge the entrance of the transfer tube; the liquid "strained" through the solid, and only liquid reached Vessel B. This bridge or porous plug always occurred at the point at which the tube was connected to Vessel A. Once in the transfer tube, the slush flowed readily. Because of the tendency to bridge at the entrance to the transfer tube, all slush transfers (Runs 3 to 20 in Table 14) were performed at high velocity. At this high velocity only one or two seconds were required to fill the receiver. Due to this short transfer time, it was not practical to measure the pressure drop. No such measurements were made, except to note that none of the transfers required a pressure greater than one atmosphere of helium gas.

The tendency of the slush to clump and adhere to the vessel walls and stirrer shaft was a problem. Unless the solid was mixed with an adequate amount of liquid, adhesion always took place. Also, when high-solid-content slush was rapidly transferred to the receiver, some of the solid would sometimes stick to the top of the receiver. No sticking was ever seen in the transfer tube. Once the slush was moving rapidly in the tube, it continued to move. However, changes in diameter or direction of pipes carrying hydrogen slush might prove troublesome.

Most transfers were attempted while the slush was still being stirred in the production vessel. When attempts were made to transfer slush of such high solid content that there was not a continuous liquid phase, channeling took place, i.e., the slush nearest to the transfer tube was forced into the tube, but slush lying farther away in the vessel did not flow rapidly enough to reach the tube entrance. As a result, when channeling started helium gas instead of slush flowed into the transfer tube.

When channeling occurred, the slush could not be transferred by gas pressurization. Other means of transfer would probably also fail in the event of channeling. A piston or centrifugal pump or even a worm gear system would fail for lack of feed if the slush were not fluid.

4.3.4 Explanation of Variations in Maximum Concentrations of Solid Which Could be Mixed and Transferred

Table 14 shows that the maximum percent solid which could be transferred under various conditions in the equipment described varied from 18 percent to 57 percent, most values being between 31 percent and 54 percent. This wide range of values was not an experimental error but represented variations in the consistency of the slush which were not attributable alone to the percent solid in the slush. The variations in consistency appeared to be the result of differences in the method of producing the slush, the chief difference being in the length of time the solid was subjected to partial melting.

Vacuum pumping of liquid hydrogen initially produced a porous solid. If the porous solid particles were allowed to partially melt, they become more dense or compact. Slush containing compact particles of solid was fluid to a much higher solid concentration than slush containing porous solid. There were indications, to be further explored, that aging of the porous solid at constant temperature would produce the same effect as partial melting. During aging, the porous solid would probably be altered into more compact particles of solid hydrogen.

When prepared by vacuum pumping, stirring, and partial melting of the solid (described in 4.2.3), the percent solid in the resulting settled slush was fairly constant and probably represented a maximum solid content for a fluid slush.

4.3.5 Conclusions and Observations

Experiments on the mixing and transfer of freshly prepared slush, i.e., slush not over five or ten minutes old, were completed. Mechanical stirring for mixing and helium pressurization for transfer appeared to be adequate in a significant range of slush compositions. In the experiments it was determined that if the slush could be mixed by mechanical stirring, it could then be transferred by helium pressurization. When the solid content was too high, mechanical stirring failed to adequately mix the slush, and it would not flow.

The fluidity of freshly prepared slush produced by vacuum pumping was found to vary with the rate of production and with subsequent treatment, especially stirring, as well as with the concentration of the solid. The solid as first produced was quite porous. If this porous solid underwent partial melting (probably accompanied by some re-formation of the solid), the solid particles became much more compact. Slush containing solid in the form of compact particles was found to be fluid at much higher solid concentrations than a slush containing the porous solid.

The mixing and transfer problems associated with freshly prepared slush were found to be dependent on concentrations of solid in the slush:

a. Under 30 Weight-Percent Solid All well-mixed slushes with a solid concentration below 30 percent were fluid.

b. 30 to 60 Weight-Percent Solid Some slushes with a solid concentration within this range were fluid while others were not. If the solid were composed of dense particles, the slush would remain fluid to the upper limit of this range; but if the solid were composed of porous solid, it often was not fluid even in the lower part of this range.

c. Over 60 Weight-Percent Solid Although fluid slushes containing up to 70 weight-percent solid could probably have been prepared, experience obtained with lesser mixtures indicated that it would be better to keep the solid content at 60 percent or below in commercial operation if fluidity were desired.

4.4 STORAGE OF HYDROGEN SLUSH

Small-scale experiments were performed for the study of the effect of storage on (a) the particle size of the solid in hydrogen slush and (b) the transfer characteristics of the slush. In these experiments, the liquid hydrogen was stirred while the solid was being formed by vacuum pumping. Stirring was stopped when the desired quantity of solid was produced, and the storage tests were made without any further stirring. The longest storage test lasted 15 hours.

4.4.1 Apparatus

The same experimental vessel (Figure 26) previously employed was used for producing and storing the hydrogen slush. Hydrogen slush was produced in the Vessel A by vacuum pumping on the liquid, with continual stirring until slush of a rather viscous nature was produced. Both stirring and vacuum pumping were then stopped. Storage was carried out under static conditions.

When the storage period was completed and the slush was to be transferred, storage Vessel A was pressurized with helium gas. In every case the slush immediately flowed up into Vessel B.

4.4.2 Measurement of Heat Leaking Into Stored Hydrogen Slush

Some of the solid hydrogen in hydrogen slush melts because of heat leaking into the storage system. Before other storage effects could be evaluated, it was necessary to determine the magnitude of this heat leak.

In the storage experiments described herein, the production and storage vessel (Figure 28) was immersed in a bath of hydrogen slush in the inner Dewar of the cryostat. Since there was slush outside the storage vessel, no heat leaked into the storage vessel through its walls. There still was a heat leak however, down the stainless steel tubing used as the stirrer shaft. This heat leak can be thought of as being divided into two vectors, the horizontal (a) and the vertical (b), as shown in Figure 28 . When the entire stirrer blade was surrounded by slush, the heat represented by both vectors was absorbed by the solid hydrogen, a part of which melted. When the slush level inside the storage vessel was low and the level of liquid hydrogen over the slush was above the top of the stirrer blade, the heat was absorbed by the upper layer of the liquid. This warmer liquid layer did not transmit its heat readily in the downward direction. A considerable portion of the heat was, however, transmitted horizontally through the walls of the vessel to the bath of hydrogen slush outside.

The rate of melting of the solid hydrogen in the storage vessel was therefore a function of the height of the slush inside the vessel, and the melting rate of solid in the stored sample of slush decreased as the slush level became lower.

The initial melting rate during storage was determined by the following procedure: Slush was first produced in the vessel by vacuum-pumping with stirring. The quantity of solid produced was determined by the "vapor-volume" method (described in 4.2.3.4). The slush was stored without stirring for a given length of time and then was again vacuum-pumped with stirring to produce 100 percent solid. Calculation of the amount of total solid produced in the two pumpings sometimes gave a value greater than the amount of liquid originally available for conversion to solid. The difference between these two quantities was accounted for by resolidification of hydrogen that melted during storage.

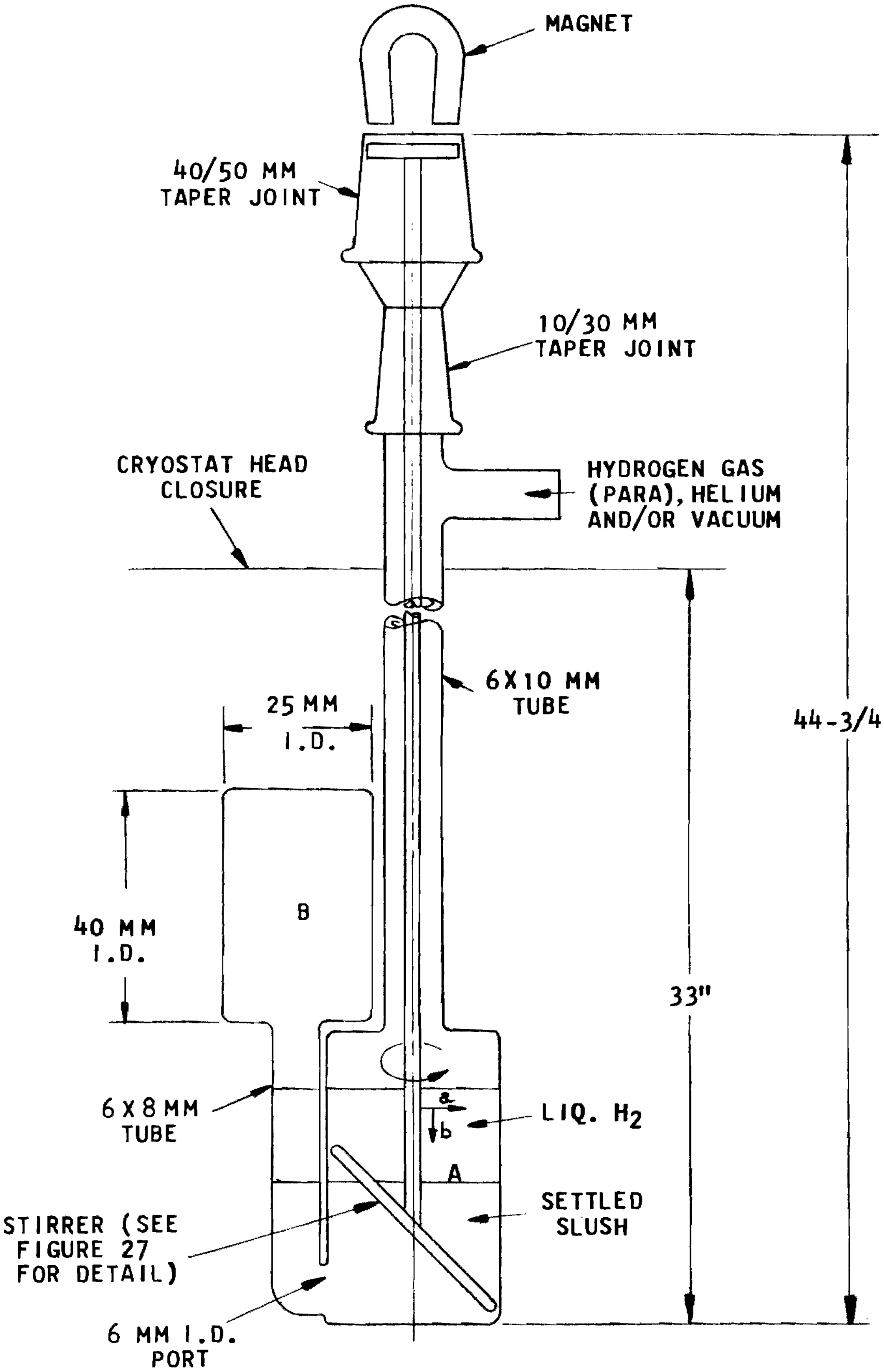

Figure 28. Experimental Hydrogen Slush Vessel

For example:

Initial solid produced	0.470 mole
Additional solid produced on second pumping	0.673
Total	1.143
Total liquid available for conversion to solid[*]	1.06
"Excess" solid	0.083 mole

Therefore 0.083 mole of solid must have melted during the storage time between the first production of solid and the final production of 100 percent solid.

This measurement of quantity of solid melted by the heat leak was applied to several samples of slush. The melting rate was found to be approximately 0.05 mole per hour in the first 60-90 minutes of storage. This represents a heat leak into the slush of 1.4 cal/hr.

4.4.3 Transfer Characteristics of Stored Slush

Three tests were made to evaluate the effect of storage on the transfer characteristics. Table 15 shows the solid hydrogen content of the three slushes as originally produced, the estimated solid concentration after storage, and the duration of storage. In all cases the material was produced by vacuum-pumping with stirring, but the slush was not stirred during storage or before transfer. Transfer of the slush from the storage vessel to the receiving vessel was accomplished by helium pressurization of the storage vessel. In all three tests transfer was easily accomplished.

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[*] Moles of liquid originally in the vessel minus the total moles of gas pumped off during the two periods of solid production.

TABLE 15

SHRINKAGE OF STORED SLUSH

Test	Time of Storage hr.	Over-all Concentration of Solid, wt-%		Concentration of Solid in the Lower Layer at End, wt-%	Relative Volume Occupied by Lower Layer, volume-% of total	
		Start	End		Actual	If no Melting
1	1.0	30	27	38	72	80
2	1.5	43	36	47	77	92
3	1.75	51	44	55	80	93

4.4.4 Particle Growth During Storage

Particle growth was observed in storage experiments. The solid hydrogen in freshly prepared slush was quite porous and appeared to be an agglomeration of many very small particles. During initial storage these particles rapidly increased in size until single particles as large as one to three mm in the longest dimension were observed. This growth was very rapid during the first hour of storage, was much slower in the second hour, and visually undetectable after two hours. Visual observation was limited to fifteen hours since this was the longest storage period.

4.4.5 Shrinkage of Slush Volume During Storage

Three storage runs (Table 15) were made in which the volume occupied by the slush was related to the total volume occupied by liquid and solid hydrogen in the vessel. All storage was without stirring so that settling of solid could take place. Initially, there was no clear supernatant liquid layer; that is, the slush was homogeneous and the slush accounted for 100 percent of the volume occupied by liquid and solid hydrogen. As the particles of solid hydrogen grew, clear supernatant liquid began to appear above the lower slush layer.

There were two possible explanations for the shrinkage in volume occupied by the slush: (1) melting of part of the solid because of heat leakage into the storage vessel, and (2) compacting of the solid particles upon storage. The quantity of solid that melted during storage was calculated in each case from a heat-leak measurement. The last column in Table 15 shows the percent of the total volume which would have been occupied by the slush layer had there been no melting.

In all cases this figure was significantly below 100 percent. It was concluded, therefore, that the shrinkage of the volume occupied by the slush was due partly to a decrease in the volume occupied by the particles as well as the melting. The bulk density of the slush increased with storage. This increase was accompanied by the particle growth described earlier in this report.

Table 15 gives data for three different storage experiments. The figures in the fifth column indicate that, as the duration of storage increases, the concentration of solid in the settled slush approaches a figure of 55 weight-percent. This upper limit is in agreement with earlier findings.

4.4.6 Maximum Concentration of Solid in Transferable Slush

A rough calculation was made of the maximum concentration of solid hydrogen slush at which the slush can be readily transferred. The basis for this calculation was the hypothesis that there must be a continuous liquid phase if the slush were to have reasonable low viscosity and thus be able to flow through pipes.

As a first approximation, it was assumed that all the particles of solid hydrogen were the same size, that each particle was spherical, and that the spherical particles were stacked vertically above one another. With these simplifying assumptions, each particle was thought of as a sphere inside a cube, all space in the cube outside the sphere being occupied by liquid. Since the volume of a sphere is $\pi d^3/6$ and the volume of a cube is d^3, where d is the common diameter of the sphere and the cube, the volume occupied by the solid phase is:

$$\frac{1/6\,\pi\, d^3}{d^3} \times 100 = 52.4 \text{ volume -\% of the total.} \qquad (109)$$

At the triple point, the density of the solid is 5.409 lb/cu.ft., and of the liquid, 4.809 lb/cu.ft. The weight of the solid phase (when d is in feet) is $5.409\pi\, d^3/6$ lb, and the weight of the liquid phase is $4.809\,(d^3 - \pi d^3/6)$ lb.

The percent solid in the slush is then given by:

$$\frac{5.409\pi\, d^3/6}{5.409\pi d^3/6 + 4.809\,(d^3 - \pi\, d^3/6)} \times 100 = 55.3 \text{ wt-\%} \qquad (110)$$

By stacking the spheres the way they are stacked in a pyramid of cannon balls, the percent of liquid volume could be somewhat reduced. Also, there are undoubtedly particle shapes which would occupy a greater proportion of the total volume than spheres. The actual particles of solid hydrogen are not spherical; they are elongated. Nevertheless, it is interesting to note that, to a first approximation, the calculated maximum weight percent solid for which there is a continuous liquid phase is roughly the same as the maximum value obtained by actual measurements in the laboratory. It therefore appears unlikely that hydrogen slush can be pumped like a liquid if its content of solid hydrogen is much above 55 weight-percent.

There is one condition under which the calculated percent of solid would be much larger than 55 weight-percent, viz., the state under which there would be a distribution of particle sizes such that small particles occupy the spaces between large particles. For hydrogen slush, this condition need not be considered seriously, since it has been found in the laboratory that the small particles either disappear or grow in an hour or two until all the particles are roughly the same size. The small particles have a greater solution pressure than the larger ones, so they tend to melt and regrow on crystals which have just started to grow. When particles have reached a size at which the solution pressure is no longer much greater than that of the other particles, the rate of growth of the larger particles becomes very small.

4.4.7 Conclusions

The very small particles first formed in the production of slush by the vacuum-pumping technique grow to particles about one mm in length. The growth was very rapid in the first hour or two of storage, but after that was too slow to be detectable. At the end of the storage period all the particles appeared to be the same general size, i.e., no particles were noticed which were much larger or much smaller than the average.

Coincident with this particle growth was a decrease in the bulk volume occupied by the slush which was apparently due to the fact that the larger particles were more compact than the porous agglomerates of small particles originally formed. The result was that a clear layer of liquid hydrogen formed above the slush. The lower (slush) layer approached a solids content of about 55 weight-percent, which agreed with the limiting value found in earlier work for the concentration of solid in the materials we have previously named "settled slush." It was shown mathematically that the upper limit of solid concentration in hydrogen slush which has a continuous liquid phase was expected to be between 50 and 60 weight-percent. This confirmed the empirical figure of about 55 weight-percent solid found as the upper limit of solid in settled slush.

After storage of up to 15 hours, the slush could still be easily transferred.

SECTION 5

LARGE SCALE EXPERIMENTAL EXAMINATION OF HYDROGEN SLUSH

The large scale experimental examination of hydrogen slush was designed to investigate the vacuum pumping production methods that had previously been studied theoretically. Investigations were also performed on transfer and storage of slush produced in the large scale examination.

5.1 APPARATUS AND INSTRUMENTATION

5.1.1 Description of Test Apparatus

The test program suggested by the analytical investigation described in Section 3 of this report required the use of a quite sophisticated apparatus to evaluate the various vacuum pumping methods of slush production. To keep heat leak at a minimum, thereby simulating the performance of the high quality equipment that will be employed in actual installations, a metal test chamber insulated with Super Insulation was utilized. Glass tankage was used inside the test chamber since visual observation of the slush formation was desired. A periscope was chosen, on the basis of utility and cost, to facilitate observation of the glass tankage contents.

A schematic diagram of the test apparatus is shown in Figure 29. The figure shows the internal components located side by side to eliminate hidden lines for easier understanding. Actually, the components were placed in a circular arrangement to fit in the cylindrical guard chamber.

The test apparatus was designed for the production of hydrogen slush by straight vacuum pumping, semiflow vacuum pumping, branched flow vacuum pumping, and cascaded branch flow vacuum pumping. In addition, it had the capability of storing the slush produced for long periods of time in the slush tank or in the storage tanks. Means were provided for transferring the slush between the various tanks.

To reduce the heat leak to a very low value, the hydrogen slush production system was installed in a stainless steel, liquid hydrogen filled guard chamber which, in turn, was shielded from ambient temperatures by multiple layer Super Insulation. The open top of the guard chamber was maintained at liquid hydrogen temperature by a Super Insulated copper-radiation shield in thermal contact with the guard chamber. To further reduce heat leak, the space around the production vessels was evacuated.

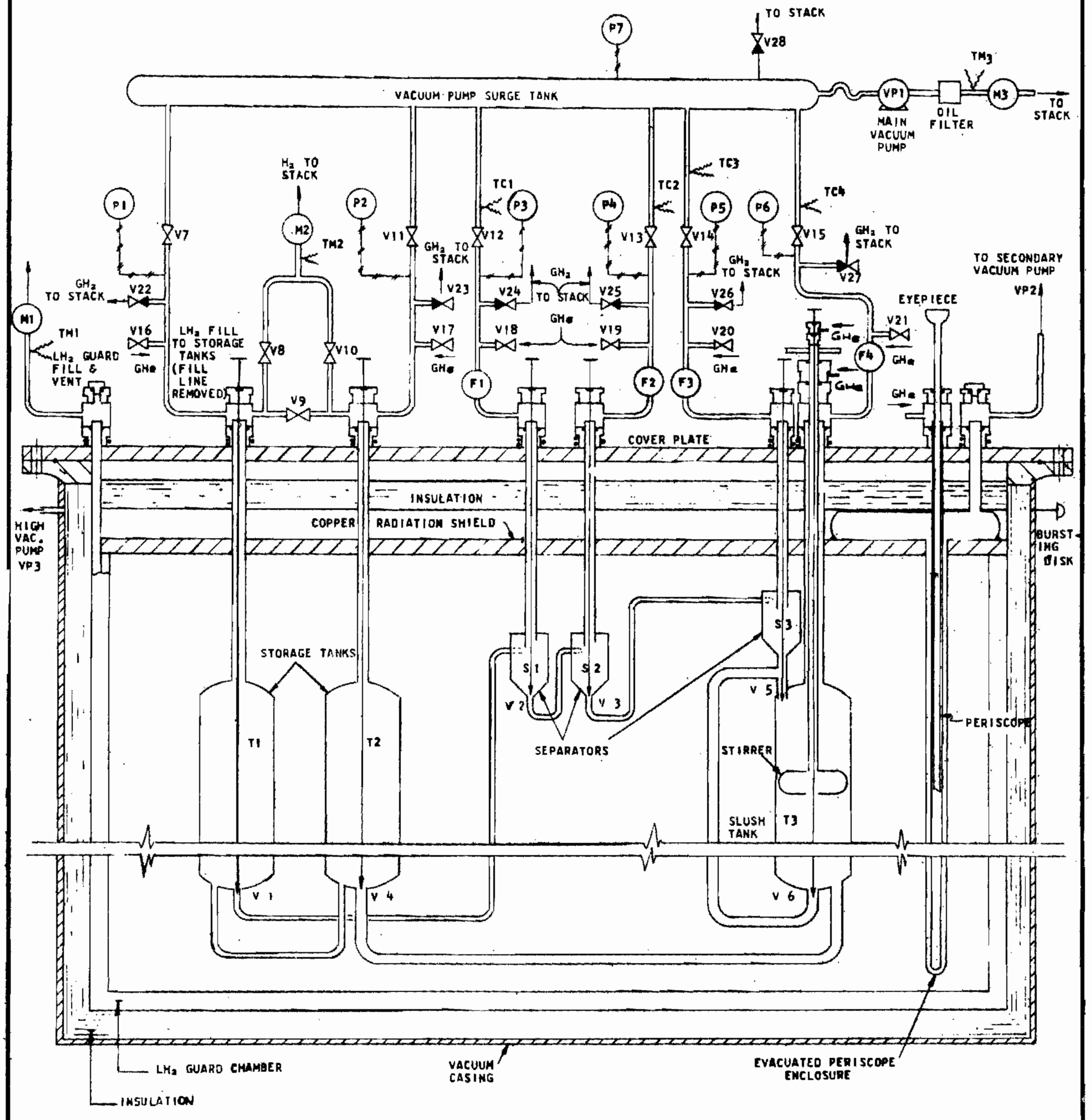

Figure 29. Experimental Apparatus for Hydrogen Slush Studies

The cold valves (V1 through V6) located within the glassware had extended stems with the stem seals fixed to the cover plate. During production, the heat leak down the valve stems was partially recovered by the cold hydrogen gas flowing to the main vacuum pump (VP1).

Visual observation of the hydrogen slush production process was provided by a vacuum-guarded periscope. The periscope was located so that all the system components could be seen by vertical and rotational movement of the periscope. The slush production process was controlled by a combination of settings of the cold valves (V1 through V6), the warm hydrogen gas flow valves (V7 through V15), and the helium pressurization valves (V16 through V21). The remaining valves (V22 through V28) are safety relief valves.

Various qualities and speeds of production could be controlled by visually observing the hydrogen slush and manipulating the appropriate valves. The pressure gauges (P1 through P7), wet drum meters (M1, M2, and M3), and flow rate meters (F1 through F4) provided data for analysis of the production processes. The several pressure levels required in the cascade and branch flow production methods were obtained by throttling the gas flow through valves V7 through V15 into a vacuum pump surge tank which was connected to a 60 cfm mechanical pump.

A 25 liter size for tanks T1 through T3 was adopted as a reasonable compromise between the difficulty of making large glass tanks and the desire for large volumes to improve the accuracy of the measurements. A large length to diameter ratio was also selected to provide high accuracy in the measurement of the liquid column heights which were used to calculate volumes. The cylindrical glass tanks T1 through T3 were nominally 7 inches in diameter and 44 inches in length. Overall dimensions of the outside guard chamber were 20 inches in diameter and 72 inches in length.

All safety precautions normally employed in the design of liquid hydrogen systems were incorporated in the design of the test apparatus. The gaseous hydrogen from the wet drum meters and the safety relief valves was piped to a vent stack which exhausted high above the laboratory. The safety relief valves were employed wherever the possibility of trapping cold fluid existed.

The stainless steel guard chamber was an annular liquid hydrogen vessel (16 in I.D. x 18 in O.D.) located inside a vertical cylindrical vacuum casing. The vacuum casing is shown in Figure 30. Super Insulation was used to allow the liquid hydrogen guard chamber to be installed without the customary liquid nitrogen shielding. Operation of the guard chamber at

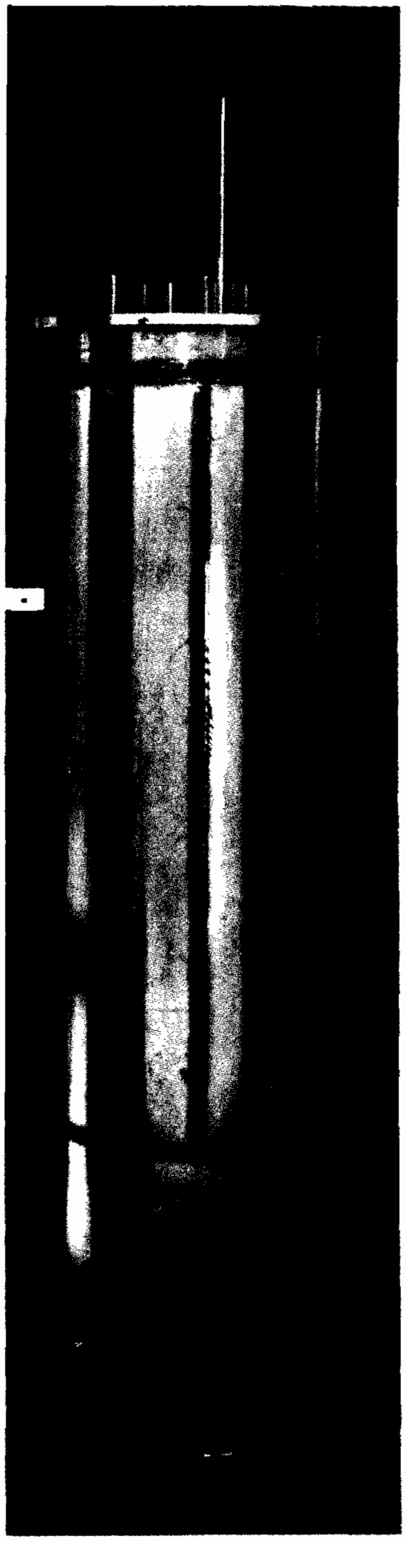

Figure 30. Side View of Guard Chamber Vacuum Casing

liquid hydrogen temperature allowed a close approach to an adiabatic system, thus reducing the heat leak to the production vessels. The temperature of the guard chamber could be reduced to slush temperature by vacuum pumping, if desired to further reduce the heat leak.

The assembled glass system prior to insertion into the guard chamber is shown in Figure 31. The stainless steel base plate rested in the lower head of the guard chamber and supported the glass system on pads of insulation. Tanks T1 and T2 were used for adiabatic storage of liquid hydrogen. Tank T3, located behind T1 and T2, was used as the slush tank. Above the tanks T1, T2, and T3 are the separators S1, S2, and S3. The assembly of tanks and separators is supported for introduction to and removal from the guard chamber by a cage formed by the base plate and a upper plywood disk connected by three removable outer rods and a center removable threaded rod. Clamping bands, used to clamp the tanks together within the cage, are removed prior to installation of the assembly into the guard chamber. The outer support rods, the central threaded rod, and the plywood disk are removed after installation.

The upper portion of Figure 31 is shown in greater detail in Figure 32. The detail of the separator piping is clearly apparent in this figure.

Figure 33 shows two views of slush tank T3 with a stirrer inside. In these views the graduation etched on the outside of the vessel which provided a scale to measure the contents are apparent. Also apparent is the silvering on a portion of the outside of the vessel. This silvering was used on all the glass vessels to provide a reflective background for periscope observation of their contents and to eliminate parallax in measurement of the contents.

A view of the installed glassware is shown in Figure 34. Clearly visible in the center are the separator tanks with the unsilvered surfaces facing the central viewing area. Other features shown are the casing flange, O-ring, vacuum casing, Super Insulation, and the guard chamber.

Figure 35 shows the copper radiation shield installed with the periscope enclosure in place. The periscope fits into the center tube, which is shielded by an evacuable annular space connected to the horizontal vessel. The guard chamber vent tube is in the lower right corner. The stirrer shaft extends up through the slush tank vent tube in the upper right corner. The remaining glass tubes in the figure are the valve access and vent tubes leading to the production vessels.

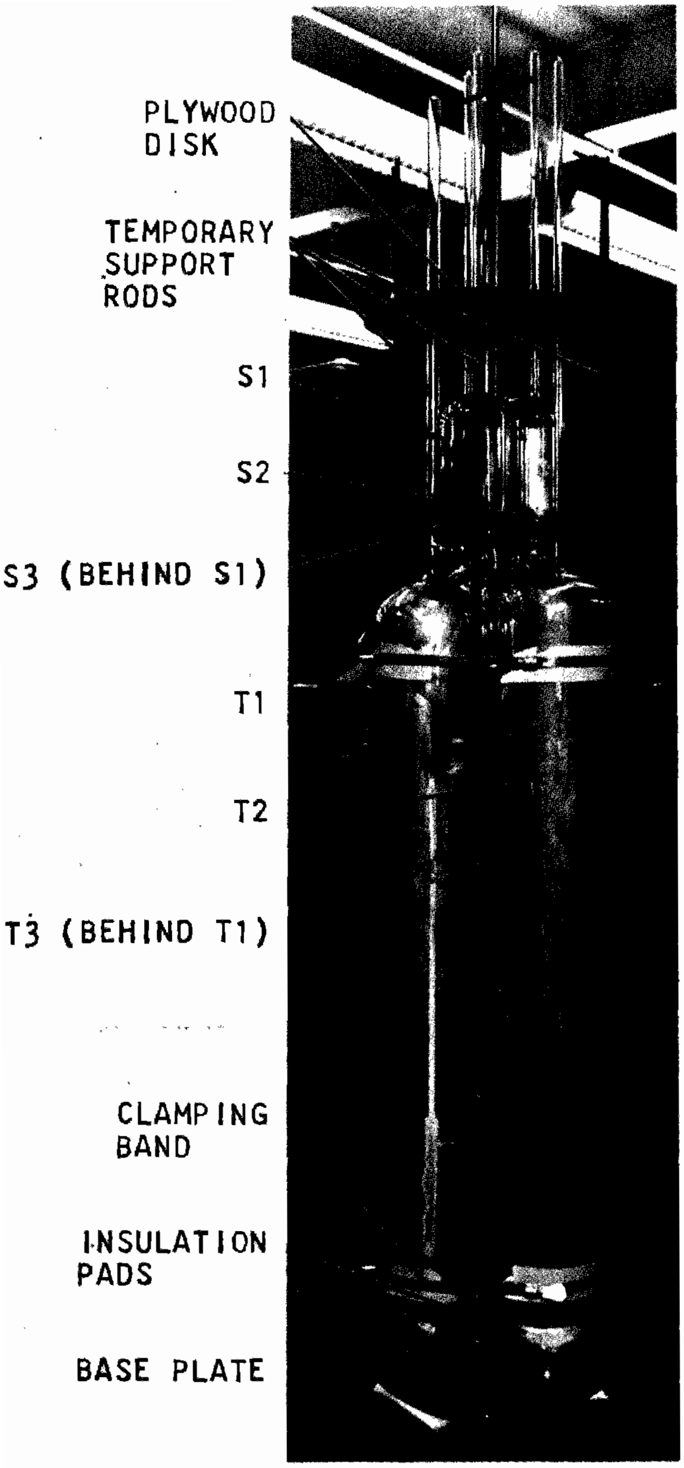

Figure. 31 Side View of Glass System

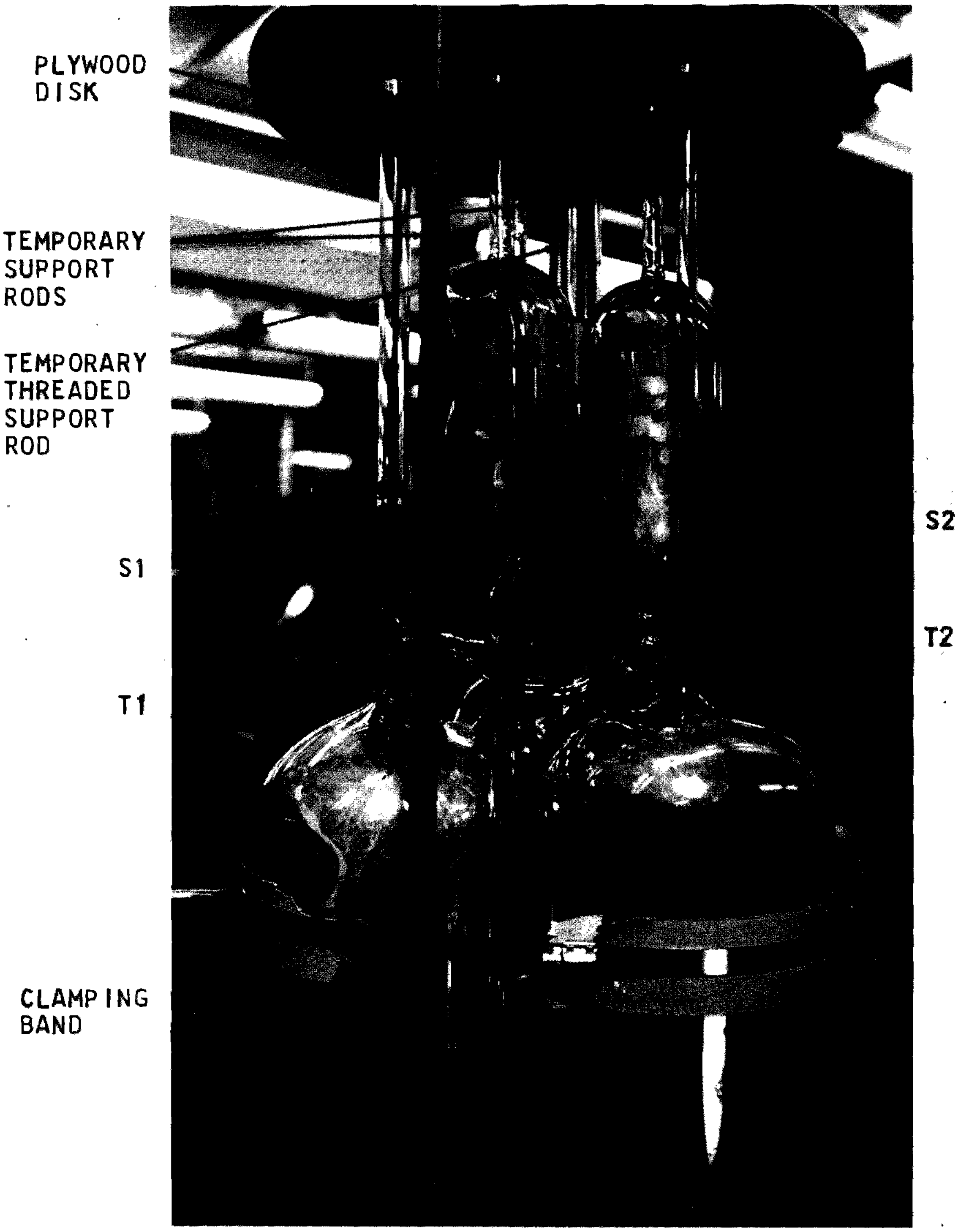

Figure. 32 Side View of Phase Separators

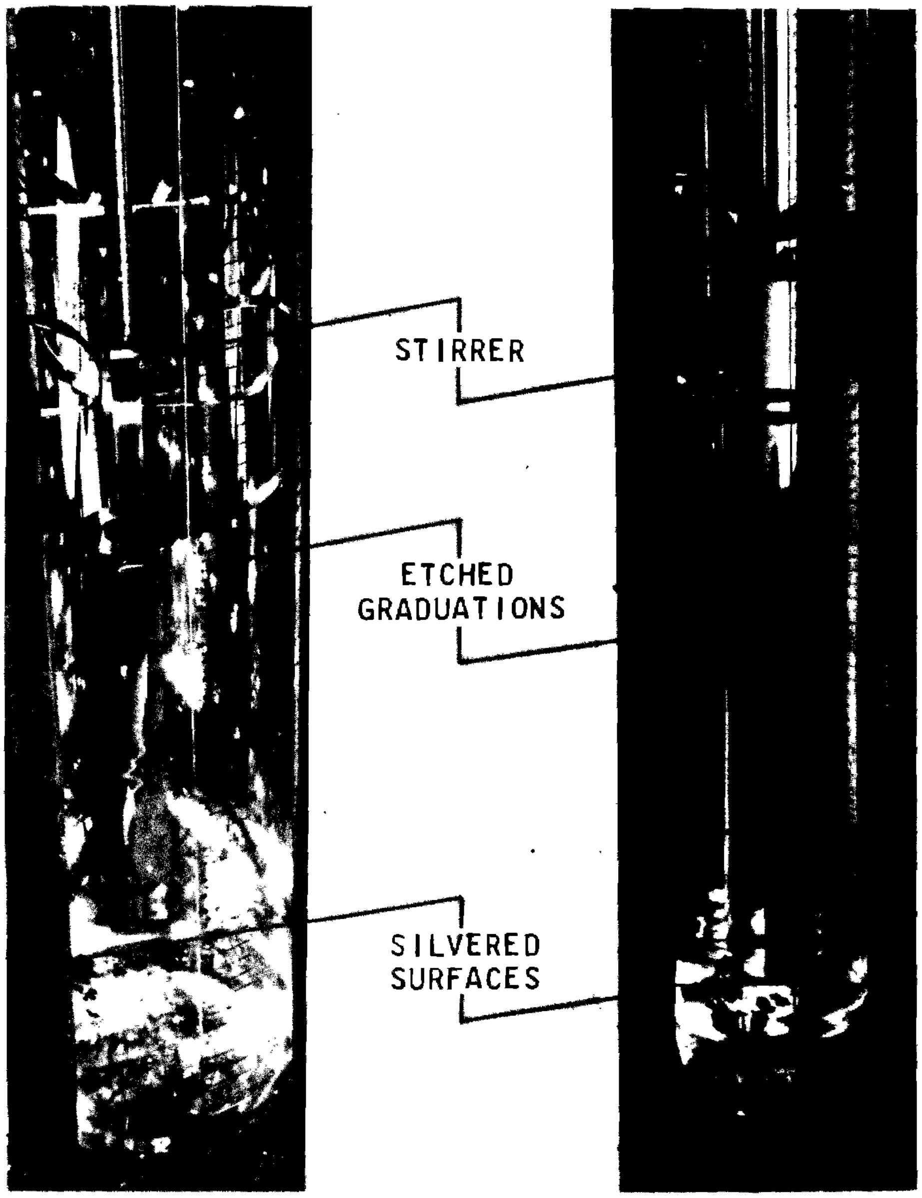

Figure 33. Glass Slush Tank T3 With Stirrer Inside

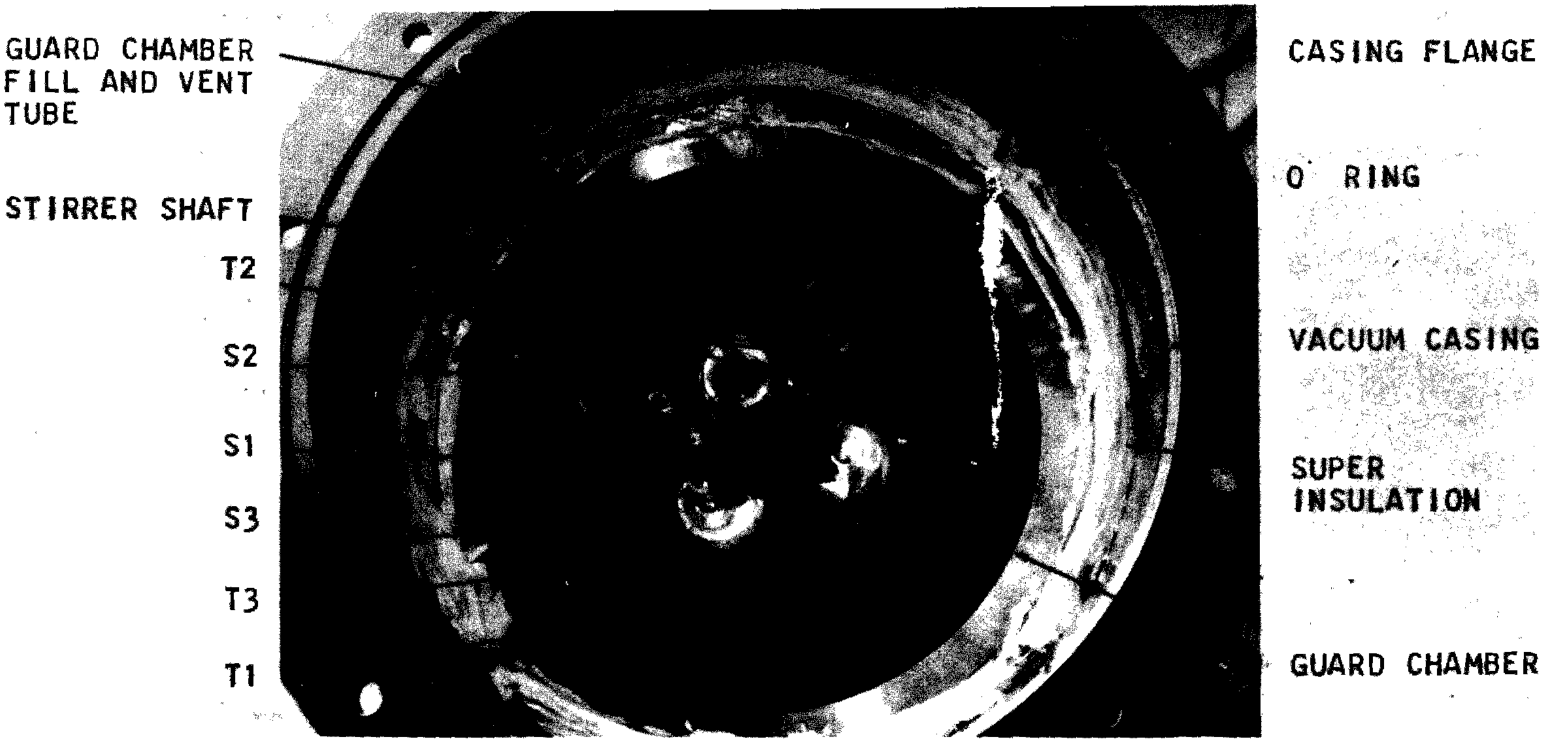

Figure 34. Top View of Glass System in Guard Chamber

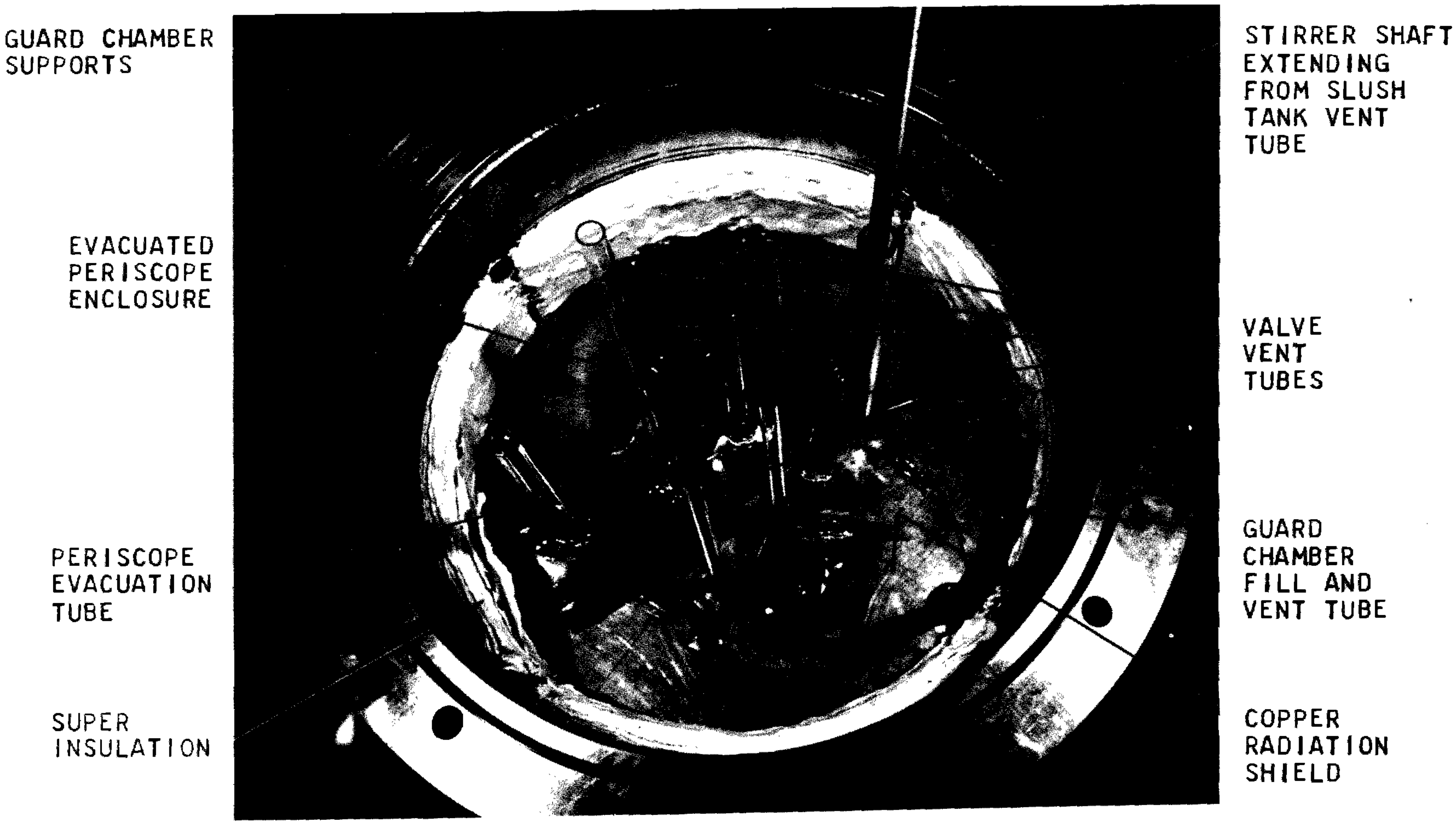

Figure 35. Top View with Radiation Shield in Place

Figure 36 shows the casing cover plate with feed throughs for the periscope, periscope evacuation tube, stirrer shaft guard chamber fill, and cold valves. Mounted on the cold valve feed throughs are brackets used to support the valve stem. Only the guard chamber fill feed through clearly shows the tee for connection to the exterior piping system. Also shown in this figure are the steam trace line and its asbestos mat cover.

5.1.2 Instrumentation Used to Obtain Data

Sufficient instrumentation was installed with the experimental apparatus to obtain the data necessary for comparing actual slush production with theoretical slush production. The parameters that required measurement were time, total gas volumes, relative gas flow rates, liquid levels, pressures, and temperatures. Visual observation of the vessel contents provided an important qualitative parameter.

5.1.2.1 Time The time intervals for various operations were determined by using a large face, synchronous, electric clock with a sweep second hand.

5.1.2.2 Total Gas Volumes The total gas volumes were measured by standard laboratory wet drum meters M1, M2 and M3. The meters were calibrated over a range of flow rates using a 5 cubic foot gas prover. All hydrogen gas being measured was passed through water bubbles to saturate the gas prior to entering the meters. Before entering the water bubbler for meter M3, the main vacuum pump exhaust gas was passed through an oil filter to prevent oil contamination of the meter. A check of system integrity was accomplished by blanking off the vacuum pump suction and observing the water bubbler and meter M3 for indications of gas flow. None was observed. As mentioned earlier in this section, safety was insured by venting all the meters directly to the stack.

5.1.2.3 Relative Gas Flow Rates Relative gas flow rates during vacuum pumping on various glass components were measured with variable area type flowmeters F1 through F4. No attempt was made to convert these gas flow rates into absolute units because of the very large corrections that would be required due to varying pressures and temperatures during the slush production. The meters were found to be more steady (less bouncing) when placed on the apparatus side of vacuum throttle valves V12 through V15 (warm hydrogen gas flow valves).

5.1.2.4 Liquid Levels Liquid Levels were measured by using a "Borescope" periscope viewing device that had been modified for cryogenic service. Built into the periscope was a light that was used to illuminate

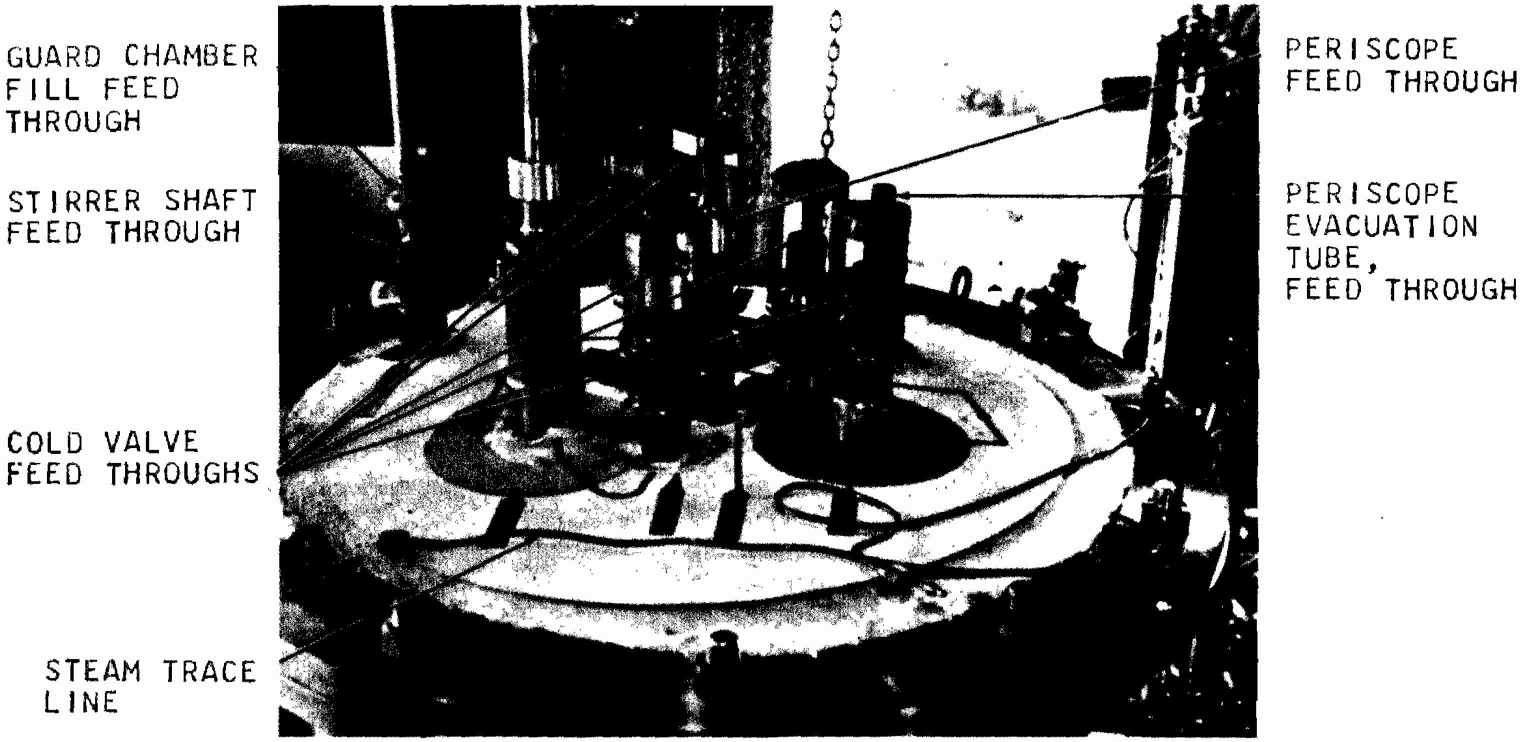

Figure 36. Casing Cover Plate Showing Feed Throughs and Steam Trace

the liquid level to be observed. The voltage to the lamp had to be kept low (15 volts) and constant to minimize heat leak to the production vessels. The low voltage resulted in a low illumination level that made photographing the vessel contents impossible. Thus, only simplified sketches of the observed phenomena were made.

To measure a level, the periscope was inserted into the test apparatus until the level was centered in the field of view. The distance from the apparatus cover plate to a reference mark near the periscope's eye piece was then measured with a meter stick to determine the height of the liquid above the zero mark on the glass tanks. The glass tanks were calibrated prior to apparatus assembly to determine the relationship between height of liquid and volume of liquid, and they were marked every 5 mm to determine liquid levels by direct observation. These marks were easily observed against a background of slush crust, but were difficult to see against a background of liquid hydrogen. As a result, the method utilizing the meter stick was consistently employed to improve accuracy.

5.1.2.5 Pressures The pressure in the glassware components was measured by pressure gauges P1 through P7 (glass mercury U tube manometers) which were mounted on an external panel. A meter stick was located between the legs of each manometer. One leg of each manometer was open to the atmosphere while the other was connected to a glassware component through the rubber vacuum hose (manifold piping) used for evacuating the glassware component (see Figure 29). During pumping, the absolute pressures indicated on the manometers were lower than the true pressure in the glassware by the value of the pressure drop in the manifold piping and in the flowmeters (F1 through F4). To obtain true pressures, all vacuum pumping was stopped momentarily. Atmospheric pressure was determined before and after a run by taking a pressure reading of the surge tank with the test apparatus valved off. Under these conditions the surge tank is normally maintained at approximately 7 microns; therefore, the pressure read on surge tank manometer (P7) is atmospheric pressure within the accuracy of the millimeter scale used.

The vacuum in the guard insulation space was measured with a tilting type McLeod gauge that had a measurement range of 0.01 to 5000 microns. This gauge was selected primarily because it is non-electric and would not cause any sparking in the laboratory. However, readings had to be taken manually since the gauge did not provide a continuous reading.

5.1.2.6 Temperatures Temperatures were measured at the locations shown on Figure 29 with copper-constantan thermocouples (TC1 through TC4) attached directly to the manifold piping. These temperatures were recorded on a 12-point temperature recorder. The temperatures at the total gas meters M1, M2 and M3 were measured with mercury-well-type thermometers, TM1, TM2, and TM3, specially designed for use with wet drum meters. This type of thermometer was used here to provide greater accuracy than could be produced with the termocouple and recorder combination. The greater accuracy was necessary at this point for computing the wet drum meter correction.

5.2 APPARATUS CHECK-OUT

The initial check-out and cooling runs of the test apparatus revealed some points of marginal design and some improper component performance. While none of the check-out problems proved insoluble they did require time, some minor apparatus changes, and some limitation on performance to achieve satisfactory operation.

The first difficulty with the apparatus occurred during assembly. The alignment of the O-ring seals in the cover plate and the extended glass tubes had to be very accurate to prevent breakage. This alignment proved difficult to achieve since the final glass blowing on the apparatus was not performed on site. Furthermore, the glassware blown on site for repairs could not be adequately annealed with the result that thermal cycling and very minor misalignment forces caused cracking due to the high internal strains. Extra careful attention to assembly and annealing, however, allowed the apparatus to be assembled and to withstand operational thermal cycles.

The principal difficulty encountered during check-out was leakage to the main insulation vacuum at the O-ring seals around the glass tubes passing through the main cover plate. These leaks were caused by excessive cooling of the O-rings by the cold hydrogen vapors vented through the glass tubes during periods of high hydrogen boiloff. Once leakage commenced the resulting insulation vacuum deterioration caused even greater hydrogen vaporization, and thus greater cooling of the O-rings which resulted in more leakage and rapid termination of the run. The installation of steam lines to keep the cover plate warm during high vaporization periods, combined with limiting the speed of hydrogen pumping, provided an adequate solution to the problem without extensive rebuilding.

A minor component failure occurred when the periscope light failed to operate at hydrogen temperatures. Though its construction and operation were carefully examined, it repeatedly failed at low temperature. The fault was attributed to the electrical contacts in the lamp circuit which opened due to thermal contraction. A simple reliable solution to the problem was achieved by supplying power to the lamp through a set of leads external to the periscope.

The Bureau of Mines Grade A helium used for apparatus pressurization introduced sufficient impurities into the cold apparatus to produce condensation on the glassware which obscurred observation. The installation of a liquid nitrogen cooled 5A Molecular Sieve trap in the helium supply line provided adequate clean-up of the impurities to prevent further difficulty from this source.

A review of the check-out problems associated with the O-ring seals indicated that these problems might have been eliminated if glass to metal joints had been made in the tubes leading from the glassware, with bellows in the metal tubes to take the strain of thermal cycling and misalignment. This type of construction had, however, been eliminated during the design because of the excessive delivery time of the glass to metal seals.

Another possible solution to the seal problem would be to use a larger diameter glass skirt around each of the tubes to which the O-ring seal would have been made. While solving the heat transfer problem, this construction might have intensified the thermal stress problem since the larger O-rings would have required larger compressive forces to make the vacuum seal. Nevertheless, this method or some functionally similar method which removes the O-ring seal from the cooled glass tubing is indicated on a requirement in glass systems which employ O-rings.

The apparatus difficulties, while overcome satisfactorily, produced a number of program delays which detracted from the experimental work. The difficulties serve to point up the fact that low temperature apparatus should be as simple as can be tolerated to perform the task and that with hybrid glass-metal apparatus it is particularly difficult to achieve a rugged design.

During apparatus check-out the glass-metal valves operated satisfactorily giving nearly dead tight closure when checked by vacuum pumping in the downstream side. Care had to be exercised in closing the valves to prevent pushing the valve plug through the glassware. During Run No. 10, to be discussed later, valve V1 was tightened too far and did crack the seat and exit tube from the bottom of tank T1.

5.3 QUALITATIVE DISCUSSION OF LARGE SCALE EXPERIMENTS

5.3.1 Run No. 1

This run was performed as an apparatus check-out. Tank T1 was filled with liquid hydrogen from a 150 liter capacity portable container. The liquid was then transferred into the separator train until separators S1 and S2 were filled. Cold valves V2 and V3 were closed, and a vacuum was slowly pulled on separator S2 until 52+ Torr was reached. During the vacuum pumping, the liquid hydrogen boiled violently. When the triple point was reached, droplets of liquid hydrogen which were splashed onto the glass wall of S2 by the violent boiling began to freeze. This solid hydrogen, quite translucent in appearance, was the first observed in the large scale test apparatus, and it provided an initial demonstration of the production ability of the apparatus. After a few minutes of observation, the heat created by the periscope light melted some of the solid that had formed near the area where the light was located. Soon after this observation the run was terminated.

During this run, a check showed that cold valves V1, V4, and V6 were not sealing tightly. Because of this, we decided to continue the experimentation in subsequent runs using the straight vacuum pumping technique until the cold valves could be modified to allow investigations of cascaded branched flow vacuum pumping and branched flow vacuum pumping.

5.3.2 Run No. 2

This run was performed as a check-out run with hydrogen slush being produced in storage tanks T1 and T2 by the straight vacuum pumping method. Liquid hydrogen was transferred from the portable storage container into storage tank T1. Since tanks T1 and T2 are interconnected, the liquid flowed from T1 to T2 until the liquid levels of both tanks were equal. All valves were then closed, and vacuum pumping was started on all the glassware. Because of small leakage in valve V4, some liquid was transferred from storage tank T2 to slush tank T3.

The solid first started to form in tanks T1 and T2 since they were pumped to a lower pressure than the rest of the glassware. Initially, the freezing liquid formed on the glass walls near the liquid level. Then, a solid crust formed on the liquid surface. The solid crust formation, which was white with semi-translucent particles, grew towards the bottom of the tank as more of the liquid became solid. During this run, approximately 14 liters of solid hydrogen were produced in the storage tanks while an additional 9 liters of liquid hydrogen remained in the slush tank.

5.3.3 Run No. 3

The purpose of this run was to again produce hydrogen slush by the straight vacuum pumping process and to investigate the ability of the stirrer to break the solid crust. The solid was produced in the slush tank where the stirrer was available for breaking and mixing the solid hydrogen. The production procedure involved filling the storage tanks with approximately 25 liters of saturated liquid hydrogen by removing valve V1 and inserting a vacuum-insulated transfer line from the portable storage container. When the fill was complete, the transfer line was removed, valve V1 replaced, and all valves closed. The liquid hydrogen was then transferred to the slush tank by opening valve V4 and pressurizing the storage tanks with gaseous helium. Valve V4 was then closed and vacuum pumping initiated on the slush tank.

With the stirrer in its highest position in the slush tank T3, the solids formed on the glass wall as in the first two runs. As the solid crust grew, it became white and opaque in appearance. Figure 37 is an artist's conception of a typical cross section of the crust formation. The tightly packed particle structure was completely bridged across the diameter of the tank and was supported by adhesion to the tank walls. The solid crust, which grew at the liquid-solid interface, was at the top surface of the boiling liquid. As the crust formed, the boiling liquid surface level moved downward in the tank.

The solid crust was allowed to grow to various thicknesses after which the stirrer was manipulated to see how effectively the crust could be broken. Crust thicknesses up to 8 cm could be broken easily by rotating and translating the stirrer. Crust thicknesses of approximately 14 cm could not be broken with the stirrer. While breaking crusts of various thicknesses, it was noted that a mass of solid hydrogen could be captured in the stirrer basket and raised above, or lowered into, the liquid. Upon withdrawal of the stainless steel stirrer blades from the liquid, the solid mass was observed to stick to the blades at the points of contact. Also, solid could be formed on the stirrer by lowering it into the liquid phase and then bringing it up into the low pressure gas phase. The solid thus formed looked like the initial solid formation on the wall of the slush tank. During manipulation, when the stirrer was forced into the crust, the crust appeared to pack readily.

5.3.4 Run No. 4

The objective of this run was to repeat the production and stirring procedures of Run No. 3 and to attempt a transfer of the solid produced. After the slush tank was filled by the same procedure used in Run No. 3, approximately two hours of vacuum pumping were required to produce the first solid formation. Crusts were then formed and broken with the stirrer, conforming the crust-breaking characteristics previously observed. During the course of this run, solids were produced with the stirrer above the liquid as in the previous runs as well as with the bottom of the stirrer positioned at the liquid surface. The crust produced while the stirrer was at the surface appeared to be "wet" and to be much softer than the crusts previously formed.

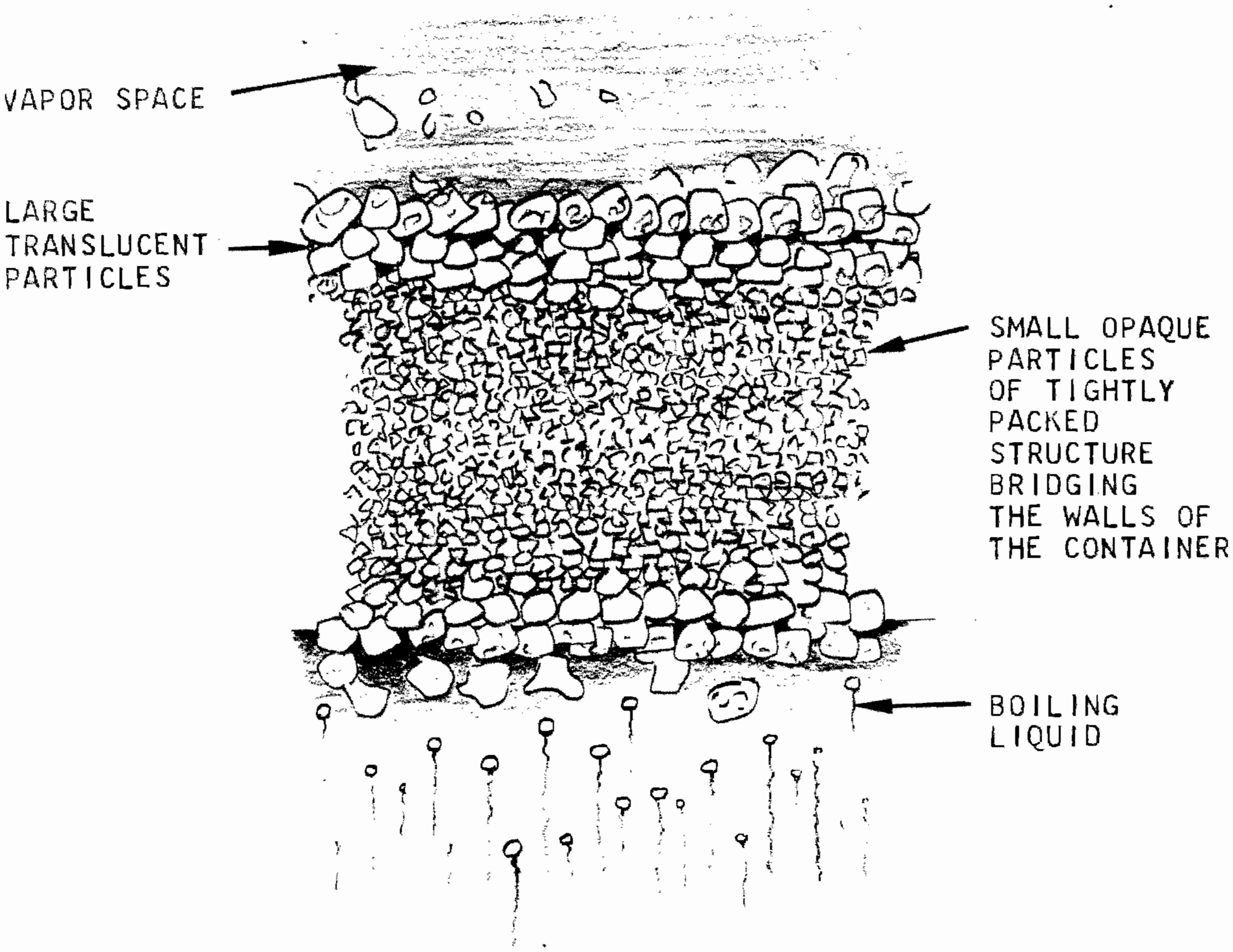

Figure 37. Typical Cross-Section of Crust Formation

When crusts of either variety were broken, solid particles could be seen dropping through the liquid. Some were quite small (less than a millimeter in diameter) while others were much larger (two to four millimeters) and were obviously unbroken sections of the crust. The first solids to drop through the liquid appeared to melt before they reached the bottom. This was probably due to a small temperature gradient in the liquid. Eventually, the solids reached the bottom of the slush tank, and a build-up of small particles could be seen (see Figure 38).

A transfer was made between slush tank T3 and separator S3 through valve V6. Valves V3, V4, and V5 were closed, and the slush tank was pressurized with helium gas while separator S3 was evacuated. Liquid hydrogen flowed through valve V6 (minimum opening diameter 0.20 inch), up the glass line, and into separator S3. It appeared that there may have been solid particles in the transferred liquid; however, the bulk of the transfer was liquid, leaving most or all of the solid behind.

5.3.5 Run No. 5

The purpose of this run was threefold: first, to gain additional straight vacuum pumping data, secondly, to determine the heat leak with the stirrer down, and thirdly, to investigate the transfer of settled slush in large scale apparatus. This run was conducted much like the fourth run with approximately three hours of pumping being required to reduce the pressure to 52+ Torr, thereby producing triple point liquid and the first solid formation.

The crust that formed on the liquid surface was broken with the stirrer each time it became 3 to 5 cm thick. The broken solids dropped to the bottom of slush tank T3 in the same manner as in Run No. 4 and started to accumulate. This layer of solids, referred to as settled slush (Figure 39) was distinguishable from liquid hydrogen since it was slightly opaque. No discrete particles could be seen in the settled slush. The top of the settled slush layer, which was not flat but rather irregular, was allowed to grow until its level coincided with that of the liquid hydrogen. The settled slush quality at that moment was calculated to be 30 percent. The stirrer was then inserted into the settled slush, which felt quite viscous and appeared to be packable.

Attempts to transfer the settled slush trough valve V4 (minimum opening diameter 0.20 inch) and into storage tanks T1 and T2 by reducing the pressure in the storage tanks to 22 Torr were unsuccessful. The pressure in the storage tanks was then increased with gaseous helium until helium was blown from storage tank T2 through valve V4 to slush tank T3 where it could

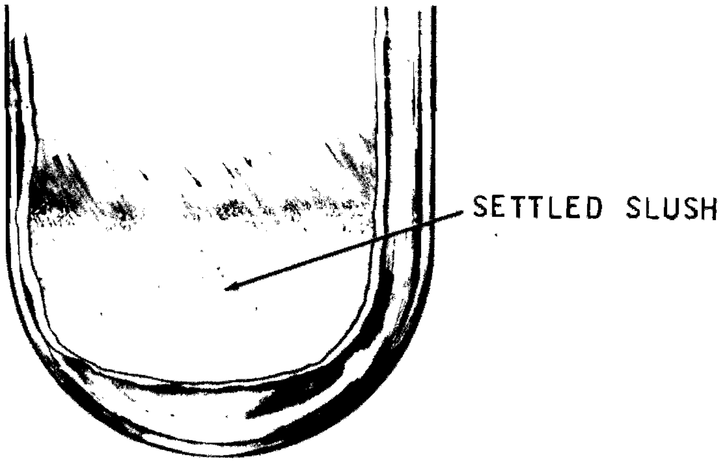

Figure 38. Buildup of Small Particles in Bottom of Slush Tank

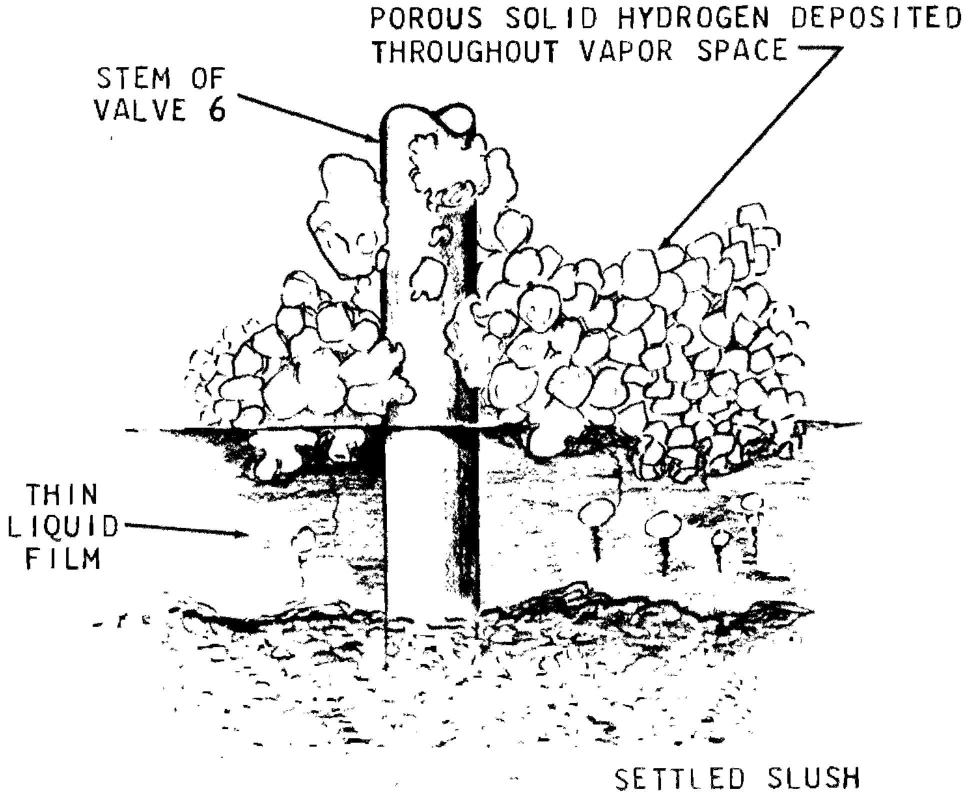

Figure 39. Typical Cross-Section of Settled Slush (Formation in Final Stages)

be seen bubbling up through the settled slush. The slush tank was then pressurized to 130 Torr and the storage tanks to 68 Torr. This caused a small amount of liquid to be transferred from the slush tank to the storage tanks. At the completion of this transfer, the solid hydrogen left behind in slush tank T3 was a completely white opaque solid.

5.3.6 Run No. 6

The object of this run was to produce hydrogen slush by melting the solid hydrogen produced by straight vacuum pumping. The run was initiated in a manner similar to the previous run. However, vacuum pumping was continued until the slush tank contents were essentially all solid. Pumping was then stopped, and the solid was allowed to melt. As melting progressed, the liquid level was observed to rise through the remaining solids. When the liquid level covered the remaining solid particles, the solid level appeared much flatter than it had appeared during formation in Run No. 5. Calculations showed the quality at this time to be 47 percent in comparison to only 30 percent in Run No. 5. A transfer of the hydrogen slush was not attempted during this run because the glassware became cloudy due to air leakage into the slush tank.

5.3.7 Run No. 7

This run was the first to utilize modified cascaded vacuum pumping, and it was conducted to investigate the possibility of expanding liquid hydrogen into a solid-vapor mixture having no liquid phase present by throttling liquid hydrogen from the separator train into the slush tank. (In the remainder of this discussion, the solid-vapor mixture will be referred to as snow.) The use of modified cascaded pumping for this run was made possible by partial correction of the valve leakage problem mentioned in the discussion of Run No. 1 on page 120. Run No. 7 is termed "modified" because all of the liquid flow from the separator train went to the top of the slush tank to produce solid. Normal cascaded vacuum pumping utilizes a split flow from the separator train with flow going to both the top and the bottom of the slush tank.

At the start of the run, the storage tanks contained approximately 24 liters of liquid hydrogen, and the slush tank was empty. All glassware valves were closed, and vacuum pumping was started on the slush tank. Valve V4, which connected the slush tank to the storage tanks, was found to be leaking slightly, allowing a small amount of liquid hydrogen to be transferred to the slush tank. This valve was tightened further, and the flow into the slush tank stopped. Pumping was continued on the slush tank, and a crust was formed on the small amount of liquid hydrogen that had leaked into the bottom of the tank. Vacuum pumping was started on the separators with the valves (V1, V2, V3, and V5) located between storage tank T1, the slush tank, and the separator train opened slightly. Liquid hydrogen then began to enter separator S1 in spurts. At this time partial vaporization of the liquid was noted. As cooldown of the separators occurred, a somewhat more steady liquid flow was accomplished through the separator train without the establishment of actual liquid levels in the separators.

The first liquid hydrogen entering the slush tank ran down the tank wall solidifying as it proceeded towards the bottom of the tank. Soon after, solid translucent stalactite type formations began to grow immediately below valve V5 (see Figure 40). Eventually, these formations bridged together into a larger mass of solid hydrogen. Some of the particles in this mass apparently had smooth surfaces as they reflected the light from the periscope. Liquid from separator S3 continued to run through the solid mass below valve V5 and down the slush tank wall. This liquid then solidified into particles which turned opaque and fell out of view, apparently to the bottom of the tank.

The mass of solid hydrogen which was formed just below valve V5 was cut loose with the stirrer. When this mass fell to the bottom of the tank, the flow of liquid coming into the tank appeared to increase. Apparently the build-up of solids below valve V5 had restricted the flow. Again the liquid ran into the tank, forming stalactites in the top of the tank. The glass wall near the bottom of the tank was covered by an opaque solid formation of small particles. Liquid continued to flow over the surface of this formation, and the opaque layer continued to build.

The mass of solid hydrogen again built up below valve V5 until a plug was formed that would not allow liquid to enter the tank. The stirrer was again moved to the top of the tank in an attempt to break the solid mass; however, the geometry of the stirrer blade was such that it would not allow a cutting action close enough to valve V5 to remove the accumulated solids. The stirrer was then lowered to the bottom of the tank where the observation was made that the solids previously cut loose did not seem to be packable.

When the plug formed in the slush tank, the liquid began to build up in separator S3. The liquid flow was shut off at storage tank T1, and separator S3 was vacuum pumped to approximately 85 Torr while the slush tank was maintained at 52 Torr. Valve V5, between separator S3 and the slush tank, was then opened wide in an attempt to flow this liquid into the slush tank. However, solids began to form above the valve, and a solid

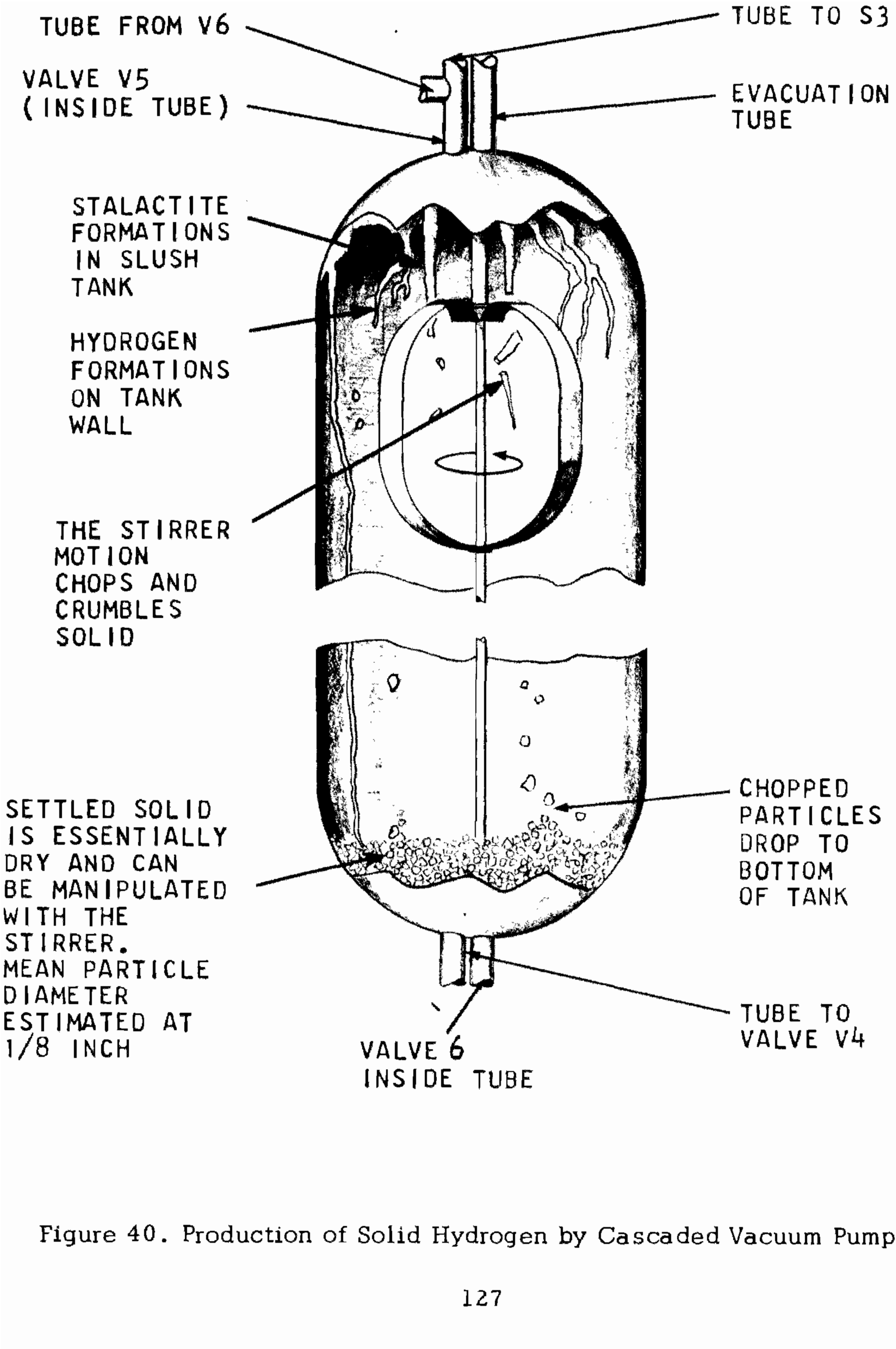

Figure 40. Production of Solid Hydrogen by Cascaded Vacuum Pumping

formation grew upward into separator S3 until all the liquid in the separator had turned to solid. This solid looked much like the crust previously produced in the straight vacuum pumping runs. The slush tank was backfilled with helium gas, and the solid plug below valve V5 melted and fell to the bottom of the tank.

The observations made during this run indicated that hydrogen snow could not be produced, at least in this particular apparatus, by throttling liquid hydrogen into a vessel evacuated to the triple point pressure. However it may be possible that by utilizing higher liquid hydrogen injection velocities than were possible with our test apparatus, or a somewhat different valve arrangement, hydrogen snow could be produced. For example, recent experiments performed by Brennan (10) with several different orifices and discharge pressures (velocities) resulted in the production of solid hydrogen having the appearance of "fluffy snow".

5.3.8 Run No. 8

The purpose of this run was threefold; first, to accurately determine the heat leak to the system during slush production with the stirrer up, secondly, to get additional data on straight vacuum pumping, and thirdly, to determine the evacuation requirements of the vapor space in the system tankage.

The heat leak was determined with approximately 15 liters of liquid hydrogen in the slush tank. The periscope was in place, and the light was shining on the slush tank. Two heat leak determinations were made; one with the slush tank maintained at approximately 380 Torr and the other with the slush tank maintained just above the triple point pressure (52+ Torr).

The heat leak determination procedure called for the evacuation of the slush tank until the desired pressure was reached and then the reduction of the pumping rate until this pressure was just maintained. The heat leak at this pressure was then determined by the amount of gas pumped to maintain equilibrium.

At the conclusion of the heat leak runs, pumping was increased on the slush tank until a crust started to form on the liquid hydrogen. This permitted experimental verification of the calculation of the specific mass requirement (SMR) for producing triple point liquid by straight vacuum pumping (see page 6).

5.3.9 Run No. 9

This run was performed to investigate the production of hydrogen slush by the semiflow vacuum pumping method. To produce slush by this method, all glassware valves were closed and the empty slush tank was evacuated to 52+ Torr. Valve V4 was then opened slightly, and liquid was allowed to slowly flow into slush tank T3. Vacuum pumping on the slush tank was adjusted so that the tank would fill with triple point liquid. When the pumping was a little too fast, solids appeared in the form of freezing particles on the tank walls at the liquid level. These solids melted when the pumping rate was reduced. Valve V4 was closed when approximately 7 liters of triple point hydrogen was in the slush tank. Pumping was continued and a crust immediately formed. The crust formed by this method was very level as compared to straight vacuum pumping crust, and it appeared that the hydrogen gas bubbles had difficulty getting through the crust to be pumped away. The crust was allowed to grow to a thickness of 9 cm and then was easily broken with the stirrer.

The boiling in the slush tank was more violent in this run than in any of the previous runs. Hydrogen droplets were splashed high into the tank where some froze and stuck to the wall.

5.3.10 Run No. 10

This run was scheduled to further investigate the modified cascaded vacuum pumping system, and it was conducted similar to Run No. 7. The first liquid into the slush tank formed stalactites growing from the tank wall. These formations grew quite long with the diameter changing very little. Instead, all the solid was formed at the tip of each formation as it grew. These stalactites, which were translucent, appeared to be quite hard (see Figure 40).

During the stalactite growth time, some liquid hydrogen was running down the tank wall and freezing. As this liquid froze it became somewhat opaque; however, liquid could still be seen running between the opaque solid formation and the glass tank wall. The stirrer was then brought down, wiping the walls very clean. No solids were left sticking to either the walls or the stirrer. As the solids accumulated in the bottom of the slush tank, they felt very crumbly when agitated with the stirrer. These solids, which were irregular in size (1 to 2 mm), could be pushed around the bottom of the slush tank with the stirrer without any evidence of their sticking together or sticking to the tank or stirrer (see Figure 40).

During the formation of the solid, it was necessary to use the stirrer to break loose the solids accumulating below valve V5. When approximately 7 liters of solids were present in the slush tank, the pumping was stopped and the solids in the top of the slush tank melted and fell to the bottom of the tank. A liquid level then appeared in the bottom of the slush tank that coincided with the level of these solids. This mixture looked like settled slush; however, this time definite solid particles could be seen suspended in triple point liquid. The solid particles were homogenous in the liquid when stirred, but when the stirring was stopped, the solids immediately settled to a very flat layer below the liquid level. When the stirrer was in the settled slush, no sticking of the solids to the stirrer was noted. The solid particles in the settled slush were not uniform in size; they looked like oblate spheroids (see Figure 41) and were not needle-like as were the particles observed in the small scale experimental apparatus.

At this point we decided to attempt a transfer of the settled slush in the slush tank to the storage tanks. Slush tank T3 was pressurized with helium gas to a slightly positive pressure, and storage tanks T1 and T2 were evacuated. Valve V4, located between the storage tanks and the slush tank was then suddenly opened. The pressure quickly equalized, and a liquid level was noted in the storage tanks. This liquid looked like it may have had some small particles in it. However, because of periscope resolution limitations, the presence of these solid particles could not be positively verified. The slush tank had no solids left in it, and the liquid hydrogen could be clearly seen. While it cannot be said with certainty that solids were transferred, it is assumed that the solids were transferred and then melted in the relatively warm storage tank. During an attempt to remove liquid from separator S1, valve V1 was tightened excessively, causing glass breakage which resulted in termination of the experimental work. Figure 42 shows the glass breakage.

5.4 QUANTITATIVE ANALYSIS OF LARGE SCALE EXPERIMENTS

5.4.1 Production of Triple Point Liquid

5.4.1.1 Pumping for Heat Leak with Stirrer Up The major source of heat leak into the production apparatus was the light on the periscope. The next largest sources were the heat transports down both the periscope and stirrer shafts from the top cover plate. Since these heat inputs were essentially independent of the low end temperature variation between 13.8°K and 20.3°K, the assumption was made that the heat leak was at a constant rate. The heat leak with the stirrer at its uppermost position was determined experimentally during Run No. 8 by adjusting the pumping rate to hold the liquid hydrogen at a constant pressure (about midway to the triple point) for a period of twenty minutes. The measured pumping rate for this run was determined as follows:

$$\text{Measured pumping rate for Run No. 8} = \frac{4.1179 \text{ ft.}^3 \text{ NTP pumped}}{20 \text{ minutes}}$$

$$= 0.205895 \text{ ft.}^3 \text{ NTP pumped per minute}$$

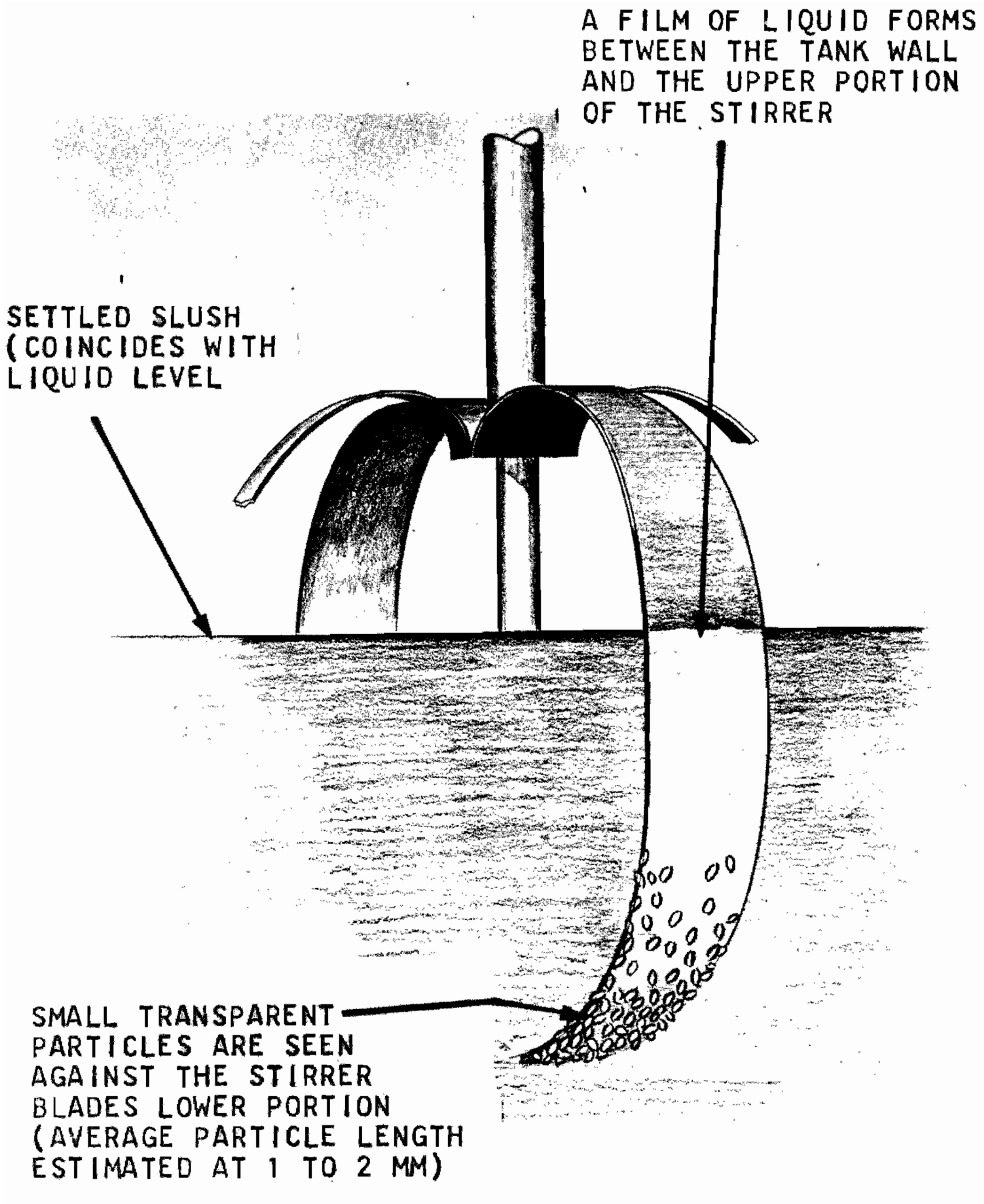

Figure 41. Typical View of Settled Slush Produced by Melting Settled Solid Hydrogen

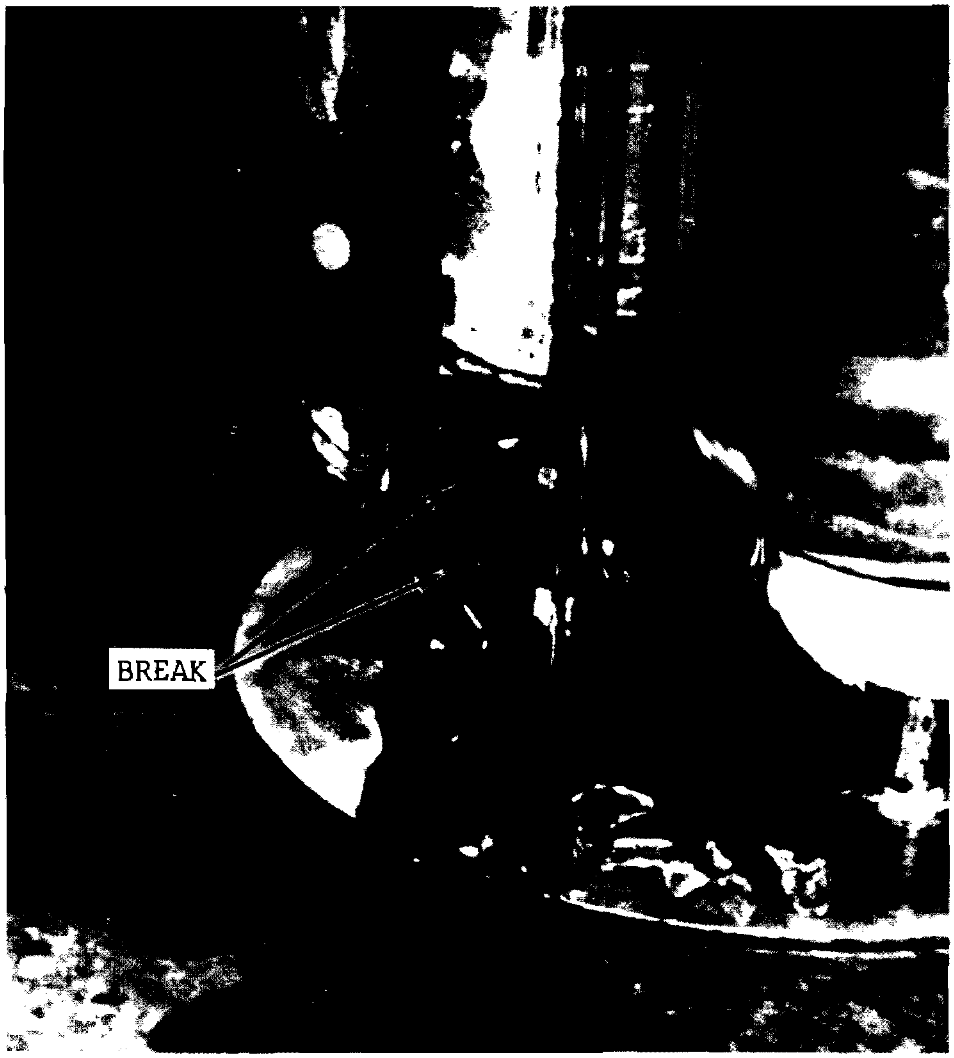

Figure 42. Glass Breakage

Attempts to use this pumping rate directly for estimating heat leak gave poor correlation of the data. As a result, a short theoretical investigation of the effects of heat leak was undertaken to determine the cause of error.

The vacuum pump, in addition to pumping to produce triple point liquid, must also pump to overcome the heat leak into the production apparatus. Furthermore, the heat leak which occurs after the production run has started boils liquid which has previously been pumped down to the triple point. Because of this, the overall effect of heat leak is greater by the magnitude of the specific mass requirement (SMR) at the level at which the heat leak occurs. For example, during a straight vacuum pumping run heat leak at the triple point boiled liquid which had previously been produced by pumping 0.1227 pound away for each pound present. As a result, the total pumping required throughout the run was 12.27 percent greater than was expected.

To avoid the considerable effort involved in determining the effect of heat leak for each run by a series of small steps, an easier method was sought. Inspection of Run No. 8 showed that approximately the same number of minutes of pumping was required for each degree Kelvin reduction in temperature. Consequently, we assumed that the use of equal temperature steps for averaging would approximate the use of equal time steps.

The effective heat leak capacity was determined by dividing the latent heat at each temperature from Mullins, Ziegler, and Kirk (1) by the specific mass requirement calculated in Section 3 for that temperature and then averaging by dividing this sum by the number of temperature intervals. Decimal fractions were used to weight the portions of a full degree at the ends.

$$\begin{array}{l}\text{Straight vacuum pumping} \\ \text{effective heat leak capacity}\end{array} = \Delta T \times \frac{\text{latent heat per temperature step}}{\text{SMR for the step}} \Big/ \Delta T \text{ increment}$$

$$\frac{0.278\,\frac{214.8}{1.0} + \frac{215.38}{1.00601} + \frac{217.03}{1.0267121} + \frac{218.05}{1.0466208} + \frac{218.5}{1.0656564} + \frac{218.44}{1.0840814}}{0.278+1+1+1+1+1+1+1+0.187}$$

$$+ \frac{\frac{217.93}{1.1019347} + \frac{217.07}{1.1193899} + (0.187)\,\frac{216.87}{1.1226949}}{0.278+1+1+1+1+1+1+1+0.187}$$

$$= 204.6718 \text{ cal./mole}$$

The effective heat leak for straight vacuum pumping with the stirrer up was found by multiplying the measured heat leak by the ratio of the latent heat during the measurement to the effective heat leak capacity.

Straight vacuum pumping effective heat leak with stirrer up

$$= \frac{.205895\ \text{ft.}^3\ \text{NTP/min. at } 217.7651\ \text{cal/mole}}{204.6718\ \text{cal./mole effective heat capacity}}$$

$$= 0.2190664\ \text{ft.}^3\ \text{NTP/min.}$$

This gave an effective heat leak of 0.2191 ft.^{3} NTP per minute, which is 6.4 percent higher than had been previously assumed.

The effective heat leak for other conditions was found in a similar manner. For semiflow vacuum pumping the effective heat leak capacity is the refrigeration available starting with atmospheric pressure liquid and ending with triple point vapor. Because the effect of the actual starting pressure is large, the effective heat leak was calculated for the actual starting conditions in the applicable runs.

$$\text{Semiflow vacuum pumping effective heat leak with stirrer up} = \frac{\text{measured heat leak times heat capacity at measured point}}{\text{enthalpy of triple point vapor} - \text{enthalpy of saturated liquid}}$$

$$= \frac{(0.205895)(217.7651)}{250.0 - 58.92}$$

$$= 0.234649\ \text{ft.}^3\ \text{NTP/min.}$$

This calculation is for a starting pressure of 760 Torr.

5.4.1.2 Pumping to Evacuate System The vapor space of the slush production system must be evacuated in order to pump down the liquid. Attempts to theoretically calculate the pumping required were unsuccessful. The data available indicated that the actual evacuation required much less pumping than the theoretically calculated mass requirement at a specified pressure level. A short theoretical investigation was undertaken to find the source of the difficulty. It was found that the isentropic removal of vapor produced a significant amount of refrigeration, thus substituting for a portion of the other pumping requirements. The remainder of the difference is assumed to be attributable to stratification of the vapor phase with only the portion of the vapor immediately above the liquid near the saturation temperature. This assumption agrees with the known tendency of hydrogen to stratify, with the fact that most of the heat leak was directed into the top of the apparatus, and with the observation that the evacuation pumping requirement was relatively independent of liquid level. Because of these considerations, it was decided to determine the evacuation requirement experimentally. Run No. 8 was used to determine the evacuation requirement because its heat leak was the most accurately known. The evacuation requirement was assumed to be the remainder of the pumping after heat leak and specific mass requirement were subtracted from the total pumping.

$$\begin{aligned}\text{Evacuation requirement for Run No. 8} &= \text{volume pumped} - \text{volume heat leak} - \text{volume for SMR}\\ &= 100.0045 - 46.0770 - 51.4657\\ &= 2.4618 \text{ ft.}^3 \text{ NTP}\end{aligned}$$

The effective evacuation requirement per Torr for the actual starting pressure was found to be 0.00354 ft.^{3} NTP per Torr.

$$\begin{aligned}\text{Effective evacuation requirement} &= \frac{2.4618}{748 \text{ Torr (Start)} - 52.89 \text{ Torr (Finish)}}\\ &= 0.0035416 \text{ ft.}^3 \text{ NTP/Torr}\end{aligned}$$

The evacuation requirement for other runs was found by multiplying the requirement per Torr times the actual pump down in Torr. A sample is given in the calculation below for Run No. 5. For the runs in which only the slush tank was evacuated, the evacuation requirement was arbitrarily assumed to be one-fourth as much as when the entire apparatus was evacuated. The calculated pumping to evacuate the system is shown for each run in Table 16.

$$\begin{aligned}\text{Evacuation requirement for Run No. 5} &= (0.0035416)(749.5 - 52.89)\\ &= 2.4671 \text{ ft.}^3 \text{ NTP}\end{aligned}$$

5.4.1.3 Pumping for Heat Leak with Stirrer Down Many of the runs had apparent heat leaks that were higher than what was measured during Run No. 8. Inspection of the data books revealed that the stirrer was in its most downward position during those runs, while it was in its most upward position during Run No. 8. It was assumed, therefore, that the higher heat leak was due to stirrer position, and the pumping for heat leak in that condition was

TABLE 16

QUANTITATIVE ANALYSIS OF LARGE SCALE EXPERIMENTS

Production of Triple Point Liquid
From Atmospheric Liquid

Run Number		1	2	3	4	5	6	7	8	9	10
Type of Run	Straight Vacuum Pumping %	X	X	100	86.96	100	100	--	100	0	0
	Semi Flow Vacuum Pumping %	--	--	0	13.04	0	0	--	0	100	0
	Cascaded Vacuum Pumping %	--	--	0	0	0	0	X	0	0	100
Starting Pressure - Torr		Atm	750	760	763	749.5	744.5	755.5	748	757.5	765
Theoretical Specific Pumping Requirement		0.123	0.122	0.1227	.124646	0.1215	0.1210	0.1222	0.1214	0.1346	0.2748
Experimental Specific Pumping Requirement		--	0.130	0.1231	.124649	0.1215	0.1207	0.1208	0.1214	0.1373	0.2734
Experimental Error %		--	+6.6	+0.33	0.0024	0	-0.25	-1.1	0	+2.0	-0.51
Quantity of 0% Slush Produced	Liters	2	17.09	15.29	13.51	20.80	15.08	1.25	13.01	5.88	--
	Ft^3 NTP	65	557.2	498.52	440.64	678.17	491.83	40.76	424.10	191.67	100.26
Vented to Atmosphere	Ft^3 NTP	0	0	4.13	8.76	0	2.17	13.21	0	--	0.86
Total Pumping Metered	Ft^3 NTP	29	--	138.45	84.34	140.14	103.32	13.15	100.00	--	39.39
Pumping for Heat Leak	Ft^3 NTP	15	23.4	78.69	37.55	55.27	40.25	20.82	46.08	14.07	12.84
Pumping to Evacuate System	Ft^3 NTP	1	2.5	2.50	0.63	2.47	2.45	0.63	2.46	0	0
Helium Pressurizing Gas Pumped	Ft^3 NTP	3	3	0	0	0	3.4	0	0	0	0
Pumping to Produce 0% Slush	Ft^3 NTP	10	72.6	61.39	54.92	82.40	59.39	4.91	51.46	26.32	27.41
Stirrer Position		Down	Down	Down	Down	Down	Down	Up	Up	Up	Down
Heat Leak Rate	Ft^3 NTP/Min	0.30	0.30	0.3004	0.3004	0.3004	0.3004	0.2191	0.2191	0.2346	0.3210
Duration of Run	Minutes	50	78	262	125	184	134	95	210.3	60	40

Production of Settled Slush and Solid Hydrogen
From Triple Point Liquid

Type of Run		--	Pump	Pump	Pump	Pump	Melt	Pump	--	--	Melt
Settled Slush Quality	% Solid	0	--	--	26.20	29.81	47.14	--	0	0	51.09
Quantity	Liters	None	--	--	5.860	14.437	7.128	--	None	None	5.215
	Ft^3 NTP		--	--	196.81	486.81	245.38	--			180.26
Density	Ft^3 NTP/Liter		--	--	33.58	33.72	34.42	--			34.565
Liquid Above Settled Slush	Liters		--	--	6.386	0.0	3.596	--			0.0
	Ft^3 NTP		--	--	208.21	0.0	117.26	--			0.0
Solid in Vapor Space	Liters		5	8.620	0.770	3.353	0.0	6.807			0.0
	Ft^3 NTP		190	316.13	28.22	122.97	0.0	249.63			0.0
Total Hydrogen in Slush Tank	Ft^3 NTP				433.24	609.78					180.26
Stirrer Position			Down	Down	Down	Down	Up	Down			Down
Heat Leak Rate	Ft^3 NTP/Min		0.2835	0.2835	0.2835	0.2835	0.2067	0.3210			
Duration of Run	Minutes	0	40	114	44	119	105	259	0	0	201
Pumping for Heat Leak	Ft^3 NTP		11	32.32	12.47	33.73	21.70	83.13			
Total Pumping Metered	Ft^3 NTP		36	73.17	21.99	68.38	36.66	131.83			
Vented to Atmosphere	Ft^3 NTP		0	0	2.77	0	0	19.62			
Pumping to Make Solid	Ft^3 NTP		25	40.85	10.31	34.65	14.96	68.32			
Solid Plus Settled Slush	Ft^3 NTP				225.03	609.78	245.38				--
Experimental Specific Pumping Requirement					0.0458	0.0568	0.0609				
Theoretical Specific Requirement for 100% Solid			0.1292	0.1292	0.1292	0.1292	0.1292	0.2737			
Solid Fraction %					35.46	43.97	47.14				
Total Solid Produced	Ft^3 NTP				79.79	268.13					
Liquid in Settled Slush	Ft^3 NTP				145.24	341.65		0.0			
	Liters				4.454	10.478					
Solid in Settled Slush	Liters				1.406	3.958					
	Ft^3 NTP				51.57	145.16					

determined from Run No. 5 by subtracting the evacuation pumping requirements and pumping for SMR from the total pumping.

$$\begin{array}{l} \text{Straight vacuum pumping effective} \\ \text{heat leak with stirrer down} \end{array} = \frac{140.1447 \text{ ft.}^3 \text{ NTP total pumping} - 2.4671 \text{ ft.}^3 \text{ NTP pump out}}{184 \text{ minutes}} - \frac{82.4112 \text{ ft.}^3 \text{ NTP for SMR}}{184 \text{ minutes}}$$

$$= 0.300361 \text{ ft.}^3 \text{ NTP/minute}$$

The effective heat leak for straight vacuum pumping with the stirrer down is 0.3004 ft.^{3} NTP/min. Table 16 describes the stirrer position, heat leak rate, and run duration for each run, as well as the calculated pumping for heat leak which is the product of the rate and the duration.

5.4.1.4 Venting to Atmosphere All gas from the tanks not being vacuum pumped during each run was vented to the atmosphere and metered to permit its inclusion in the calculations. This gas represented the portion of the system heat leak which was taken at atmospheric pressure, and it was subtracted from the calculated pumping for heat leak. The gas vented to the atmosphere is shown for each run in Table 16 .

5.4.1.5 Helium Pressurizing Gas Helium gas was used in Runs 1, 2, and 6 for pressure transfer of liquid hydrogen from one part of the apparatus to another. The quantity of gas used during each transfer was determined by recording the change in pressure of the high pressure helium supply cylinder and consulting a supply cylinder calibration chart. The helium gas used was assumed to be pumped or vented to the atmosphere along with the hydrogen gas, and it was subtracted from the total metered gas to determine the total hydrogen gas metered. That the helium gas did not have a greater effect is probably due to stratification in the apparatus. The helium pressurizing gas used for each run is shown in Table 16 .

5.4.1.6 Total Pumping Metered The exhaust of the vacuum pump was metered and the readings corrected to NTP (70°F and 760 Torr, dry basis) using the perfect gas laws. The partial pressure of the water vapor in the meter was taken from the tables by Keenan and Keyes (11). The local barometric pressure was obtained from the surge tank manometer when there was no flow through the vacuum pump. The vacuum pump blank-off pressure had been previously checked to be approximately 7 microns. The corrected meter readings are shown for each run in Table 16.

Corrected total pumping metered for heat leak in Run No. 8

$$= \text{(meter correction)} \left(\frac{\text{Barometric pressure - water vapor pressure}}{\text{standard pressure}}\right)$$

$$\times \left(\frac{\text{standard temperature}}{\text{test temperature}}\right) \text{(meter start - meter finish)}$$

$$= 1.0440 \times \frac{744 \text{ Torr} - 19.426 \text{ Torr}}{760 \text{ Torr}} \times \frac{530 \text{ Rankine}}{531 \text{ Rankine}} \times 422.810 - 418.665$$

$$= 4.1179 \text{ ft.}^3 \text{ NTP.}$$

5.4.1.7 Pumping to Produce Triple Point Liquid The pumping to produce triple point liquid is the algebraic sum of the gas quantities: total pumping metered; plus gas vented to atmosphere, minus pumping for heat leak minus pumping to evacuate the system, minus helium pressurizing gas pumped. These quantities are presented in Table 16.

5.4.1.8 Quantity of Triple Point Liquid Produced The quantity of triple point liquid produced was determined by visually gauging the various tanks and referring to the tank calibration. When the "zero" level mark was observed in the center of the field of view of the periscope, a reference mark on the periscope eyepiece was found to be 29.7 cm above the top surface of the top flange of the guard chamber. A meter stick was used to gauge the tanks by centering the liquid level in the field of view and measuring to the reference mark.

During assembly of the apparatus, the tanks were calibrated with water. The slush tank, for example, contained 1.25 liters of water at the zero mark and 23.15 liters at the 95, or full, mark. The best fit with the calibration gave the following expression for the slush and storage tank contents:

Slush tank contents (liters) = (meter stick reading cm - 24.278) (0.23053)

Storage tank contents (liters) = (meter stick reading cm - 25.145) (0.23053)

The total quantity of triple point liquid produced is listed in Table for each run in both liters and in ft.^3 NTP. The content per liter of triple point liquid is given as 32.60602 ft.^3 NTP. For example:

Volume of liquid in slush tank at triple point in Run No. 4 = (82.9-24.278) (0.23053) = 13.514 liters

Where 82.9 cm was the meter stick reading

$$\text{Quantity of triple point liquid in Run No. 4} = (13.514 \text{ liters})(32.6060 \text{ ft.}^3 \text{ NTP/liters})$$

$$= 440.641 \text{ ft.}^3 \text{ NTP}$$

5.4.1.9 Experimental Specific Pumping Requirement The experimental specific pumping requirement is the ratio of the pumping required to produce triple point liquid to the quantity of triple point liquid produced, and it is listed for each run in Table 15 .

$$\text{Experimental specific pumping requirement for Run No. 4} = \frac{54.924 \text{ ft.}^3 \text{ NTP pumped}}{440.641 \text{ ft.}^3 \text{ NTP produced}}$$

$$= 0.124646$$

5.4.1.10 Theoretical Specific Pumping Requirement The theoretical specific pumping requirement is the specific mass requirement (SMR) minus 1. The specific mass requirement was calculated for the actual starting pressure of each run, in the same manner as in Section 3. The properties were obtained by interpolating the tables from Mullens, Ziegler, and Kirk (1).

$$\text{Theoretical specific pumping requirement for Run. No. 5} = \frac{\frac{14.6146 + 14.7080}{2} - 3.939}{\frac{14.6146 + 14.7080}{2} - 3.9919} [1.1159876] - 1$$

$$= 0.1215208$$

The starting pressure, type of run, and theoretical specific pumping requirements are tabulated for each run in Table 16 .

In Run No. 4, the calculation of the theoretical specific pumping requirement was complicated by leakage through valve V4 during the run. Gauging of the storage tank at the beginning and end of the run gave the portion of the starting liquid which had leaked through valve 4. The first liquid leaked while the slush tank was at atmospheric pressure and was pure straight vacuum pumping; the last liquid leaked while the slush tank was at the triple point and was pure semiflow vacuum pumping. Therefore, the effect of the leaked liquid was assumed to be as if half of it had been pure semiflow and half straight vacuum pumping. The theoretical specific pumping requirement was obtained by weighing the theoretical pumping requirements by the fraction produced each way. Because the experimental data gave the fraction of starting liquid, it was necessary to use the reciprocals of the specific mass requirements to determine the split in terms of triple point liquid produced.

$$\text{Theoretical specific pumping requirement for Run No. 4} = \frac{1}{\frac{0.26176}{2}\;\frac{1}{1.123045} + \frac{0.26176}{2}\;\frac{1}{1.135332}} -$$

$$= 0.124649$$

The split reported in Table 16 is for the fractions of the triple point liquid produced each way.

5.4.1.11 Experimental Error The experimental error is the ratio of the experimental specific pumping requirement to the theoretical specific pumping requirement minus 1. Thus, for Run No. 4, the experimental error is

$$\frac{0.124646}{0.124649} - 1 = -0.0000241$$

$$\text{or } -0.0024\%$$

The experimental error for each run is shown in Table 16 .

5.4.2 Comparison of Experimental Results and Theoretical Calculations

5.4.2.1 Run No. 1 The primary purpose of this run was to check-out the apparatus. The small quantity of zero percent slush produced in the phase separators could not be accurately gauged. No correlation between theoretical and experimental valves could be obtained.

5.4.2.2 Run No. 2 The primary purpose of Run No. 2 was also check-out. The reported time of reaching the triple point was assumed to be considerably late and, therefore, the correlation is poor with an approximate experimental error of 6.6 percent.

5.4.2.3 Run No. 3 An excellent experimental agreement with the theoretical pumping requirement was obtained during this run with an error of only .33 percent.

5.4.2.4 Run No. 4 In Run No. 4, only the slush tank was evacuated. Leakage through valve V4 during the run gave part straight vacuum pumping and part semiflow vacuum pumping. Despite the complexity introduced by the leakage, an excellent correlation was obtained with an experimental error of only .0024 percent.

5.4.2.5 Run No. 5 The experimental error for Run No. 5 is zero by definition because this run was used to determine the heat leak with the stirrer down. Since Runs No. 3, 4, 6, and 10, which were also used to determine heat leak with the stirrer down, had excellent experimental correlation, it is assumed that an excellent correlation was achieved for Run No. 5.

5.4.2.6 Run No. 6 During Run No. 6 there was a large air leak into the vacuum pumping system. The tare pumping rate to overcome this leak was metered after the run was completed and the leakage during the run was calculated as 10.3627 cubic feet. This quantity was subtracted from the raw meter reading,and the net corrected to NTP is reported in Table 16 . Despite this difficulty with leakage (which also caused an obscuring of vision in the observation of the interior of the apparatus), an excellent correlation was obtained with an experimental error of .25 percent.

5.4.2.7 Run No. 7 This run was a modified cascaded vacuum pumping run and ordinarily would not have produced any triple point liquid. There was, however, some leakage through valve V4 in the early part of the run which placed a small quantity of liquid in the bottom of the slush tank. The pumpdown of the slush tank to prepare for the cascaded run also achieved the pumpdown of this small quantity of liquid. A reasonably good correlation was obtained (experimental error of 1.1 percent) considering the tiny quantity of triple point liquid involved. The liquid level was just enough to read the zero calibration mark. In fact, the expectable slush tank gauging error of ±0.1 cm (±0.023 liters) could account for the experimental error. The remainder of the run was 100 percent solid.

5.4.2.8 Run No. 8 The experimental error for Run No. 8 is zero by definition because this run was used to determine the pumping required to evacuate the system and the heat leak with the stirrer up. Since Runs No. 7 and 9 also had the stirrer up and the correlation for these runs was reasonably good, it is assumed that a good correlation was also achieved for Run No. 8.

5.4.2.9 Run No. 9 This run was a semiflow vacuum pumping run, which is a continuous process rather than a batch process; and, therefore, the data reported are for only a selected time interval during the run. Exact matching of the pumping speed to obtain steady-state conditions at the triple point liquid point was difficult, and the resulting run cycled from the production of small quantities of solid with the liquid to the production of slightly warm liquid. The time interval used for data reporting was selected with starting and finishing conditions as alike as possible, but some error was probably present. The boiling during this run was quite violent, splashing liquid droplets up on the walls of the tank where some solids were formed. Through we were not able to precisely determine the quantity of solid formed during the run, the fact that solid was noted agreed with the finding that the experimental pumping requirement was greater than the theoretical requirement to produce zero solid. An unknown difficulty with one of the wet drum meters during this run gave an impossibly low value for the pumping accomplished. As a result the pumping was determined by gauging the storage tanks as well as the slush tank and using the lost liquid as the total pumping. Due to the unavoidable gauging error of this method in comparison of the accuracy of gas measurement with a meter, this may have contributed to the experimental error. It is concluded that only a fair correlation was achieved for this run (experimental error of 2.0 percent), but it is close enough to verify the theoretical specific pumping requirement.

5.4.2.10 Run No. 10 This was a cascaded vacuum pumping run (see 3.1.4 for definition of this method) in which no liquid was produced. Instead, only 100 percent solid was produced. The data shown in Table 16 are for a selected time interval during the run. Because of the porous nature of the solid and the irregular shapes of the stalactites, etc. formed, we were able to gauge the volume of solid hydrogen produced. The quantity of solid produced was determined by gauging the liquid removed from the storage tanks and subtracting the gas removed from the system. Although the physical location of the stirrer was at the top of the slush tank, its heat leak effect was the same as if it were down because the solid hydrogen was being produced in the top of the slush tank. An excellent correlation was obtained with only a .51 percent experimental error.

5.4.2.11 Conclusions There are two major conclusions which were drawn at this point as a result of the preceding experiments. They are:

1. The experimental program verified the theoretical specific mass requirements for the various vacuum methods of producing triple point liquid as being well within the expectable experimental error.

2. Estimation of the effects of heat leak must take into account the thermodynamic pecularities of the production method used, especially for straight vacuum pumping, if meaningful results are to be obtained. The averaging method discussed in paragraph 5.4.1.1 appears to be a reasonably accurate short method of estimating these effects.

5.4.3 Production of Settled Slush and Solid Hydrogen

5.4.3.1 Effective Pumping for Heat Leak The effective pumping for heat leak was adjusted for the latent heat at the triple point from Mullins, Ziegler, and Kirk (1) in a manner similar to paragraph 5.4.11 and its sample calculations. The stirrer position, effective heat leak rate, duration, and pumping for heat leak are shown for each run in Table 16.

5.4.3.2 Venting to Atmosphere and Total Pumping Metered These quantities were obtained and converted to cubic feet NTP in the same manner as that described in paragraphs 5.4.1.4 and 5.4.1.6, and are shown in Table 16.

5.4.3.3 Pumping to Produce Solid The pumping to produce solid is the algebraic sum of the gas quantities: total pumping metered; plus gas vented to atmosphere; minus pumping for heat leak. These quantities are presented in Table 16.

5.4.3.4 Liquid above Settled Slush Where there was clear liquid above the settled slush, the quantity was gaged in the same manner discussed in paragraph 5.4.1.8 and is listed in Table 16.

5.4.4 Discussion of Solid Produced During Individual Runs

5.4.4.1 Run No. 1 This was a check-out run in which only a tiny quantity of solid was produced; it was not measured in any way.

5.4.4.2 Run No. 2 This was also a check-out run. A large quantity of solid hydrogen was produced, but no settled slush was prepared. The quantity of solid was determined by dividing the pumping to make solid by the theoretical specific pumping requirement to make solid, and it is listed in Table 16 under "Solid in Vapor Space" as 5 liters. However, the space occupied by solid was crudely estimated as equivalent to 14 liters, indicating an apparent solid porosity of 9 liters or 65 percent by volume. Because of the crudity of the measurements for this run, the numbers are severely rounded off. For sample calculations, refer to those in Run No. 3.

5.4.4.3 Run No. 3 In this run the presence of settled slush was not confirmed since the techniques for detecting its presence had not yet been developed. The several operators of the apparatus took turns observing through the periscope, and some thought they saw a lower region that was slightly less crystal clear than the triple point liquid. Others felt that this region was a slight haze of cloudiness on the glassware. None of the operators were able to distinguish a level or interface between the clear liquid and whatever was below. Without this observation, it is not possible to compute the properties of the settled slush. The quantity of solid produced was determined by dividing the pumping to make solid by the theoretical specific pumping (from Section 3) required to make solid, and it is listed in Table 16 as "Solid in Vapor Space." The calculations for determining the quantity of solid were performed as follows:

$$\begin{aligned} \text{Solid made in Run No. 3} &= (\text{Volume metered} - \text{volume heat leak})/\text{SMR} \\ &= (73.1678 - 32.3152)/0.1292274 \\ &= 316.1296\ \text{ft.}^3\ \text{NTP of solid} \end{aligned}$$

$$\text{Volume of solid in Run No. 3} = \frac{316.1296 \text{ ft.}^3 \text{ NTP}}{36.674 \text{ ft.}^3 \text{ NTP/liter}}$$

$$= 8.6199 \text{ liters}$$

5.4.4.4 Run No. 4

During this run a technique was developed for locating the level of the settled slush by following a piece of the broken crust with the periscope as it settled slowly down through the liquid. When it stopped moving and disappeared, the interface was assumed located. Once the interface between settled slush and clear liquid was initially located by this technique, it could be detected visually after some practice. However, when the interface was lost from the field of view, it was difficult to locate again without externally setting the periscope at the last known measured location or by following another piece of broken crust. With additional practice in observing the interface, it was observed as being extremely iregular rather than level. An apparent "level," to be used for gauging the volume of the settled slush and the volume of the clear liquid above it, was visually estimated from the irregular interface.

An additional problem involved the solid hydrogen that was lifted into the vapor space by the stirrer during crust breaking operations and the solid deposited on the tank walls and stirrer. Since it was not possible to gauge the volume of these solids, it was necessary to develop a procedure to determine how much of the solid produced was in the settled slush and how much was in the vapor space.

The total hydrogen in the slush tank at the end of the run was determined by gauging the quantity of liquid in the slush tank at the start of the run, gauging the quantity of liquid leaked from the storage tanks into the slush tank, and subtracting the gas removed from the apparatus by pumping and venting.

$$\begin{array}{lrl}
\text{Total hydrogen in slush tank} & = 440.6407 \text{ ft.}^3 & \text{NTP in slush tank at} \\
\text{at the end of Run No. 4} & & \text{start of run} \\
 & - \ 21.9913 \text{ ft.}^3 & \text{NTP removed by pumping} \\
 & - \ \ 2.7676 \text{ ft.}^3 & \text{NTP removed by venting} \\
 & + \ 17.3586 \text{ ft.}^3 & \text{NTP leaked from storage tanks} \\
 & \overline{} & \text{to slush tank} \\
 & 433.2404 \text{ ft.}^3 & \text{NTP in slush tank at end} \\
 & & \text{of run}
\end{array}$$

The portion of this hydrogen that was composed of solid, located in the vapor space, and settled slush, located in the bottom of the slush tank, was obtained by subtracting the quantity of liquid located above the settled slush.

Solid and settled slush in Run No. 4

$$\begin{array}{rl} = \ 433.2404\text{ ft.}^3 & \text{NTP total} \\ -\ \underline{208.2088}\text{ ft.}^3 & \text{NTP liquid above settled slush} \\ 225.0316\text{ ft.}^3 & \text{NTP solid and settled slush} \end{array}$$

The leakage through valve V4 during this run (see discussion for Run No. 4 in paragraph 5.4.1.10) was determined by gauging the storage tanks at the start and end of the run, then subtracting the gas vented from the storage tanks.

Leakage through valve V4 in Run No. 4

$$\begin{array}{rl} = \ 17.3586\text{ ft.}^3 & \text{NTP gone from storage tanks} \\ -\ \underline{2.7676}\text{ ft.}^3 & \text{NTP vented} \\ 14.5910\text{ ft.}^3 & \text{NTP leaked} \end{array}$$

The pumping required to convert this liquid to triple point liquid was determined by multiplying it by the theoretical specific pumping requirement for semiflow production of zero percent slush.

Pumping to make triple point liquid from leakage in Run No. 4

$$\begin{aligned} &= (0.1353321)\,(14.5910) \\ &= 1.9746\text{ ft.}^3\text{ NTP} \end{aligned}$$

This quantity of pumping was subtracted in the usual method to determine the pumping required to make solid.

Pumping to make solid in Run No. 4

$$\begin{array}{rl} = \ 21.9913\text{ ft.}^3 & \text{NTP pumped} \\ -\ 12.4725\text{ ft.}^3 & \text{NTP heat leak} \\ +\ 2.7676\text{ ft.}^3 & \text{NTP vented} \\ -\ \underline{1.9746}\text{ ft.}^3 & \text{NTP for leakage} \\ 10.3118\text{ ft.}^3 & \text{NTP} \end{array}$$

Since the experimental specific pumping requirement is the ratio of the pumping required to make solid to the quantity of solid and settled slush, it is calculated as follows for Run No. 4.

Experimental specific pumping requirement for Run No. 4

$$\begin{aligned} &= \frac{10.3118\text{ ft.}^3\text{ NTP}}{225.2088\text{ ft.}^3\text{ NTP}} \\ &= 0.0458238 \end{aligned}$$

The percentage of solid in the total of solid plus settled slush is the ratio of the experimental specific pumping requirement to the theoretical specific pumping requirement for making 100 percent solid from triple point liquid.

Percentage of solid in Run No. 4 $= \frac{0.0458238 \text{ experimental specific pumping requirement}}{0.1292274 \text{ theoretical specific pumping requirement}}$

$= 0.354598$

$= 35.4598$ percent solid

or 64.5402 percent liquid

The remainder of the 100 percent (64.5402 percent)is the percentage of liquid in the solid and settled slush. The quantity of liquid in the solid and settled slush was determined by multiplying this liquid percentage by the quantity of solid and settled slush.

Liquid in solid and settled slush in Run No. 4 $= (0.645402)\ (225.0316)$

$= 145.2359 \text{ ft.}^3 \text{ NTP}$

It was assumed that none of this liquid was clinging to the solid in the vapor space and that all of it was in the settled slush. The volume occupied by this liquid was determined in the following manner

Volume of liquid in settled slush in Run No. 4 $= \frac{145.2359 \text{ ft.}^3 \text{ NTP}}{32.606 \text{ ft.}^3 \text{ NTP/liter}} = 4.4543$ liters

and subtracted from the gauged volume of the settled slush to determine the volume occupied by the solid in the settled slush.

Volume of solid in settled slush in Run No. 4 = 5.8605 gauged volume of settled slush

4.4543 volume of liquid in settled slush

1.4062 volume occupied by solid in settled slush

The quantity of solid in the settled slush is determined by the following calculation.

Quantity of solid in settled slush in Run No. 4 $= (1.4062 \text{ liters})\ (36.674 \text{ ft.}^3 \text{ NTP/liter})$

$= 51.5707 \text{ ft.}^3 \text{ NTP}$

The solid percentage in the settled slush is calculated in the following manner.

$$\text{Solid percentage in the settled slush in Run No. 4} = \frac{51.5707 \text{ ft.}^3 \text{ NTP}}{51.5707 + 145.2359 \text{ ft.}^3 \text{ NTP}}$$

$$= 0.26203745$$

$$= 26.2 \text{ percent solid in settled slush}$$

The rounded values from the preceding calculations are reported in Table 16 . The remainder of the solid produced is reported as solid in vapor space.

5.4.4.5 Run No. 5 In this run the production of settled slush was continued until the last of the clear liquid above the settled slush had just disappeared. As with Run No. 4 there was a lot of solid in the vapor space, and the same procedure for reduction of data was employed except that there was no leakage through valve V4, and there was no clear liquid above the settled slush. The results of the calculations for this run are reported in Table 16 .

5.4.4.6 Run No. 6 In this run the stirrer was in its upper position while excess solid was formed and then allowed to melt. Because of the melting there was no solid in the vapor space at the end of the run. The level of the settled slush formed by melting was very flat and could be easily seen and accurately gauged. The data was reduced by the same procedure as in Run No. 4 except that there was no leakage through valve V4, and there was no solid in the vapor space. The solid fraction of 47.14 percent reported in Table 16 was determined 105 minutes after reaching the triple point (44 minutes after the start of melting). Further calculations gave solid fractions of 43.49 percent at 83 minutes (22 minutes melting) and 46.20 percent at 99 minutes (38 minutes melting). Pumping was stopped 61 minutes after the triple point was reached, at which time melting started.

5.4.4.7 Run No. 7 In this modified cascaded vacuum pumping run, 100 percent solid was produced from atmospheric pressure liquid. The quantity of solid produced was determined in the same manner used in Run No. 3.

5.4.4.8 Run No. 8 The only solid produced was the tiny quantity needed to detect the arrival at the triple point.

5.4.4.9 Run No. 9 Only a small quantity of solid was produced

5.4.4.10 Run No. 10 Settled slush was produced by using cascaded vacuum pumping to make 100 percent solid, then allowing it to melt. Both the hard, dry solid and the melting slush were vigorously stirred. The melting was continued until there was exactly zero liquid above the settled slush. The volume of the settled slush was gauged and the quantity of hydrogen in the slush tank determined in the same manner for the other runs. Because there was no solid in the vapor space and no liquid above the settled slush, the entire quantity of hydrogen in the slush tank was in the settled slush. This allowed direct calculation of the density.

$$\text{Density of settled slush in Run No. 10} = \frac{180.2556 \text{ ft.}^3 \text{ NTP}}{5.2150 \text{ liters}}$$

$$= 34.565 \text{ ft.}^3 \text{ NTP per liter}$$

The solid percentage in the settled slush was determined on a density basis.

$$\text{Solid fraction in settled slush in Run No. 10} = \frac{\dfrac{1}{32.606} - \dfrac{1}{34.565}}{\dfrac{1}{32.606} - \dfrac{1}{36.674}}$$

$$= 0.510948$$

$$= 51.09 \text{ percent}$$

Note that the method of determining the solid percentage in the settled slush for Run No. 10 is a method not previously discussed; it is the only method which does not require destruction of the slush or special preparation. It does, however, require accurate knowledge of the volume and of the mass, which in turn require that the vessel be calibrated and a record be kept of the mass balance. Although this method could be cumbersome in full size equipment, it may be the only method available when the heat balance is not known due to upsets in heat leak or other variables.

5.4.5 Discussion of Large-Scale Slush Production Results

When settled slush was produced by pumping (Runs No. 4 and 5), the quality was approximately 30 percent solid. When settled slush was produced by first making solid, then allowing it to partially melt (Runs No. 6 and 10), the quality was about 50 percent solid.

There were also other differences. The appearance of the lower solid content slush was very much like the perfectly clear triple point liquid, being only slightly less transparent. The appearance of the higher solid content slush was less clear and might be described as being translucent. Most observers saw individual particles, but one did not. The lower solid content slush could not be transferred by straightforward means (see paragraphs 5.3.4 and 5.3.5), but the failure to transfer may have been due to technique rather than the properties of the slush. It is believed that the slush with higher solid content was transferred as described in paragraph 5.3.10 (Run No. 10), although it cannot be absolutely proved since all of the solid melted as soon as it entered the storage tank. The settled slush with low solid content exhibited about the same percentage as the freshly-made lowest solid content slush produced in the small scale apparatus (Section 4). Thus, the low solid content settled slush apparently stayed at low solid content in the large apparatus even after the portion first made had aged as much as two hours.

The heat leak into the bottom of the slush tank during these runs was extremely low as a result of the periscope being kept at a higher level than normal in order to observe the crust breaking, etc., and the stirrer being lowered only enough to break crust. Although the longer of the two solid content runs (Run No. 5, 119 min.; Run No. 4, 44 min.) showed a higher solid content than the shorter (29.81% versus 26.20%), this does not necessarily indicate than an aging process is operative since the experimental error in the method of determining the solid content may well be greater than the difference between the two.

The solid percentage of the low solid content settled slush was observed to be at the low end of the experimental results shown by the small scale tests of freshly made slush. This might well have been due to the very short time required to start partial melting of the freshly made slush in the small apparatus. The higher solid content settled slush produced by partially melting solid in the large scale apparatus had approximately the same solid fraction as the settled slush produced by partial melting in the small scale apparatus. The difference between the solid fractions in Runs No. 6 and 10 may be due to melting from 100 percent solid in Run No. 10 and from mostly solid with some liquid in Run No. 6, or it may be due to the vigorous stirring before and during melting in Run No. 10. Also, it is likely that the difference might be attributed to the experimental error in the computation method. The solid percentage in the decreasing quantity of settled slush in Run No. 6 seemed to be increasing very slightly with time during melting, but this may have been due to experimental error. No verification of this observation was obtained from Run No. 10 since the slush produced in this run is the result of a different production process from that used in Run No. 6.

5.4.6 Characteristics of Low Solid Content Settled Slush

Although the major objective of the larger scale experimental work was to verify the vacuum pumping production methods, some additional information was discovered about the characteristics of the low solid content hydrogen slush produced by straight vacuum pumping. The type of slush produced is apparently influenced by the heat leak and stirring action during the production process.

Based on work with the small apparatus, it was assumed that a flowable mixture of particles would form from the broken crust that settled down through the liquid. However, the evidence all points to the conclusion that these particles did not form during straight vacuum pumping even after as much as two hours since:

1. By visual observation through the periscope we noted that the settled slush retained the same appearance as the agglomerates produced in the small apparatus before particles formed.
2. The solid fraction was calculated at 30 percent when vacuum pumping as compared with 31 percent to 38 percent values for agglomerates and 55 percent for particles in the small apparatus.
3. Manipulation of the large apparatus stirrer in the settled slush gave the slush a tendency to pack rather than behave as a fluid mixture, even when a mass of the material was lifted clear of the liquid;
4. The top surface of the settled slush produced by vacuum pumping was rough rather than smooth and level as in the small apparatus.
5. The solid in the vapor space readily adhered to the tank walls and stirrer blades of the large apparatus.
6. The settled slush could not be transfered by any of the techniques employed in the large scale apparatus.

Based on the assumption that the different results were due to the different characteristics of the apparatus used, it may be necessary when using large apparatus to heat or violently stir settled slush to produce the 55 percent solid flowable mixture of particles achieved with the small apparatus. When the slush was deliberately partially melted in the large apparatus, the higher solid fraction was achieved and the slush lost its sticking characteristic.

The heat leak in the large apparatus is about one-hundredth as much per pound of hydrogen as in the small apparatus. It may be that the higher heat leak is necessary to grow flowable particles by partial melting or it may be necessary to have a heat leak into the pipelines for successful transfer. Various means of adding heat in a production plant include using electric heaters; introducing gaseous hydrogen, warm liquid hydrogen, or warm gaseous helium; using gaseous helium warming coils; or deliberately designing the equipment with a high heat leak.

The stirrer in the large apparatus was designed primarily as a crust breaker and could not impart a violent stirring action to all of the settled slush at once. The stirrer in the small apparatus nearly filled the entire volume of the apparatus and could be used to beat the settled slush violently at the same time it was breaking the crust. Violent stirring action in the settled slush may be necessary to start the particle growing process. Because such a stirrer would be a major problem in a large tank, it may be necessary to produce the slush in small batches in small tanks that can be completely filled with a stirrer and then transfering the flowable slush to a large storage tank. If this be the case, the comparative economics of the various production methods will change.

SECTION 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

1. The most practical methods of producing large quantities of hydrogen slush are the vacuum pumping methods because of their relatively low capital and operating costs and their simple operation.

2. Because the operating costs of the vacuum pumping slush production systems are almost entirely due to the value of the hydrogen pumped away, the operating costs could be further reduced by integrating the slush production plant with a liquid hydrogen plant, where the pumped hydrogen could be recovered.

3. Of the vacuum pumping methods theoretically investigated, the cascaded branched flow vacuum pumping process shows the lowest total cost for the production of 75,000 lbs. of 50 percent solid slush in seven days. Under other conditions, straight vacuum pumping might provide lowest cost, depending on the production time and total quantity produced.

4. The theoretical specific mass requirements of the vacuum pumping systems were verified experimentally to be well within the expectable measurement error of the large scale test apparatus.

5. The practicability of producing hydrogen slush by vacuum pumping methods was demonstrated by the operation of the large scale apparatus.

6. The upper limit of solid content in settled slush produced by vacuum pumping was found to be in the order of 50 percent to 55 percent. This solid fraction also appeared to be the upper limit of flowable mixtures.

7. Solid hydrogen with no observable liquid phase can be produced. This material, which on a gravimetric basis is nearly 100 percent solid, has high porosity and non-flowability which make it unattractive. There are some indications, however, that this porous solid might be compacted by mechanical means to achieve greater density.

8. The settled slush produced by straight vacuum pumping was found to contain a maximum of approximately 30 percent solid. The flowability of this low solid content mixture was not observed during the experiments (see paragraph 5.3.5 and 5.3.6).

9. The 50 percent solid content settled slush can be produced by two methods: first, by making excess porous solid and then partially melting it to obtain all slush with no excess liquid; secondly, by making low solid content (30 percent) slush and then partially melting it to obtain a much lesser quantity of 50 percent solid slush plus excess triple point liquid. When 100 percent solid is partially melted to obtain 50 percent solid settled slush, the amount of pumping required is that for 100 percent solid, or double what would be required if the 50 percent solid settled slush were produced directly.

10. Successful transfer of hydrogen slush requires careful techniques, and the minimum procedure required has not yet been established. It appears that close temperature and/or pressure control of the receiving vessel are required together with a high velocity during transfer.

11. The effects of heat leak, which were not included in the theoretical analysis, can be an important consideration. Particular care is required in estimating the effects of heat leak for the straight vacuum pumping process, because the heat leak at the end of the batch preparation boils liquid for which pumping had previously been expended. A workable estimating procedure is discussed in paragraph 5.4.1.1.

12. None of the four methods developed for determining solid content have been found to be entirely satisfactory, and a direct reading instrument is desirable, if not essential. The two melting methods for determining solid content (heat balance and volume change) are unsatisfactory for process control because they require destruction of the slush. The production heat balance method is workable only while the slush is being produced or stored under carefully controlled conditions and depends on accurate knowledge of the heat balance. For operations involving transfer, it would not be satisfactory. The density determination method requires accurate measurement of the volume occupied by the slush and an accurate record of the mass of the slush in that volume. This last method is subject to gross errors in the answer for small errors in the measurements.

13. A practicable method of fueling vehicle tankage with 50 percent solid slush can probably be developed based on:

a. production of excess solid and partial melting to obtain flowable 50 percent solid settled slush

b. flowing the mixture into a pre-cooled vehicle tank though a pipeline. Upgrading the solid to a higher solid content on board the vehicle might be achieved through additional development efforts utilizing helium gas injection cooling.

6.2 RECOMMENDATIONS

During the performance of the studies and experiments detailed in this final report on Contract No. AF 33(657)-10248, the requirements for further examination of several aspects of hydrogen slush production, transfer, and storage became apparent. A final review of these requirements, taking into consideration the experience gained to date, has resulted in the recommendations presented here in both summary and detailed forms. We have selected these particular recommendations for discussion because they represent immediate problems to the overall hydrogen slush program. There are a number of other areas which may well merit further investigation in the furture.

6.2.1 Summary

1. Techniques and processes should be developed for obtaining higher solid percentages for storage in the space vehicle tankage since the advantage of hydrogen slush as a propellant increases markedly with increases in the solid percentage. Some of the attractive possibilities for further investigation include packing porous solid into dense solid chunks, growing dense particles as stalactitie-type formations, and upgrading a maximum flowable mixture after it is on board the vehicle.

2. The vacuum pumping production processes should be further investigated to develop techniques for making flowable settled slush of the highest possible solid content since these processes promise the lowest costs for volume slush production.

3. The flowability of the various hydrogen slush mixtures should be further investigated: techniques should be developed to handle these mixtures in complicated vehicle fueling systems; or, simplified systems capable of handling hydrogen slush should be developed.

4. A practical method of measuring the solid percentage in hydrogen slush should be developed. The greatest need is for a method applicable to flight-weight tankage.

5. The solubility of helium in hydrogen slush of various qualities should be determined to see whether this will present a problem in diluting the fuel.

6.2.2 Discussion of Recommendations

6.2.2.1 Production of Greater than 50 Percent Solid The first recommendation presented in this section has already been well recognized, as evidenced by the award of Contract No. AF 33(615)-1357, "Research of Production Techniques for Obtaining over 50 Percent Solid in Slush Hydrogen."

6.2.2.2 Vacuum Pumping Production Methods The results of the theoretical investigation, as verified by the experimental efforts to date, have clearly indicated that some form of the vacuum pumping technique will be the most economical method of producing hydrogen slush of up to fifty percent quality. However, we have found that a number of problems exist in predicting the type of slush to be formed. Consequently, we recommend a study aimed at completing the development of a practical, economical slush production method.

To achieve this goal, one of the major objectives of the recommended study must be to determine the mixing requirements. The stirring mechanism used in the small scale experiments (Section 4) nearly filled the dewar which would be inpractical in large apparatus. Using that stirrer, however, a settled slush was obtained which appeared very promising for transfer, provided the transfer was made at relatively high linear velocities immediately after mixing the slush. The stirring device used in the large scale experiments (Section 5) was primarily designed to break up the crust formation at the top of the liquid-gas interface and, apparently, a different hydrogen slush formation was obtained. The first task under the recommended study, therefore, should be to design a stirring device which will serve both functions, i.e. breaking up of the crust formation, as well as complete mixing of the solid-liquid mixture. For application to large storage tanks (e.g. 75,000 lbs.), it is hoped that a fairly simple crust breaking device, perhaps having a rotary and oscillatory motion and operating at fairly slow speeds, can be used. The mixing of the settled slush phase might best be done by a small, relatively high speed, propeller or fan located at the bottom of the tank. A study to develop such equipment should consist of a design phase, construction of appropriate test equipment of at least 30 gallon capacity, and a test phase utilizing several configurations of stirring devices.

Work to date has also shown that heat in-leakage to the slush particles has a significant effect on their characteristics. This may account for some of the differences noted between the small and the large scale testing where the heat input to the fluid was different by two orders of magnitude. In order to study these effects, a means of varying the heat leak to the slush producing equipment should be incorporated. Considering the 30 gallon production-storage equipment, this could be done by varying the heat leak through the stirrer and mixer by varying the degree of vacuum in the insulation space, or preferably, by controlled electrical heating.

This study should also have the goal of investigating the long-term storage of settled slush. Experiments should be conducted for periods of up to one week. Separate tests should be conducted with the fluid in a quiescent state as well as when it is agitated by the stirring device.

At the conclusion of the experimental phase, existing designs for liquid hydrogen storage and transport equipment should be examined to determine what modifications, if any, would be necessary to handle hydrogen slush. Two important needs which would have to be considered are:

1. Stirring devices
2. Helium pressurization provisions for transfer and long-term storage under a helium atmosphere, so that subatmospheric storage could be eliminated.

6.2.2.3 Transfer Properties of Hydrogen Slush While conclusive results were not attainable in the large scale test program, the small scale testing did indicate that high linear velocities and thorough mixing were necessary in order to transfer hydrogen slush. In the absence of these conditions, the solid tended to form a bridge at the entrance to the transfer piping which acted as a strainer in the liquid. The major problem in the transfer of hydrogen slush is the tendency of the solid to adhere to vessel walls, the stirrer shaft, and other surfaces within the storage or production equipment. In order to achieve a practical slush production and transport system, we recommend a study to further examine these effects which influence the transfer of the slush.

The production equipment described in earlier sections of this report and a relatively simple piping configuration incorporated between this equipment and a dump-tank would be adequate to perform an evaluation of the sticking problem. The variables to be considered would be stirring speed (degree of agitation) and transfer velocity through the piping. Having determined minimum linear velocities and stirring requirements for the simple piping configuration, additional complexity would be incorporated into the piping system in the form of elbows, valves, and other flow restrictions to develop data for correlation in some manner similar to that used for correlating pressure drop data.

A further task of the study should be to investigate the degree of slush degradation (decreased percent solid) caused by transfer under varying conditions and the static charge effect during high velocity transfers.

6.2.2.4 Hydrogen Slush Quality Meter The hydrogen slush work performed to date has been limited by the need for visual observation of the slush formed. This limitation will remain until a more thorough understanding of the formulation of solid-liquid mixtures is gained. However, before the overall slush program can progress very far it is essential that a quality meter be developed which will measure the percent solid formed and indicate its characteristics.

If the assumption can be made that the settled slush mixture is nearly homogeneous or if a representative sampling of the slush mixture can be noted by some orientation throughout the vessel, beta-ray attenuation may be the most promising method of approach. Its applicability, however, is entirely dependent upon the homogeneity of the mixture, and it may not be applicable to measuring overall characteristics directly when the slush mixture is in the form of a solid crust, a liquid layer, and a layer of settled slush.

Another promising source of data regarding the characteristics of the slush mixture may be the power required for the stirring device located in the bottom of the tank. Depending upon the flow velocities through this device, it might be instrumented to determine the viscosity of the mixture of settled slush. Information applicable to this approach will be forthcoming from the efforts Linde Division is currently devoting to Contract No. AF 33(657)-11098, "Research on Rheologic and Thermodynamic Properties of Solid and Slush Hydrogen."

6.2.2.5 Solubility of Helium The application of gaseous helium to hydrogen slush production, storage, and transfer is evident from the description of its use in this report. Slush upgrading will very probably be by means of helium gas injection cooling; transfer can be by pressurization with helium gas; storage and transport of slush hydrogen will be accomplished with the slush under a helium atmosphere. It is necessary, therefore, to know the solubility of helium gas in slush hydrogen.

The works of Streett (8), Smith (12), and Roellig and Giese (13) are described in Appendix I of this report. These investigators have studied the solubility of helium in hydrogen liquid at atmospheric and higher pressures. However, to date, no one has investigated the solubility of helium in slush hydrogen. The initial phase of such a study should be the solubility in a static slush system containing various solid percentages. Upon completion of this phase, the dynamic effects of transferring slush hydrogen by means of helium pressurization, wherein the gas-phase would become entrained with the solid-liquid phase, should be analyzed and investigated. The result of this study should be an understanding of the helium solution and mixing with various percentages of solid hydrogen and adequate means of predicting the quantity of helium that would be injected into a vehicle engine utilizing hydrogen slush produced, stored, and transferred in helium pressurized apparatus.

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APPENDIX I

LITERATURE SURVEY

A.1 SOLUBILITY AND RATE OF DIFFUSION OF HELIUM IN LIQUID HYDROGEN

A.1.1 Summary

There are only two papers of the literature surveyed in which experimental work on the solubility of helium in liquid hydrogen is reported, and there are no papers which report anything on the solubility of helium in mixtures of solid and liquid hydrogen or in solid hydrogen alone. The results reported in the two papers (12, 13) are plotted in Figure 43. It can be seen from this Figure that the results are quite different. As an example of the difference, one paper(12) gives the solubility in liquid hydrogen at a partial pressure of 7 atm. helium and a temperature of about 20°K as 1.1 mole-percent, the other paper(13) as 11.05 mole-percent.* A study of the papers offers little evidence as to which one of them (if either) has the correct results. Possibly the greatest sources of error in both of them lie in the sampling and analysis steps. Although the methods used in the two investigations are quite different from each other, both of them seem reasonably sound except for the method used for temperature determination in the second paper(13). Even here, the maximum error is probably not over 1.1°K, which is small compared to the discrepancies in solubility values between the two papers.

A theoretical examination of Smith's data by Brazinsky and Gottfried(14) showed reasonable thermodynamic consistency. Thus, in the absence of better data, Smith's values of solubility have been adopted in this report.

The diffusion coefficient, D, for helium in liquid hydrogen was measured by Castagnoli(15) over the temperature range 15.74°K to 20.25°K. His results are shown in Figure 44. Using Smith's data (Figure 43) for the solubility of helium in liquid hydrogen and Castagnoli's data (Figure 44) for the diffusion coefficient, it can be estimated that the initial (maximum) rate with which helium used to pressurize liquid hydrogen would dissolve in the liquid hydrogen would be 1.67×10^{-8} lb. helium per square foot of liquid surface area

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* After the completion of this survey, we found that a doctoral dissertation entitled "Liquid-Vapor Equilibrium in the System Normal Hydrogen - Helium" by W. B. Streett, University of Michigan, 1963, had recently been published. The solubility data obtained by Streett are in fairly close agreement with those of S. R. Smith, reported here in Figure 43 and in Tables 17, 18, and 19. A copy of Streett's dissertation was received too late for inclusion of his data in this report.

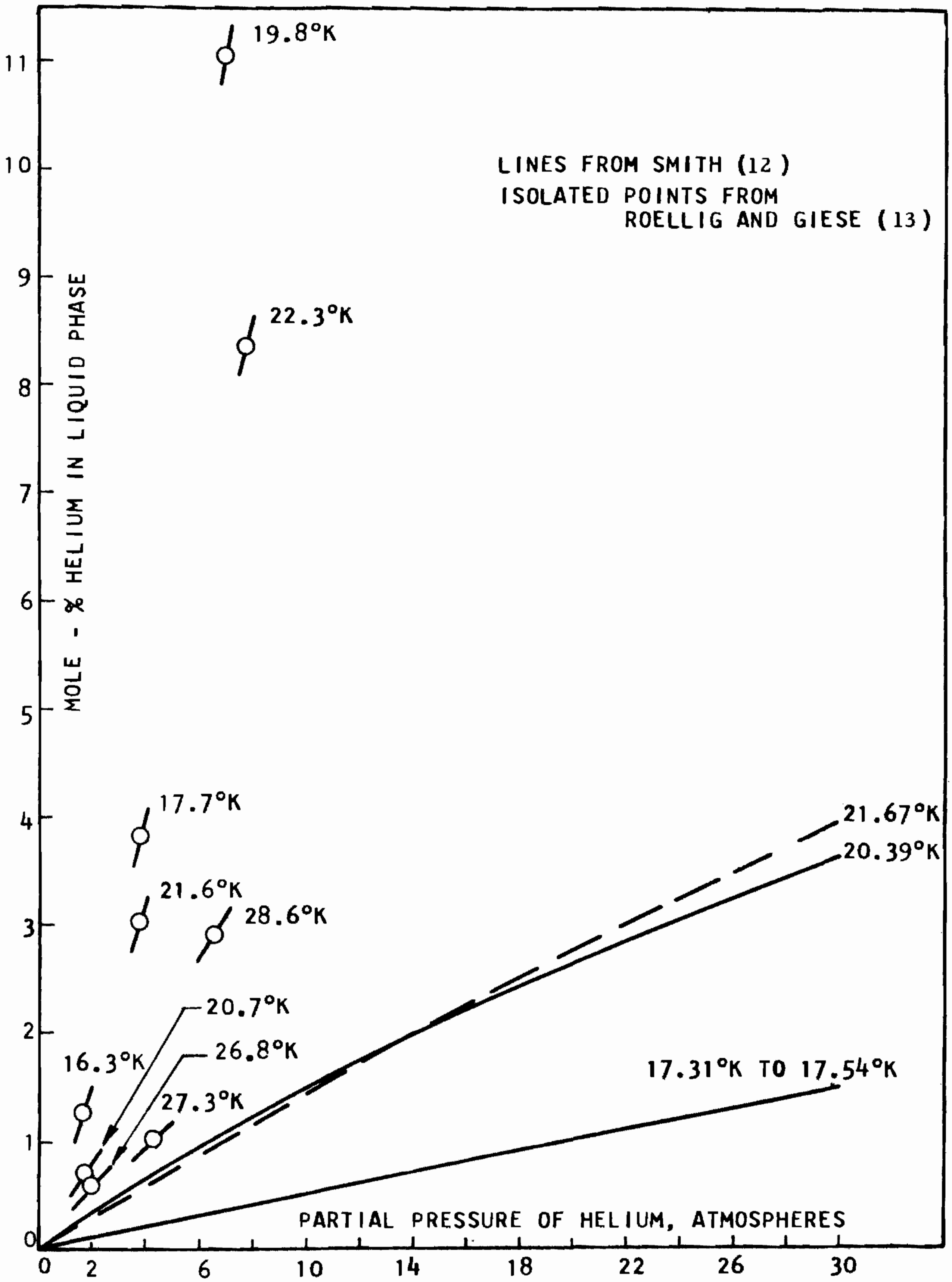

Figure 43. Literature Values for the Solubility of Helium in Liquid Hydrogen

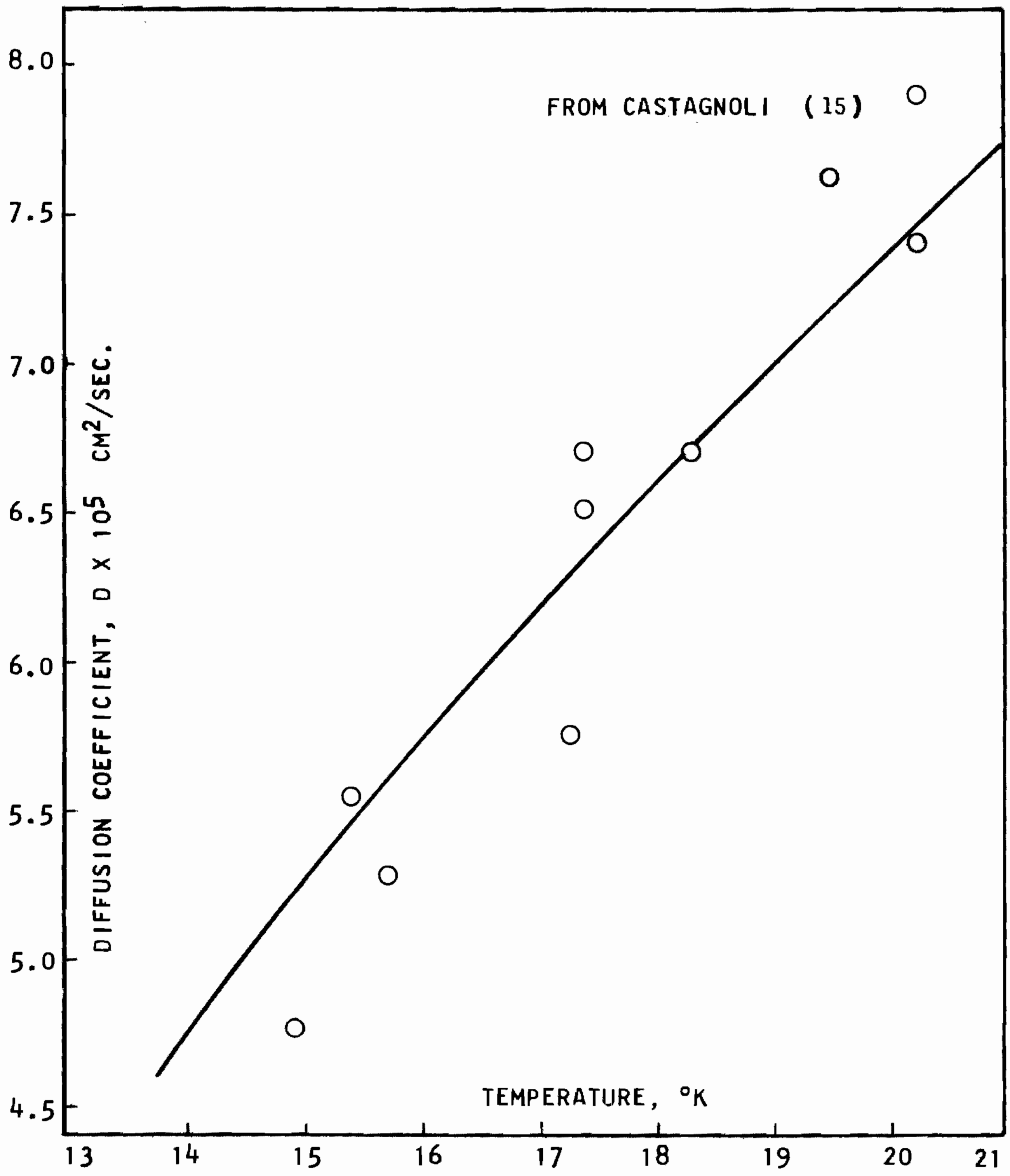

Figure 44. Rate of Diffusion of Helium in Liquid Hydrogen

per second at a helium partial pressure of 3 atm. and a temperature of 13.8°K. This indicates that, if stirring is kept to a minimum, liquid hydrogen or hydrogen slush can be pressurized with helium for short periods of time with very little loss of helium and very little dilution of liquid hydrogen by helium.

A.1.2 Data of S. R. Smith for Solubility of Helium in Normal Liquid Hydrogen

The results given by Smith(12) are detailed in Tables 17, 18 and 19, and shown as three curves in Figures 43 and 45. In Figure 43, the measured solubilities are plotted versus the partial pressure of helium; in Figure 45, the solubilities are plotted versus total absolute pressure (hydrogen plus helium). When there is no helium present, the pressure is due solely to the vapor pressure of the liquid normal hydrogen, which is as follows:

17.4°K	0.35 atm.
20.39°K	1.00 atm.
21.67°K	1.50 atm.

Although there was a slight variation of the temperature for the data plotted on these curves, they are essentially isotherms; any errors of a few tenths of a degree due to temperature variations are far outweighed by other sources of error. The temperatures are given to the second decimal place because that is the way Smith gave them in his tables of data, but the second decimal place has no significance with respect of the solubility figures. The curves for 20.39°K and 21.67°K cross. To indicate clearly which is which, the curve for 21.67°K has been drawn with broken lines.

TABLE 17

RESULTS REPORTED BY SMITH FOR ABOUT 17.4°K

Sample	Temp., °K	Total Pressure psia	Total Pressure atm. abs.	Partial Pressure of He, atm. abs.	Mole-% He Gas	Mole-% He Liquid
K1A	17.4	48	3.27	2.72	83.4	0.19
K1B	17.4	48	3.27	2.73	83.5	0.20
K2A	17.4	83	5.65	5.09	90.1	0.22
K2B	17.4	83	5.65	5.13	90.8	0.28
K7A	17.31	96	6.53	6.00	91.8	0.27
K7B	17.31	96	6.53	6.00	91.8	0.31
K3A	17.49	141	9.59	8.97	93.5	0.45
K3B	17.49	141	9.59	8.96	93.4	0.51

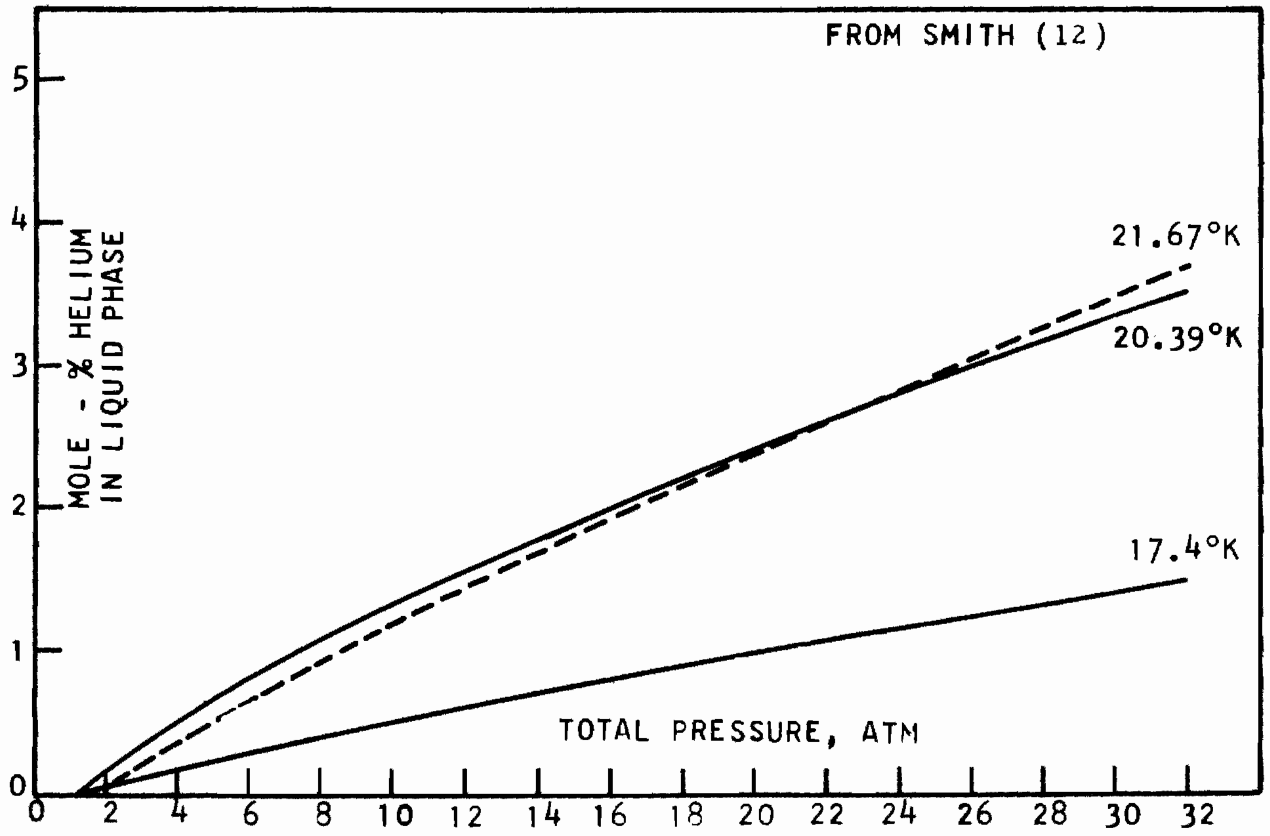

Figure 45. Literature Values for the Solubility of Helium in Liquid Hydrogen

TABLE 17 (CONTINUED)

RESULTS REPORTED BY SMITH FOR ABOUT 17.4°K

Sample	Temp., °K	Total Pressure psia	Total Pressure atm. abs.	Partial Pressure of He, atm. abs.	Mole-% He Gas	Mole-% He Liquid
K4A	17.54	207	14.08	13.28	94.3	0.67
K4B	17.54	207	14.08	13.30	94.4	0.74
K5A	17.47	316	21.50	20.43	95.0	1.05
K5B	17.48	316	21.50	20.43	95.0	1.08
K6A	17.40	358	24.36	23.19	95.2	1.11
K6B	17.40	358	24.36	23.19	95.2	1.15

TABLE 18

RESULTS REPORTED BY SMITH FOR 20.39°K*

Sample	Total Pressure psia	Total Pressure atm. abs.	Partial Pressure of He, atm. abs.	Mole-% He Gas	Mole-% He Liquid
H1A	63	4.29	3.12	72.9	0.59
G2A	102	6.94	5.73	82.5	0.87
G3A	177	12.04	10.50	87.2	1.53
G4A	256	17.42	15.50	89.0	2.16
G5A	291	19.80	17.86	90.2	2.47
H3A	365	24.84	22.40	90.2	2.95
H3B	365	24.84	22.40	90.2	2.97
F2B	376	25.58	23.03	90.0	2.89
F1A	405	27.56	24.86	90.2	3.06

---

* No temperatures are given for the individual runs.

TABLE 19

RESULTS REPORTED BY SMITH FOR 21.67 K*

Sample	Total Pressure psi	Total Pressure atm. abs.	Partial Pressure of He, atm. abs.	Mole-% He Gas	Mole-% He Liquid
L6A	157	10.68	8.93	83.6	1.21
L6B	157	10.68	8.94	83.7	1.36
L5A	386	26.27	22.96	87.4	3.06
L5B	386	26.27	22.90	87.2	3.13

Since Smith produced his liquid hydrogen by condensing gas originally at room temperature, his liquid is normal (75 percent ortho) hydrogen. For industrial and rocket purposes, it is the solubility of helium in para-hydrogen that is of interest, but there is probably only a slight difference in the solubility in the two liquids.

A.1.2.1 Smith's Experimental Method Hydrogen from a compressed-gas cylinder at room temperature was condensed into the pressure vessel in which the solubility was to be measured. A gaseous mixture of helium and hydrogen at a known pressure was then bubbled continuously through the liquid normal hydrogen which was kept at a known temperature. The gas mixture was continuously recirculated by means of a high-pressure gas-circulating pump external to the cryostat. The bubbling action stirred the liquid phase and produced close contact between the gas liquid phases, thus helping to establish equilibrium. Samples were withdrawn from both phases and analyzed by means of a mass spectrometer. The temperature was measured by a calibrated copper-constantan thermocouple.

A.1.2.2 Possible Sources of Error Smith's method appears theoretically sound. The greatest source of experimental error seems to have been in the analysis of the gas phase. Smith states (12, p. 18) that he had to turn the gas-circulating pump off about 15 minutes before sampling the gas phase to avoid getting too high a hydrogen concentration in the gas phase. He ascribes this high hydrogen concentration to a spray of liquid hydrogen thrown up out of the equilibrium vessel by the circulating pump.

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* More complete data for the range 21.65 to 21.95°K are given (under the nominal temperature of 21.8°K) in Table I of Drayer and Flynn (16). Drayer's and Flynn's table was obtained by reading values from Smith's Figure 11 (12, p. 28). See also Tables 6 and 7 in Smith (12, pp. 26-27).

In Table 20 a comparison is shown for a few of Smith's runs of the partial pressures (in atm.) of hydrogen as determined by multiplying Smith's gas-phase hydrogen concentrations by the total pressure and by the use of Raoult's law, i.e., by multiplying the mole-fraction of hydrogen in the liquid phase by the vapor pressure of pure liquid normal hydrogen as given in the National Bureau of Standards "Compendium" (17, section 6.002). If Raoult's law applies and if Smith's analytical results are correct, the two figures for the partial pressure would be the same. Instead, the partial pressure calculated from Smith's gas analysis is always higher than the pressure expected from Raoult's law, and the ratio of the two pressures increases rapidly as the total pressure increases. The lowest value of the ratio is 1.16 at 20.39°K and a total pressure of 4.29 atm.; the highest value is 3.37 at 17.4°K at a total pressure of 24.36 atm. It is evident that either Raoult's law does not apply, or that Smith's hydrogen analyses are too high, or some of both is true.

There is evidence that Smith's gas analyses actually were too high in hydrogen. He carried out an experiment (12, p. 30) in which he bubbled helium through liquid hydrogen and analyzed the gas phase without recirculating it. In this way he found only 1.5 mole-percent hydrogen in the gas phase versus 12 percent when the gas was recirculated. While it would not be expected that complete equilibrium would be established by just bubbling the helium through once, one would expect a somewhat closer approach to equilibrium than Smith's figures would indicate. It seems entirely possible, therefore, that hydrogen gas was vaporized from liquid spray carried into the recirculating gas stream and that this extra hydrogen caused Smith to obtain too high a figure for hydrogen in the gas phase analysis. The period of 15 minutes' waiting mentioned by Smith would not have corrected this error. However, the most important thing is the analysis of the liquid phase rather than that of the gas phase, and there is no indication in Smith's dissertation of possible sources of error in the liquid phase analysis.

A.1.2.3 Other Literature Related to Smith's Work

Brazinsky and Gottfried (14) performed a theoretical analysis of Smith's results and concluded that the results are "reasonably consistent" thermodynamically. These authors also discuss the fugacity of hydrogen in both the gas and liquid phases. In view of the uncertainty of Smith's results, a more extended discussion of the thermodynamics has not been undertaken.

Drayer and Flynn (16) used the data of Smith (12) to calculate "K-factors" for both helium and hydrogen. The K-factor is defined as y/x, in which y is the mole fraction of a component in the vapor phase and x is

TABLE 20

COMPARISON OF MEASURED AND THEORETICAL PARTIAL PRESSURES OF HYDROGEN

Sample	Temp. °K.	Total Pressure, atm.	Mole-% H_2 in Gas	Partial Pressure of H_2 Measured	Raoult's Law	Ratio	Mole-% H_2 in Liquid	Vapor Pressure of Pure n-H_2 atm.
K1A	17.4	3.27	16.6	0.541	0.35	1.55	99.81	0.35
K2A	17.4	5.65	9.90	0.559	0.35	1.60	99.78	0.35
K7A	17.31	6.53	8.24	0.538	0.33	1.63	99.73	0.33
K3A	17.49	9.59	6.53	0.626	0.38	1.65	99.55	0.38
K4A	17.54	14.08	5.69	0.800	0.40	2.00	99.33	0.40
K5A	17.47	21.50	4.96	1.07	0.38	2.82	98.95	0.38
K6A	17.40	24.36	4.84	1.18	0.35	3.37	98.89	0.35
H1A	20.39	4.29	27.1	1.16	1.00	1.16	99.61	1.00
F1A	20.39	27.56	9.8	2.70	0.97	2.78	96.94	1.00
L6A	21.67	10.68	16.4	1.75	1.48	1.18	98.79	1.50
L5A	21.67	26.27	12.6	3.31	1.45	2.28	96.94	1.50

the mole fraction of the same component in the liquid phase. The following is quoted from Drayer and Flynn (16, pp. 2 and 4):

> "Initially a plot of K versus P (total pressure) was prepared for each component. The data did show some scatter, especially for helium K-factors. The best smooth curve was drawn through the plotted points and this curve was then transferred to another plot.
>
> "It should be noted that the 20.4° and 21.8°K isotherms for helium cross at approximately 10 atmospheres. Since the Boyle point of helium is near 20°K, one would expect a reversal of the gas solubility in that region. This is in fact shown by the data."

A.1.3 Data of Roellig and Giese

The results published by these authors (13) are given in Table and are plotted as isolated points on Figure 43. Each point has a segment of a straight line drawn through it, which, if extended, would intersect the origin. The line segments indicate very roughly the general trend of solubility at the given temperatures. Figure 43 shows that the results reported by Roellig and Giese are quite different from those of Smith.

The results of Roellig and Giese could not be plotted in Figure 45 because neither the total pressures nor any data from which they can be calculated are given in the paper.

TABLE 21

EXPERIMENTAL RESULTS REPORTED BY ROELLIG AND GIESE

Run No.	Temperature °K	Partial Pressure of He, atm. abs.	Solubility of He in Liquid H_2 Mole-%
1	16.3	1.86	1.26
2	17.7	3.77	3.80
3	19.8	7.01	11.05
4	20.7	1.77	0.69
5	21.6	3.67	3.01
6	22.3	7.64	8.35
7	26.8	1.98	0.59
8	27.3	4.32	1.03
9	28.6	6.50	2.89

A.1.3.1 Roellig and Giese's Experimental Method

The gas and liquid phases were contained in a "solubility chamber" partly made of glass. The chamber is described in a separate paper (18). Both phases were stirred, and equilibrium was well established. In all runs, the gas phase was sampled and analyzed by means of a mass spectrometer. In some of the runs the liquid phase was sampled and the samples analyzed with a mass spectrometer. In other runs, the quantity of helium in the liquid was calculated by subtracting the amount of helium computed from the pressure and analysis to be in the gas phase from the total (measured) amount of helium introduced into the solubility chamber.

No analyses are reported in the publication (13). The total pressures were measured but are not given. The temperatures of the solution were not measured, but were calculated from the chart given by Chelton and Mann (19, p. 19) for the vapor pressure of para-hydrogen versus temperature using the assumption that the vapor pressure of hydrogen for a liquid mixture of hydrogen and helium obeys Raoult's law. The article does not state whether the liquid used was para- or normal-hydrogen, but this would probably make very little difference.

A.1.3.2 Possible Sources of Error

If Smith's data (Table 20) are correct, the assumption that Raoult's law holds for the He-H_2 system is not valid. An indication of the possible errors in temperature caused by the method of calculation used by Roellig and Giese was obtained by recalculating two temperatures using the appropriate partial-pressure ratios from Smith's data (Table 22) and the appropriate vapor pressures from Chelton and Mann (19, p.19). These calculations yield temperatures of 17.4°K and 21°K.

TABLE 22

RECALCULATION OF TWO OF ROELLIG AND GIESE'S TEMPERATURES

Temp. Calculated by Roellig and Giese (13), °K	16.3	21.6
Vapor Pressure for Pure p-H_2 (19, p. 19), psia	3.2	21.5
Ratio from Table 20	1.6	1.16
Recalculated Vapor Pressure, psia	5.11	25.0
Temp. from Vapor Pressure Curve (19, p. 19)	17.4	22.2

A.1.4 Critical Items in Solubility Measurements

As a result of the various possible sources already listed, we have concluded that any future experimental determinations of solubility should consider the following critical points:

1. Establishment of equilibrium between the gas and liquid phases and homogeneity within each phase.
2. Sampling of both the phases in such a way that the equilibrium is not disturbed and so that the composition of the samples is the same as that of the respective phases.
3. Accurate gas analyses.
4. Accurate measurements of temperature and pressure.

A.1.5 Rate of Diffusion of Helium in Liquid Hydrogen

Castagnoli (15) measured the rate of diffusion of helium in liquid hydrogen. He did not state whether the hydrogen was normal or para, but judging from the description of his apparatus, the liquid was probably normal. In any case, the experimental error in his determinations was probably much greater than any differences in the rate of diffusion in para or in normal liquid hydrogen.

Castagnoli found that the best fit to his experimental values is given by the equation

$$D = 20 \exp\left(-\frac{20}{T}\right) 10^{-5} \text{ cm}^2 \text{sec.}^{-1} \tag{111}$$

The curve in Figure 44 represents this equation. The points calculated by the writer from the equation are listed in Table 23 along with Castagnoli's experimental values. The experimental values have been plotted in Figure 44 to show the scatter of the points.

A.1.5.1 Application

The application of the values (solid curve in Figure 44) for the diffusion coefficient is illustrated by the following problem:

What is the rate of diffusion of helium into liquid hydrogen at a helium partial pressure of 2.724 atm. and a temperature of 17.4°K?

TABLE 23

DIFFUSION COEFFICIENTS FOR HELIUM IN LIQUID HYDROGEN

Temperature °K	D, cm^2/sec.		
	Exp.	Calc.	
14.90	4.75	-	x 10^{-5}
15.00		5.28	
15.40	5.55	-	
15.74	5.27	-	
16.00		5.73	
17.00		6.17	
17.25	5.74	-	
17.38	6.70	-	
17.38	6.50	-	
18.00		6.58	
18.30	6.69	-	
19.00		6.98	
19.50	7.62	-	
20.00		7.36	
20.25	7.90	-	
20.25	7.40	-	

Note: All values of D are to be multiplied by 10^{-5}.

The exact calculation of such a diffusion rate is very complicated, but a good approximation may be made by starting with the equation

$$J = D \frac{\partial c}{\partial x} \tag{112}$$

in which

J = the net rate of diffusion, in moles per second, of a mobile component across a surface area of one cm^2.

D = the diffusion coefficient, $cm^2 sec.^{-1}$

$\frac{\partial c}{\partial x}$ = the concentration gradient of the mobile component in a direction normal to the plane of the area through which the rate of the diffusion is being calculated, in moles/cm^3 per cm of length in this (normal) direction. This equation applies fairly rigorously only for the diffusion of a gas into a solid in the absence of a thermal gradient, but it is a good first approximation for diffusion into a liquid.

The concentration gradient of helium to a depth of one centimeter may be roughly approximated by assuming: that the first layer of liquid hydrogen with which the helium comes in contact is saturated with helium; that at a distance of one centimeter from the liquid hydrogen surface, the concentration of helium is zero; and that the gradient over the distance of one centimeter is linear. At a helium partial pressure of 2 atm., the solubility of helium at 17.4°K is given by Smith's work as about 0.12 mole-percent (lowest curve on Figure 43). Although Smith's work was doen with normal hydrogen, the solubility would probably be about the same for para-hydrogen (p-H_2). The smoothed values of the density of liquid p-H_2 (20) are:

$$0.0367970 \text{ mole/cm}^3 \text{ at } 17.000°K$$
$$0.0363119 \text{ mole/cm}^3 \text{ at } 18.000°K$$

The density variation in this range is nearly linear. Linear interpolation gives 0.03660 mole/cm^3 for 17.4°K. The concentration of helium at saturation is therefore:

$$0.03660 \times 0.0012 = 4.4 \times 10^{-5} \text{ mole/cm}^3$$

Since the concentration is assumed to go from this value to zero over a distance of one cm,

$$\frac{\partial c}{\partial x} \cong 4.4 \times 10^{-5} \text{ mole cm}^{-3}\text{cm}^{-1}$$

From Figure 44 , D = $6.34 \times 10^{-5} cm^2 sec.^{-1}$ at 17.4°K. Therefore,

$$J \cong 6.34 \times 10^{-5} \times 4.4 \times 10^{-5}$$

$$J \cong 2.79 \times 10^{-9} \text{ mole cm}^{-2}\text{sec.}^{-1}$$

Converting to engineering units,

$$J' = \frac{2.79 \times 4.003 \times (30.48)^2}{453.6} \times 10^{-9} = 2.30 \times 10^{-8} \text{lb. He ft}^{-2}\text{sec.}^{-1}$$

at 17.4 °K at a He partial pressure of 3 atm.

Reliable data are not available for the solubility of helium in liquid hydrogen at the triple point (For para-hydrogen this is 13.813 °K.). Assuming, however, that the solubility of helium at 13.8 °K is about the same as at 17.4 °K, we can estimate the rate of diffusion at 13.8 °K as follows:

From Figure 44 , the value of D at 13.8 °K is 4.60×10^{-5}.

Therefore,

$$J' \cong \frac{4.60}{6.34} \times 2.30 \times 10^{-8} \cong 1.67 \times 10^{-8} \text{lb. ft}^{-2}\text{sec.}^{-1}$$

at a partial He pressure of 3 atm. and a temperature of 13.8 °K.

Since the net rate of diffusion of helium is greatest when the helium pressure is first applied to the liquid hydrogen, this value of J' may be taken as a maximum. We therefore conclude that, when helium at a partial pressure of 3 atm. is applied to the surface of liquid hydrogen at 17.4° K, the helium will at first penetrate the hydrogen at a rate of about 2.3×10^{-8} lb. per second per square foot of surface area exposed to the helium. After some helium has dissolved, this rate of penetration will decrease. On the other hand, if there is stirring of any kind, the quantity of liquid surface xposed to the helium will be increased, and the total rate with which helium dissolves in the liquid will, of course, be correspondingly increased.

A.2 VAPOR PRESSURE OF SOLID AND LIQUID PARAHYDROGEN

A.2.1 Summary

The best literature values noted for the vapor pressure of solid and liquid parahydrogen are given in Table 24 and plotted in Figures 46 and 47

A.2.2 Discussion

A new paper on the vapor pressure of p-hydrogen (actually 99.79 percent p-hydrogen, 0.21 percent o-hydrogen) , written by Weber *et al.* (21)

TABLE 24

VAPOR PRESSURE OF SOLID AND LIQUID PARAHYDROGEN

	Temp., °K	Vapor Pressure		
		atm. abs.	psia	torr
Solid	10	0.00259	0.0380	1.97
	11	0.00747	0.1098	5.68
	12	0.0184	0.2704	14.0
	13	0.0399	0.5864	30.4
Triple Point	13.803	0.0695	1.0214	52.8
	14	0.0779	1.1448	59.3
	15	0.1326	1.9487	100.9
	16	0.2130	3.1302	161.9
	17	0.3250	4.7762	247.0
	18	0.4758	6.9924	361.6
	19	0.6727	9.8860	511.2
	20	0.9231	13.566	701.1
B.p.	20.268	1.0000	14.696	760
Liquid	21	1.2334	18.126	
	22	1.6127	23.700	
	23	2.0691	30.407	
	24	2.6105	38.364	
	25	3.2453	47.693	
	26	3.9818	58.517	
	27	4.8285	70.960	
	28	5.7939	85.147	
	29	6.8869	101.210	
	30	8.1176	119.296	
	31	9.5006	139.621	
	32	11.0513	162.410	

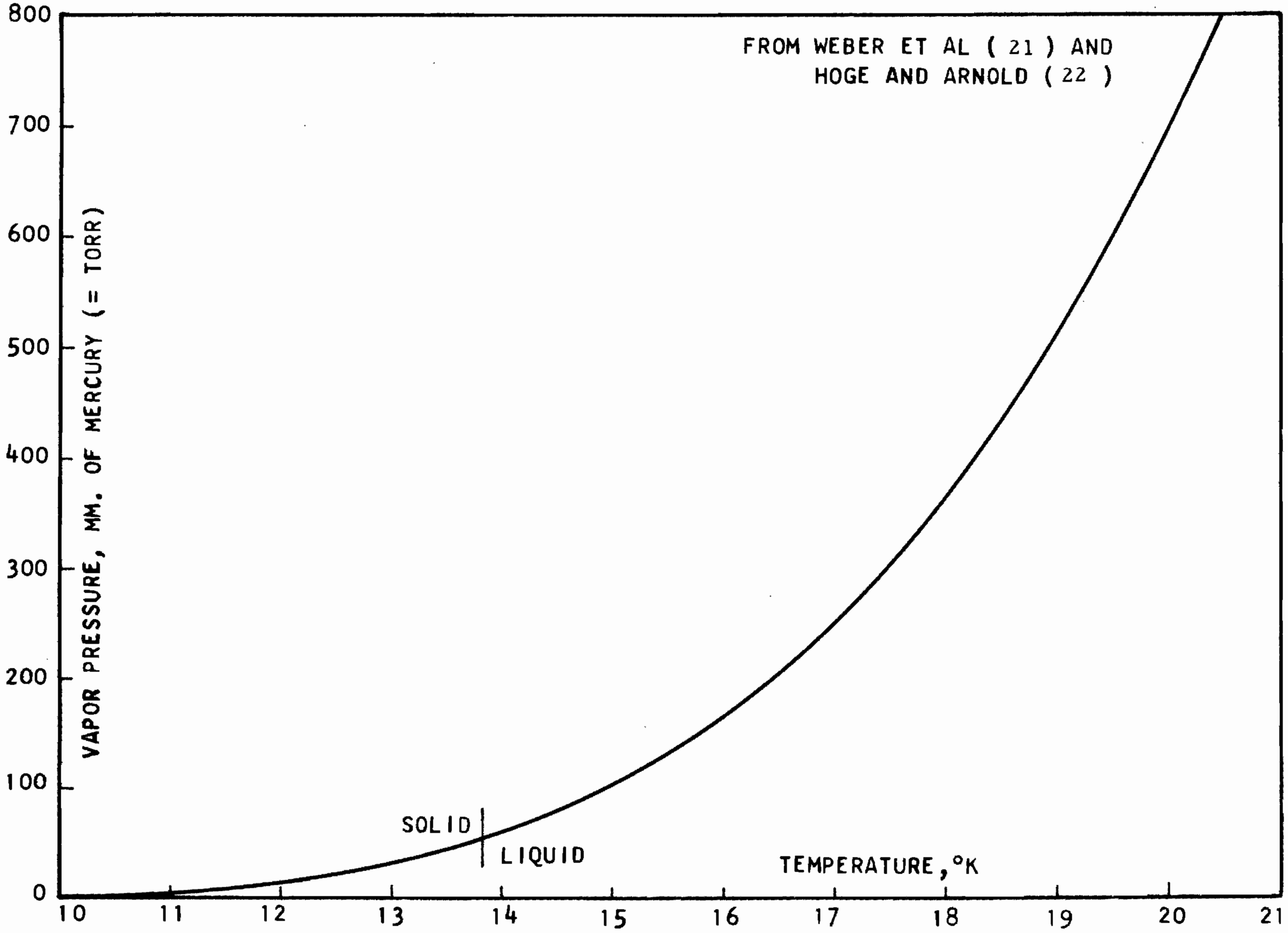

Figure 46. Vapor Pressure of Solid and Liquid Parahydrogen in Torr

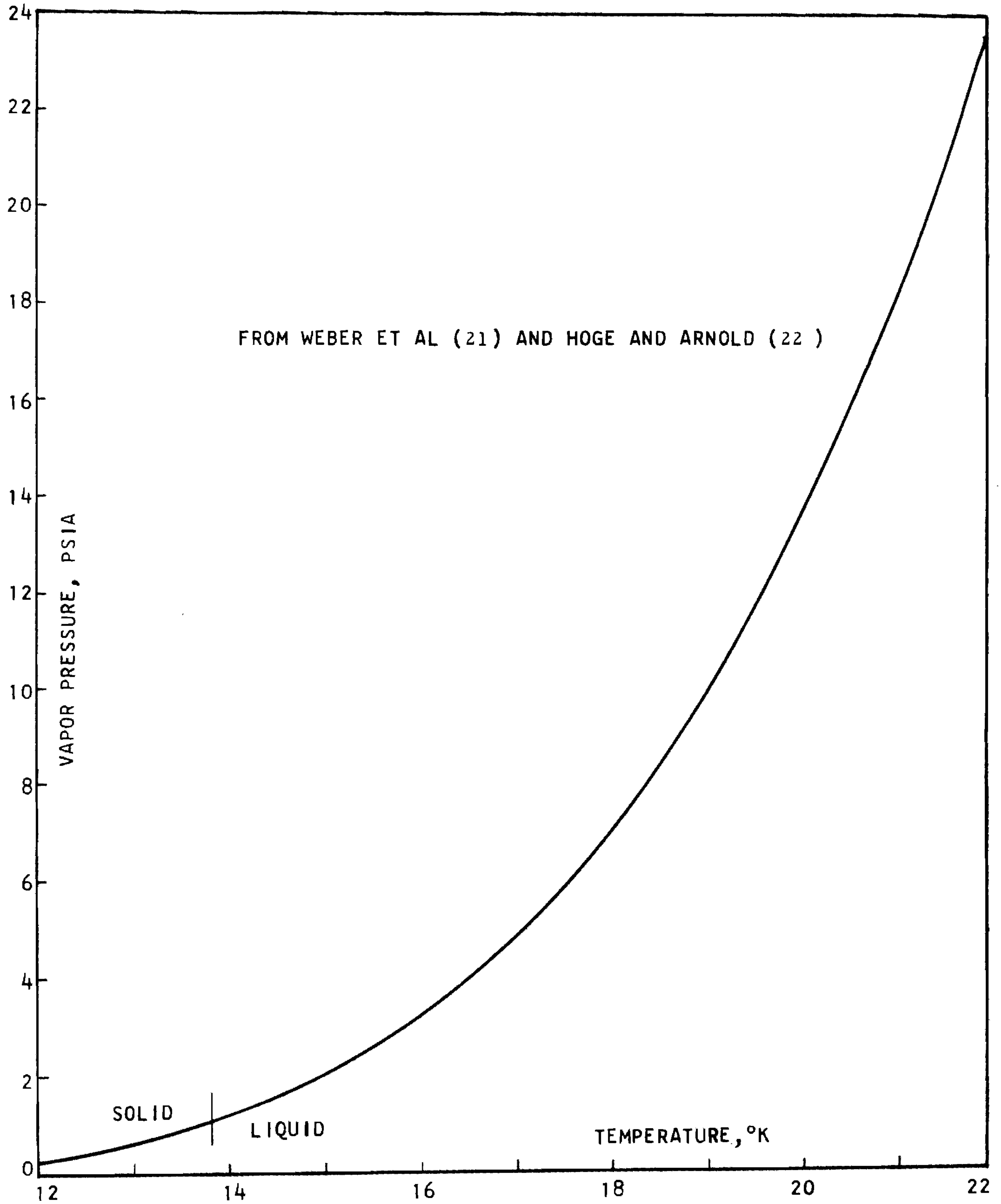

Figure 47. Vapor Pressure of Solid and Liquid Parahydrogen in psia

of the National Bureau of Standards, has recently appeared. New points were determined at temperatures above the normal boiling point (20.268 °K), and these were correlated with the best values at temperatures below the boiling point, namely those of Hoge and Arnold (22). According to Weber (21), a correction of 0.01° must be made in the temperatures used in the earlier work:

$$T(\text{Hoge and Arnold}) - 0.01 = T\ (\text{NBS-1955})$$

Table 24 gives the smoothed values from Hoge and Arnold's Table 8 (22, p. 71) in the temperature range 10°K to 20°K, corrected for the 0.01° temperature change by linear interpolation. Linear interpolation is not theoretically correct, but the error is small because the pressure change corresponding to 0.01° is small. The corrected value of the triple point of p-hydrogen is 13.803 °K.

Table 24 also gives the values between 20°K and 32°K from column 3 of Table 2 in Weber <u>et al.</u> (21, p. 237). Except for the pressure at the normal boiling point, the figures in Table 24 are smoothed values which fit the experimental values very closely. (At the boiling point the calculated value is 0.9999 instead of the experimental value of 1.0000 atm. abs.)

According to Weber <u>et al</u>. (21), vapor pressures in the temperature range between the triple point and the boiling point are given within the experimental deviations by the equation;

$$\log_{10} P\ (\text{atm.}) = 1.772454 - \frac{44.36888}{T} + 0.02055468\ T \qquad (113)$$

Between the boiling point and 29°K, Weber <u>et al</u>. (21), derived the equation:

$$\log_{10} P\ (\text{atm.}) = 2.000620 - \frac{50.09708}{T + 1.0044} + 0.01748495\ T \qquad (114)$$

Some of the values in Table 24 have been plotted in Figures 46 and 47 for rapid interpolation. If more exact values are needed, they may be calculated from the equations given above.

No values for the vapor pressure of p-hydrogen at temperatures below 10°K have been found. For n-hydrogen, measurements have been made down to 7.43°K (23).

A.3 MEASUREMENT OF LOW TEMPERATURES

A.3.1 Introduction

This subject has been well covered by R. B. Scott in Chapter V, "Low-Temperature Thermometry," of his book Cryogenic Engineering (24), by G. K. White in his book Experimental Techniques in Low-Temperature Physics (25), and by K. D. Timmerhaus in Chapter 4 of Applied Cryogenic Engineering (26). It is, necessary here therefore, to only outline briefly the principal pertinent points and to cover some of the literature published since these books were written. The chief interest here is in the laboratory or engineering measurement of temperatures to an accuracy within about 0.1 °K.

A.3.2 Use of Vapor Pressure

In research on hydrogen slush it may be convenient to use the vapor pressure of liquid para-hydrogen as an indication of temperature. For example, if a bath of liquid para-hydrogen surrounds an experimental vessel, the temperature may be obtained by measuring the gas-phase pressure. It is essential that the bath be stirred so that the pressure measured will be the true equilibrium vapor pressure. A table and two graphs (Table 24 and Figures 46 and 47) of values for the vapor pressure of para-hydrogen were given earlier in this Appendix.

It should be noted that dissolved impurities change the vapor pressure of the liquid; their presence, therefore, leads to errors in the temperature determined by measuring the vapor pressure of liquid hydrogen. However, very few materials are soluble in liquid para-hydrogen. The impurities which could modify the vapor pressure are pretty well limited to ortho-hydrogen, helium, and perhaps neon.

A.3.3 Thermocouples

Thermocouples are convenient for use at low temperatures as well as high if the proper precautions, listed by Scott (24, pp. 119-128), are employed. At temperatures below 20°K, the two best thermcouples consist of gold alloyed with 2.11 atom-% cobalt used with pure copper, or this same gold-cobalt alloy used with an alloy of silver containing 0.37 atom-% gold. The silver alloy, called "normal silver," is preferable because it has a lower thermal conductivity than copper. Constantan may be used instead of the gold-cobalt alloy, either with copper or with the silver alloy. The gold alloy has a much higher sensitivity than constantan, but this advantage is partly offset by larger spurious voltages in the gold-cobalt caused by inhomogeneities in the wire if the inhomogeneities lie in regions of temperature change.

For accurate work, all thermocouples must be calibrated. It is necessary only to calibrate a given thermo couple at a few temperatures in the range of interest. The values thus obtained are compared with a standard table, and either a correction curve for the deviation from the standard is plotted, or, when the corrections for the tabulated values are small, a correction is calculated for any given point by linear interpolation (27, p. 150).

Powell, Caywood, and Bunch (28) of the National Bureau of Standards have published voltage calibration tables for the following thermocouples: gold-cobalt versus copper, constantan versus copper, "normal" silver versus copper, alumel versus chromel, and constantan versus iron. These authors also give valuable information on the use of the thermocouples. The same calibration values and some additional information have been published by Powell, Bunch, and Corruccini (27). The first three columns in Table 25 give figures from reference (27). The fourth column was calculated from the data in columns 2 and 3.

TABLE 25

THERMOELECTRIC POTENTIAL DIFFERENCES IN MICROVOLTS FOR THE BEST LOW-TEMPERATURE THERMOCOUPLES

Temperature °K	Gold 2.1 atom-% Cobalt versus Copper	Silver 3.7 atom-% Gold versus Copper	Gold 2.1 atom-% Cobalt versus Silver 3.7 atom-% Gold
1	0.53	0.00	0.53
2	2.09		2.09
3	4.66		4.66
4	8.22		8.22
5	12.74	0.00	12.74
6	18.20		18.20
7	24.57		24.57
8	31.83		31.83
9	39.96		39.96
10	48.93	0.01	48.92

TABLE 25 (CONTINUED)

THERMOELECTRIC POTENTIAL DIFFERENCES IN MICROVOLTS FOR THE BEST LOW-TEMPERATURE THERMOCOUPLES

Temperature °K	Gold 2.1 atom-% Cobalt versus Copper	Silver 3.7 atom-% Gold versus Copper	Gold 2.1 atom-% Cobalt versus Silver 3.7 atom-% Gold
11	58.72		58.70
12	69.30		69.30
13	80.65		80.61
14	92.75		92.75
15	105.6	0.07	105.53
16	119.1		119.0
17	133.2		133.1
18	148.1		148.1
19	163.5		163.3
20	179.6	0.2	179.4
21	196.4		196.2
22	213.7		213.4
23	231.7		231.2
24	250.1		249.6
25	269.1	0.6	268.5

Note: These voltages are with respect to a mythical reference junction kept at 0°K. The method used by the Bureau of Standards to obtain these values is described in reference (27), page 141.

The method used at the National Bureau of Standards at Boulder Colorado (29, p. 541) for making thermocouple junctions with the gold-cobalt wire involves briefly dipping a twisted pair of the thermocouple wires into a molten pool of eutectic soft solder which is held near its melting point. Caution must be observed since either prolonged dipping or higher solder temperatures will cause the gold-cobalt to dissolve in the solder pool.

Other workers have successfully welded or silver-soldered these thermocouples.

Powell and Caywood (30) have tested several thermocouples besides those mentioned above, but none proved to be as useful for low-temperature work. These less useful thermocouples were: constantan versus iron, alumel versus chromel, and gold-palladium versus platinum-iridium.

Thermocouples have the disadvantage that a reference junction kept at a fixed temperature must be used. In making low-temperature measurement it is best to keep the temperature of the reference junction at a temperature that is not far from the temperature being measured (e.g., boiling helium, hydrogen or nitrogen). This technique often improves the absolute accuracy of the measurements by avoiding spurious emf's arising from temperature gradients in the region of inhomogeneities in the thermocouple wire (24, pp. 120-121); however, the benefit of keeping the reference junction at a low temperature is lost if the wire between the junctions is allowed to pass through a warm zone.

A.3.4 Resistance Thermometers

A.3.4.1 Platinum Resistance Thermometers Platinum resistance thermometers have not usually been used at temperatures below about 20°K because of their low sensitivity at there temperatures. Recently, however, a new type of platinum resistance thermometers has been described (31, p. 798) which has a resistance of about 1380 ohms and a sensitivity of about 0.04 ohm per degree at 5°K, increasing to 0.12 ohm at 10°K; this thermometer has been successfully used down to 7°K. When platinum resistance thermometers are to be used at low temperatures, a bridge capable of measuring small voltages with precision must be used.

A.3.4.2 Germanium Resistance Thermometers A sensitive resistance thermometer for use at temperatures below 10°K is made of suitably doped germanium (24, pp. 132-134; 26). Even though quite expensive, this type of thermometer is coming into rather common use because, if well made by the manufacturer, they are stable and give reproducible readings without frequent recalibration.

When high accuracy and a reproducibility of ± 0.001°K is required, germanium thermometers are apparently much better than carbon thermometers. When measurements are to be made only to ± 0.1°K, carbon thermometers come sufficiently close to equilibrium within a few minutes, but it took several weeks at 4.2°K for some carbon thermometers to come within 0.001°K of equilibrium in tests made by Edlow and Plumb (32). A germanium thermometer reached equilibrium within 0.001 °K in a little over an hour; moreover, the germanium thermometer retained reproducibility within a millidegree at 4.2 °K during experiments carried out over a period of several months. Other authors have found even better reproducbility for germanium thermometers, viz., $\pm 10^{-4}$ °K (24, p. 133).

A.3.4.3 Carbon Resistance Thermometers Carbon thermometers are far less expensive than germanium thermometers, but the carbon thermometers have the disadvantage that they usually are subject to loss of calibration when thermally cycled. The quality and sensitivity of carbon thermometers varies considerably among different manufacturers (33, p. 68).

When carbon thermometers are employed, they should be recalibrated at three different temperatures each time they are to be reused for low-temperature service after having been allowed to warm to room temperature (25, p.126). Conveniently, the three points may be the boiling point and triple point of hydrogen and the boiling point of helium. Alternatively, if a hydrogen bath is well stirred and the vapor pressure can be read accurately, any three points between the boiling point and triple point may be used. Temperature measurements with properly calibrated carbon thermometers of good quality are accurate ±0.1 °K or better (34).

A convenient way to obtain the temperature values corresponding to resistances measured on carbon thermometers is to use the equation of Clement and Quinnell (35):

$$\log R + K/\log R = A + B/T \qquad (115)$$

where R = resistance, ohms
T = temperature, °K
A, B, and K = constants derived from calibration.

Typical values of the three constants of Equation (115) for temperatures between 4 °K and 20 °K are: A = 3.687, B = 2.931 and K = 3.343 (34).

A.3.4.4 Thermistors Thermistors are sensitive at liquid hydrogen temperatures, have reproducible outputs, and are small enough to act as point sensors (36). They are capable of measuring temperatures to an accuracy of better than 0.05 °K, provided they are calibrated under the exact conditions for which they are to be used (33).

A.3.5 Gas Thermometers

Gas thermometers are usually not as easy to use as the other types of thermometry mentioned above, but they represent the most accurate means yet devised for determining the true thermodynamic temperature (24, p. 112). They are usually employed for making accurate calibrations of other thermometers, although they are occasionally used for direct temperature measurements. Din and Cockett (33, p. 72) describe a helium-filled thermometer bulb connected by capillary tubing to a Bourdon gauge, for industrial low-temperature use.

A.4 RHEOLOGY OF LIQUID AND SOLID HYDROGEN

A.4.1 Introduction

Rheology is the study of the flow properties of matter. It is of interest in connection with the motion of condensed hydrogen inside tanks and the transfer of liquid hydrogen or hydrogen slush from one container to another.

A.4.2 Viscosity of Liquid Hydrogen

The most important rheological property of liquids is the viscosity. A number of measurements have been reported for the viscosity of liquid hydrogen at saturation pressure, but no reports have been found in the literature for the viscosity at pressures greater than those of the vapor pressure at the temperature of each measurement. No comparison of the viscosity of para-hydrogen with that of normal-hydrogen has been found; in fact, none of the articles in which viscosities are reported give the o-p composition of the hydrogen used. It is assumed that the composition for which measurements were reported was in all cases that of normal (75 percent ortho) hydrogen, because the usual method of preparing liquid hydrogen for the measurement of physical properties is to condense gaseous normal-hydrogen into the vessel in which the properties are to be measured.

Results of viscosity measurements on liquid hydrogen have been published in a number of different papers. In all cases the liquid hydrogen is under its own vapor pressure. In the first major compilation (9) of the properties of hydrogen, published by the National Bureau of Standards in 1948, two main sets of results were mentioned: those of Johns (37) and those of Keesom and MacWood (38). Johns used the capillary flow method, whereas the other investigators measures the logarithmic decrement of an oscillating disk or sphere in liquid hydrogen. The results of these different measurements were not in agreement, but lay on roughly parallel lines when plotted against temperature (9 , p. 452). Since the NBS scientists had no reason to think that one method was superior to the other, they drew a curve between the two sets of reported values and used this curve to give the "most probable values."

In 1940 and 1941, Van Itterbeek and Van Paemel published papers (39) describing some viscosity measurements on liquid hydrogen which were not mentioned in the Bureau of Standards compliation. The values given in these publications did not agree with any of the previous work, and apparently they may now be ignored, because in 1962, Van Itterbeek and Van Paemel, together with H. Zink, published a brief paper (41) presenting new measurements without reference to even their own previous work. They give some "corrected" (probably recalculated) values of Keesom and MacWood which agree fairly well with their new results, and they point out that a lone 1917 Leiden value (40) falls close to their new curve. Neither the Bureau of Standards review (9) nor Van Itterbeek et al. (41) mention any way of reconciling the latter's results with those of Johns (37).

The result is that the curve selected by the Bureau in 1948 (9) as most probable is still a good compromise. Perhaps the most probable values should be weighted slightly more toward the lower values since all the better measurements made by oscillating disk or sphere methods are found to give values which are in fairly good agreement, thus leaving only the capillary results of Johns (37), with their higher values, in disagreement with the rest.

Table 26 gives the values of Johns (37) and the most recent values published by Van Itterbeek and his associates (41). Both sets of values are plotted in Figure 48 . The curve labeled "best" in Figure 48 was drawn between the other two curves, and values read from it are also given in Table 26. These values are weighted slightly toward the lower curve except at higher temperatures, where the results of Johns are possibly a little more reliable.

The viscosity measured (40) in Leiden in 1917 at the boiling point of liquid hydrogen is also plotted in Figure 48.

The viscosity of liquid hydrogen is extremely low, as can be seen by comparing the values in Table 26 with the values (in micropoise) for the following liquids:

	0°C	50°C	100°C
Water	17,921	5,494	2,838
Ethyl alcohol	17,730	7,020	-
Benzene	-	4,420	-
Normal-Hexane	4,010	2,480	-

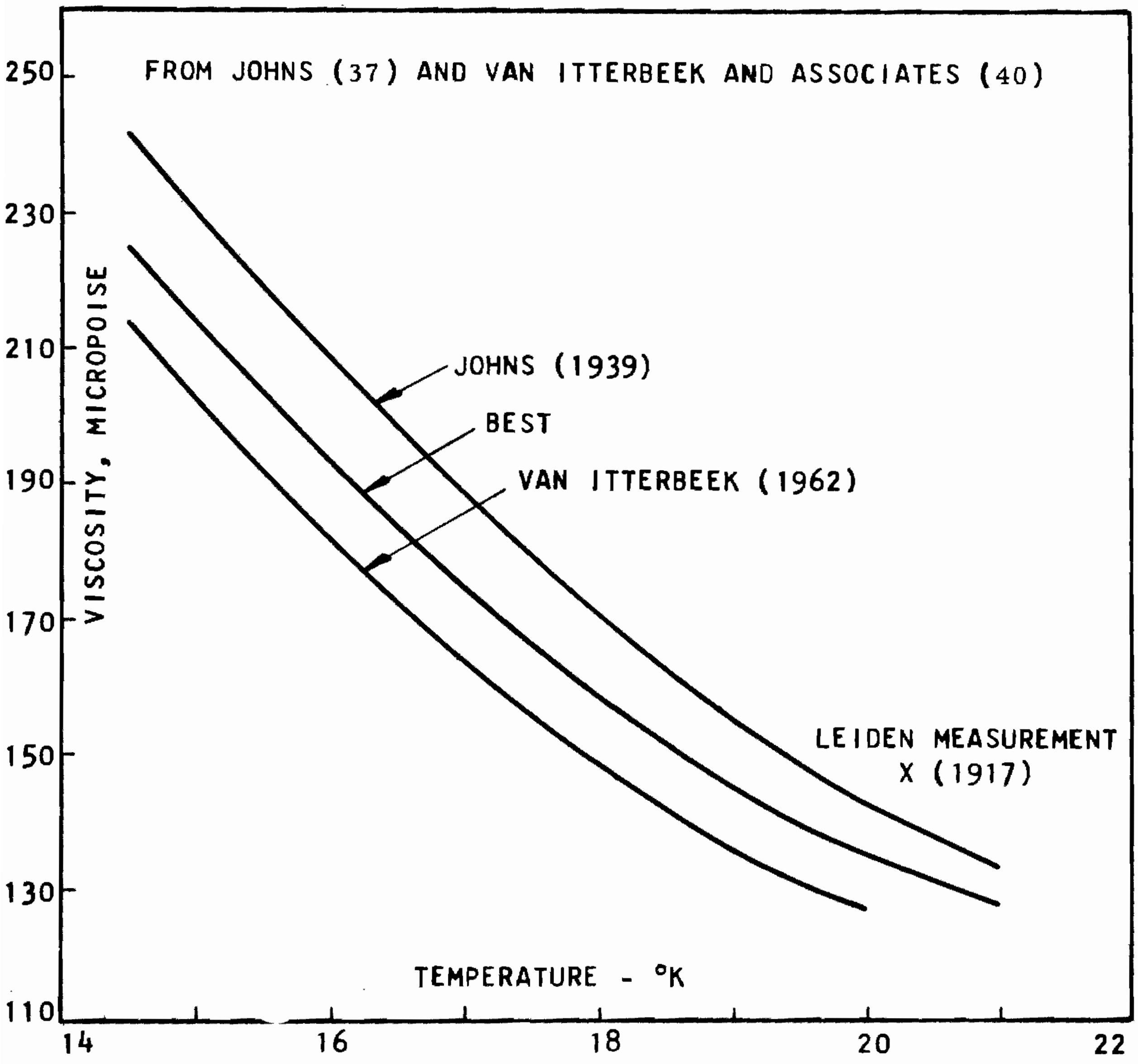

Figure 48. The Viscosity of Liquid Hydrogen

TABLE 26

VISCOSITY OF LIQUID HYDROGEN AT SATURATION PRESSURE

	Viscosity, micropoise		
Temp. °K	Johns (37) 1939	Van Itterbeek (41) 1962	"Best" Values
14.5	241.8	213	225
15.0	230.3	201	214
16.0	209.0	182	193
17.0	189.1	164	174
18.0	170.5	150	158.5
19.0	154.6	136	145
20.0	142.5	127.5	135
21.0	133	-	-

Note: It is believed that the liquid hydrogen used in making these measurements was normal (75% ortho).

A.4.3 Extrusion of Solid Normal Hydrogen

In the cases of solids, important rehological properties are deformation and extrusion. Extrudability is one measure of deformability.

The only rheological study of solid hydrogen found in the literature is that of Stewart (42), in which extrusion measurements at 4.2 °K are reported. Stewart points out that when pressure is to be applied to a solid at very low temperatures, it is necessary to design the apparatus so that a minimum of heat can leak into the cryogenic solid. He accomplished this by the use of long stainless steel tubes 3/4 in. O.D. with a wall thickness of 0.06 in. These "compression members" were attached to a conventional hydraulic press at room temperature. Through these members, forces up to 1.5 tons could be applied to 1/4 in. diameter damples kept at 4.2 °K. The low temperature was maintained by a bath of liquid helium; once the apparatus had been cooled down, less than 100 cc of liquid helium per hour was lost by evaporation from the cryostat.

Stewart (42) found that the most convenient measure of plastic flow strength is the applied pressure required to cause extrustion of cylindrical samples through an axial hole of smaller diameter than the diameter of the cylinder. At 4.2 °K, the only temperature at which he made any measurements, Stewart found that it took a pressure of 232 atmospheres to extrude solid hydrogen rapidly and smoothly through a 1/8 in. diameter hole, starting with a cylindrical sample 1/4 in. in diameter and 1/2 in. long. This pressure was reproducible within about ± 10 percent.

Stewart compared the extrudability of solid hydrogen with that of the alkali metals and with solid neon, argon, krypton and nitrogen. Of all these materials, hydrogen was extruded at the lowest pressure; it was the most plastic and transmitted pressure the best. In fact, solid hydrogen flows so easily that in the earlier measurements it was extruded through the small annular space between the piston and the cylinder wall; this undesired extrusion led to loss of the sample. The difficulty was eliminated by use of a metallic potassium packing seal. Even at 4°K, potassium was found to be plastic enough to flow and seal off the space around the piston.

Solid argon and krypton samples were shattered at 4.2 °K instead of being extruded.

The theory of the flow of plastic solids has been discussed by Prager (43).

A.4.4 Determination of Viscosity of Liquid Hydrogen Under Pressure

It would be of interest to measure some of the rheological properties which are not now known for condensed hydrogen systems. Since liquid hydrogen may, in the future, be transported in pipes under pressure, it is desirable to measure its viscosity at pressures above saturation.

The three principal types of methods of measuring viscosity are those using rotating disks and other rotating devices, falling bodies (44.45), and flow through capillary tubes. It would probably not be practical to use the rotating disk method in a pressure vessel if the drive shaft for the disk must emerge through the pressure casing, because the resistance encountered by the shaft in going through a packing gland is likely to be greater than the resistance of the fluid to the motion of the disk. It also seems rather difficult to have the whole mechanism submerged in the liquid hydrogen whose viscosity is being measured.

The rate with which a sphere or other solid object falls through a liquid when the rate of all has attained constant velocity is a measure of the viscosity of the liquid. It may be possible to build a pressure vessel with a narrow window for determining visually the rate of fall of the object released magnetically or otherwise from outside the apparatus. Another possibility is to employ a radioactive object and measure its rate of fall by the detection of radiation at several points; this would require the use of a radiation detector that will operate at liquid hydrogen temperatures, unless a method can be devised whereby gamma radiation could be detected outside the pressure vessel in such a way as to show the location of the falling object.

Bridgman (46, 44 p. 87) and Dow (44, p. 88) used apparatus of a type first suggested by Lawaczeck (44 , p. 87) in determining the viscosity of 45 liquids at pressures up to 12,000 atm. In this apparatus a hollow tubular vessel, made of steel, falls inside a steel pressure tube 6 mm I.D. The clearance between the hollow vessel and the tube is very small (3.g., 0.0125 cm for water), and the length of fall in 3 cm. Electrical contact points near the ends of the vessel are used to signal, through insulated electrodes in the pressure tube, the position of the vessel in the pressure tube. It would appear that a modification of this method could be used to determine the viscosity of liquid hydrogen under pressure.

The use of the capillary flow method is another possibility. Two pressure vessels, each equipped with a piston, could be connected by a capillary tube with the whole apparatus (except the tubes through which the pressure is transmitted to the pistons) being submerged in a stirred liquid hydrogen bath kept at the desired temperature. One vessel would be filled with liquid hydrogen. The differential pressure acorss the capillary (and between the pistons) would be kept sufficiently small so that a viscosity measurement could be made by timing the rate at which one of the pistons moves when the differential pressure is applied.

R. B. Dow (47) has reviewed the subject of the measurement of rheological properties under high pressure.

A.4.5 Rheology of Hydrogen Slush

Nothing has been found in the literature on the properties of hydrogen slush. Most of the recent literature discussions of the rheology of suspensions of solids in liquids deal with collodial suspensions rather than with suspensions of crystallites in a two phase single component system such as hydrogen slush. For example, in a symposium (48) published in 1961 on the rheology of suspensions, there is not a single contribution on suspensions of crystals in liquids. The closest thing found in the literature is a discussion of the rheology of sand-water mixtures (49).

A modern treatment of viscosity is given in the book by Bird, Stewart, and Lightfoot (50). This book gives five representative mathematical models (empirical equations) which can be used to express the rheology of suspensions. After experimental data on the apparent viscosity of hydrogen slush become available, it can be determined which of these models best represents the facts.

APPENDIX II

SAMPLE CALCULATIONS FOR THEORETICAL INVESTIGATIONS OF HYDROGEN SLUSH PRODUCTION TECHNIQUES

B.1 SYMBOLS

The symbols used in the calculations discussed both here and in Section 3 are listed below:

A	area
c	specific heat
D	distance between plates
g	acceleration of gravity
H	enthalpy
H	height of exchanger plates
h	specific enthalpy
k	thermal conductivity
m	helium mass
N_{Ra}	Raleigh number
P	pressure
Q	total heat to be removed
q	slush quality in percent
S	entropy
s	specific entropy
SMR	specific mass requirement
T	temperature
U	heat transfer coefficient
V	vapor volume
v	specific volume
W	refrigeration capacity in watts
X	gas evolved during expansion (fraction)
X	interval starting mass based on unit final product mass
x	liquid mass
Y	mass pumped for an interval based on unit final product mass
y	vapor mass
z	solid mass

α	convection modulus
β	cubic expansion coefficient
Δ	increment
Σ	summation
λ	latent heat of vaporization of helium
μ	free convection heat transfer coefficient
η	viscosity
π	product
ρ	density
τ	time interval
θ	temperature difference between heat exchanging streams

Superscripts

*	isenthalpic expansion
'	triple point conditions

Subscripts

atm	atmospheric
avg	average
$e\theta$	condition $\theta°$ from T
f	final condition
g	gas
He	helium
H_2	hydrogen
i	initial condition
L	liquid
n	normal conditions
norm	normal
o	original liquid condition for a process or series of steps
$o\theta$	condition $\theta°$ from T_o
p	constant pressure
q	slush of quality q
r	refrigerator
s	solid
sat	saturated condition
solid	all solid
T	temperature
t	terminal liquid condition for a process or series of steps and triple point conditions
v	vapor
1	first step
2	second step

B.2 CALCULATIONS

All thermodynamic properties used in the following calculations were obtained from Mullins, Ziegler, and Kirk (1). Physical data are from NBS Compendium (17) and Cryogenic Data Book (19).

B.2.1 STRAIGHT VACUUM PUMPING

B.2.1.1 Specific Mass Requirement

TABLE 1

Equation (3a), giving column 2 in Table 1

$$SMR_{if} = \frac{s_{V_{avg}} - s_{Lf}}{s_{V_{avg}} - s_{Li}}$$

with T_i = 20.278 and T_f = 20.00°K and

$$SMR = \frac{\frac{14.595 + 14.708}{2} - 3.939}{\frac{14.595 + 14.708}{2} - 4.003}$$

$$= 1.0060102$$

and with T_i = 20.00°K and T_f = 19.00°K

$$SMR = \frac{\frac{15.135 + 14.708}{2} - 3.713}{\frac{15.135 + 14.708}{2} - 3.939}$$

$$= 1.02057819$$

Equation (8), giving column 3 in Table 1

$$SMR_{ot} = \prod_{o}^{t} SMR_{if}$$

where o = 20.278°K and t = 19.00°K

$$SMR = (1.0060102)\ (1.02057819)$$

$$= 1.02671207$$

Equation (13), giving SMR_{tq}, the SMR from triple point liquid to all solid:

$$SMR_{solid} = \frac{(s_S - s_V)}{(s_L - s_V)}$$

$$= \frac{-17.730}{-15.701}$$

$$= 1.12922744$$

B.2.1.2 Pumped Volume Requirement

TABLE 2

Equation (19), giving the first entry of column 3 in Table 2:

$$Y_{if} = SMR_{ot} \ (SMR_{if} - 1)/SMR_{if}$$

$$= (1.2269499)\ (0.0060102)/(1.0060102)$$

$$= 0.00670731 \text{ Lb.}$$

Equation (24), giving the first entry of column 4 in Table 2:

$$V_{Tif} = Y_{if} / \rho_{Tif\ avg}$$

For the table, T is the saturation temperature, and

$$= \frac{0.00670731 \text{ Lb.}}{0.081 \ \text{Lb/Ft.}^3}$$

$$= 0.083 \text{ Ft.}^3\text{/Lb. of triple point liquid}$$

Equation (18), giving the second entry in column 3 of Table 2:

$$Y_{if} = X_i \ (SMR_{if} - 1)/SMR_{if}$$

$$= (1.2202426)\ (0.02057819)/1.02057819$$

$$= 0.02250196 \text{ Lb.}$$

Equation (21), giving the starting mass for above calculation of the second entry:

$$X_{i+1} = X_i - Y_{if}$$

$$= 1.2269499 - 0.00670731$$

$$= 1.2202426 \text{ Lbs.}$$

B.2.2 SEMI-FLOW VACUUM PUMPING

B.2.2.1 Specific Mass Requirement

TABLE 3

Equation (34), giving column 2 of Table 3:

$$SMR^*_{ot} = (h_{Lo} - h_{vt})/(h_{Lt} - h_{vt})$$

$$= \frac{33.13 - 250.00}{58.92 - 250.00}$$

$$= 1.1349696$$

Equation (13), giving column 3 of Table 3:

$$SMR_{solid} = 1.12922744$$

Equation (35), giving column 4 of Table 3:

$$SMR^*_{os} = SMR^*_{oq} \text{ where } q = 100$$

$$SMR^*_{os} = (SMR^*_{ot})\ (SMR_{solid})$$

$$= (1.1349696)\ (1.12922744)$$

$$= 1.28168306$$

B.2.2.2 Pumped Volume Requirement

Combining Equations (17) and (24), giving column 5 in Table 3:

$$V_{\text{sat ot}} = \frac{SMR_{ot} - 1}{\rho_{\text{Tif avg}}}$$

$$= \frac{0.1349696}{0.0078}$$

$$= 17.30379 \text{ Ft.}^3$$

B.2.3 CASCADED VACUUM PUMPING

B.2.3.1 Specific Mass Requirement

TABLE 4

Equation (33), giving column 2 of Table 4:

$$SMR^*_{if} = (h_{Lf} - h_{vf})\ (h_{Li} - h_{vf})$$

where i = 760 Torr and f = 500 Torr

$$SMR^*_{if} = \frac{52.76 - 269.86}{58.92 - 269.86}$$

$$= 1.029202$$

and with i = 500 Torr and f = 200 Torr

$$SMR^*_{if} = \frac{42.74 - 261.25}{52.76 - 261.25}$$

$$= 1.048059$$

Equation (8), giving column 3 of Table 4:

$$SMR^*_{ot} = \prod_{o}^{t} SMR^*_{if}$$

where o = 760 Torr and t = 200 Torr

$$SMR_{ot} = (1.029202)\ (1.048059)$$

$$= 1.078664$$

B.2.3.2 Pumped Volume Requirement

TABLE 5

Equation (18a), giving the first entry of column 3 in Table 5:

$$Y_{if} = X_i \; (SMR^*_{if} - 1)/SMR^*_{if}$$

where $X_i = SMR^*_{ot}$ at $q = o$

$$Y_{if} = (1.127967)\;(0.029202)/1.029202$$

$$= 0.032004 \text{ Lb.}$$

Equation (42), giving the first entry of column 4 in Table 5:

$$V_{Tif} = Y_{if} / \rho_{Tf}$$

$$= \frac{0.032004}{0.057}$$

$$= 0.561474 \text{ Ft.}^3$$

Equation (21), giving the starting mass for the second increment of column 3 in Table 5:

$$X_{i+1} = X_i - Y_{if}$$

$$= 1.127967 - 0.032004$$

$$= 1.095963$$

Equation (18a), giving the second entry in column 3 of Table 5:

$$Y_{if} = X_i \; (SMR^*_{if} - 1)/SMR^*_{if}$$

$$= (1.095963)\;(0.048059)/1.048059$$

$$= 0.050256 \text{ Lb.}$$

B.2.4 HELIUM GAS REFRIGERATOR COOLING METHOD

B.2.4.1 Batch Process

TABLE 6

Equation (43), averaged for the increment from 19°K to 21°K, gives the first entry of column 1 for Table 6:

$$Q_{if} = X_i (h_{sat\ i} - h_{sat\ f})$$

for $T_i = 21.0°F$ and $T_f = 19.0°K$ and $X_i = 1$

$$Q_{if} = (62.49 - 53.01)/2$$

$$= 4.74 \text{ cal/mole °K}$$

$$= 4.24 \text{ Btu/Lb. °K}$$

Equation (60) gives the first entry of column 2 for Table 6:

$$\tau_{if} = 7.04 \ _{avg} D (h_i - h_f)/k\alpha^{1/3} \theta_L^{4/3}$$

$$= (7.04)(4.42) D (4.24)/(1.83 \times 10^{-5})(4.51 \times 10^3) 41$$

$$= 39.1 D \text{ sec/°K}$$

Equation (59b) gives the first entry of column 3 for Table 6:

$$W_L = 0.142 K\alpha^{1/3} \theta^{4/3}/\rho_{avg} D$$

$$= (0.142)(3.29 \times 10^{-5})(5.45 \times 10^3) 18.8/4.42 D$$

$$= 0.1085/D \text{ Btu/sec. lb.}$$

$$= 115/D \text{ watts/lb.}$$

The convection modulus α in equations (59b) and (60) is given in equation (53) as:

$$\alpha = \rho^2 C p g \beta/\eta k$$

For 20°K

$$\alpha = (4.42)^2(4.24)(32.2)(0.0182)/(9 \times 10^{-6})(3.29 \times 10^{-5})$$

$$= 163.5 \times 10^9/\text{ft.}^3\ {}^\circ\text{K}$$

where the physical properties are from references 1, 17 and 19.

TABLE 7

Equation (43) gives for the first column in Table 7:

$$Q_{if} = X_i\ (h_{sat\ i} - h_{sat\ f})$$

for $T_i = 20.278°\text{K}$ and $T_f = 20°\text{K}$ and $X_i = 1$

$$Q_{20.278 \to 20} = 58.92 - 57.59 = 1.33 \text{ cal/mole}$$

$$= 1.192 \text{ Btu/lb.}$$

for $T_i = 15.0°\text{K}$ and $T_f = 14°\text{K}$ and $X_i = 1$

$$Q_{15-14} = 37.23 - 33.76 = 3.47 \text{ cal/mole}$$

$$= 3.11 \text{ Btu/lb.}$$

Equation (46a) gives the second column in Table 7:

$$\tau_{if} = Q_{if}/W_{if}$$

which for $W_{if} = Q_{15-14}$ yields

$$T_{20.278 \to 20}/T_{15-14} = 1.192/3.11 = 0.383$$

TABLE 8

Equation (44) gives for the first column in Table 8:

$$Q_{tq} = qx\ (h_{tL} - h_{ts})$$

and for $q = 50\%$

$$Q_{t50} = 0.5\ (33.13 - 5.096) = 0.5\ (28.03) = 14.02 \text{ cal/mole}$$

$$= 12.55 \text{ Btu/lb.}$$

Equation (47a) gives the second column in Table 8:

$$\tau_q = Q_q/W_q$$

which for $W_q = Q_{15-14}$ and $q = 50\%$ yields

$$\tau_{50} = 12.55/3.11 = 4.04$$

Equation (48b) gives the last column in Table 8:

$$\tau_{oq} = (\sum_{o}^{t} Q_{if} + Q_{tq})/W_q$$

which for $W_q = Q_{15-14}$ and $q = 50\%$ yields

$$\tau_{o\to 50} = (23.03 + 12.55)/3.11 = 11.47$$

B.2.4.2 Flow Process

TABLE 9

Equation (75) gives the second column in Table 9:

$$T_{ro} = T_t - e_L - q\,[\,T_{oe} - (T_t - e_L)\,]\,(h_{ot} - h_{os})/(h_o - h_{ot})$$

for $q = 50\%$, $T_{oe} = 20°K$, $e_L = 1$ and

$$T_{ro} = 13.8-1-0.5[\,20-(13.8-1)]\,(33.13-5.10)/(58.92-33.13)$$

$$= 12.8 - 0.5\,[7.2]\;(28.03/25.79)$$

$$= 12.8 - 3.9$$

$$= 8.9°K$$

Equation (76) gives the third column in Table 9:

$$T_{mean} = [\,T_{oe} - T_{ro}\,]/\ln\,(T_{oe}/T_{ro})$$

for $q = 50\%$, $T_{oe} = 20°K$ and $e_L = 1$, $T_{ro} = 8.9°K$ and

$$T_{mean} = [\,20-8.9\,]/\ln\;20/8.9$$

$$= 11.1/\ln 2.25$$

$$= 13.7°K$$

B.2.5 LIQUID HELIUM COOLING

B.2.5.1 Batch Process

TABLE 10

Equation (79) gives the first entry in the second column of Table 10:

$$(m/x)_{ot} = (h_o-h_t)/(\lambda+c_p[(T_o+T_t)/2-4.2)]$$

$$= (52.61-29.58)/(8.8+2.38[20.28+13.8)/2-4.2])$$

$$= 23.03/39.7 = 0.581$$

Equation (80) gives the helium requirement to produce the desired quality slush from triple point liquid.

$$(m/x)_{tq} = q(h_t - h_s)/(\lambda + c_p[T_t - 4.2])$$

for $q = 50\%$

$$(m/x)_{t-50} = 0.5(29.58-4.55)/8.8+2.45[13.8-4.2])$$

$$= 12.52/32.3 = 0.387$$

Equation (81) gives the remaining entries in Table 10:

$$(m/x)_{oq} = (m/x)_{ot} + (m/x)_{tq} = 0.968$$

B.2.5.2 Flow Process

TABLE 11

Equation (83) gives the second column in Table 11:

$$(m/x)_q = [(h_o-h_t) + q(h_t-h_s)]/[\lambda+c_p(T_{oe}-4.2)]$$

for $q = 50\%$ and with $T = 20°K$

$$(m/x)_{50} = [(52.61-29.58+0.5(29.58-4.55)]/[8.8+2.37(20.4.2)]$$

$$= [23.03 + 0.5 \cdot 25.03]/[8.8 + 2.37(15.8)]$$

$$= 35.6/46.3 = 0.767$$

Equation (87) gives the last column in Table 11:

$$\theta_i = T_i - T_{o\theta} + (x/mc_p)(h_o - h_i)$$

for $q = 50\%$ and with $T_i = 13.81°K$, $T_{o\theta} = 20°K$ and $T_o = 20.28°K$

$$\theta_{13.8} = 13.81 - 20 + [1/(0.767)(2.37)](52.61 - 29.58)$$

$$= -6.19 + 23.03/(0.767)(2.37)$$

$$= -6.19 + 12.7 = 6.5°K$$

B.2.6 HELIUM INJECTION COOLING

TABLE 12

Equation (96) gives the second and third columns of Table 12:

$$V_{He(if)n} = V_{sat(if)} \ [(P_o - P_{y(if)})/P_{atm}](T_{norm}/T_{if})$$

For the first entry in the second column $T_i = 20.278°K$, $T_f = 20.0°K$, $V_{sat(if)} = 0.083$ from column 4 of Table 2:

$$V_{He(if)n} = 0.083 \ [(760 - 735)/760] \ (294.27/20.14)$$

$$= [0.083(25)/760] \ (14.6)$$

$$= 0.0398 \text{ ft.}^3 \text{ NTP}$$

For the first entry in the third column of Table 12, $T_i = 20.278$, $T_f = 20.0°K$, but $V_{sat(if)} = 0.094$ from column 6 of Table 2:

$$V_{He(of)n} = 0.094 \ [(760 - 735)/760] \ (294.27/20.14)$$

$$= [0.094(25)/760] \ 14.6$$

$$= 0.0449 \text{ ft.}^3 \text{ NTP}$$

APPENDIX III

COST ESTIMATION PROCEDURE FOR HYDROGEN SLUSH PRODUCTION SYSTEMS

This appendix describes the procedures used to develop general costs for hydrogen slush production system components. It also presents the basic assumed costs for the cryogenic fluids used in these production systems. The procedures described here are used to develop detailed production system costs in Appendix IV, where the example of producing 75,000 pounds of 50 percent slush in seven days is presented, and also in Appendix V, where detailed examples of maintaining and upgrading hydrogen slush are presented.

C.1 COST FACTORS

The costs for the hydrogen slush production systems were separated into two general catagories. They are initial capital investment and operating costs.

C.1.1 Initial Capital Investment

For the systems presented in Appendix IV, the initial capital investment items considered were: vacuum pumps, slush storage tanks, and helium gas refrigerators. Other capital items which were not considered included: cryogenic pipelines, heat exchangers, phase separators, instrumentation, and labor. The cryogenic pipelines were not considered because the distance between components in an actual system can be extremely variable. To be assessed with any accuracy, the cost of heat exchangers, phase separators, instrumentation, and labor would require a much more detailed systems analysis than the scope of this contract permitted.

C.1.2 Operating Costs

Items considered under operating costs include: Hydrogen losses (vaporized liquid used for cooling), helium losses, and electrical power. Other operating cost items not considered include: heat leak, pressure drop, and labor. For the examples presented in Appendix IV, inclusion of these items was considered beyond the scope of the contract.

C.2 COST DETERMINATION OF CAPITAL INVESTMENT ITEMS

C.2.1 Vacuum Pump Cost

A commercially available vacuum pump, installed at Cape Kennedy, was used as the basis for an extrapolation which was performed to estimate costs for similar vacuum pumps with varying capacities and compression ratios. This extrapolation was then used to construct a general vacuum pump cost graph which relates the cost of a pump to its capacity at a given suction and exhaust pressure.

The following data were obtained from the vacuum pump at Cape Kennedy.

Suction pressure	8.5 psia
Discharge pressure	16 psia
Compression ratio	1.88
Capacity	89.7 cfm
Cost	$31,500

This pump is designed to operate at cryogenic temperatures with hydrogen gas.

The requirements imposed on the vacuum pump in our theoretical work on hydrogen slush production are:

Suction pressure	51 mm Hg
Discharge pressure	765 mm Hg
Compression ratio	15
Capacity	varied

Extrapolation of data obtained from the vacuum pump at Cape Kennedy has been performed according to a 0.87 exponential scale factor currently used for scaling of process compressors. The probable error of using this approximation is ±28.3 percent. This percentage is determined from the "Six-Tenths Factor" described in Reference (51).

The same exponential scale factor has been used to compute both the different capacities and the different number of stages.

Using the data given, the required number of stages to accomplish the proposed vacuum can be determined as follows:

$$\begin{pmatrix}\text{compression ratio}\\ \text{of available pump}\end{pmatrix}^{\begin{pmatrix}\text{required number}\\ \text{of stages}\end{pmatrix}} = \begin{array}{l}\text{compression ratio of}\\ \text{required pump}\end{array}$$

$$(1.88)^{N} = 15$$

$$N = 4.27$$ (This number is used rather than an integral number for cost estimation purposes.)

With the required number of stages know, the cost of a 89.7 cfm pump to create a vacuum of 51 mm Hg. and discharge at 765 mm Hg. pressure can be calculated in the following manner:

$$\begin{pmatrix}\text{required number}\\ \text{of stages}\end{pmatrix}^{(\text{scale factor})} \begin{pmatrix}\text{pump cost}\\ \text{for one stage}\end{pmatrix} = \begin{array}{l}\text{pump cost for}\\ \text{required number}\\ \text{of stages}\end{array}$$

$$(4.27)^{0.87} \times \$31{,}500 = \$112{,}000$$

The cost for this pump is plotted on Figure 49 , and it can be obtained by tracing a line with slope 0.87 in the log-log paper. Note that the line passes through $112,000 when the pump capacity is 98.7 cfm. This corresponds with the above calculation.

The costs for the other suction pressures (100, 200, and 500 Torr presented in Figure 49 were plotted in a similar manner.

C.2.2 Slush Storage Tank Costs

The required storage capacity was determined for the production systems, and a cost of $2 per gallon was assumed from costs of existing, field erected, large liquid hydrogen tanks. From this value, Figure 50 was prepared to show tank cost in $/pound versus the slush quality for the various production systems. How the tank costs presented in Figure 50 were determined is discussed in the following paragraphs.

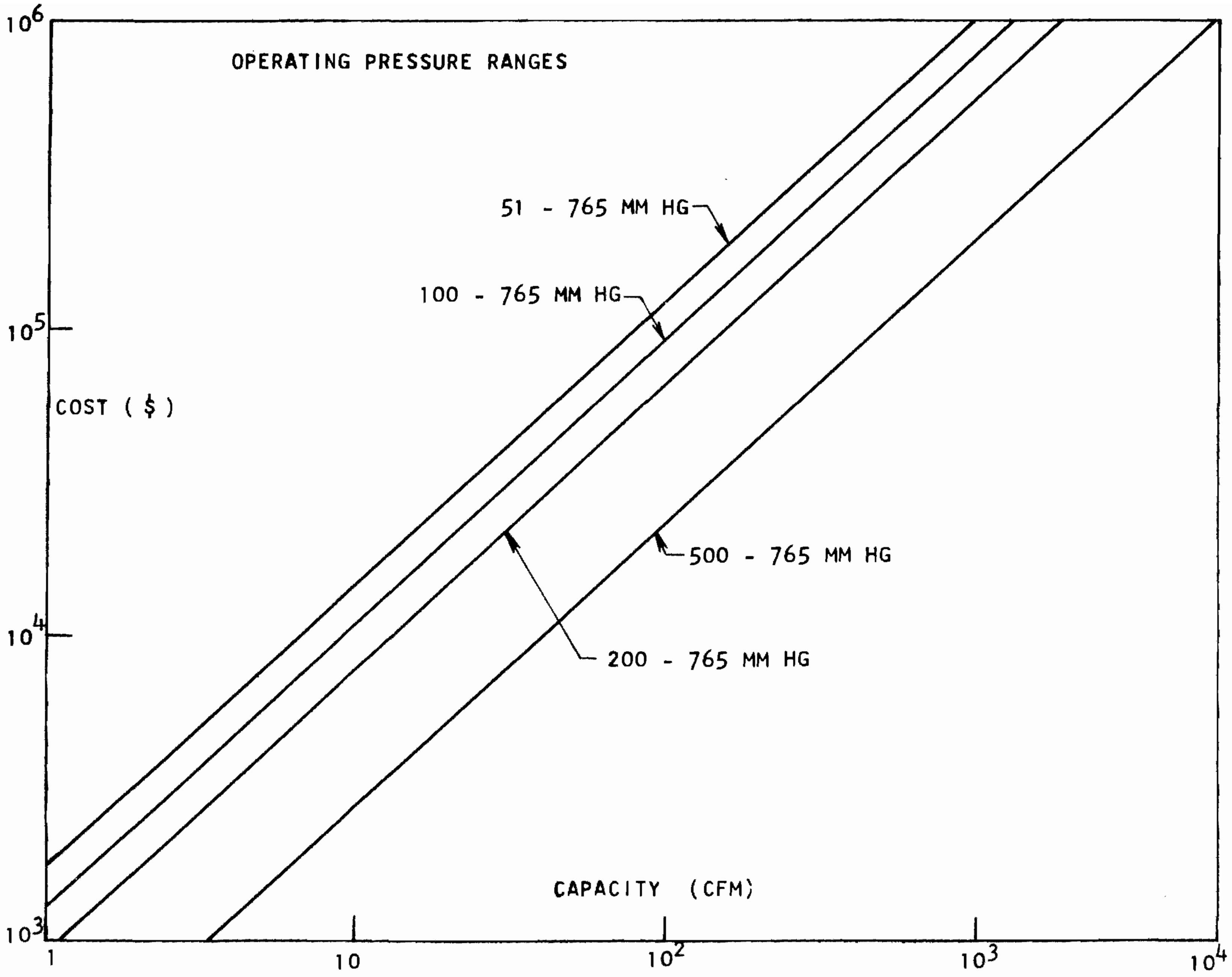

Figure 49. Capital Investment for Vacuum Pumps Operating at Indicated Pressure Ranges

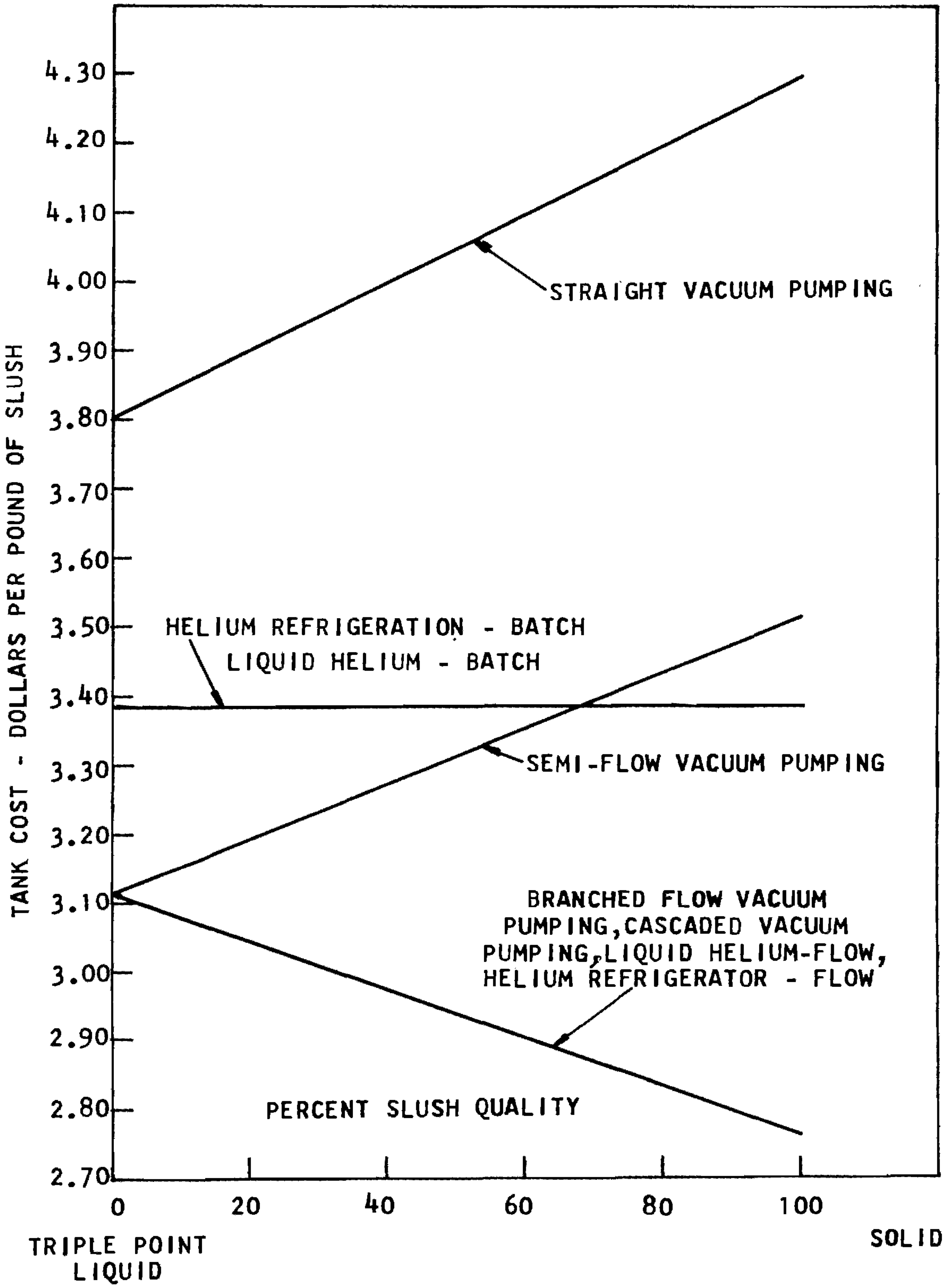

Figure 50. Capital Investment in Vacuum Insulated Tankage

C.2.2.1 Straight Vacuum Pumping The slush storage tank costs for this system are based on the fact that the tank is initially filled with saturated liquid hydrogen at 760 Torr. The quantity of liquid hydrogen initially required for a given slush quality is the quantity of slush desired times the specific mass requirement (SMR) for the quality desired.

$$\begin{array}{l}\text{tank cost}\\ \text{per pound of}\\ \text{triple point}\\ \text{liquid produced}\end{array} = \frac{\begin{array}{c}\text{1 pound product}\\ \text{(SMR triple point liquid)}\end{array}}{\begin{array}{c}\text{density of saturated}\\ \text{liquid hydrogen (lb./ft.}^3\text{)}\end{array}} \times \frac{\text{tank cost}}{\text{gallon}} \times \begin{array}{c}\text{gallon per ft.}^3\\ \text{conversion factor}\end{array}$$

$$= \frac{1.12269499 \text{ (lbs.)}}{4.419 \text{ (lb./ft.}^3} \times \frac{\$2.00}{\text{gallon}} \times \frac{7.481 \text{ gallons}}{\text{ft.}^3}$$

$$= \$3.8013 \text{ per lb. of triple point liquid}$$

$$\begin{array}{l}\text{tank cost}\\ \text{per pound of}\\ \text{solid produced}\end{array} = \frac{(1.26777797)}{4.419 \text{ lb./ft.}^3} \times \frac{14.962 \text{ (\$)}}{\text{ft.}^3}$$

$$= \$4.2925 \text{ per lb. of solid}$$

C.2.2.2 Semiflow Vacuum Pumping The slush storage tank for this system is initially filled with triple point liquid hydrogen. The tank can therefore be smaller than the straight vacuum pumping system tank since the density of the liquid hydrogen is increased.

$$\begin{array}{l}\text{tank cost}\\ \text{per pount of}\\ \text{triple point}\\ \text{liquid produced}\end{array} = \frac{\text{lbs. produced}}{\text{density of triple point liquid (lb./ft.}^3\text{)}} \times \frac{\text{tank cost (\$)}}{\text{ft.}^3}$$

$$= \frac{1 \text{ (lb.)}}{4.809 \text{ lbs./ft.}^3} \times \frac{\$14.962}{\text{ft.}^3} = \$3.1112 \text{ per lb. of triple point liquid}$$

$$\begin{array}{l}\text{tank cost}\\ \text{per pound of}\\ \text{solid liquid}\end{array} = \frac{\begin{array}{c}\text{1 (lb. produced)}\\ \text{SMR triple point liquid}\to\text{solid}\end{array}}{\text{density of triple point liquid (lbs./ft.}^3\text{)}} \times \frac{\text{tank cost (\$)}}{\text{ft.}^3}$$

$$= \frac{1.292663}{4.809} \times \frac{\$14.962}{\text{ft.}^3}$$

$$= \$3.5134 \text{ per lb. of solid}$$

C.2.2.3 Branched Flow Vacuum Pumping, Cascaded Vacuum Pumping, Liquid Helium (Flow), and Helium Refrigerator (Flow)

The slush storage tankage required for these systems must only be large enough to accomodate the much more dense hydrogen slush. As these systems are all flow type systems, the desired quality hydrogen slush is produced immediately upon entering the tank, and as a result extra tank capacity to accommodate the less dense hydrogen liquid is not needed.

tank cost per pound of triple point liquid produced = \$3.112/lb. of triple point liquid (see semiflow vacuum pumping paragraph C.2.2.2, for details of calculations)

tank cost per pound of solid produced

$$= \frac{\text{1 lb. produced}}{\text{density of solid lbs./ft.}^3} \times \frac{\text{tank cost (\$)}}{\text{ft.}^3}$$

$$= \frac{1\ \text{(lb.)}}{5.409\ \text{lbs. ft.}^3} \times \frac{\$14.962}{\text{ft.}^3}$$

= \$2.7674 per lb. of solid

C.2.2.4 Liquid Helium (Batch) and Helium Refrigerator (Batch)

In these two production systems there is no loss of liquid hydrogen. However, regardless of the slush quality produced, the tank must initially be filled with saturated liquid hydrogen at 760 Torr. The tank cost per pound of slush is therefore constant and is not dependent on slush quality.

tank cost per pound of slush produced

$$= \frac{\text{1 lb. produced}}{\text{density of saturated liquid hydrogen lbs./ft.}^3} \times \frac{\text{tank cost (\$)}}{\text{ft.}^3}$$

$$= \frac{1\ \text{(lb.)}}{4.419\ \text{lbs. (ft.}^3\text{)}} \times \frac{\$14.962}{\text{ft.}^3}$$

= \$3.3858 per lb. slush

C.2.3 Helium Gas Refrigerator Costs

On the basis of data extrapolated from actual and purposed refrigeration systems in the range of 5 -20°K, Figure 51 was prepared to show the approximate selling price versus the mean operating temperature for various refrigerator capacities.

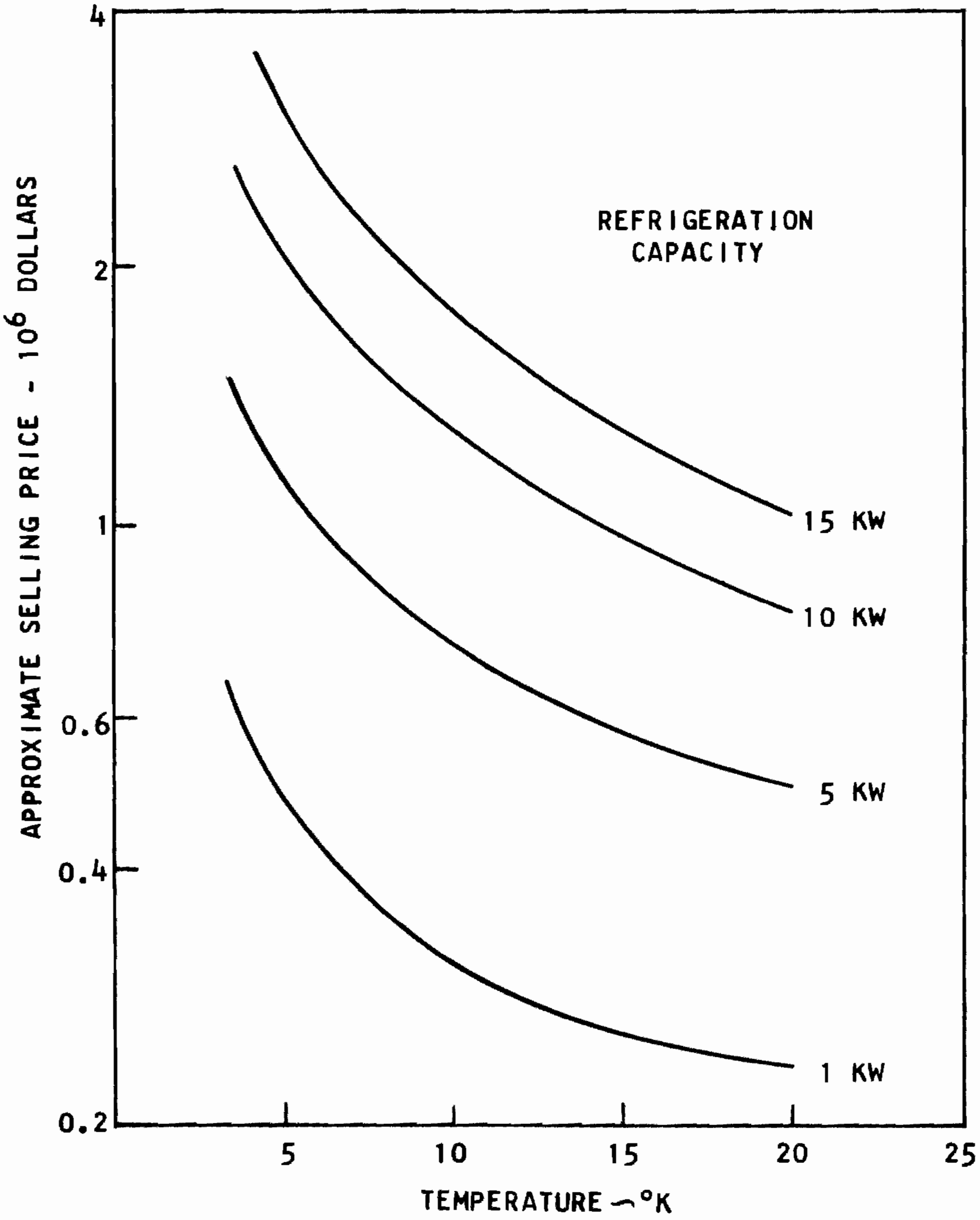

Figure 51. Approximate Selling Price for Helium Refrigerators Versus Mean Temperature of Refrigerant

C.3 CALCULATION OF OPERATING COST

C.3.1 Hydrogen Losses

The operating costs of the vacuum pumping systems are shown on Figure 52. These costs consist entirely of hydrogen losses. The hydrogen loss is calculated from the specific mass requirement and is estimated at $0.50 per pound.

operating cost to produce all solid hydrogen by straight vacuum pumping = (SMR-1) x \$0.50/lb.

= .26777797 x \$0.50/lb.

= \$.133888 per lb. of solid product

Table 27 tabulates the operating costs for the other vacuum pumping systems. These costs were calculated as above.

TABLE 27

TABULATED OPERATING COSTS

FOR VACUUM PUMPING SYSTEMS

System	Dollars Per Lb. Of: Triple Point Liquid Product	Solid Product
Straight Vacuum Pumping	0.061347	0.133888
Semifolw and Branched Flow Vacuum Pumping	0.067485	0.140841
Cascaded Vacuum Pumping	0.063983	0.136888

C.3.2 Helium Losses

The liquid helium used with the liquid helium cooling production process was assumed to cost $7.75 per liquid liter.

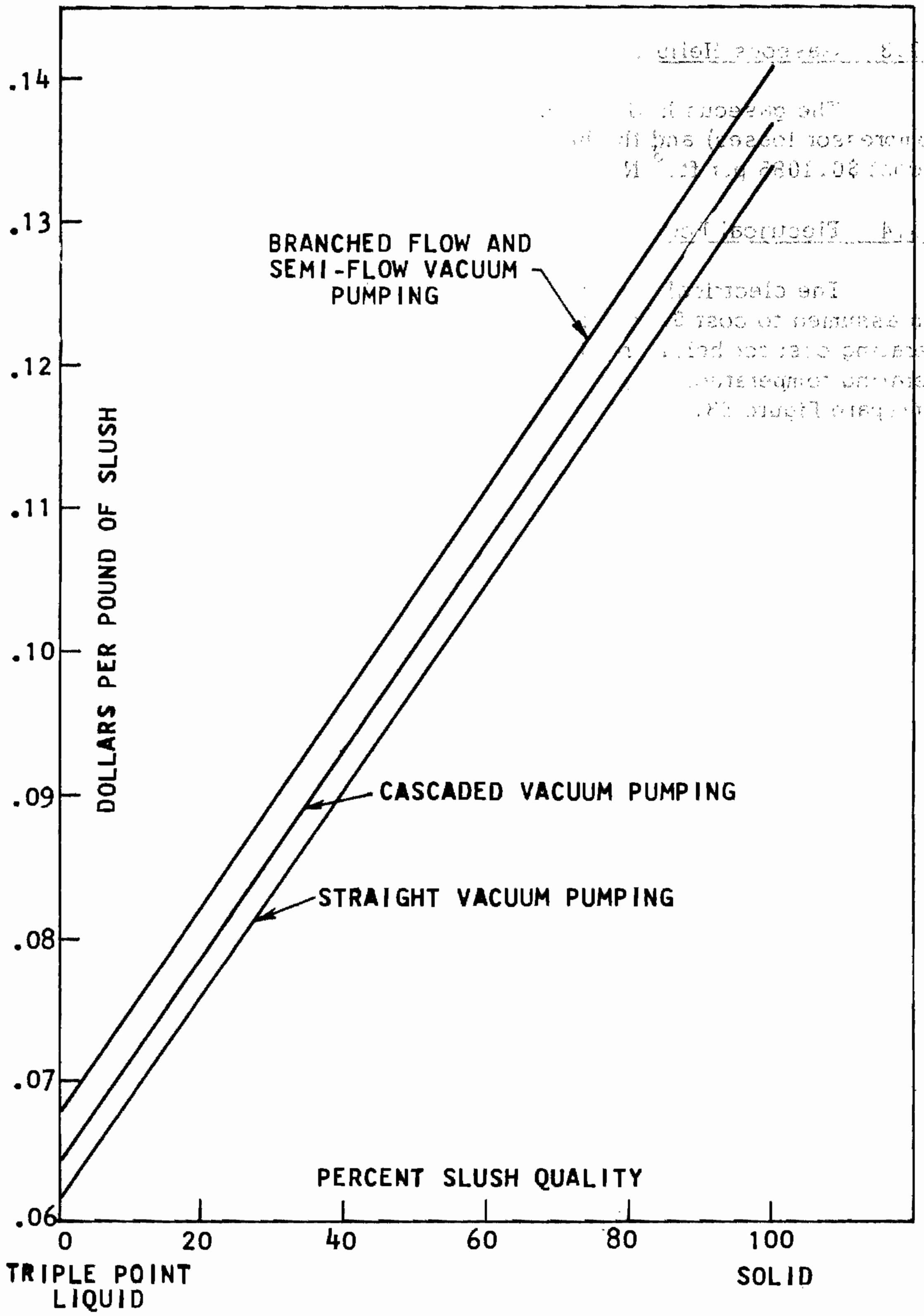

Figure 52. Operating Costs of Vacuum Pumping Systems (Hydrogen Losses)

C.3.3 Gaseous Helium

The gaseous helium used with the Joule-Thomson production system (compressor losses) and the helium gas injection cooling system was assumed to cost \$0.1085 per $ft.^3$ NTP.

C.3.4 Electrical Power

The electrical power used for operation of the helium gas refrigerator was assumed to cost \$.01 per kilowatt-hour. Figure 53 is a graph showing the operating cost for helium refrigerators on a KW per KW capacity versus the mean operating temperature. Operating data from commercial refrigerators was used to prepare Figure 53.

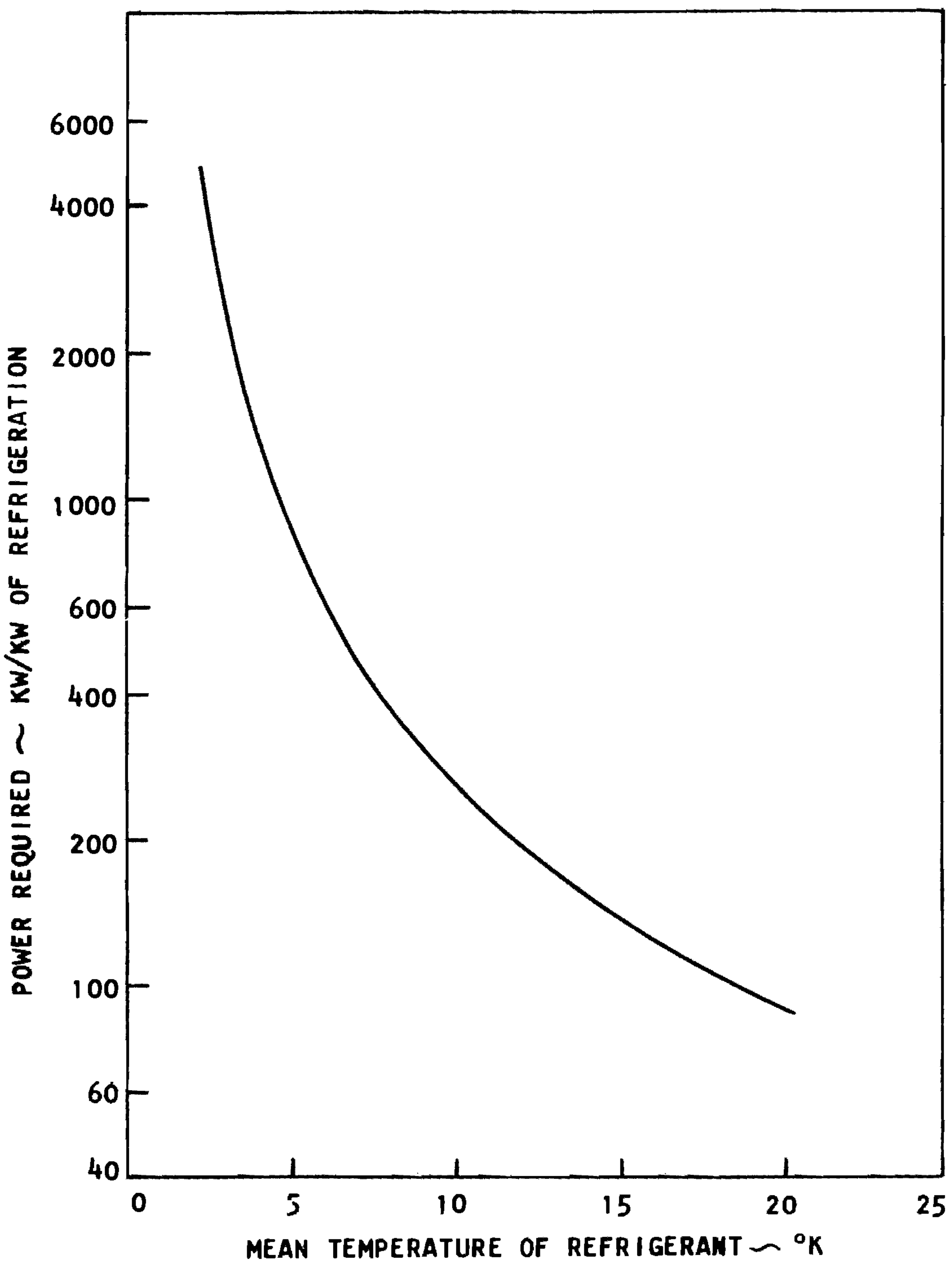

Figure 53. Power Required for Operation of Helium Gas Refrigerators

APPENDIX IV

ESTIMATED CAPITAL AND OPERATING COSTS FOR THE PRODUCTION OF 75,000 LBS. OF 50 PERCENT QUALITY HYDROGEN SLUSH IN SEVEN DAYS

The estimated capital investment and operating costs for the production of 50 percent quality hydrogen slush in a period of seven days are calculated in this appendix for all but two of the production systems described in Section 3. The excluded systems, venturi cooling and compression and expansion of liquid hydrogen, are not discussed here because they do not appear practical when compared to the other production systems. A summary of the total costs calculated in this appendix is presented in Table 28.

D.1 STRAIGHT VACUUM PUMPING

D.1.1 Capital Investment

The capital investment for this system includes the cost of the vacuum pump and the system tankage. The pump cost is based on the assumption that all the hydrogen gas will be pumped at the triple point pressure necessary to produce hydrogen slush and that the pump will be capable of operating at this pressure. It should be understood, however, that the volume of hydrogen gas that must be removed to reach the triple point is calculated with the knowledge that pumping will be performed at successively lower pressure.

D.1.1.1 Vacuum Pump It can be seen from Figure 10 that 13.5 ft.^{3} of hydrogen gas must be removed for each pound of 50 percent hydrogen slush produced. The pump capacity may now be determined as follows:

$$\text{cfm} = \frac{\text{lbs. to be produced}}{\text{days for production}} \times \frac{\text{day to minutes}}{\text{conversion factor}} \times \frac{\text{ft.}^3\text{ gas removed}}{\text{per lb.}}$$

$$= \frac{75{,}000 \text{ lbs.}}{7 \text{ days}} \times \frac{1 \text{ day}}{24 \times 60 \text{ min}} \times \frac{13.5 \text{ ft.}^3}{\text{lb.}}$$

$$= 100.4 \text{ cfm}$$

The cost of a pump with this capacity is $122,000. See C.2.1 in Appendix III and Figure 49 for a description of the cost estimation procedure used to obtain this cost.

TABLE 28

COMPARISON OF CAPITAL AND OPERATING COSTS TO PRODUCE 75,000 POUNDS OF 50 PERCENT SLUSH IN SEVEN DAYS

Hydrogen Slush Production Systems	Total Capital Costs	Total Operating Cost
Straight Vacuum Pumping	425,750	7,320
Semi-Flow Vacuum Pumping	483,250	7,815
Branched Flow Vacuum Pumping	455,500	7,815
Cascaded Vacuum Pumping	346,500	7,540
Helium Gas Refrigerator (Batch)	953,950	1,950
Helium Gas Refrigerator (Flow)	880,500	1,410
Cooling With Liquid Helium (Batch)	253,950	2,043,000
Cooling With Liquid Helium (Flow)	220,500	1,618,000
J-T Cooling of a Helium-Hydrogen Mixture	720,500	22,750
Helium Gas Injection Cooling	303,750	1,924,464

D.1.1.2 Tankage Tankage costs for straight vacuum pumping are determined in a manner described in C.2.2. of Appendix III and graphed in Figure 50. From these sources, the tankage costs are set at $4.05 per pound of 50 percent slush. Thus:

Tankage costs = $4.05 x 75,000 lbs. = $303,750

The total capital investment for the production of 75,000 lbs. of 50 percent hydrogen slush by straight vacuum pumping is:

Pump cost	$ 122,000
Tankage cost	$ 303,750
Total	$ 425,750

D.1.2 Operating Costs

The operating costs for this production system are based entirely on the hydrogen waste during production. Since the cost of the hydrogen waste per pound of 50 percent quality hydrogen slush produced by this system is $0.0976 (see C.3.1 in Appendix III and Figure 52), the operating cost for this system is $7,320.

D.2 SEMIFLOW VACUUM PUMPING

D.2.1 Capital Investment

The capital investment for this production system is composed of the vacuum pump and system tankage cost.

D.2.1.1 Vacuum Pumps Using the procedure described in D.1.1.1 in conjunction with Figure 10 , a pump capacity of 198.7 cfm is found to be required for this system. From the graph on Figure 49 we find that the cost of a pump with this capacity is $235,000.

D.2.1.2 Tankage From Figure 50, a tankage cost of $3.31 per pound of slush to be produced is obtained. Thus:

Tankage costs = $3.31 x 75,000 lbs. = $248,250

The total capital investment for the production of 75,000 lbs. of 50 percent hydrogen slush by semiflow vacuum pumping is:

Pump cost	$	235,000
Tankage cost	$	248,250
Total	$	483,250

D.2.2 Operating Costs

The operating costs for this production system are graphed in Figure 52 as $0.1042 per pound of 50 percent slush to be produced.

$0.1042/lb. x 75,000 lbs. = $7,815

D.3 BRANCHED FLOW VACUUM PUMPING

D.3.1 Capital Investment

The capital investment for this system includes the vacuum pump and system tankage costs.

D.3.1.1 Vacuum Pump The data from Figure 10 and the procedure from D.1.1.1 is used to obtain a pump capacity of 198.7 cfm for this production systems. The cost of a pump with the capacity is graphed in Figure 49. as $235,000.

D.3.1.2 Tankage Figure 50 sets a tankage cost of $2.94 per pound of slush for this system. Thus:

Tankage costs = $2.94 x 75,000 lbs. = $220,500

Branched flow vacuum flow production of 75,000 lbs. of 50 percent hydrogen slush requires a total capital investment of:

Pump cost	$	235,000
Tankage cost	$	220,500
Total	$	455,500

D.3.2 Operating Costs

From Figure 52 we obtain an operating cost for this production system of \$0.1042 per pound of 50 percent slush to be produced.

$$\$0.1042/\text{lb.} \times 75{,}000 \text{ lb.} = \$7{,}815$$

D.4 CASCADED VACUUM PUMPING

D.4.1 Capital Investment

Capital investments for this production system include the cost of vacuum pumps for three separators and the slush tank as well as the cost of the system tankage.

D.4.1.1 Vacuum Pumps The required pump capacities are derived by utilizing the procedure explained in D.1.1.1 with data obtained from the lower portion of Figure 10 . The cost of pumps with these capacities are then obtained from the graph in Figure 49. Thus:

A 4-46 cfm capacity pump for the 500 Torr separator costs	\$ 1,650
A 15-63 cfm capacity pump for the 200 Torr separator costs	\$ 11,800
A 14-88 cfm capacity pump for the 100 Torr separator costs	\$ 15,800
A 80-06 cfm capacity pump for the slush tank costs	\$ 101,000
Total	\$ 130,250

The cost of an equivalent staged pump is obtained as follows:

$$\left(\frac{130{,}250}{101{,}000}\right)^{.87} \times 101{,}000 \quad \$ \; 126{,}000$$

D.4.1.2 Tankage The tankage requirements for this system are the same as those given in D.3.1.2 for the branched flow vacuum pumping system. Thus:

$$\text{Tankage costs} = \$2.94 \times 75{,}000 \text{ lbs.} = \$220{,}500$$

The total capital investment required for the production of 75,000 lbs. of 50 percent hydrogen slush by the cascaded vacuum pumping method is:

Pump cost	\$ 126,000
Tankage cost	\$ 220,500
Total	\$ 346,500

D.4.2 Operating Costs

An operating cost of \$0.1005 per pound of 50 percent slush to be produced is obtained from Figure

\$0.1005/lb. x 75,000 lb. = \$7,540

D.5 HELIUM GAS REFRIGERATION

There are two processes (Batch and Flow) for producing hydrogen slush by helium gas refrigeration. As shown in the process discussions, the refrigerator capacity is the same for both processes for the production of a given quantity and quality of slush in the same time period. The temperature level of the refrigerators for each process is, however, different leading to different operating costs. The tankage required is also different leading to a different capital investment for the two processes.

D.5.1 Helium Gas Refrigerator Batch Process

The capital investment for the batch process consists of the cost of the refrigerator and the process tankage, while the operating costs are the power costs to run the refrigerator. The investment and operating expenses for the process are developed in the paragraphs below.

D.5.1.1 Refrigerator

The refrigerator capacity required is determined through the use of equation (46) after having calculated the total heat to be removed by the use of equation (45) and Tables 7 and 8. From Table 7, the total heat to be removed to produce triple-point liquid is Q_{if} = 23.03 Btu/lb. and from Table 8 the heat to be removed from triple-point liquid to produce 50 percent slush is

Q_q = 12.52 Btu/lb. so that the total heat to be removed in producing 50 percent slush is:

$$Q_{o50} = 23.03 + 12.52 = 35.55 \text{ Btu/lb.}$$

and for 75,000 lbs. of final product

$$\begin{aligned} Q_{o50} &= 35.55 \cdot 75,000 \\ &= 2,666,250 \text{ Btu} \end{aligned}$$

The capacity of a single refrigerator operating constantly for seven days to produce this quantity of slush is given by equation (46).

$$\begin{aligned} W_{o50} &= Q_{o50}/T \\ &= 2,666,250/7\text{x}24 \\ &= 15,870 \text{ Btu/hr.} \\ &= 4.65 \text{ KW} \end{aligned}$$

In the process discussion it was shown that a single refrigerator operating at an average temperature below the triple point of hydrogen could accomplish the desired refrigeration with a fixed heat exchanger installation in the production tank. It was further shown that a refrigerator which produced an average temperature of 11°K at the heat exchange surfaces would be a reasonable choice to provide relatively constant cooling rate throughout the process. Such a refrigerator would have to have an average temperature somewhat below 11°K, and for costing purposes an average temperature for the refrigerator of 10°K is assumed.

From Figure 51, the cost of a 4.65 KW 10°K refrigerator is approximately $700,000.

D.5.1.2 Tankage

The tankage for this batch process is determined from Figure 50 to be $3.386 per pound of 50 percent slush produced so that for 75,000 pounds

$$\begin{aligned} \text{Tankage cost} &= 75,000 \text{ x } 3.386 \\ &= \$253,950 \end{aligned}$$

The total capital investment for producing 75,000 pounds of 50 percent slush in seven days by the helium gas refrigeration batch process is the sum of the refrigerator and tankage costs:

Refrigerator cost	\$ 700,000
Tankage cost	\$ 253,950
Total Investment	\$ 953,950

D.5.1.3 Helium Gas Refrigerator Batch Process Operating Cost

The operating cost for this system is the power required to operate the refrigerator. From Figure 53 it requires 250 KW per KW of refrigerator capacity to operate at a mean temperature of 10.0°K. The operating cost is calculated as follows:

$$\text{Total power} = 250 \times 4.65$$

$$= 1162 \text{ KW}$$

For seven-day operation at \$0.01 per kilowatt hour the cost is:

$$\text{Operating cost} = (1162)(7)(24)(0.01)$$

$$= \$1,950$$

D.5.2 Helium Gas Refrigerator Flow Process

The flow process employs the same refrigerator capacity as the batch process, but its average temperature is lower so that the investment and operating costs are different. The tankage volume is also different, contributing to the difference in investment cost.

D.5.2.1 Refrigerator

The refrigerator capacity as calculated for the batch process is 4.65 KW. The average temperature for the flow process is given in Table 9 of the process discussion. For 50 percent slush the average temperature of heat exchange surface at the liquid is 13.8°K. Using the same 1°C temperature difference for the gas temperature gives 12.8°K as the mean temperature for the refrigerator. The cost of a 4.65 KW 12.8°K refrigerator from Figure 51 is $600,000.

D.5.2.2 Tankage

The tankage for this flow process is determined from Figure 50 to be $2.94 per lb. of 50 percent slush produced so that for 75,000 pounds:

$$\text{Tankage cost} = 75{,}000 \times 2.94$$

$$= \$220{,}500$$

The total capital investment for producing 75,000 pounds of 50 percent slush in seven days by the helium gas refrigeration process is the sum of the refrigerator and tankage costs:

Refrigeration cost	$ 600,000
Tankage cost	$ 220,500
Total Investment	$ 820,000

D.5.3 Helium Gas Refrigerator Flow Process Operating Cost

The operating cost for this system is the power required to operate the refrigerator. From Figure 53 it requires 180 KW per KW of refrigerator capacity to operate at a mean temperature of 10.0°K. The operating cost is calculated as follows:

$$\text{Total power} = 180 \times 4.65$$

$$= 837 \text{ KW}$$

For seven-day operation at $0.01 per kilowatt hour the cost is:

$$\text{Operating cost} = (837)(7)(24)(0.01)$$

$$= \$1410$$

D.6 COOLING WITH LIQUID HELIUM

D.6.1 The Liquid Helium Flow Process

The liquid helium flow process requires a production tank with an internal helium reservoir and a heat exchanger to transfer heat from the liquid hydrogen to the helium.

D.6.1.1 Capital Investment for Batch Process

The capital investment for this process is considered to be the tankage cost only. The cost of the heat exchangers required are not considered, and the small volume of the internal reservoir for the liquid helium is not considered to affect the total volume of the system. From Figure 50 the tankage cost for a batch process is \$3.386 per pound of slush produced. The investment for this process is therefore:

$$\text{Capital Investment} = 75{,}000 \times 3.386$$

$$= 253{,}950$$

D.6.1.2 Operating Cost for Batch Process

The operating cost for this process is the cost of the liquid helium required. From Table 10 in the process description, the helium requirement to produce 50 percent slush is given as 0.968 lbs. per lbs. of slush. For 75,000 lbs. of product, the operating cost @ \$7.75 per liter of liquid helium is:

$$\text{Operating Cost} = (7.75)(75{,}000)(.968)(28.32)/7.8$$

$$= \$1{,}908{,}000$$

$$= \$2{,}043{,}000$$

D.6.2 The Liquid Helium Flow Process

The liquid helium flow process includes a heat exchanger for the recovery of the sensible heat in the venting helium gas in addition to the production tankage and heat exchanger.

D.6.2.1 Capital Investment In the Flow Process

As in the batch process, the cost of the heat exchangers is not considered, and the small liquid helium reservoir is not considered to have any effect on the tankage costs. From Figure 50, the tankage cost for this process is $2.94 per pound of 50 percent slush to be produced. The investment for this process is therefore

Capital Investment = 75,000 x 2.94 = $220,500

D.6.2.2 Operating Cost

The operating cost for this process is the cost of the liquid helium required. From Table 11 in the process description, we find that the helium requirement to produce 50 percent slush is given as 0.767 pounds per pound of slush to be produced. For 75,000 pounds of product, the helium required is

Helium Required = (75,000)(0.767) = 57,500 lbs.

With a liquid helium cost of $7.75 per liter, the operating cost for this process is

Operating Cost = (7.75)(57,500)(28.32)/(7.8)

= $1,618,000

D.7 JOULE-THOMSON COOLING OF A HELIUM-HYDROGEN MIXTURE

D.7.1 Capital Investment

The capital investment for this process includes the cost of the refrigerator system and the product storage tank.

D.7.1.1 Joule-Thomson Refrigeration System

A complete cost estimate was not made for this system, but the cost would be in the neighborhood of $500,000.

D.7.1.2 Tankage

For this process the tank must be included to correlate it with previous systems. The tank cost at $2.94 per pound of 50 percent slush is $220,500.

	$500,000
	200,500
Total Capital Investment	$720,500

D.7.2 Operating Costs

Power cost 110,000 KWH $0.01/KWH	$ 1,100
Hydrogen Losses (precooler) 8,500 pounds at $0.50/pound	$ 4,250
Hydrogen losses (compressor) at 1/2 percent loss per hour; 400 pounds (part of 8500 pounds precooler loss)	Zero Additional
Helium losses (compressor) at 1/2 percent loss per hour, 160,000/ft.^{3} NTP at $0.1085 per cubic foot NTP	$ 17,400
Total	$ 22,750

D.8 PRODUCTION OF HYDROGEN SLUSH BY HELIUM GAS INJECTION

D.8.1 Capital Investment

The capital investment for this process is considered to be the tankage cost only. From Figure 50 the tankage cost for this process is $4.05 per pound of 50 percent slush (same as straight vacuum pumping) the investment for this process is therefore

Capital investment = 75,000 x 4.05

= 303,750

D.8.2 Operating Cost

The operating cost for this process is the cost of the gaseous helium used for injection and the cost of the hydrogen evaporated.

D.8.2.1 Gaseous Helium From Table 12 in the process description the amount of gaseous helium required to produce 50 percent slush per pound is calculated as follows.

$$\text{Helium Requirement} = 67.0131 + (404.1672 - 75.6730)/.5$$

$$= 235.5901 \text{ ft.}^3 \text{ He NTP/lb. 50 percent slush}$$

The cost of helium for producing 75,000 pounds of 50 percent slush at $0.1085 per cubic foot is

$$\text{Helium Cost} = (75{,}000)\,(235.5901)\,(0.1085)$$

$$= \$1{,}917{,}000$$

D.8.2.2 Hydrogen Loss The hydrogen loss for this process is considered the same as the Straight Vacuum Pumping Process and is $7,320. The total operating cost for this process is therefore

Helium Cost	$1,917,000
Hydrogen Loss	7,320
	$1,924,320

APPENDIX V

MAINTAINING AND UPGRADING HYDROGEN SLUSH BY HELIUM GAS INJECTION COOLING

The capital and operating costs for maintaining and upgrading 75,000 pounds of hydrogen slush by helium gas injection cooling are presented in both summary and detailed forms in this appendix.

E.1 SUMMARY

E.1.1 Maintaining Hydrogen Slush

The cost of maintaining 75,000 pounds of 50 percent quality hydrogen slush is composed of the capital investment and operating costs to balance the system heat leak. For a well insulated 75,000 pound capacity space vehicle storage tank, the heat leak is estimated to be 9,000 Btu/hr. or 0.125 Btu/lb.hr. This is equivalent to 0.5 percent solid melting per hour during ground hold.

E.1.1.1 Capital Investment The capital investment is the cost of the following three items:

1.	A 126.23 cfm capacity vacuum pump for producing 561 pounds of 50 percent slush per hour	$ 155,000
2.	A 561 pound capacity hydrogen slush storage tank @ $4.05 per pound of slush to be stored	$ 2,272
3.	A 466.7 pound capacity liquid hydrogen storage tank @ $2.00 per gallon of liquid to be stored	$ 1,578
	Total	$ 158,850

E.1.1.2 Operating Costs The operating costs include the costs of the gaseous helium used to produce solids and of the liquid hydrogen used for slush make-up and cooling gaseous helium.

1.	122,939 ft.^{3} NTP of gaseous helium @$0.1085 per ft.^{3} NTP	$ 13,339
2.	1137.2 pounds of liquid hydrogen @$.50 per pound	$ 569
	Total	$ 13,908 per hour

E.1.2 Upgrading Hydrogen Slush

The cost of upgrading 75,000 pounds of 50 percent hydrogen slush to 60 percent hydrogen slush after loading the 50 percent quality on board the space vehicle includes capital investment and operating costs. These costs are predicated on the assumption that a 7 day time period is allowed for the upgrading.

E.1.2.1 Capital Investment The capital investment consists of the cost of a vacuum pump and two storage tanks.

1.	A 14.44 cfm capacity vacuum pump for producing 10,783 pounds of 50 percent slush in seven days	$ 20,500
2.	A 10,783 pound capacity hydrogen slush storage tank @ $4.05 per pound of slush to be stored	$ 43,671
3.	A 8,785 pound capacity liquid hydrogen storage tank @ $2.00 per gallon of liquid to be stored	$ 29,743
	Total	$ 93,914

E.1.2.2 Operating Costs These costs are composed of the cost of the gaseous helium required to maintain the total pressure of 760 Torr in the space vehicle tank during the helium gas injection and the cost of the liquid hydrogen used for cooling the helium gas and slush make-up.

1.	2,313,276 ft.^{3} NTP of gaseous helium @ $0.1085 per ft.^{3} NTP	$ 250,990
2.	21,679 pounds of liquid hydrogen @$.50 per pound	$ 10,837
	Total	$ 261,827

E.2 DETAILED DISCUSSION

E.2.1 Maintaining Hydrogen Slush

To maintain 75,000 pounds of 50 percent quality hydrogen slush loaded aboard a space vehicle for a one hour ground hold, the heat leak during the hold time must be balanced by producing additional hydrogen slush by helium gas injection cooling of the triple point liquid and adding an amount of 50 percent slush equal to the amount of triple point liquid used to produce refrigeration during the injection process. Since the heat leak in this case is estimated at 0.125 Btu per pound of stored slush and the heat required to melt 1 percent slush to triple point liquid is 0.2503 Btu per pound, the percent solid melted per hour is

$$\frac{0.125\ \text{Btu/lb.}}{0.2503\ \text{Btu/lb./percent solid}} = 0.499\ \text{percent solid melting per hour.}$$

To replace the solids melted to triple point liquid by the heat leak, 0.499 percent solid must be produced by helium gas injection cooling during the hour. Table 12 on page 70 states that 328.4942 ft.^{3} NTP of helium gas is required to produce one pound of solid hydrogen from triple point liquid while maintaining the total pressure at 760 Torr during the production process. Therefore, the amount of helium gas required to produce 0.499 percent solid from 75,000 pounds of 50 percent slush would be

$$\frac{(328.4942\ \text{ft.}^3\ \text{NTP helium gas})^*}{1\ \text{lb. (all solid from triple point liquid)}} \times \frac{0.00499}{\text{hr.}} \times 75{,}000\ \text{lbs.}$$

$$= \quad 122{,}939\ \text{ft.}^3\ \text{NTP helium gas required per hour}$$

The cost of this gaseous helium at $0.1085 per pound (see C.3.4 in Appendix III) is $13,339.

Prior to injection, the helium must be cooled to 13.813°K. This cooling is accomplished in two steps. Step one utilizes liquid hydrogen to cool the helium to 20.278°K, and step two uses separately produced 50 percent slush to further cool the helium to 13.813°K.

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* See Table 12 on page 70.

The amount of liquid hydrogen required to perform step one is calculated as follows:

Mass of helium to be cooled = 122,934 ft.^3

or

122,934 ft.^3 x 0.01034 lb./ft.^3 = 1271 lbs. of helium gas

The amount of heat to be removed from this helium gas is

$$
\begin{aligned}
Q &= (\text{Enthalpy of helium @ } 294.27°\text{K} - \text{Enthalpy of helium @ } 20.278°\text{K}) \\
&= (663.42 - 51.27) \\
&= 612.15 \text{ Btu/lb. of helium gas}
\end{aligned}
$$

The refrigeration capacity available from the liquid hydrogen used to cool the helium to 20.278°K is

$$
\begin{aligned}
Q &= \text{Heat of vaporization of hydrogen} + (\text{Enthalpy of hydrogen @ } 294.27°\text{K} - \text{Enthalpy of hydrogen @ } 20.278°\text{K}) \\
&= 193 + (1783.21 - 308.68) \\
&= 1667.53 \text{ Btu/lb. of liquid hydrogen}
\end{aligned}
$$

Thus, the amount of liquid hydrogen requied to cool the 1271 pounds of gaseous helium to 20.278°K is

$$1271 \left(\frac{612.15}{1667.53}\right) = 466.7 \text{ lbs. of liquid hydrogen.}$$

The amount of 0.50 percent quality hydrogen slush required to accomplish step two is calculated as follows:

The heat removal required from the helium gas is

$$
\begin{aligned}
Q &= (\text{Enthalpy of Helium @ } 20.278°\text{K} - \text{Enthalpy of helium @ } 13.813°\text{K} \\
&= (51.27 - 36.63) \\
&= 14.64 \text{ Btu/lb. of helium}
\end{aligned}
$$

Refrigeration available from converting 50 percent hydrogen slush to 20.278°K liquid is

$$\begin{aligned} Q &= (\text{Enthalpy of hydrogen @ } 20.278°\text{K} - \text{Enthalpy of 50 percent of hydrogen slush} \\ &= (52.61 - 17.06) \\ &= 35.55 \text{ Btu/lb. of hydrogen} \end{aligned}$$

Thus, the amount of 50 percent quality hydrogen slush required to cool the gaseous helium to 13.813°K is

$$1271 \left(\frac{14.64}{35.55}\right) = 538.5 \text{ lbs. of 50 percent slush.}$$

When the slush aboard the space vehicle melts, it creates triple point liquid. The total amount of triple point liquid thus produced is

$$0.00499 \times 75{,}000 \text{ lbs.} = 374.26 \text{ lbs. triple point liquid.}$$

Because of vaporization loss, this amount of triple point liquid, when cooled by helium gas injection, will yield

$$\frac{374.26}{SMR_{0 \text{ percent to 50 percent slush}}} = \frac{374.26}{1.064613} = 351.54 \text{ lbs. of 50 percent slush.}$$

Since 374.26 pounds are needed and only 351.54 pounds are availalbe, 22.72 (374.26 - 351.54 = 22.72) pounds of 50 percent hydrogen slush must be made up from a separate source. This amount added to the 538.5 pounds of slush required to cool the helium from 20.278°K to 13.813°K brings the total externally produced slush required to 561 pounds.

As shown in Figure 10 , the production of 50 percent hydrogen slush by straight vacuum pumping requires the removal of 13.5 ft.^{3} of hydrogen gas per pound of slush to be produced. The volume removed in this case is

$$\frac{13.5 \text{ ft.}^3}{\text{lb.}} \times 561 \text{ lbs.} = 7573 \text{ ft.}^3 \text{ of hydrogen gas}$$

Since the slush is to be produced in one hour, the required vacuum pump capacity is

$$\frac{7.573 \text{ ft.}^3}{60 \text{ min.}} = 126.23 \text{ cfm.}$$

It can be seen from Figure 49 that a vacuum pump with this capacity would cost \$155,000.

The tankage cost for the production of the 561 pounds of slush is

$$\$4.05/\text{lb.} \times 561\text{ lbs.} = \$2.272.$$

The tankage cost for the liquid hydrogen used to cool the helium gas is

$$\frac{466.7\text{ lbs.}}{4.419\text{ lb./ft.}^3} \times \frac{\$2.00}{\text{gal}} \times \frac{7.481\text{ gal.}}{\text{ft.}^3} = \$1578$$

The cost of the liquid hydrogen used to maintain the hydrogen slush is

$$\$.50/\text{lb.} \quad (466.7\text{ lbs.} + 561\text{ lbs.}/1.195236) = \$569.$$

E.2.2 Upgrading Hydrogen Slush

To upgrade 75,000 pounds of 50 percent slush to 60 percent slush after loading on the space vehicle (assuming negligible heat leak), the hydrogen slush is further cooled by helium injection cooling. See Figure 21 for a flow diagram of this process.

The amount of 50 percent slush required to produce 75,000 pounds of 60 percent slush is 75,000 pounds times the specific mass requirement to go from 50 percent to 60 percent slush.

$$75{,}000\text{ lbs.} \times 1.012139 = 75{,}910\text{ lbs. of 50 percent slush}$$

The amount of triple point hydrogen that must be evaporated to upgrade 75,910 pounds of 50 percent slush to 60 percent slush is 910 pounds. Therefore, 910 pounds of 50 percent slush must be added during the process. The volume of this hydrogen is

$$\frac{910\text{ lbs.}}{.0078\text{ lb./ft.}^3} = 116{,}666\text{ ft.}^3\text{ hydrogen gas @ }13.813^\circ\text{K and }52 + \text{Torr.}$$

The amount of gaseous helium required to maintain the total pressure at 760 Torr while evaporating 910 pounds of triple point hydrogen is

$$116{,}666 \frac{(760-52.8)}{760} \times \frac{294.27}{13.81} = 2{,}313{,}276 \text{ ft.}^3 \text{ NTP}$$

The cost of this helium @ \$0.1085 ft.^{3} = \$250,990.

As in E.2.1, the helium must be precooled to 13.813°K before it is used to upgrade the hydrogen. The helium is first cooled to 20.278°K by liquid hydrogen. The mass of helium to be cooled is

$$2{,}313{,}267 \text{ ft.}^3 \times 0.01034 \text{ lb./ft.}^3 = 23{,}930 \text{ lbs.}$$

The amount of heat to be removed from the helium is

Q = (Enthalpy of helium @ 294.27°K - Enthalpy of helium @ 20.278°K)

= (663.42 - 51.27)

= 612.15 Btu/lb. of helium gas

The refrigeration capacity available from the liquid hydrogen used to cool the helium to 20.278°K is

Q = heat of vaporization of hydrogen + (Enthalpy of hydrogen @ 294.27°K - Enthalpy of hydrogen @ 20.278°K)

= 193 + (1783.21 - 308.68)

= 1667.53 Btu/lb. of liquid hydrogen

Thus, the amount of liquid hydrogen required to cool the 23,930 pounds of gaseous helium to 20.278° is

$$23{,}900 \left(\frac{612.15 \text{ Btu}}{1667.53}\right) = 8{,}785 \text{ lbs. of liquid hydrogen.}$$

The amount of 50 percent slush required to further cool the gaseous helium to 13.813°K is calculated as follows:

The heat removal required from the helium gas to reduce the temperature from 20.278°K to 13.813°K

Q = (Enthalpy of helium @ 20.278°K - Enthalpy of helium @ 13.813°K

$$= (51.27 - 36.63)$$

$$= 14.64 \text{ Btu/lb. of helium}$$

Refrigeration available by converting 50 percent hydrogen slush to 20.278°K liquid is

$$Q = (\text{Enthalpy of hydrogen @ } 20.278°\text{K} - \text{Enthalpy of 50 percent hydrogen slush})$$

$$= (52.61 - 17.06)$$

$$= 35.55 \text{ Btu/lb. of hydrogen}$$

Thus, the amount of 50 percent quality hydrogen slush required to cool the gaseous helium to 13.813°K is

$$23{,}930 \left(\frac{14.64}{35.55}\right) = 9{,}873 \text{ lbs. of 50 percent slush.}$$

The mass of hydrogen slush required for cooling and makeup is

$$9{,}873 \text{ lbs.} + 910 \text{ lbs.} = 10{,}783 \text{ lbs. of 50 percent slush.}$$

Since the production of 50 percent slush by straight vacuum pumping requires the removal of 13.5 ft.^{3} of hydrogen gas per pound of slush to be produced, as shown in Figure 10, the volume removed in this case is

$$\frac{13.5 \text{ ft.}^3}{\text{lb.}} \times 10{,}783 \text{ lbs.} = 145{,}571 \text{ ft.}^3 \text{ of hydrogen gas.}$$

Assuming that the slush is to be produced in seven days, the required vacuum pump capacity is

$$\frac{145{,}571 \text{ ft}^3}{7 \text{ days} \times \frac{24 \text{ hr.}}{\text{day}} \times \frac{60 \text{ min.}}{\text{hr.}}} = 14.44 \text{ cfm.}$$

The tankage cost for the production of the 10,783 pounds of slush is \$4.05 /lb. x 10,783 lbs. = \$43,671.

The tankage cost for the liquid hydrogen used to cool the helium gas is

$$\frac{8.785 \text{ lbs.}}{4.419 \text{ lb./ft.}^3} \times \frac{\$2.00}{\text{gal.}} \times \frac{7.481 \text{ gal.}}{\text{ft.}^3} = \$29,743$$

The cost of the liquid hydrogen used to upgrade the hydrogen slush is the cost of the hydrogen to cool the helium gas to 20.278°K plus the hydrogen to further cool the helium to 13.813°K and the cost of the makeup 50 percent slush.

$$\$0.50/\text{lb.}\ (8,785 + 10,783/1.195236) = \$10,837$$