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HYDROGEN SLUSH DENSITY REFERENCE SYSTEM

FINAL REPORT

by

D. H. Weitzel, L. T. Lowe, D. A. Ellerbruch,

J. E. Cruz, and C. F. Sindt

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NATIONAL BUREAU OF STANDARDS REPORT

HYDROGEN SLUSH DENSITY REFERENCE SYSTEM

FINAL REPORT

to

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

by

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U.S. DEPARTMENT OF COMMERCE

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ABSTRACT

A hydrogen slush density reference system was designed for calibration of field-type instruments and/or transfer standards. The device is based on the buoyancy principle of Archimedes. The solids are weighed in a low-mass container so arranged that solids and container are buoyed by triple-point liquid hydrogen during the weighing process.

Several types of hydrogen slush density transducers were developed and tested for possible use as transfer standards. The most successful transducers found were those which depend on change in dielectric constant, after which the Clausius-Mossotti function is used to relate dielectric constant and density.

Key words: Capacitance; density reference system; density transducers; density transfer standard; dielectric constant; hydrogen slush; microwave; nuclear radiation attenuation.

HYDROGEN SLUSH DENSITY REFERENCE SYSTEM[*]

D. H. Weitzel, L. T. Lowe, D. A. Ellerbruch,

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1. Introduction

The purpose of the hydrogen slush density reference system is for calibration of field type instruments and/or transfer standards. The transfer standard is an instrument which can be used in or on a storage tank or pipeline containing slush hydrogen, but which will not be a fixed or permanent part of the facility instrumentation. The transfer standard thus provides a method for traceability of facility instrumentation to the primary density reference system.

2. Design Considerations

2.1 General

For a density reference system, it is advisable to work directly with mass and volume. Several methods for hydrogen slush weighing were considered before a system was designed to take advantage of the already well known density of triple-point liquid hydrogen. Triple-point liquid will always be one component of the solid-liquid mixture known as hydrogen slush. The triple-point liquid density is given by Roder, et al.[1], as 77.017 kg m^{-3}, with an uncertainty of ±0.1 percent, and the triple-point solid density is given by Dwyer, et al.,[2] as 86.59 kg m^{-3}, with an uncertainty of ±0.3 percent. A hydrostatic weighing method was accordingly conceived which would take advantage of the more accurate of these two, i.e., the triple-point liquid density.

2.2 A Method for Slush Density Measurement

When considering density determination for slush hydrogen, which is neither solid nor liquid but a variable mixture of these two phases, it might seem unlikely that the advantages of Archimedes' Principle could be applied. This is not the case, however, as will be shown.

Consider a light weight container suspended from a weighing system as shown in figure 1. The container is suspended inside a dewar which is closed by a gas-tight top plate. The mass transducer is in a separate housing above the top plate, but communicates with the dewar atmosphere through a clearance hole provided for the suspension member. The first step is to zero and calibrate the weighing system; this is done with calibration weights in the column above the top plate.

The empty container is weighed, then filled with triple-point liquid hydrogen from a separate cryostat as represented in figure 2. The mass of the full container is noted, the empty mass is subtracted, and the net mass of the liquid contained is recorded as M_ℓ.

Figure 3 shows the cryostat completely full of triple-point liquid. The mass of the container is again noted. This buoyed mass of the "empty" container is a constant of the apparatus, and a method is provided for zeroing the weighing system with this exact mass suspended from it.

Slush is now introduced, as shown in figure 4. This is done by lifting the container up against a plate which has screened holes in it, and then transferring slush from the same cryostat which previously provided triple-point liquid. The solids are retained while the excess liquid is transferred back to the slush generator. When a convenient solid
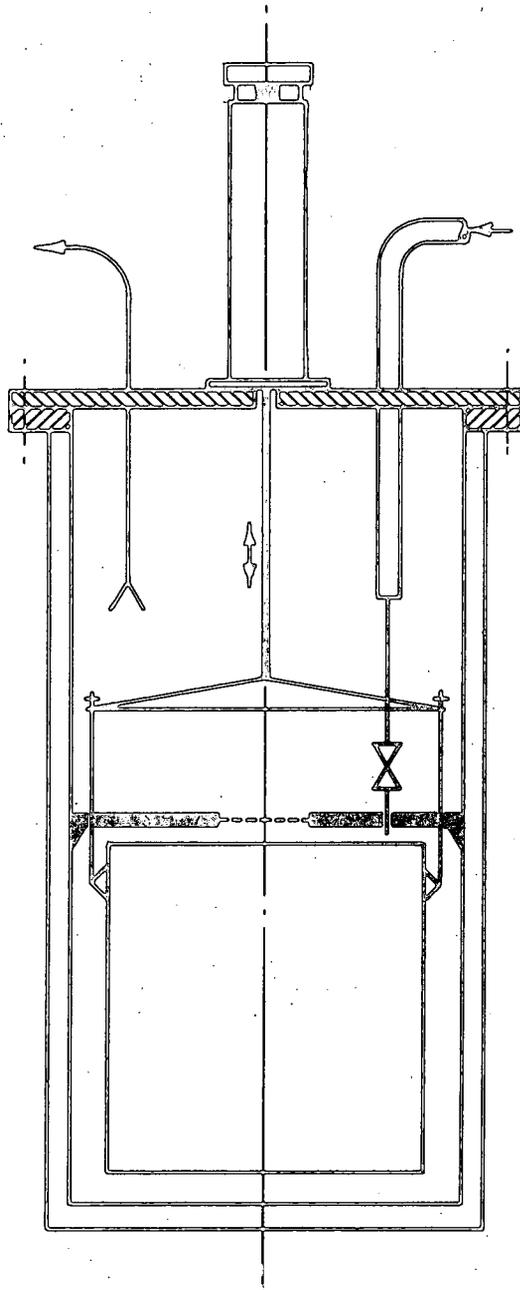
Figure 1.   Empty Weigh=Can in Cryostat.

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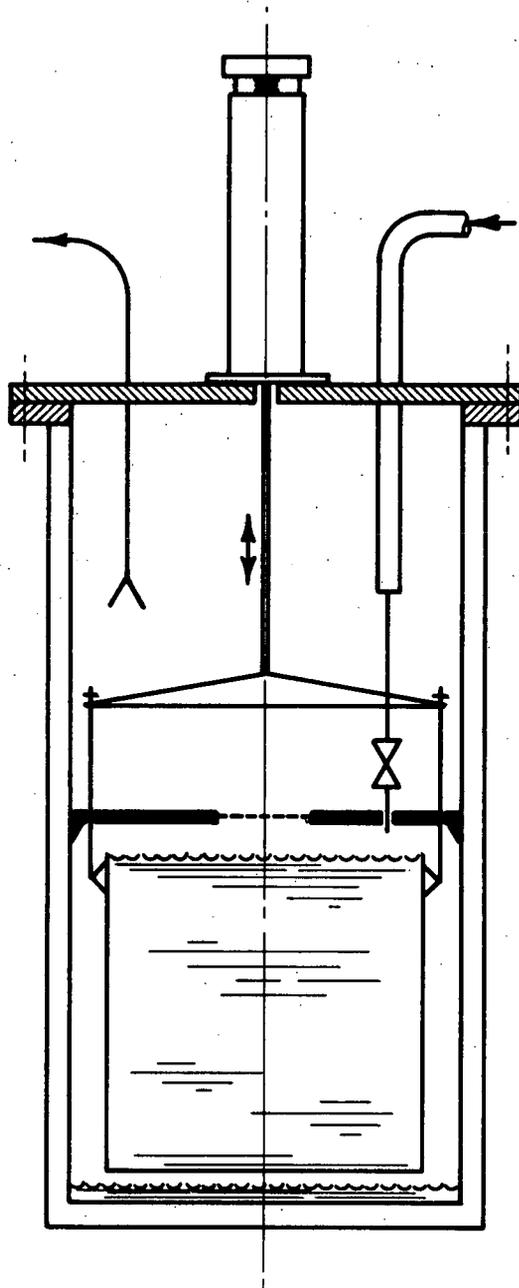
Figure 2.   Weigh-Can Filled with Triple-Point Liquid Hydrogen.
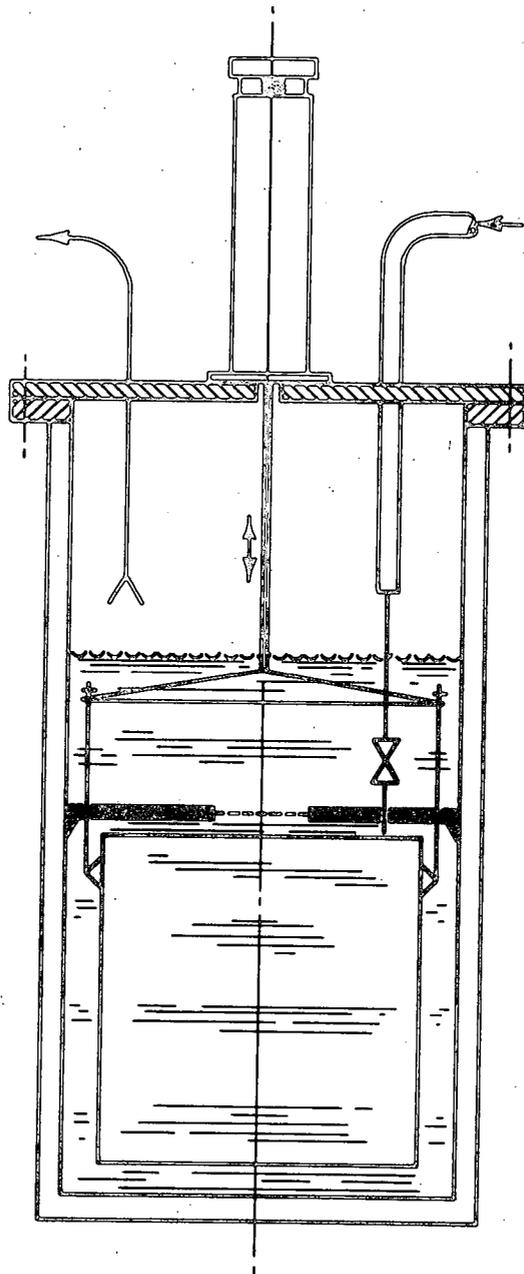
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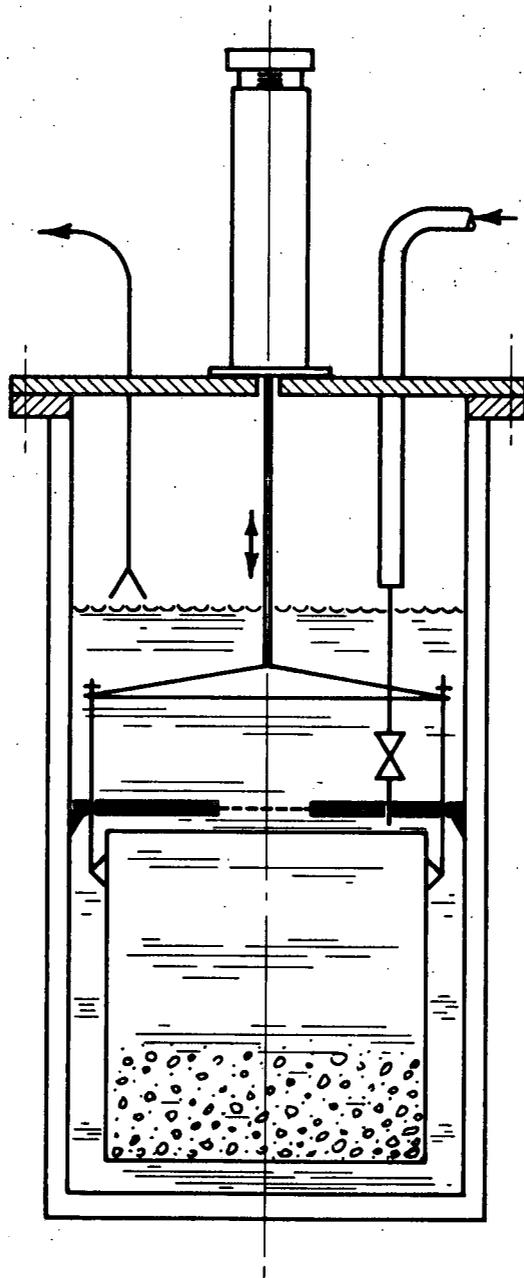
Figure 4.   Hydrogen Slush in Weigh-Can, Cryostat Filled with
            Triple-Point Liquid.

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fraction has been added to the liquid, the final weighing is made. After subtracting the buoyed mass of the "empty" container, the buoyed mass of the solid hydrogen is known. This is designated as M_b, the variable parameter which will yield the desired density ρ for each sample of slush.

The functional relation between the slush density ρ, the triple-point liquid density ρ_ℓ, and the masses M_ℓ and M_b can be easily derived. The mass of the slush in the container is equal to ρV, where V is the volume. The mass of the liquid before any solid was present was $\rho_\ell V$. The difference between these two masses is exactly M_b, the buoyed mass of the solid hydrogen in the container. Thus

$$\rho V - \rho_\ell V = M_b .$$

Since the volume V is equal to M_ℓ / ρ_ℓ, the following relationships can be written:

$$\rho = \frac{M_b}{V} + \rho_\ell = \frac{M_b \rho_\ell}{M_\ell} + \rho_\ell \text{ or}$$

$$\rho = \rho_\ell \left(\frac{M_b}{M_\ell} + 1 \right) \tag{1}$$

where

ρ = slush density

ρ_ℓ = triple-point liquid density

M_b = buoyed mass of solid

M_ℓ = mass of triple-point liquid which just fills the container.

Equation (1) separates ρ into two factors, one of which (ρ_ℓ) is a measured physical constant taken from the literature. Its use introduces

a constant systematic error, whereas the other factor $(M_b/M_\ell + 1)$ will introduce both systematic and random errors.

Thus, the experimental measurements required to obtain the slush density ρ are M_b and M_ℓ, both of which are determined by direct weighing. The magnitude of M_ℓ will be about 2000 g for an inner container having a diameter of 28 cm and depth of 37 cm. The magnitude of M_b will vary from a few grams for a low solid fraction to about 137 g for 60 percent solid fraction.

2.3 Error Analysis

It is instructive at this point to make some reasonable assumptions about the weighing system and calculate the accuracy with which an unknown slush density can be determined. If calibration masses and a suitable method for their application and removal during the experiment are provided, it should be quite easy to determine both M_b and M_ℓ to within ±0.5 percent of their true values. In order to make a better example, however, assume that the inaccuracy in the weighing can be as much as ±2.0 percent.

A general expression for compounding of errors in y, where $y = f(x_1, x_2, \ldots, x_n)$ is

$$\left(dy\right)^2 = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right)^2 \left(dx_i\right)^2 \tag{2}$$

if the components of error dx_i are independently distributed and symmetrical with respect to positive and negative values.[3] These are reasonable assumptions for the situation represented by equation (1). Accordingly,

$$\left(d\rho\right)^2 = \left(\frac{\partial\rho}{\partial\rho_\ell}\right)^2\left(d\rho_\ell\right)^2 + \left(\frac{\partial\rho}{\partial M_b}\right)^2\left(dM_b\right)^2 + \left(\frac{\partial\rho}{\partial M_\ell}\right)^2\left(dM_\ell\right)^2.$$

Typical values for the variables are

$$M_b \quad = \quad 117 \text{ g (the value for a solid fraction of 0. 50)}$$
$$M_\ell \quad = \quad 2000 \text{ g}$$
$$\rho_\ell \quad = \quad 77.017 \text{ kg m}^{-3}.$$

From these values and the assumed fractional errors in weighing, together with the ±0. 1 percent uncertainty in ρ_ℓ, the uncertainties are:

$$\frac{dM_b}{M_b} \quad = \quad 0.02, \text{ or } dM_b = 2.34 \text{ g}$$

$$\frac{dM_\ell}{M_\ell} \quad = \quad 0.02, \text{ or } dM_\ell = 40.0 \text{ g}$$

$$\frac{d\rho_\ell}{\rho_\ell} \quad = \quad 0.001, \text{ or } d\rho_\ell = 0.077 \text{ kg m}^{-3}.$$

The partial derivatives are:

$$\frac{\partial\rho}{\partial\rho_\ell} \quad = \quad \left(\frac{M_b}{M_\ell} + 1\right) = 1.05856$$

$$\frac{\partial\rho}{\partial M_b} \quad = \quad \frac{\rho_\ell}{M_\ell} \quad = \quad 0.03854$$

$$\frac{\partial\rho}{\partial M_\ell} \quad = \quad \frac{-\rho_\ell M_b}{M_\ell^2} \quad = \quad -0.002256.$$

From equation (2),

$$(d\rho)^2 \quad = \quad 0.00665 + 0.00814 + 0.00818, \text{ or}$$

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$$(d\rho)^2 = 0.0230, \text{ from which}$$

$$d\rho = \pm 0.15 \text{ kg m}^{-3}.$$

Note that the three terms which add together to get $(d\rho)^2$ are approximately equal in magnitude even though the uncertainty in the triple-point liquid density (which gives the first term) is ± 0.1 percent, whereas the uncertainty in each of the two weighings is ± 2.0 percent, or 20 times as great. This comes about because of the functional relationship expressed in equation (1). By making use of Archimedes' Principle it is possible to capitalize heavily on the high degree of accuracy with which the triple-point liquid density ρ_ℓ is known.

To carry this example through, equation (1) is used to find the mean ρ for a solid fraction of 0.50. Thus

$$\rho = \rho_\ell \left(\frac{M_b}{M_\ell} + 1 \right) = 77.017 \left(\frac{117}{2000} + 1 \right)$$

$$= 81.35 \text{ kg m}^{-3}.$$

The fractional error in ρ is

$$\frac{d\rho}{\rho} = \pm \frac{0.15}{81.35} \text{ or } \pm 0.18\%.$$

From these considerations it may be concluded that the density of hydrogen slush can be determined at 0.50 solid fraction with an uncertainty of less than ± 0.2 percent if a weighing system which is accurate to ± 2.0 percent is used. Figure 5 shows how the uncertainty in slush density ρ will vary for the assumed system as the density itself is varied. A scale of mass fraction solid (sometimes called "quality") is shown for comparison with density. The uncertainty is shown in kg m^{-3} as well as percent of measured mean density.

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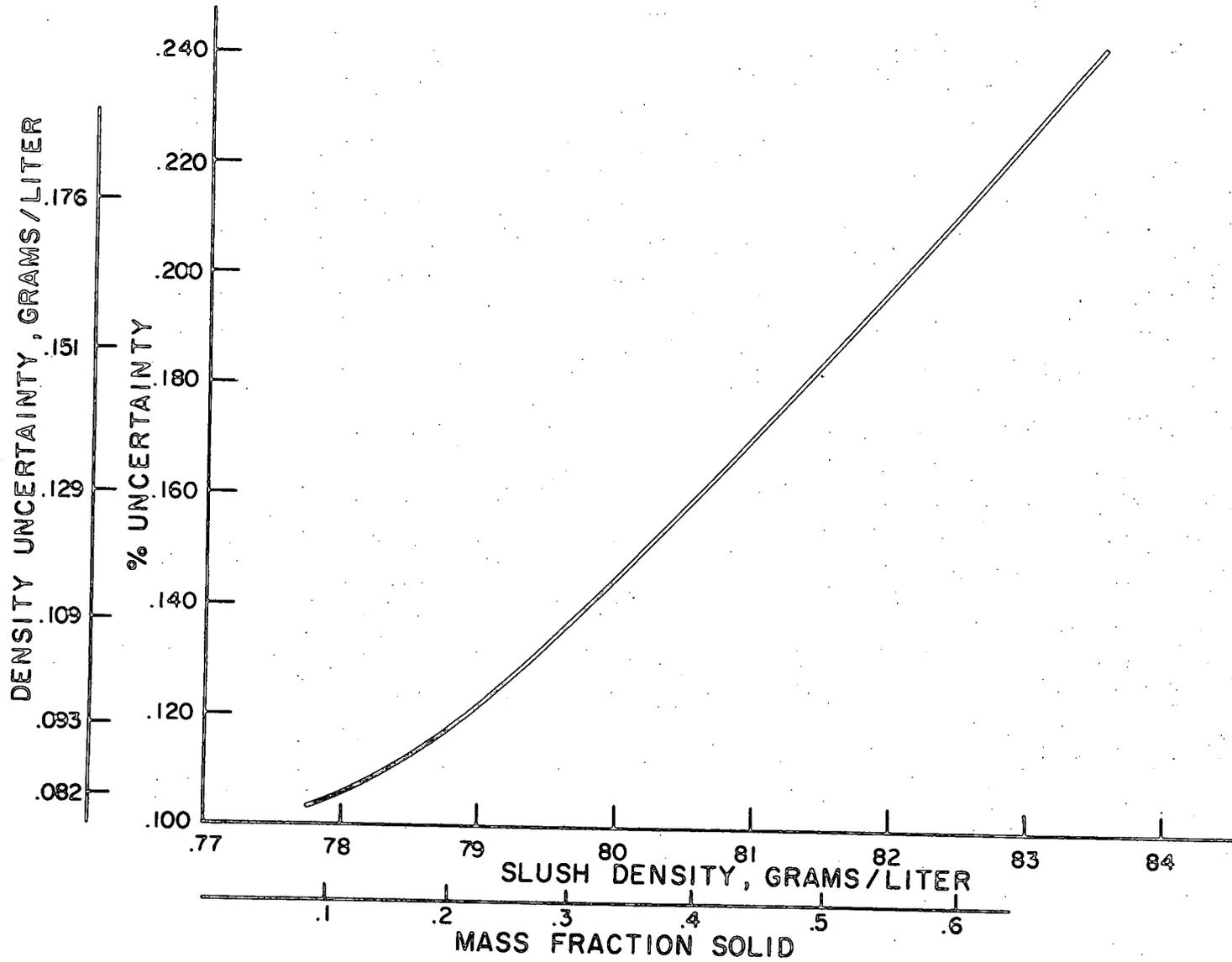
Figure 5.   Error Analysis Results.

2.4 Slush Quality Error

It is often convenient to use the concept of "quality" by which is meant the mass fraction of solid in the liquid-solid mixture. Conversion from slush density to slush quality is, of course, a purely mathematical manipulation and cannot introduce any new experimental error which is traceable to the density reference system. The conversion from density to quality does, however, introduce a new physical constant along with the uncertainty in our present knowledge of that constant. The constant is ρ_s, the triple-point density of solid hydrogen, which is given in reference [2] as 86.59 kg m^{-3}, with an uncertainty of ±0.3 percent.

If we now examine the equation which converts density to mass fraction of solid (quality) we can see how much additional uncertainty is introduced into our statement of results. The expression for mass fraction of solid in terms of the slush, liquid, and solid densities, is

$$F = \frac{\rho_s (\rho - \rho_\ell)}{\rho (\rho_s - \rho_\ell)}. \tag{3}$$

For ρ we substitute from equation (1), which gives

$$F = \frac{\rho_s M_b}{(M_b + M_\ell)(\rho_s - \rho_\ell)}. \tag{4}$$

This expresses F in terms of the experimental variables M_b and M_ℓ and the systematic parameters ρ_ℓ and ρ_s. The partial derivatives are

$$\frac{\partial F}{\partial M_b} = \frac{\rho_s M_b}{(\rho_s - \rho_\ell)(M_b + M_\ell)^2}$$

$$\frac{\partial F}{\partial M_\ell} = \frac{-\rho_s M_b}{(\rho_s - \rho_\ell)(M_b + M_\ell)^2}$$

$$\frac{\partial F}{\partial \rho_\ell} = \frac{-\rho_s M_b}{(M_b + M_\ell)(\rho_s - \rho_\ell)^2}$$

$$\frac{\partial F}{\partial \rho_s} = \frac{-M_b \rho_\ell}{(M_b + M_\ell)(\rho_s - \rho_\ell)^2} \ .$$

Values for the experimental variables and systematic parameters together-
er with their uncertainties are:

$$M_b = 117.01 \pm 0.58 \text{ g} \quad \text{(for 0.500 mass fraction)}$$
$$M_\ell = 1998 \pm 10 \text{ g}$$
$$\rho_\ell = 77.017 \pm 0.077 \text{ kg m}^{-3}$$
$$\rho_s = 86.59 \pm 0.26 \text{ kg m}^{-3}.$$

If we make these substitutions and square the results, we have (without
designating units):

$$\left(\frac{\partial F}{\partial M_b}\right)^2 = 1.63 \times 10^{-5}$$

$$\left(\frac{\partial F}{\partial M_\ell}\right)^2 = 5.57 \times 10^{-8}$$

$$\left(\frac{\partial F}{\partial \rho_\ell}\right)^2 = 0.271$$

$$\left(\frac{\partial F}{\partial \rho_s}\right)^2 = 0.215 \ .$$

Also we have

$$(dM_b)^2 \;=\; (0.58)^2 \;=\; 0.342$$

$$(dM_\ell)^2 \;=\; (10)^2 \;=\; 100$$

$$(d\rho_\ell)^2 \;=\; (0.077)^2 \;=\; 5.93 \times 10^{-3}$$

$$(d\rho_s)^2 \;=\; (0.26)^2 \;=\; 6.76 \times 10^{-2}.$$

The uncertainty in F can now be approximated, as was done for ρ, by use of equation (2). Thus, when $F = 0.500$, for which the value of M_b is 117.01 ±0.58 g/ℓ, we have

$$\left(dF\right)^2 = \left(\frac{\partial F}{\partial M_b}\right)^2 \left(dM_b\right)^2 + \left(\frac{\partial F}{\partial M_\ell}\right)^2 \left(dM_\ell\right)^2 + \left(\frac{\partial F}{\partial \rho_\ell}\right)^2 \left(d\rho_\ell\right)^2$$

$$+ \left(\frac{\partial F}{\partial \rho_s}\right)^2 \left(d\rho_s\right)^2$$

$$= (5.57 \times 10^{-6}) + (5.57 \times 10^{-6}) + (1.61 \times 10^{-3}) + (1.45 \times 10^{-2})$$

$$= 1.61 \times 10^{-2}$$

$$dF = \pm 0.013.$$

The fractional error in F is

$$\frac{dF}{F} = \frac{0.013}{0.50} = \pm 0.026 \text{ or } \pm 2.6\%.$$

Thus, the uncertainty in the mass fraction F is about 24 times as great as the uncertainty in the slush density ρ when both are expressed as fractional errors at 0.500 solid fraction. This is purely a consequence of introducing the relatively uncertain physical constant ρ_s into our expression for slush density. As our knowledge of ρ_s improves, the statement of solid mass fraction (quality) can be given with correspondingly less uncertainty.

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2.5 Error Due to Heat Leak

One more source of experimental error should be considered before the analysis is complete. This has to do with heat leak into the inner container. Any such heat influx will continuously change the slush density by melting some of the solid. Thus, the density ρ becomes a function of time, and it is necessary to determine this time dependence. A preliminary task is to analyze the accuracy with which this can be done. Since there will always be some elapse of time between a density determination and a readout from a transfer standard which is in place and being calibrated, it is apparent that the time dependence of ρ must be known with a high degree of accuracy.

In order to define the functional relationship between ρ and elapsed time t, note that in equation (1),

$$\rho = \rho_\ell \left(\frac{M_b}{M_\ell} + 1 \right),$$

it will be M_b which varies with time as heat leaks into the inner container. Therefore

$$\frac{d\rho}{dt} = \frac{\rho_\ell}{M_\ell} \frac{dM_b}{dt} .$$

It is the solid mass M_s, however, rather than the buoyed mass M_b, which varies directly with heat influx, so write

$$M_b = M_s - \rho_\ell V_s = M_s - \rho_\ell \frac{M_s}{\rho_s} = M_s \left(1 - \frac{\rho_\ell}{\rho_s} \right).$$

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Then

$$\frac{dM_b}{dt} = \left(1 - \frac{\rho_\ell}{\rho_s}\right)\frac{dM_s}{dt} = \left(1 - \frac{\rho_\ell}{\rho_s}\right)\frac{1}{H}\frac{dQ}{dt} ,$$

where

H   is heat of fusion and

$\frac{dQ}{dt}$ is heat influx.

This substitution gives

$$\frac{d\rho}{dt} = \frac{\rho_\ell}{M_\ell H}\left(1 - \frac{\rho_\ell}{\rho_s}\right)\frac{dQ}{dt} .$$

This is an exact expression showing that the time variation of slush density is directly proportional to heat leak into the inner container. If the system is at steady state, all terms on the right side of the equation are constants, although they all have uncertainties associated with them. The values and uncertainties are known for all of the constants except dQ/dt, for which the symbol W is used. Thus

$$d\rho = -A\, dt \qquad\qquad (6)$$

where

$$A = \frac{W\rho_\ell}{M_\ell H}\left(1 - \frac{\rho_\ell}{\rho_s}\right),$$

and the negative sign is introduced to show that density decreases with time. Integration of (6) from t_0 to t_1 gives

$$\rho_1 - \rho_0 = -A(t_1 - t_0).$$

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Note that $(t_1 - t_0)$ is a fixed time interval, which is designated T_1. Then

$$-A = \frac{\rho_1 - \rho_0}{T_1} = -\frac{W\rho_\ell}{M_\ell H}\left(1 - \frac{\rho_\ell}{\rho_s}\right),$$

from which

$$-W = \frac{M_\ell \rho_s H(\rho_1 - \rho_0)}{T_1 \rho_\ell (\rho_s - \rho_\ell)}.$$

Since ρ_1 and ρ_0 are not independent variables, use equation (1) from which

$$\rho - \rho_0 = \frac{\rho_\ell}{M_\ell} (M_{b1} - M_{b0}).$$

Then

$$-W = \frac{\rho_s H(M_{b1} - M_{b0})}{T_1 (\rho_s - \rho_\ell)}. \tag{7}$$

Equation (7) gives W in terms of independent experimental variables $(M_{b1}, M_{b0}, \text{ and } T_1)$ and systematic parameters $(\rho_s, \rho_\ell, \text{ and } H)$. Now express the constant A in these terms, giving

$$\frac{d\rho}{dt} = -A = \frac{\rho_\ell (M_{b1} - M_{b0})}{T_1 M_\ell}. \tag{8}$$

Equation (8) gives the variation of slush density with time, based on a preliminary experiment performed during the time interval T_1. M_{b0} and M_{b1} are load cell readings taken at the beginning and end, respectively, of the time interval T_1.

The expression for a final slush density ρ, which is determined by obtaining an initial density ρ_0 and correcting it for the solid melted during an elapsed time interval T_2, can now be written as

$$\rho = \rho_0 + \int_{t_0}^{t_2} \frac{d\rho}{dt}\, dt$$

$$= \rho_0 + \frac{\rho_\ell (M_{b1} - M_{b0})}{T_1 M_\ell} (t_2 - t_0)$$

$$= \rho_0 + \frac{T_2 \rho_\ell (M_{b1} - M_{b0})}{T_1 M_\ell}. \tag{9}$$

Here T_1, M_{b1}, and M_{b0} refer to the preliminary experiment which gave equation (8). T_2 and ρ_0 refer to any subsequent slush density determination. Since ρ_0 is not the independent variable, however, refer once more to equation (1) and write

$$\rho_0 = \rho_\ell \left(\frac{M_b}{M_\ell} + 1 \right)$$

which can be substituted into equation (9). This gives

$$\rho = \frac{\rho_\ell}{M_\ell} \left[\left(M_b + M_\ell \right) + \frac{T_2}{T_1} \left(M_{b1} - M_{b0} \right) \right], \tag{10}$$

where M_b is the load cell reading taken at the beginning of the time interval T_2.

Equation (10) is the final working equation for the slush density reference system. It shows all of the variables and systematic parameters which enter into a density determination. To be complete, then,

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we should perform a final error analysis of this equation, which has been done in Appendix A. The result shows that the heat leak correction can be incorporated into the slush density determination without addition of any significant new uncertainty.

3. Design Details

Appendix B contains detailed shop and assembly drawings of the weighing cryostat and slush generator in their final configurations. The system was designed and built essentially as described in section 2.2.

3.1 Weighing System

A light-weight (850 g) aluminum weigh-can having a volume of 23.2 ℓ (see Appendix B, figure 2B) is suspended from a load cell which is in a separate housing above the top plate of the weighing cryostat. Between the top plate and the load cell is a cylinder, with windows (see figure 3B) in which are suspended a series of calibration masses. The weigh-can may be lifted from the load cell suspension at any time, and one or more of the calibration masses can be substituted.

The method of weigh-can suspension and counterbalance is shown in figure 6. A flexure beam attached to the lower side of the top plate makes it possible to remove almost all of the empty (submerged) weigh-can mass from the load cell. This provides maximum sensitivity for determination of M_b, the buoyed mass of the solids in the weigh-can. A gum rubber damper at the top of the suspension was found to be helpful in avoiding load transducer oscillations. The gum rubber section also prevents overstraining the suspension when the weigh-can is locked against its stationary cover after a weighing has been completed.

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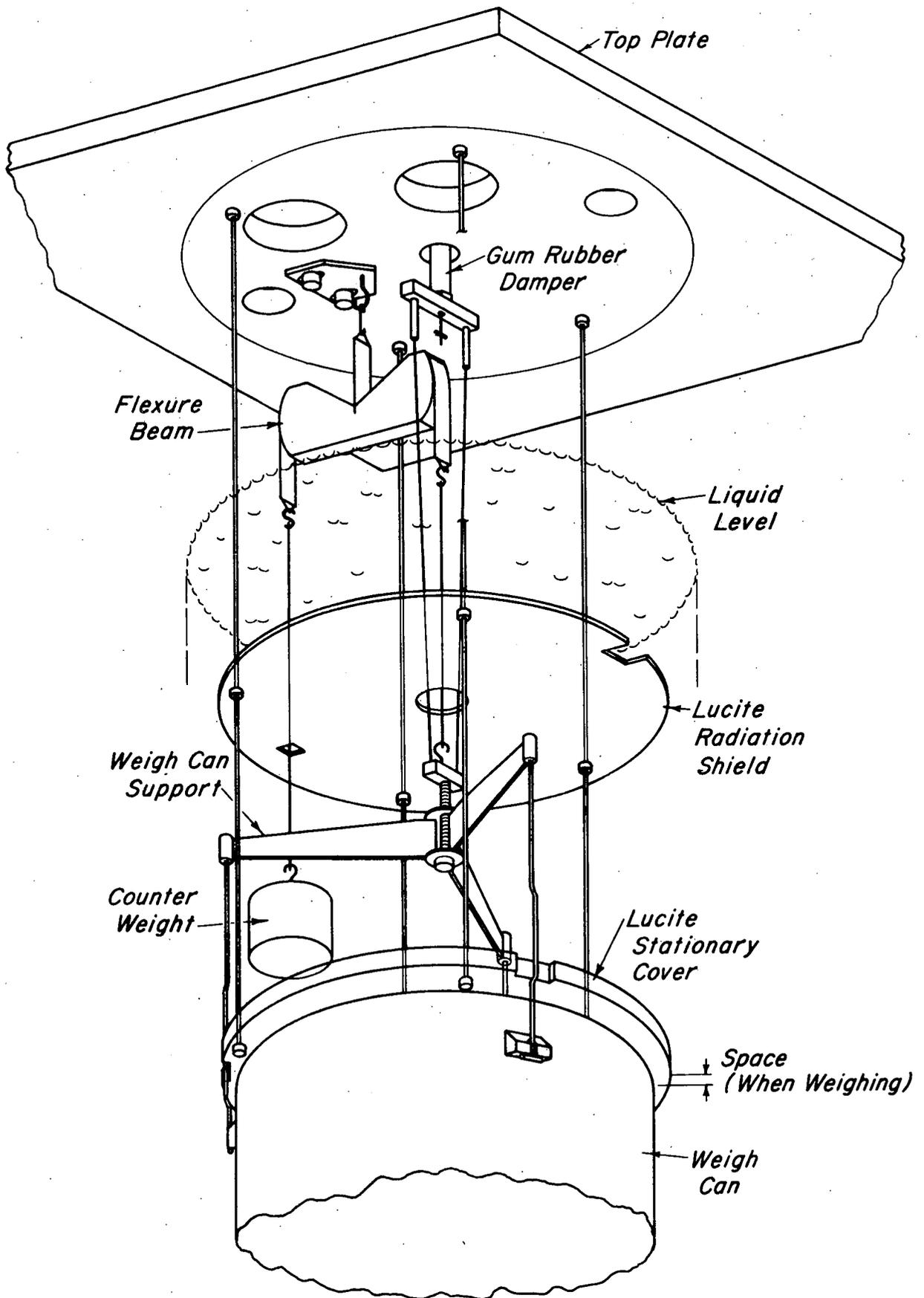
Figure 6.   Weigh-Can Suspension System.

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The top plate and calibration-weight column were designed to accommodate any load cell or force transducer which could be mounted on the framework provided. Early in the program Mr. Harlan Harman, Chief of the Pressure and Thrust Section in the Instrument and Development Branch of the MSFC kindly provided us with several force-balance units which had been successfully used as differential pressure transmitters. It was suggested that we could attach the top of the weigh-can and calibration-weight suspension system to the midpoint of one bellows of the force-balance differential pressure transmitter, and use it as a sensitive weighing device without any further modification. This proved to be a very satisfactory method for determination of M_ℓ and M_b. The transmitter is an electronic force-balance system in which the DC current required to maintain a null is measured to indicate the force (of gravity, in our application). The unit used on the density reference system has a sensitivity of about 0.05 mA per gram weight, which can be converted to voltage for readout and recording by placing a stable resistor in series with the force motor. A 500 Ω resistor was used, giving a sensitivity of 25 mV/g. Overall short-term stability was ±0.5 g or better when weighing loads on the order of 100 g.

3.2 Stirring Method

After a determination of average slush density in the weigh-can has been made, it is of no value unless it can be accurately correlated with the reading of another instrument, i. e., it must be correlated with a reading or series of readings from the transfer standard which is being calibrated. The transfer standard transducer will usually be located inside the weigh-can volume; its weight will be supported by the fixed plate which forms the weigh-can cover between weighings. When the can

is lowered for weighing it no longer contacts the cover, so it and attachments to it are not weighed. The important point, however, is that the transfer standard transducer must sense the <u>average</u> density of the weigh-can contents. This can be accomplished only to the extent that the slush is kept homogeneous while density transducer readings are being taken. An effective stirring arrangement is accordingly of paramount importance to usefulness of the density reference system.

An important restraint on design of the stirring method was the fact that any blades or surfaces wide enough to effectively move the solids would also support a significant amount of solids when the stirring was stopped for a weighing. If the blades were attached to the "outside world", a new uncertainty in M_b would be introduced. To circumvent this problem, the magnetic method illustrated in figure 7 was designed. A low-mass rotor inside the weigh-can carries eight slender bar magnets which link flux with eight large alnico bar magnets attached to an iron wheel which surrounds the cryostat. The various dimensions and materials are as shown in figure 7.

A variable-speed air motor and a friction drive arrangement are used to turn the large magnet wheel. Strength of flux linkage was found to be adequate for all conditions except when starting to stir a full load of well-settled heavy slush.

The magnet wheel and air motor assembly are supported on an aluminum platform which can be lowered by means of cables into a pit beneath the cryostat. This arrangement allows the magnetic linkage to be removed for accurate weighing of the slush. The same aluminum platform supports the cryostat shell (dewar) and lowers it into the pit, along with the magnet wheel, when access to the interior of the cryostat is required.

PLASTIC ROTOR

ALUMINUM WEIGH-CAN

IRON DRIVE WHEEL
1" x 1¼" CROSS SECTION

1"x1"x3" ALNICO MAGNETS
ON DRIVE WHEEL

¼" x ½" x 3" ALNICO
MAGNETS ON ROTOR

22¼" D.

14" D.

12" D.

11" D.

WEIGH-CAN HANGER

ALUMINUM WEIGH-CAN

PLASTIC ROTOR AND
ELEVATING SPIRAL

MAGNETS

FIXED PLASTIC COVER

IRON WHEEL

AIR MOTOR

NON-MAGNETIC STAINLESS
STEEL DEWAR, EVACUATED
ALUMINIZED MYLAR
MULTI-LAYER INSULATION

ELEVATOR FOR DEWAR
AND/OR MAGNET WHEEL

SLEEVE
BEARING

FRICTION DRIVE

Figure 7.   Magnetic Stirring Method.

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A second restraint on the stirring method was the requirement that as much as possible of the weigh-can interior be kept open for installation of density-sensing devices. This led to the rotating plastic spiral which is shown in figure 8. The combined stirring and elevating action of the four-bladed plastic rotor and four-turn spiral provides a very effective stirring action. Homogeneity of the stirred slush can be tested by observing the readout value of any stable density transducer while changing the speed of the stirring rotor. If there is no noticeable change in density readout, it can be assumed that the liquid-solid mixture is homogeneous over the chosen range of stirring speeds.

3.3 System Operation

Auxiliary systems required to provide the hydrogen slush in the weighing cryostat include the slush generator, liquid supply vessel, vacuum-jacketed transfer lines, pumping capability for the "freeze-thaw" method of slush production[4], and hydrogen and helium gas supplies for pressurization, purging, and transfer operations.

Figure 9 is a photograph of the control panel board, which incorporates a schematic diagram of the system. From left to right are represented the vacuum pump, water-warmed heat exchanger, slush generator, and weighing cryostat. Figure 10 is a general view of the cryostat assembly as seen from the left end of the control panel during a run. In the right-hand side of the dewar support framework is the slush generator, which is connected with a valved and vacuum-jacketed transfer line to the 175-liter supply dewar at the far right of the picture. In the foreground is a 50-liter liquid nitrogen dewar for filling the generator radiation shield. The weighing cryostat is in the left-hand portion of the framework and connects to the generator with a second vacuum-jacketed transfer line, which can be seen above the top plates. The

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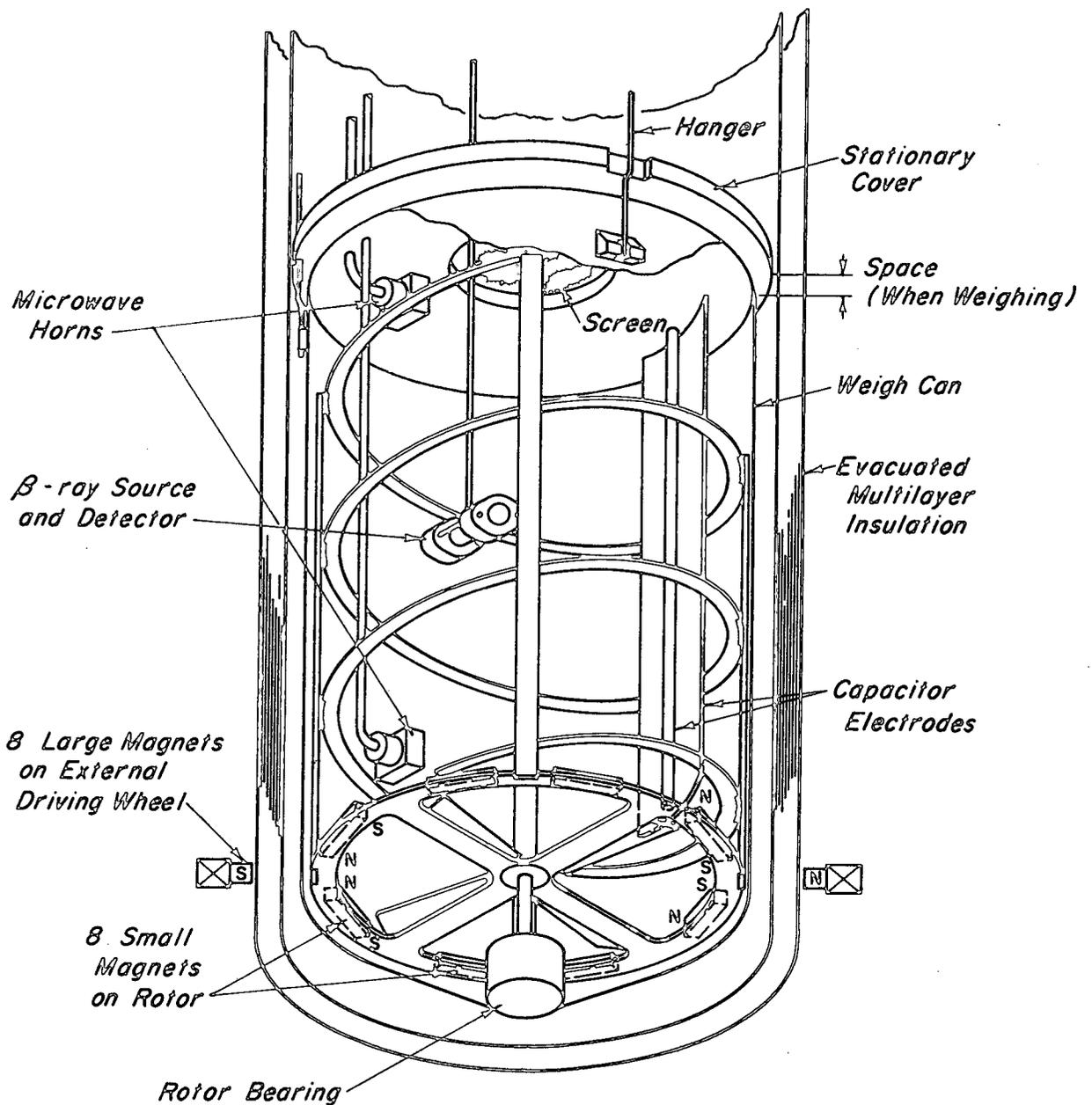
Figure 8. Weigh-Can Interior Showing Stirring Rotor and Density Transducers.

Labels on figure:
- Hanger
- Stationary Cover
- Space (When Weighing)
- Weigh Can
- Evacuated Multilayer Insulation
- Capacitor Electrodes
- Screen
- Microwave Horns
- β-ray Source and Detector
- 8 Large Magnets on External Driving Wheel
- 8 Small Magnets on Rotor
- Rotor Bearing
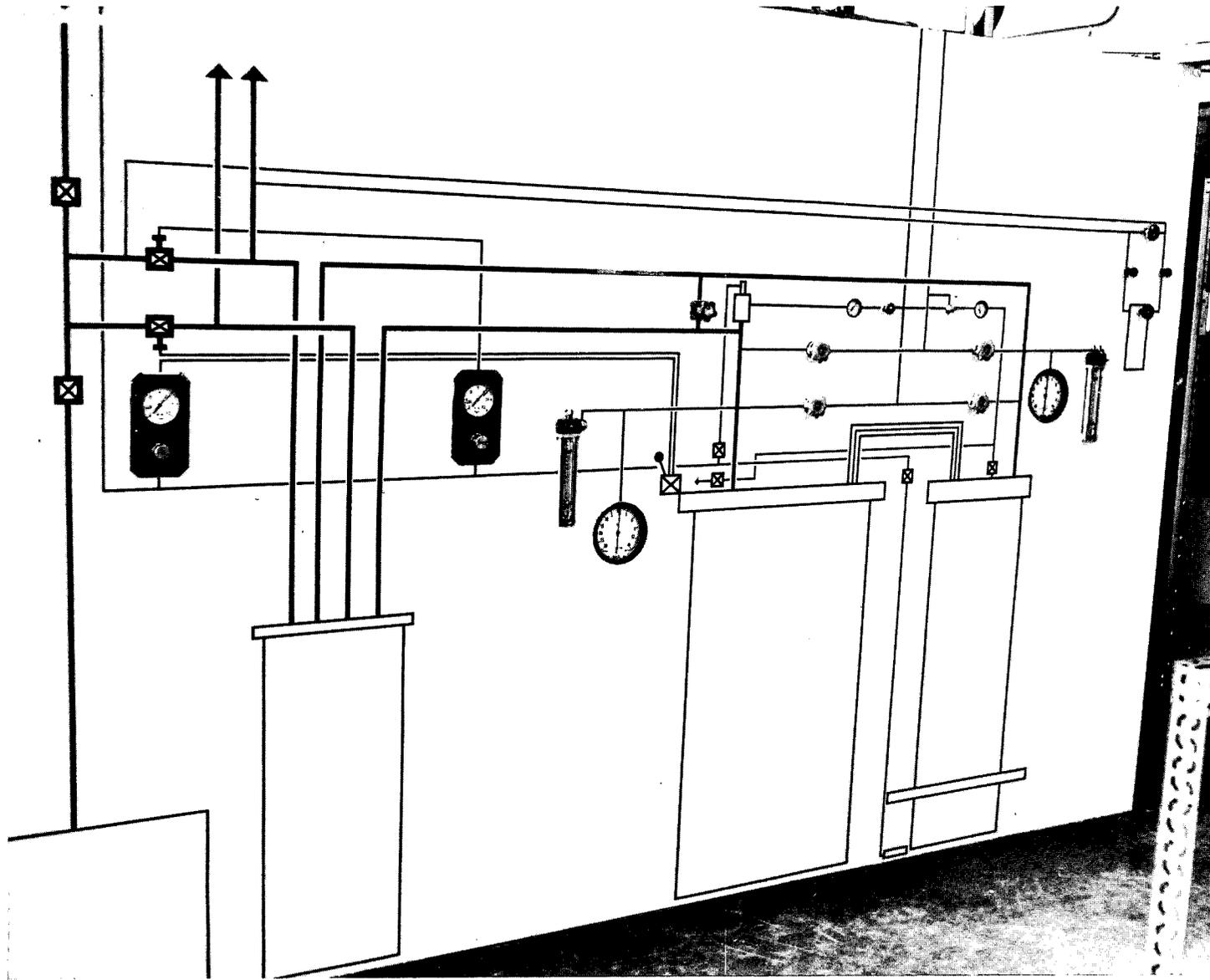
Figure 9.   Panel Board and Flow Diagram.
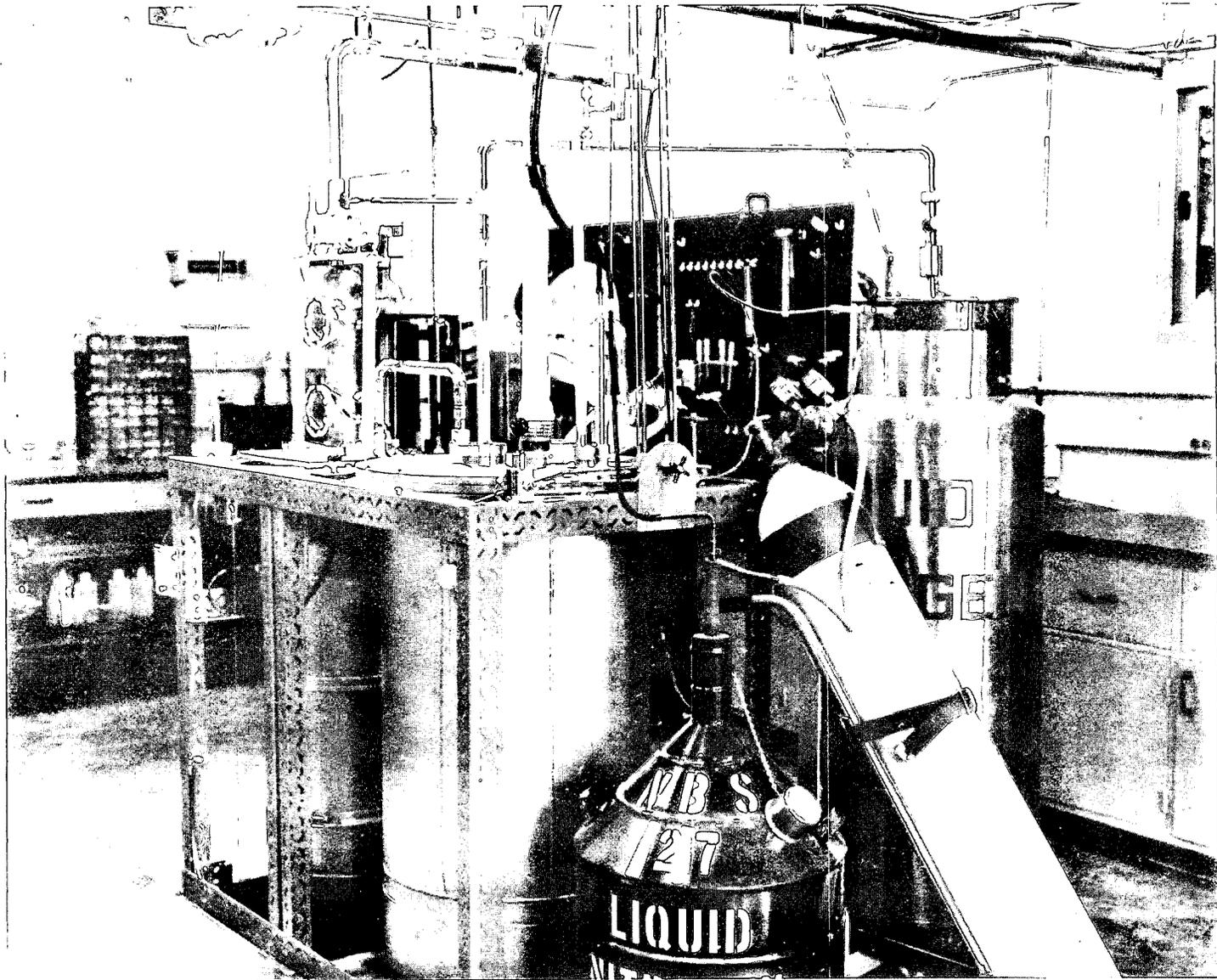
Figure 10. General View of Assembled System.

calibration-weight column and force-balance unit are above the cryostat; the magnet drive wheel is out of sight in the pit below the cryostat. Figure 11 shows the weighing cryostat open, as it might appear between runs, with the weigh-can exposed and ready to be removed from its suspension.

The general operation procedure is as follows:

(1)   Purge and pump cycles for cleanup of system.

(2)   Fill generator radiation shield with liquid nitrogen.

(3)   Connect 175-liter liquid hydrogen supply dewar to generator.

(4)   Fill generator with LH_2 and simultaneously cool weighing cryostat.

(5)   With generator full and some liquid in weigh-can, bring both vessels to triple-point pressure.

(6)   Fill weigh-can with triple-point liquid and weigh. (This gives M_ℓ, one of the system constants, and does not need to be repeated for each run.)

(7)   Transfer more liquid from generator, overflowing the weigh-can, and fill dewar. Maintain liquid at triple point with throttling valves and manostat.

(8)   Adjust force-balance unit to zero reading.

(9)   Generate slush, and transfer to weigh-can. Transfer surplus liquid back to generator and repeat until desired solid fraction resides in weigh-can. (Be sure that weigh-can is in closed position for this operation.)

(10)   Stir and read density as shown by transducer under test. Log on magnetic tape.

(11)   Lower the magnetic drive wheel a foot or more below the cryostat.
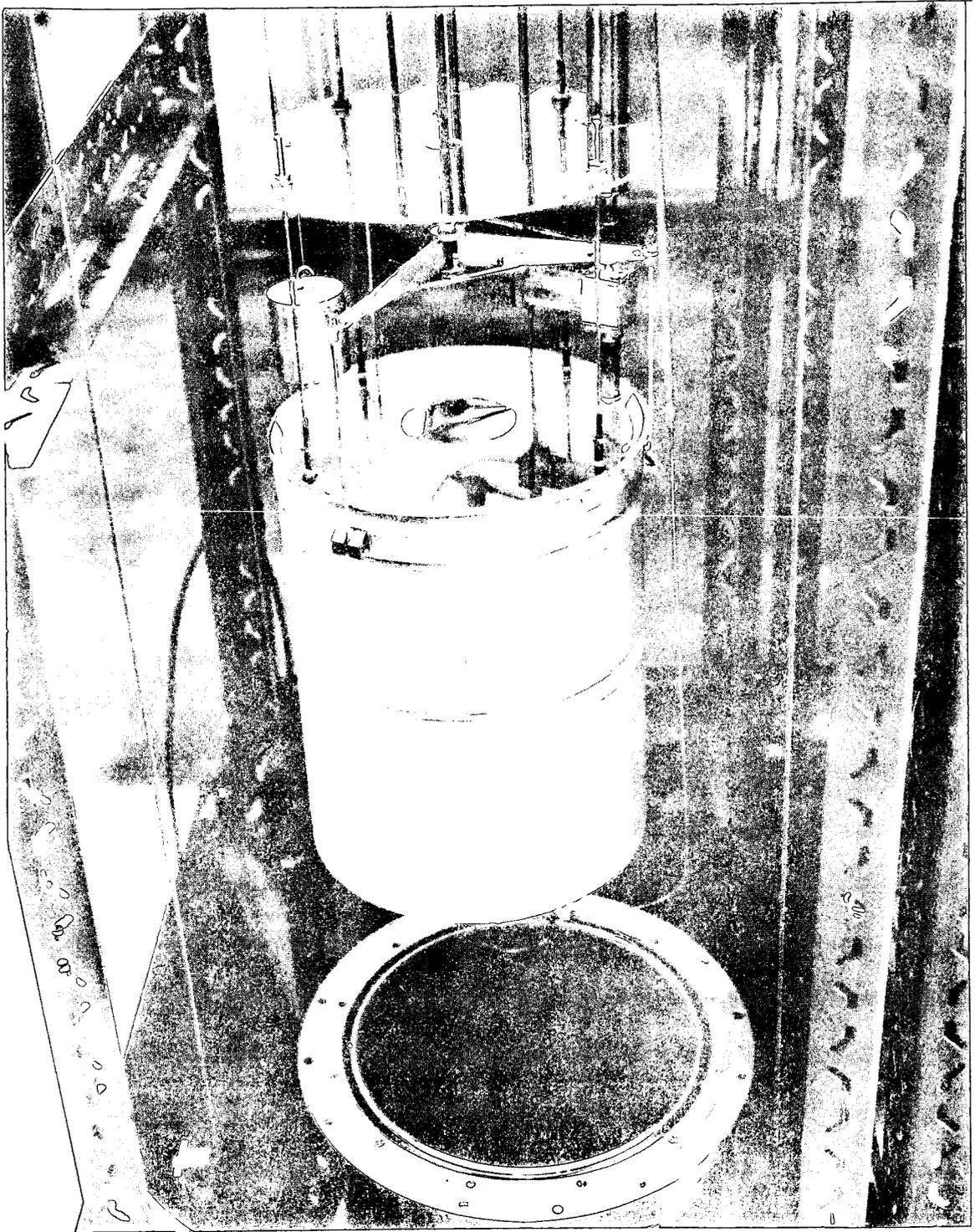
Figure 11. Cryostat Interior with Weigh-Can.

(12) Lower the weigh-can onto the force-balance suspension and observe readout on digital voltmeter and parallel-connected chart recorder. Log on magnetic tape. Alternate weigh-can with calibration weights until maximum accuracy is obtained.

(13) To make the heat leak correction, observe the time vs. weight drift and record data required for extrapolation back to the density transducer readout time.

(14) Repeat steps (9) through (13) as necessary.

4. Density Transducer Tests

Of the many measurable effects which are known to vary with density, five were chosen for study as hydrogen slush density transducers and possible development as a slush density transfer standard. The five methods were:

1. Attenuation of beta radiation,
2. Attenuation of gamma radiation,
3. Dielectric change in a fixed capacitor,
4. Microwave transmission characteristics, and
5. Velocity of sound.

Methods 3 and 4 are based on changes in relative dielectric constant and were found to be the best candidates.

4.1 Beta-Ray Attenuation

If a source of beta radiation is placed a suitable distance from a detector in liquid or slush hydrogen, the count-rate of beta particles reaching the detector is an accurate indicator of the density of the fluid. A system based on this principle was built by a private company under NASA contract and was extensively studied in the density reference system.

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The beta-ray attenuation system uses sealed sources containing strontium-90 and encapsulated "surface barrier" radiation detectors. Each detector contains a 50-mm^2 active area, 500 microns thick, housed in a stainless steel capsule with a 0.002-inch-thick stainless steel window. The source housing contains a sealed 15 millicurie strontium-90 beta source. For additional safety, the source housing is fabricated with a second stainless steel window 0.001-inch thick. Source-to-detector spacing is made variable by means of small rods sliding through holes in the detector housing. See figure 12.

Beta particles from the source are absorbed by the detector, thereby producing minute electrical pulses. These are fed through a preamplifier to a linear amplifier which shapes and further amplifies the pulses, after which they go to a discriminator where those below a given energy threshhold are blocked out. The discriminated pulses can then be counted directly, or they can be converted to a DC signal proportional to the pulse rate. The method is diagramed in figure 13.

The source and detector assembly shown in figure 12 has windows spaced 4 cm apart. A 1/4-inch stainless steel tube supports this "probe", provides means for evacuation and helium back-fill of the detector housing, and carries the signal lead. The source capsule is "permanently" sealed, with no provision for evacuation or back filling. This was a safety judgement, but is presently subject to some question.

Parameters investigated in the density reference system were source-to-detector spacing, discrimination level, reliability, and both long and short term accuracy.

Since hydrogen slush is normally a non-homogeneous mixture, an ever present problem for any density transducer is representative
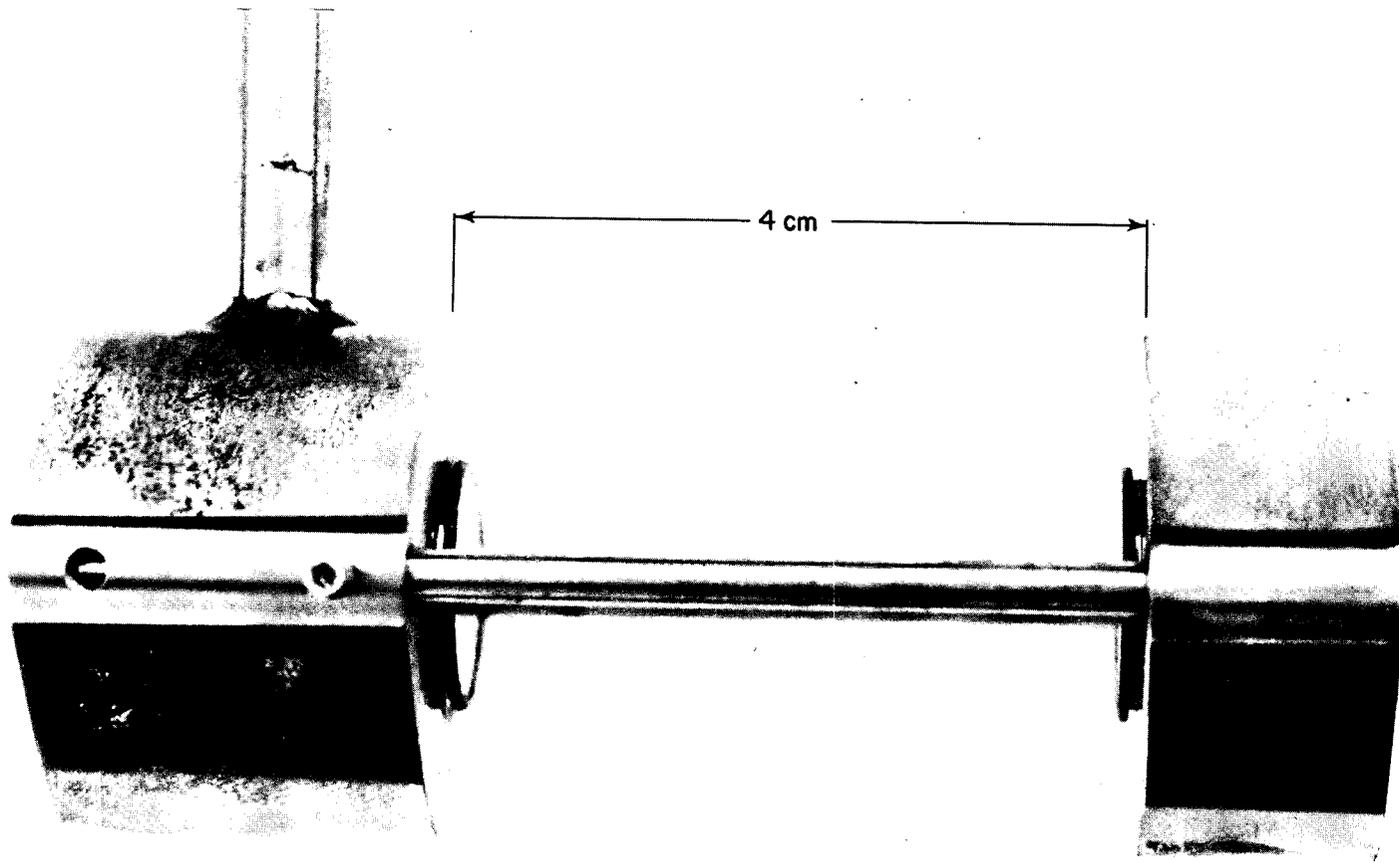
Figure 12. Beta-Ray Source and Detector.
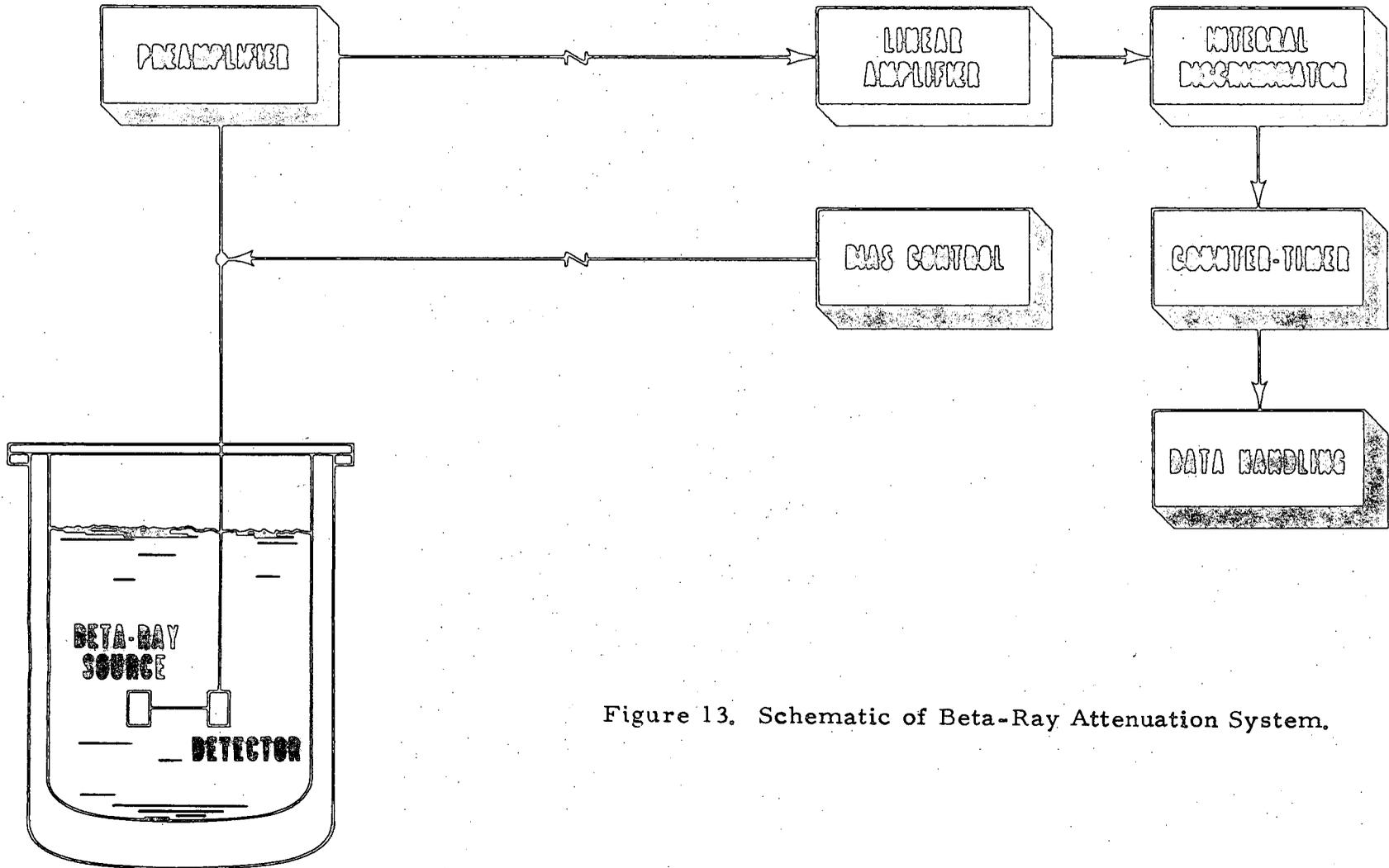
Figure 13. Schematic of Beta-Ray Attenuation System.

sampling. For the beta-ray attenuation system, this requires adequate separation between source and detector windows, but if spacing is too great there will not be a sufficiently high count for fast response or good statistics. After a considerable amount of experimentation it was determined that a 4-cm spacing and an energy discrimination level which gave approximately 3×10^4 counts per second at triple-point liquid hydrogen density was a good set of conditions for work in the density reference system.

Data were first taken with a strip-chart recorder connected to the analog output provided by the equipment, but this was soon replaced by a counter-timer with a magnetic tape printer, so the data reduction could be done by computer. The computer program produced means, slopes, and standard deviations, as well as machine-made graphs of density vs. count-rate. The latter relationship was found to be linear within the limits of experimental error. On a few plots a slight change in the slope at triple point was found, i. e., a small difference in $\Delta c/\Delta \rho$ when going from the liquid into the slush region, but these were subsequently attributed to imperfect mixing of the slush. The slope, which represents sensitivity of the method, averaged about 5×10^3 counts s^{-1} per kg m^{-3} density change.

A series of runs with two of the probes in the density reference system covered a period of six months and involved approximately 10 complete cooldown/warmup cycles. Performance was relatively stable over this period. Data from the last four of these runs, representing more than 1000 stable count-rate vs. density observations, were carefully analyzed. It was concluded that the equipment was capable of measuring hydrogen liquid or slush density with an uncertainty of no more than one percent over the range of 71 to 81 kg m^{-3}, i. e., from

normal boiling liquid to 0. 45 solid fraction, with no indication of loss of accuracy at the extremes of this range. The uncertainty is based on a statistical scatter of the count rates within a $\pm 2\sigma$ error band, i. e. , 95 percent confidence, and also includes the 0. 2 percent uncertainty contributed by the density reference system.

Subsequent experience with these and the additional three detectors provided did, however, turn up some serious long-range stability problems. All of the detectors became noisy over a period of less than a year of service, and two of the five yielded very little satisfactory data. The two detectors which were extensively tested in the density reference system were later installed in a one-m^3 vessel used for solid fraction up-grading. One detector performed well over a period of several weeks; the other exhibited an erratic base count-rate and gave very little useful data in the new installation. Finally, the source housing on one of the probes suffered a ruptured window. The inner seal remained intact, so no contamination resulted, but the incident casts doubt on the method of source packaging.

After completion of the program all of the detectors were returned to the manufactuer for examination and reconditioning. In addition to detector breakdown, complexity of the associated electronics is a disadvantage of the beta-attenuation system. For point density sensing, however, it is a workable method, and could be used as a transfer standard for providing traceability to a density reference system.

4. 2 Gamma Ray Attenuation

Our experience with gamma ray attenuation for liquid and slush hydrogen density measurement has been documented in other publications.[5, 6] Two densitometers of this type have been used at NBS. The densitometers used cesium 137 sealed sources, one 4 curies, the other

17 curies, and ionization chambers as detectors. Sources and detectors were mounted externally on opposite sides of the storage vessel; the beam penetrated the walls of the vessel as well as the contained hydrogen. For both vessels the beam traversed 0.76 m of hydrogen liquid or slush, and a little more than half of the attenuation took place in the hydrogen.

It was determined that the response (ionization current) was accurately linear with density, so frequent checks on calibration of the instruments could be made by using vapor pressure of well-stirred liquid to determine a range of liquid densities from normal boiling to triple point, then extrapolating this line into the slush region in order to read out slush densities. Sensitivity figures depend on the dropping resistance and amplifier used to convert the ionization current to a measurable millivolt signal. Typical values were 0.7 mV per kg m^{-3} change in hydrogen slush density.

The only real problem experienced with the gamma-ray densitometers was drift, which was apparently related to small temperature changes in the environment of the amplifiers and high-megohm resistors. This area requires refinement, but should not be an insurmountable problem. There are, however, three basic disadvantages to these systems:

(1)   Not transferable without loss of calibration,

(2)   Relatively high radiation hazard, and

(3)   Stronger sources required for larger vessels.

In the early part of the density reference system program, it was assumed that the gamma-ray method should be evaluated in the weighing cryostat, and bracketing was provided to accommodate the 4-curie-source system. As the program progressed, however, it was apparent that the

disadvantages listed above virtually eliminated this form of instru-
mentation as a density transfer standard, and that nothing would be
gained by further testing of the gamma system in its available form.
It is possible that a gamma-ray source and detector system could be
developed for placement inside a storage vessel. This might be similar
to the beta-ray attenuation system, but without the limitation of short
source-to-detector path lengths. Such systems have been proposed and
if one becomes available it would be profitable to test it in the density
reference system.

4.3 Capacitance Method

For any capacitor of simple, fixed geometry, the measured
electrical capacitance varies directly with the dielectric constant of the
medium between the electrodes. The relation between dielectric constant
and density is, for hydrogen, quite well represented by the Clausius-
Mossotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} = P\rho \qquad (11)$$

where

ϵ is dielectric constant

ρ is density

P   is specific polarization, a property having dimensions
of reciprocal density.

The polarization "constant" P has been found to increase by
about 0.1 percent when hydrogen changes from liquid to 0.5 solid frac-
tion at triple-point pressure. [6]

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The dielectric constant for triple-point liquid hydrogen is 1.25158.[6] The dielectric constant for any slush sample can therefore be obtained with high accuracy from the ratio of the capacitance of the condenser with sample to the capacitance in triple-point liquid. Having determined ϵ, the density of slush is calculated from the Clausius-Mossotti equation. Table 1 is a tabulation of ϵ, ρ, and P for hydrogen from normal-boiling to 0.5 solid fraction.

Equation (11) can be written

$$\epsilon = \frac{1 + 2P\rho}{1 - P\rho} = \frac{(1 - P\rho) + 3P\rho}{1 - P\rho} = 1 + \frac{3P\rho}{1 - P\rho}.$$

The variation in ϵ is then given by

$$d\epsilon = \left(\frac{\partial\epsilon}{\partial P}\right)dP + \left(\frac{\partial\epsilon}{\partial\rho}\right)d\rho = \frac{3\rho dP + 3Pd\rho}{(1 - P\rho)^2}. \tag{12}$$

Triple point liquid density is 77.017 kg/m³; 0.5 solid fraction slush density is 81.526 kg/m³. The corresponding polarizability values are 1.0046 and 1.0056 cm³/g. Using the average of these values for ρ and P and the difference between the extremes for dP and dρ we have

$$d\epsilon = \frac{3 \times 0.07927 \times 0.0010 + 3 \times 1.0051 \times 0.00451}{(1 - 1.0051 \times 0.07929)^2}$$

$$= 2.81 \times 10^{-4} + 1.61 \times 10^{-2}.$$

This is the change in ϵ which results when hydrogen changes from triple-point to 0.5 solid fraction slush. The first term is due to the change in polarizability; the second term is due to the change in density. If we start from the triple-point liquid value of $\epsilon = 1.25158$, the polarizability term accounts for a change in ϵ of 0.02 percent, while the density term accounts for a 1.3 percent change.

Table 1

Density, Dielectric Constant, and Polarizability

for Hydrogen from Normal Boiling to 0. 5 Solid Fraction Slush

ρ (g cm^{-3})	ϵ	P (cm^{3}g^{-1})	$d\rho/d\epsilon$
.07076	1.22971	1.0051	
.07085	1.23000	1.0051	.0834303
.07113	1.23100	1.0051	.0876160
.07142	1.23200	1.0050	.0874520
.07171	1.23300	1.0050	.0872880
.07200	1.23400	1.0050	.0871245
.07228	1.23500	1.0050	.0869612
.07257	1.23600	1.0050	.0867975
.07286	1.23700	1.0049	.0866344
.07314	1.23800	1.0049	.0864714
.07343	1.23900	1.0049	.0863085
.07372	1.24000	1.0049	.0861457
.07400	1.24100	1.0049	.0859831
.07429	1.24200	1.0048	.0858207
.07457	1.24300	1.0048	.0856584
.07486	1.24400	1.0048	.0854962
.07514	1.24500	1.0048	.0853342
.07543	1.24600	1.0047	.0851724
.07571	1.24700	1.0047	.0850107
.07600	1.24800	1.0047	.0848491
.07628	1.24900	1.0047	.0846877
.07657	1.25000	1.0046	.0845265
.07685	1.25100	1.0046	.0843654
.07702	1.25158	1.0046	
.07713	1.25200	1.0046	.0816585
.07741	1.25300	1.0047	.0773903
.07769	1.25400	1.0048	.0771717
.07797	1.25500	1.0048	.0769633
.07824	1.25600	1.0049	.0767551
.07852	1.25700	1.0049	.0765471
.07880	1.25800	1.0050	.0763393
.07907	1.25900	1.0051	.0761317
.07935	1.26000	1.0051	.0759243
.07962	1.26100	1.0052	.0757171
.07990	1.26200	1.0053	.0755101
.08017	1.26300	1.0053	.0753033
.08045	1.26400	1.0054	.0750966
.08072	1.26500	1.0055	.0748902
.08100	1.26600	1.0055	.0746842
.08127	1.26700	1.0056	.0744782
.08134	1.26723	1.0056	

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The above analysis applies when all of the dielectric between the capacitor electrodes is either liquid or slush, i. e. , when the capacitor is totally submerged and when the density distribution is uniform. Non-uniform distribution will result if the electrode spacing is too close and/or if mixing of the slush does not produce a homogeneous fluid.

After some preliminary testing of various capacitor configurations, the design shown in figure 14 was developed for testing in the density reference system. The capacitor is composed of a 1.27-cm-diameter brass rod 33 cm long which is rigidly supported 0.64 cm away from a section of thin-wall brass cylinder. The cylinder section has a radius of 8.5 cm, arc length of 8.3 cm, and extends 2.5 cm beyond the rod at each end. The section of cylinder forms one electrode; the adjacent rod is the other. The capacitance in triple-point liquid (77.017 kg m^{-3}) was 18.667 pf. The capacitor was located near the perimeter of the weigh-can, and the stirring pattern was such that solids were raised and swirled in a circular path between the electrodes.

From the assumption that the capacitance is directly proportional to the relative dielectric constant, it follows that

$$C = A\epsilon = A(1.25158) = 18.667 \text{ pf},$$

giving a geometrical constant of

$$A = 14.915 \text{ pf},$$

which is the "empty space" capacitance. Since a capacitance measurement of 18 pf having an uncertainty of ±0.001 pf or less can readily be obtained with shielded leads and a good three-terminal capacitance bridge, it is apparent that the relative dielectric constant, and hence the apparent density of the fluid between the electrodes, can be obtained with high accuracy.

0.64 cm

1.27 cm Dia.

8.3 cm

r = 8.5 cm

Socket head screw with lock washer

Dielectric material

2.5 cm

38 cm

2.5 cm
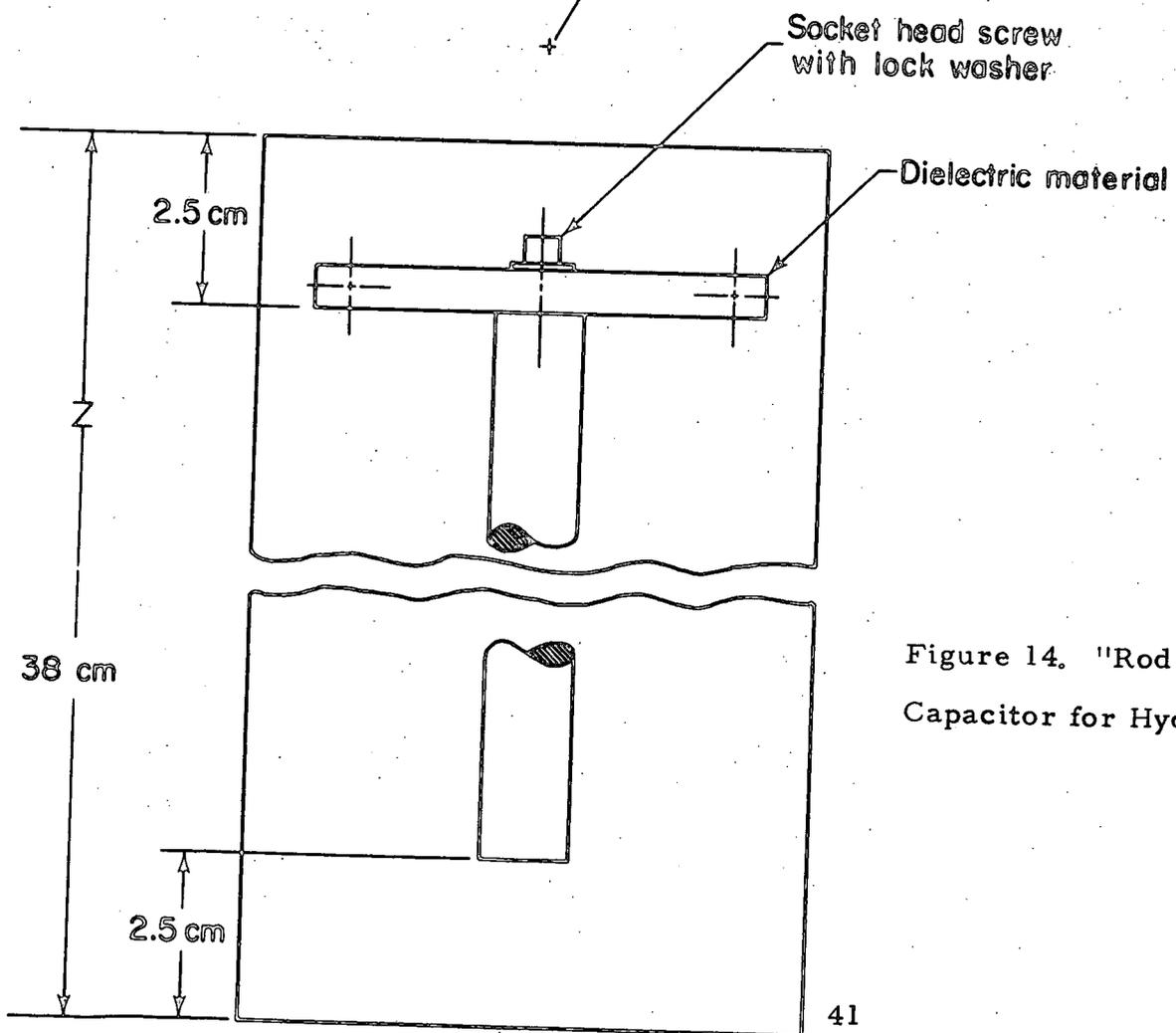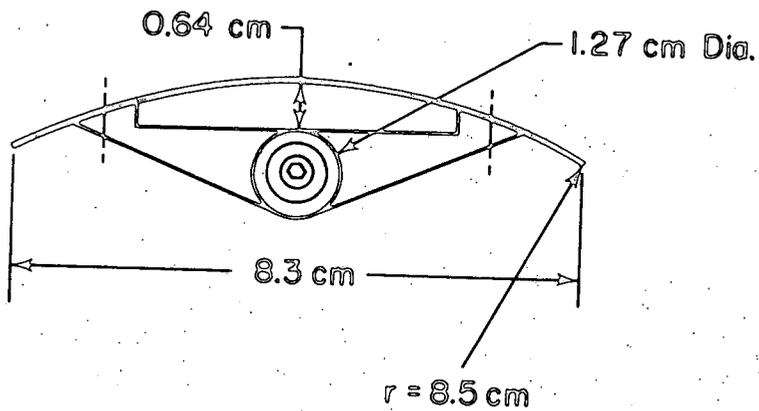
Figure 14. "Rod to Blade" Capacitor for Hydrogen Slush.

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A capacitance uncertainty of 0.001 pf in 18 pf is about 0.005 percent, so an uncertainty in ϵ of 0.01 percent is not unreasonable. From equation (12) it is possible to obtain the corresponding uncertainty in density. Using density and polarizability values for 0.5 solid fraction slush, and assuming 0.1 percent uncertainty in the value of P, gives the following:

$$\rho = 81.526 \text{ kg m}^{-3} = 0.0815 \text{ g cm}^{-3}$$
$$P = 1.0056 \text{ cm}^3 \text{ g}^{-1}$$
$$dP = 1.0056 \times 10^{-3}$$
$$d\epsilon = 1.2679 \times 10^{-4}.$$

Then equation (12) is

$$d\epsilon = \frac{3(0.0815 \times 1.0056 \times 10^{-3} + 1.0056 \times d\rho)}{(1 - 1.0056 \times 0.0815)^2}$$

$$1.2679 \times 10^{-4} = \frac{0.2459 \times 10^{-3}}{0.8427} + \frac{3.0168 \ d\rho}{0.8427}$$

$$= 2.918 \times 10^{-4} + 3.580 \ d\rho$$

$$-1.650 \times 10^{-4} = 3.580 \ d\rho$$

$$d\rho = 4.61 \times 10^{-5} \text{ g/cm}^3$$

$$\frac{d\rho}{\rho} = \frac{4.61 \times 10^{-5}}{8.15 \times 10^{-2}} = 5.66 \times 10^{-4}$$

$$= 0.057\%.$$

The conclusion of the analysis is that the apparent density of the slush between the capacitor electrodes can be obtained with an accuracy which exceeds that of the density reference system, the reasons being that (1) the dielectric constant of triple-point liquid hydrogen is better known than the density, and (2) it is easier to make accurate comparisons of capacitors than masses.

The principal values of testing capacitors in the density reference system were (1) to develop a good capacitor geometry for representative sampling, and (2) to develop the best possible stirring pattern for maintaining a homogeneous mixture of slush.

The capacitance method can, of course, be used for "point" as well as "zone" sensing of liquid or slush density. A popular capacitor design for sensing at a given level in a vessel is a "bullseye" made up of several concentric rings of small cross section rod or wire. Tests in the density reference system were made to determine the minimum spacing between rings which would allow slush to fall through rather than be supported by a horizontal "bullseye" capacitor.

It was found that very slight agitation of the fluid, or very slight vibration of the capacitor, such as would usually be present in containers under field conditions, would prevent the settling solids from bridging across rings spaced one cm apart. Capacitance-type point sensors of this kind will give the density in the immediate vicinity of the probe, and from the density the phase, whether vapor, liquid, or slush, at the level of the sensor will be apparent.

4. 4 Microwave Method for Dielectric Measurement

The capacitance measurements described above result in density determination because the dielectric constant of the fluid between the capacitor electrodes can be derived from the capacitance. An alternative method for measurement of dielectric constant is based on time delay in propagation of a microwave signal. The density then follows from the Clausius-Mossotti function. Two advantages of the microwave method are:

1) The sample is an unrestricted column of fluid between two microwave horns which can be spaced any desired distance apart.

2) The output signal is a frequency, which can be easily transmitted to a data center or, alternately, can be converted to a proportional voltage signal.

The method is illustrated in figure 15. The microwave signal generator is swept in frequency over its spectrum. The signal travels from the generator to the mixer by two paths, the reference and the test channels. It is assumed that both paths are dispersionless.

The instantaneous frequencies of the two signals fed into the mixer are designated f and f′ and both vary linearly at the same time rate. The frequencies differ, however, because of the time delay in the signal going through the fluid in the cryostat.

The test signal undergoes a total phase shift given by

$$t = \frac{d\varphi}{d\omega} = \frac{\ell}{c}\sqrt{\epsilon},$$ (14)

where t is the group delay time, ℓ is the distance between horn faces, and c is the free-space velocity of propagation.

A finite change in the dielectric constant of the fluid produces a finite change in the group delay time,

$$\frac{\partial t}{\partial \epsilon} \Delta\epsilon = \Delta t = \frac{\ell}{2c} \frac{\Delta\epsilon}{\sqrt{\epsilon}} .$$

The frequency of the signal generator is swept over the bandwidth $(f_2 - f_1)$ in time t_s. The average rate of change of frequency is,

$$\frac{\Delta f}{\Delta t} = \frac{(f_2 - f_1)}{t_s} .$$

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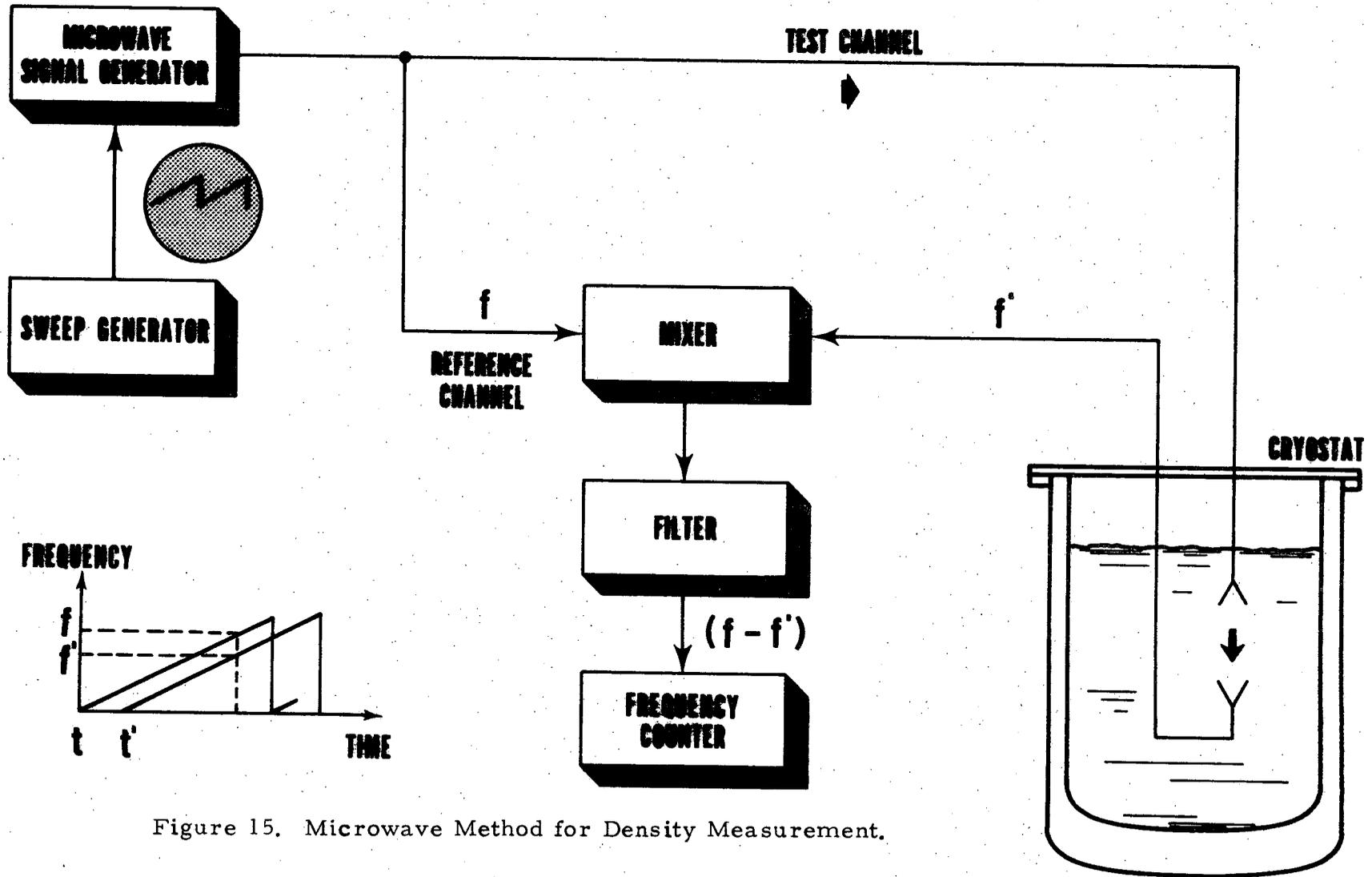
Figure 15. Microwave Method for Density Measurement.

The difference between the instantaneous reference and test frequencies is

$$\Delta f = \frac{(f_2 - f_1)\ell}{2ct_s\sqrt{\epsilon}} \Delta\epsilon,$$

from which

$$\Delta\epsilon = \frac{2ct_s\sqrt{\epsilon}}{(f_2 - f_1)\ell} (f_2 - f_1). \tag{15}$$

The mixer, then, is essentially a product demodulator. Its output spectrum contains f and f' frequency sums and differences, but all except the difference, $f_2 - f_1$, are filtered out.

An analysis of the variation in equation (15) can be made to estimate the accuracy with which the change in dielectric constant ($\Delta\epsilon$) can be measured. Typical values and associated uncertainties are as follows:

t_s = 10^{-3} seconds; $dt_s = \pm 10^{-5}$ seconds, the sweep period of the signal generator.

c = 3×10^{10} cm/s; $dc = \pm 1$ cm/s, the free space velocity of electromagnetic radiation.

ϵ = 1.25158, $\sqrt{\epsilon}$ = 1.119; $d\sqrt{\epsilon} = \pm 10^{-5}$, the dielectric constant of triple-point liquid hydrogen.

Δf = 50 Hz; $d(\Delta f) = \pm 0.1$ Hz, a typical frequency shift and the uncertainty of the counter used.

$(f_2 - f_1)$ = 3×10^9 Hz; $d(f_2 - f_1) = \pm 10^7$, the frequency sweep of the generator.

ℓ = 90 cm; $d\ell = \pm 0.2$ cm, the distance between horn faces.

The root mean square error is

$$\left[\frac{d(\Delta\epsilon)}{\Delta\epsilon}\right]_{rms} = \left[\left(\frac{10^{-5}}{10^{-3}}\right)^2 + \left(\frac{1}{3\times10^{10}}\right)^2 + \left(\frac{10^{-5}}{1.119}\right)^2 + \left(\frac{10^{-1}}{50}\right)^2 \right.$$

$$\left. + \left(\frac{10^7}{3\times10^9}\right)^2 + \left(\frac{2\times10^{-1}}{90}\right)^2\right]^{\frac{1}{2}}$$

$$= (10^{-4} + 10^{-21} + 8\times10^{-11} + 4\times10^{-6} + 10^{-5} + 5\times10^{-6})^{\frac{1}{2}}$$

$$= 1.1\times10^{-2} = 1.1 \text{ percent.}$$

Conversion from $\Delta\epsilon$ to $\Delta\rho$, i. e., from change in dielectric constant to change in density, is again by way of the C-M function, as explained in section 4. 3.

Most of this error in the $\Delta\epsilon$ measurement results from uncertainty in the sweep period of the signal generator, which could be improved with a better instrument. It is likely that an uncertainty of ±0.5 percent or less could be achieved by this microwave method of slush density measurement, but we were not able to develop readout instrumentation to demonstrate this within the scope of the density reference system contract.

One of the principal difficulties experienced with the microwave studies in the density reference system was the lack of sufficient open space in the weigh-can interior. This was partly because the program schedule required simultaneous evaluation of more than one transducer, but there was also considerable difficulty because of the proximity of the stirring rotor and spiral. These moving surfaces caused spurious reflections of the microwave signal, resulting in uncertainty in the "true" time delay measurement.

To obtain additional data, under more favorable conditions, a swept frequency microwave system was installed in the one-m^3 hydrogen slush upgrading vessel. Figure 16 shows data obtained in the upgrader for various levels of settled slush. The microwave horn faces were 90 cm apart; the lower horn face was 20 cm above the dewar bottom. The settled slush depths shown in figure 16 refer to distances above the lower horn face. The balance of the sample column, reaching to the upper horn, is assumed to be triple-point liquid. The effective dielectric constant thus becomes a direct function of the settled slush level.

The system was normalized, i.e., Δf set equal to zero, with triple-point liquid between the horns. When slush was introduced, a frequency shift proportional to the change in effective dielectric constant was observed, as shown in figure 16. The mean or effective density then derives from the Clausius-Mossotti function; the deviation from linearity of ϵ vs. ρ in the C-M function is about 0.8 percent over the density range from triple point liquid to freshly settled slush having a density of about 81.1 kg/m^3.

An independent estimate of density can be made by assuming a density for settled slush based on previous experience. A reasonable estimate for fresh settled slush is 81.1 kg/m^3, i.e., a solid mass fraction of 0.45. The average density of the column then becomes the weighted averages of the triple point liquid and settled slush depths. A density scale based on this assumption is shown on the right side of figure 16.
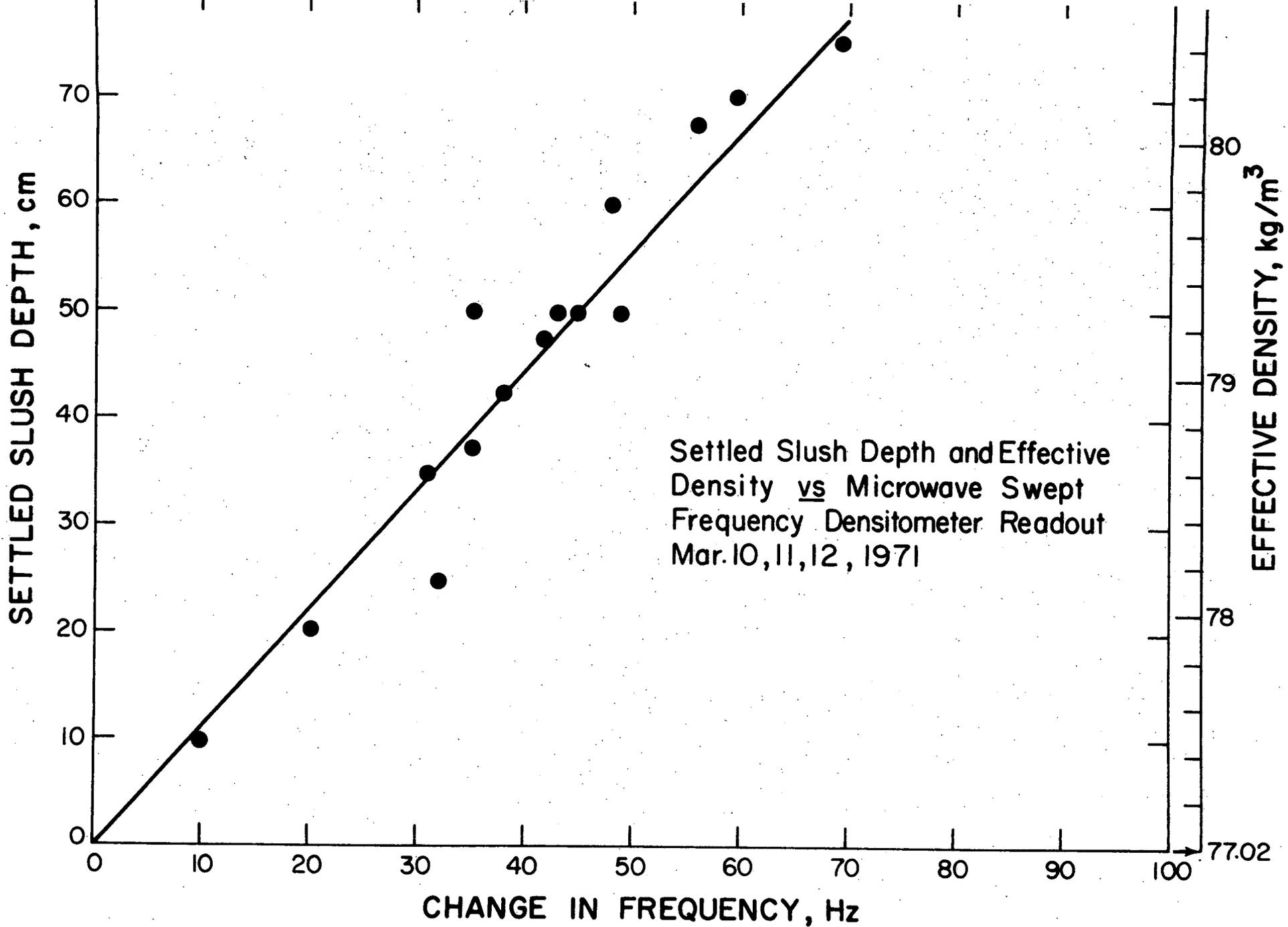
Figure 16.   Settled Slush Density Data Obtained by Microwave Method.

This is simply another way of expressing the settled slush depth, and the two vertical scales are proportional to one another. A test of the method is to plot the frequency shift against either vertical scale and observe the scatter of the data points and the deviation from linearity. The data indicate that the method can be used to locate a settled slush level to within about five centimeters if the above assumptions regarding liquid and settled slush densities are made. Conversely, if an unknown density distribution is assumed, the mean density can be determined with a sensitivity of a few tenths of a kg/m^3. It appears, at this point, that some refinement of readout instrumentation is all that would be required to make this method competitive with the more common capacitance measurement method.

4.5 Velocity of Sound

One more method of hydrogen liquid and slush density sensing was tested in the density reference system. This was velocity of sound, which has been measured as a function of density in fluid parahydrogen by Younglove[7]. His results are shown plotted in figure 17, from which it is apparent that a density change of 0.001 g cm^{-3} (1 kg m^{-3}) or less, is detectable by this method.

The transducer shown in figure 18 was designed for testing in the density reference system. It consists of two quartz crystals held a fixed distance apart in an open framework which allows free passage of fluid between the crystal faces. Of major concern, of course, was the question of effect of solid particles, i.e., slush in the sonic path.

We were able to duplicate Younglove's results in the liquid phase between normal-boiling and triple-point densities, but even a small solid
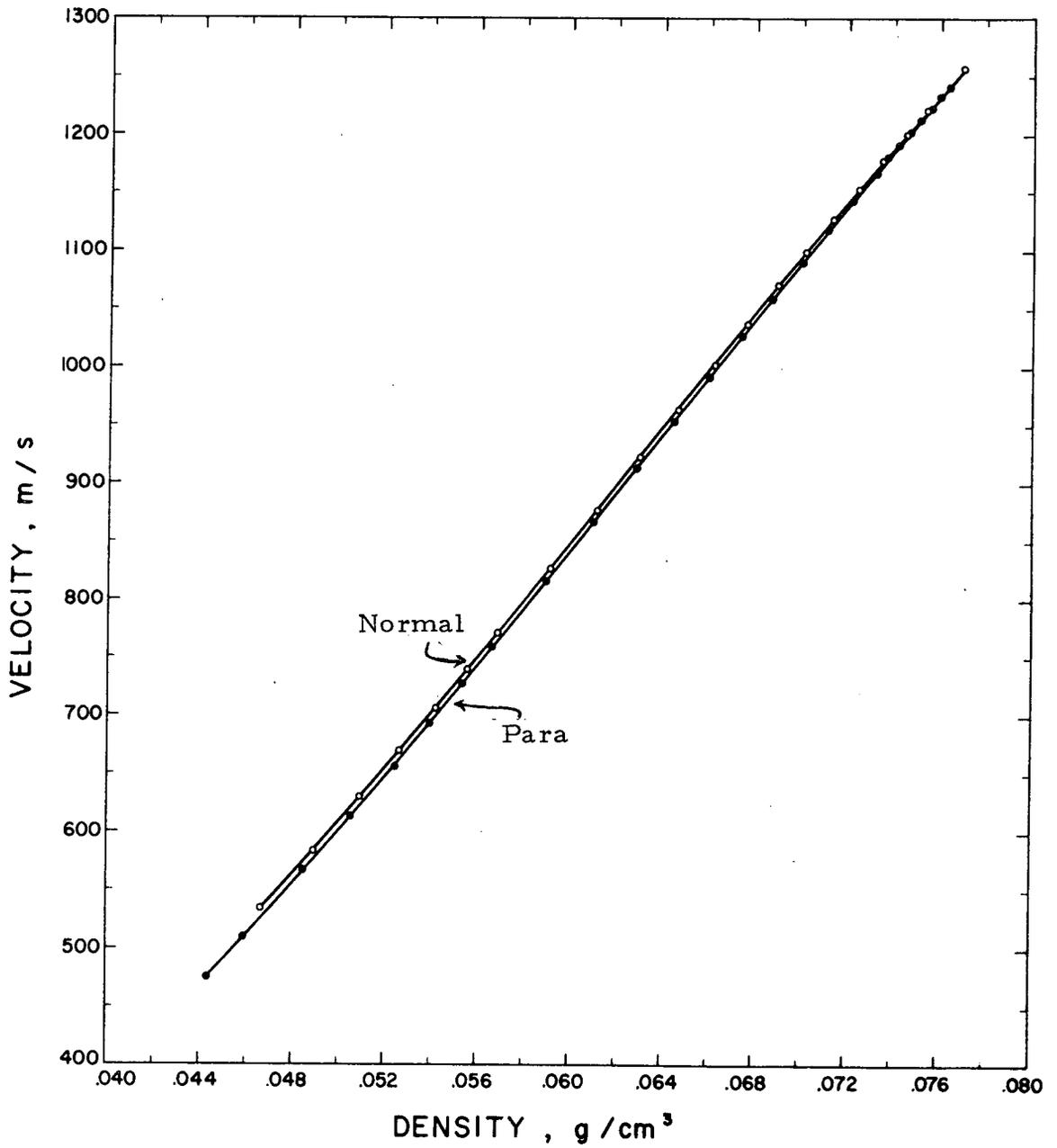
Figure 17. Younglove Data for Velocity of Sound in Hydrogen.
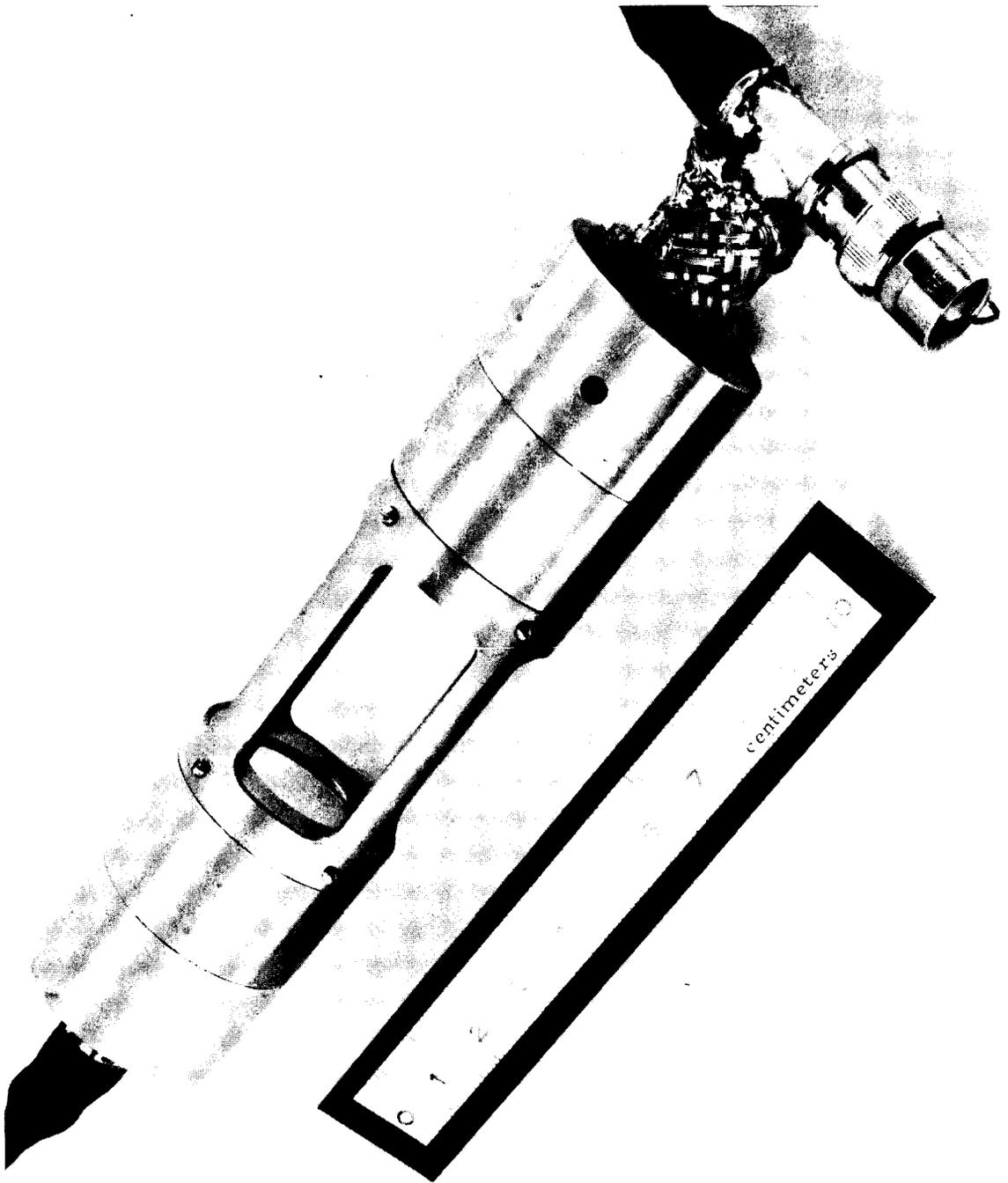
Figure 18. Velocity of Sound Transducer for Density Measurement.

fraction resulted in scatter of reflected frequencies, making it impossible to achieve the constructive interference on which the method depends. Accordingly, it must be concluded that sonic methods do not look promising for slush density measurements.

5. Summary

Table 2 summarizes the hydrogen slush density transducer testing, with emphasis on the characteristics necessary for a slush density transfer standard. Beta-ray attenuation can give densities with uncertainties of ± 1.0 percent, and may be worth considering for point density sensing in some applications. Gamma-ray attenuation offers higher accuracy, but is not at present suitable for use as a transfer standard. Methods depending on change in dielectric constant are the simplest and most predictable, as well as the most accurate, for fluids which have a known dielectric constant vs. density relationship. The Clausius-Mossotti function provides this relationship for hydrogen.

The direct comparison of capacitances in a stable capacitor of simple geometry is the recommended method for hydrogen slush density measurements. A capacitor design which allows free passage of slush between the electrodes was developed and tested with satisfactory results in the density reference system. A much larger version of this "rod-to-blade" capacitor design is being used with a high degree of success in a one-m^3 hydrogen slush upgrading vessel at NBS. Still larger versions have been designed for installation in 11.4 m^3 and 87 m^3 slush vessels which are part of a new facility under construction at the George C. Marshall Space Flight Center in Huntsville.

It is not really necessary to calibrate the capacitors in the density reference system. All that is required is one accurate reading of the

Table 2

Hydrogen Slush Density Transducer Summary

	β	γ	C	MW
Density Uncertainty	1%	0.5%	0.5%	0.5%
Special Advantages	Simple Probe	No Probe	Simple System	Large Sample
Special Problems	1. Complex Electronics 2. Detector Breakdown	1. Radiation Hazard 2. Not Transferable	Sampling	Spurious Reflections
Transfer Standard	Possible	No	Yes	Possible

capacitance with triple-point liquid hydrogen between the electrodes. After this, the dielectric constant and corresponding density can be obtained for any slush sample. The temperature does not change, of course, so no temperature correction is required. It is important to be assured, however, that slush passes freely between the electrodes; this can be tested by stirring the mixture at several speeds until a stable slush density reading is obtained.

6. References

1. Il. M. Roder, L. A. Weber, and R. D. Goodwin, "Thermodynamic and Related Properties of Parahydrogen from Triple Point to 100 K at Pressures to 340 Atmospheres," NBS Monograph 94 (1965).

2. R. F. Dwyer, G. A. Cook, O. E. Bernwaldt, and H. E. Nevins, "Molar Volume of Solid Parahydrogen Along the Melting Line," J. Chem. Phys. 43, p. 801 (1965).

3. E. B. Wilson, Jr., "An Introduction to Scientific Research," Mc Graw-Hill Book Co., Inc. (1952).

4. D. B. Mann, P. R. Ludtke, C. F. Sindt, and D. B. Chelton, "Liquid-Solid Mixtures of Hydrogen Near the Triple Point," Adv. in Cryo. Engr. 11, p. 207, Plenum Press (1966).

5. D. H. Weitzel, C. F. Sindt, and D. E. Daney, "Hydrogen Slush Density Reference System," Adv. Cryo. Engr. 13, p. 523, Plenum Press (1968).

6. B. A. Younglove, "Polarizability, Dielectric Constant, Pressure, and Density of Solid Parahydrogen on the Melting Line," J. Chem. Phys., 48, 9 (1968).

7. B. A. Younglove, "Speed of Sound in Fluid Parahydrogen," J. Acous. Soc. Am. 38, 3 (1965).

Appendix A

The final working equation of the density reference system is

$$\rho = \frac{\rho_\ell}{M_\ell} \left[\left(M_b + M_\ell \right) + \frac{T_2}{T_1} \left(M_{b1} - M_{b0} \right) \right].$$

The terms in the equation are

ρ	=	slush density,
ρ_ℓ	=	triple-point liquid hydrogen density,
M_b	=	buoyed mass of solids in weigh-can,
M_ℓ	=	mass of triple-point liquid which exactly fills the weigh-can,
T_2	=	elapsed time between slush density transducer reading and the weighing for determination of M_b,
T_1	=	time interval between weighings made to determine heat leak,
M_{b1}	=	buoyed mass of solids at end of interval T_1, and
M_{b0}	=	buoyed mass of solids at beginning of interval T_1.

A consistent set of values for the experimental variables, and the value of the one systematic parameter ρ_ℓ, are as follows:

$$M_b = 117 \pm 2.34 \text{ g}$$
$$M_{b0} = 117 \pm 2.34 \text{ g}$$
$$M_{b1} = 92.5 \pm 1.85 \text{ g}$$
$$T_1 = 8000 \pm 10 \text{ s}$$
$$T_2 = 900 \pm 1 \text{ s}$$
$$M_\ell = 2000 \pm 40 \text{ g}$$
$$\rho_\ell = 77.017 \pm 0.077 \text{ kg m}^{-3}.$$

It is assumed that all of the weighings may contain uncertainties of as much as ±2 percent. The values of M_b and M_{b0} are for 0.50 solid fraction slush. The value of M_{b1} was obtained by assuming a heat influx to the slush in the weigh-can of 2.0 watts. (The actual heat influx measured during several experiments was about 1.3 watts.) The time intervals T_1 and T_2, together with their uncertainties, are reasonable estimates.

The partial derivatives obtained from the working equation are as follows:

$$\frac{\partial \rho}{\partial M_b} = \frac{\rho_\ell}{M_\ell}$$

$$\frac{\partial \rho}{\partial M_{b0}} = \frac{-\rho_\ell T_2}{M_\ell T_1}$$

$$\frac{\partial \rho}{\partial M_{b1}} = \frac{\rho_\ell T_2}{M_\ell T_1}$$

$$\frac{\partial \rho}{\partial T_1} = \frac{\rho_\ell T_2 \left(M_{b1} - M_{b0}\right)}{M_\ell T_1}$$

$$\frac{\partial \rho}{\partial T_2} = \frac{\rho_\ell \left(M_{b1} - M_{b0}\right)}{M_\ell T_1}$$

$$\frac{\partial \rho}{\partial M_\ell} = \frac{\rho_\ell T_2 \left(M_{b0} - M_{b1}\right)}{M_\ell^2 T_1} - \frac{\rho_\ell M_b}{M_\ell^2}$$

$$\frac{\partial \rho}{\partial \rho_\ell} = \frac{M_b + M_\ell}{M_\ell} - \frac{T_2 \left(M_{b0} - M_{b1}\right)}{M_\ell T_1} .$$

Each term of the form $(\partial \rho / \partial \chi)^2 \, (d\chi)^2$ can now be evaluated. The results are as follows:

For $\chi = M_b$, $(3.85 \times 10^{-2})^2 (2.34)^2 = 8.12 \times 10^{-3}$

For $\chi = M_{b0}$, $(4.33 \times 10^{-3})^2 (2.34)^2 = 1.04 \times 10^{-4}$

For $\chi = M_{b1}$, $(4.33 \times 10^{-3})^2 (1.85)^2 = 6.45 \times 10^{-5}$

For $\chi = T_1$, $(1.10 \times 10^{-4})^2 (10)^2 = 1.21 \times 10^{-6}$

For $\chi = T_2$, $(-1.18 \times 10^{-4})^2 (1)^2 = 1.39 \times 10^{-8}$

For $\chi = M_\ell$, $(-2.21 \times 10^{-3})^2 (40)^2 = 7.83 \times 10^{-3}$

For $\chi = \rho_\ell$, $(1.06)^2 (0.077)^2 = 6.63 \times 10^{-3}$.

From the above tabulation, it is easy to see which terms contribute most to the final uncertainty in ρ. The two percent uncertainties in M_b and M_ℓ each contribute slightly more than the 0.1 percent uncertainty in the triple-point liquid density ρ_ℓ. None of the new variables introduced by the heat leak correction make a significant contribution to the final uncertainty.

The total squared uncertainty in ρ is obtained by adding the tabulated values, which gives $(d\rho)^2 = 0.0227$ kg m^{-3}, or $d\rho = 0.15$ kg m^{-3}. The relative error, for 0.5 solid fraction slush, is $0.15/81.35 = \pm0.18$ percent.

Appendix B

Drawing Number
D-6180

Figure 6.
WEIGHING CRYOSTAT

Figure 1B.   Cutaway of Assembled
H₂ Slush Density Cryostat.

Figure 2B. Weigh-Can Details

Drawing Number D-6178

Drawing Number
D-6182-1

Figure 3B.   Calibration Weight Column.

Drawing Number
D-6179

Figure 4B.   Dewar for Density Reference System.

Sub-Assembly F
Make five.

Sub-Assembly G
Make two.

Matr: Brass
Make two.

Matr: Type 304 Stainless
Make two.

Sub-Assembly D
Make two.

Matr: Brass
Make two.

Do Not Make!

Sub-Assembly

Sub-Assembly E

Figure 5B.   Top Plate Sub-Assemblies.

Drawing Number
D-6181-1

Figure 6B.   Top Plate Details.

Drawing Number
D-6183-1

N₂ vent

Liquid N₂ in

~10"

Agitator drive shaft

Sub-Assembly A
D-6180

Slush H₂
transfer line

1½" Veeco Valve,
modified to serve as
relief valve, one req'd.

O-ring Coupling
Three Req'd

Glass

Glass

Weld

Glass

Pictorial Position
of Shaft

½" Veeco Coupling
One Req'd.

True Position
of Shaft

13"

SLUSH CONTAINER ASSEMBLY
Ref. Dwg. D-6192

RADIATION SHIELD ASSEMBLY
Ref. Dwg. D-6189

VACUUM JACKET ASSEMBLY
Ref. Dwg. D-6191

Drawing Number
D-6184-1

Figure 7B.   General Assembly 50 Liter Hydrogen
Slush Generator.

94479
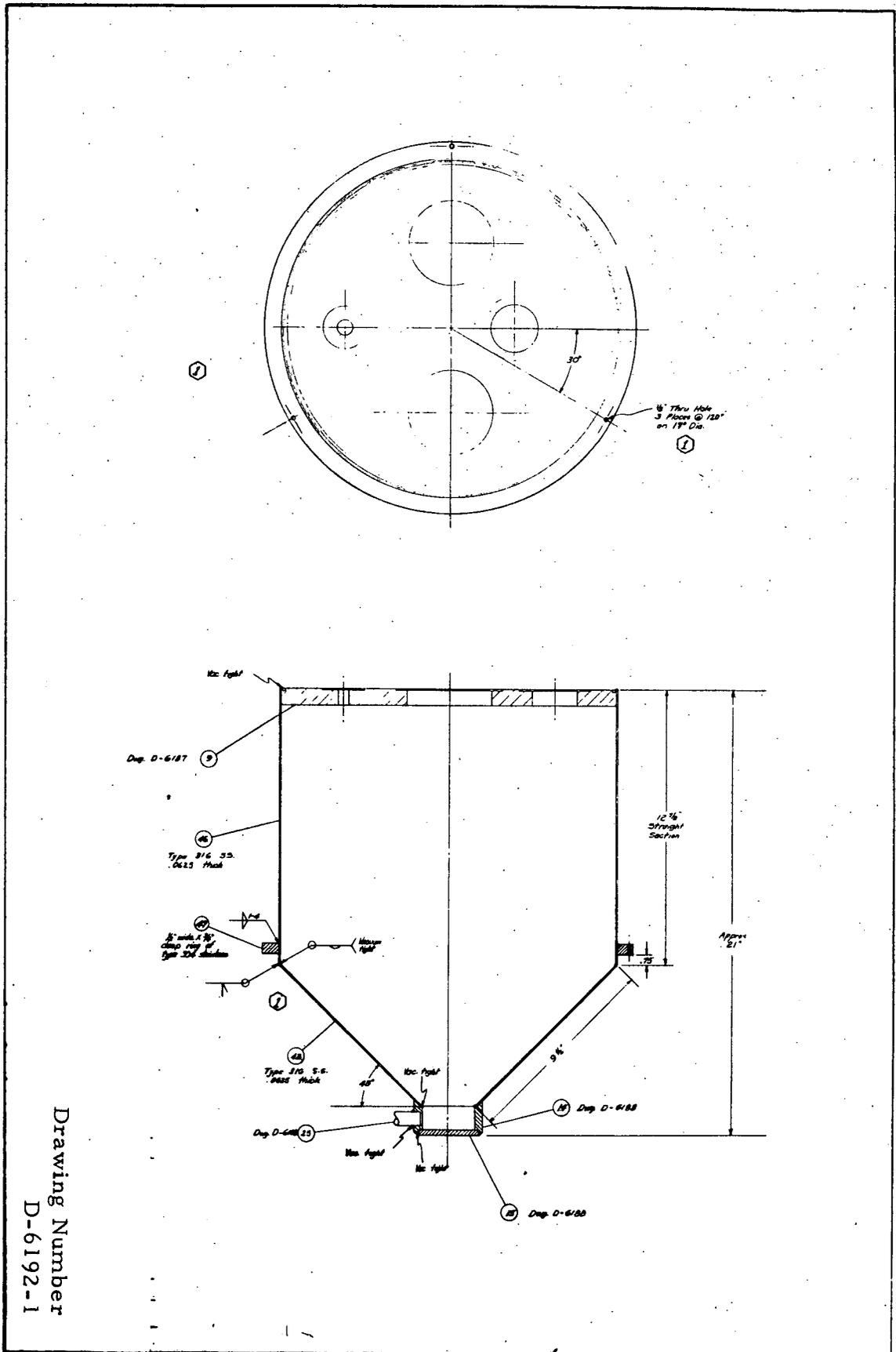
Figure 8B.   Slush Container of Generator.

Drawing Number D-6189-7

Figure 9B.   Nitrogen Cooler Radiation Shield.
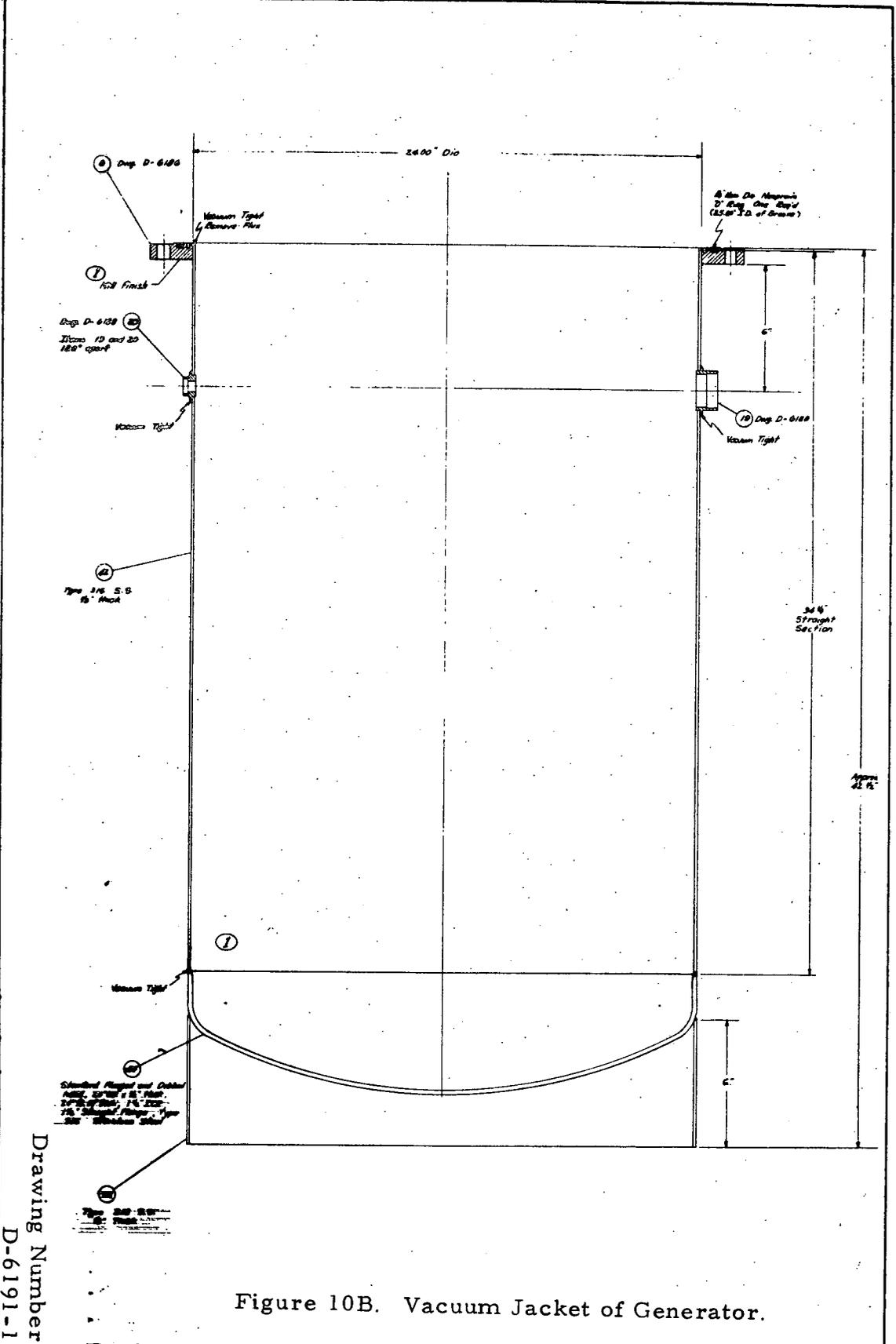
Figure 10B. Vacuum Jacket of Generator.

TOP VIEW

BOTTOM VIEW
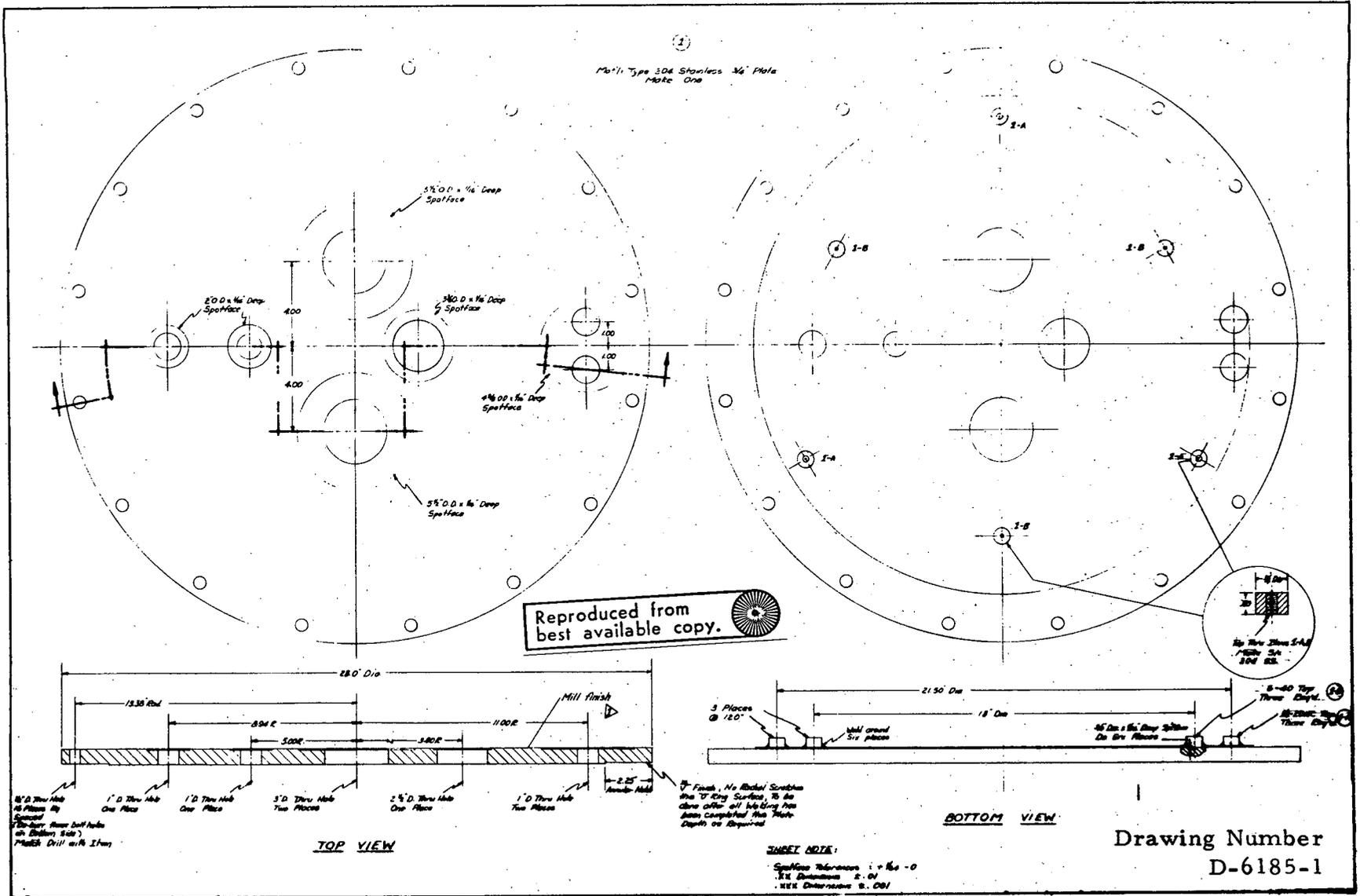
Figure 11B. Generator Top Plate.

Drawing Number
D-6185-1

Figure 12B.   Top Plate for Slush Container of Generator.
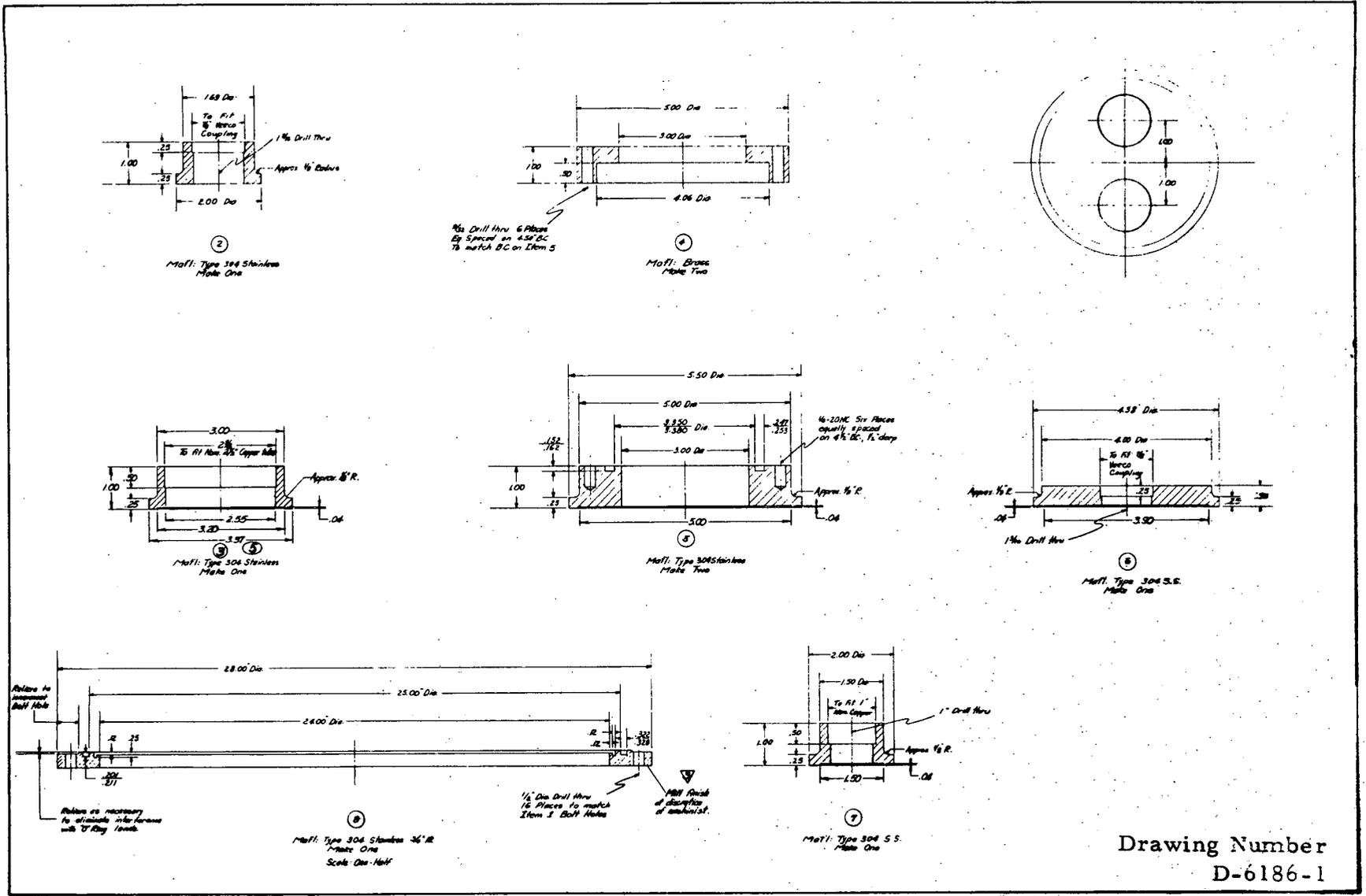
Drawing Number
D-6187-1

Figure 13B. Generator Details 2-8.

Figure 14B.   Generator Details 14-26.

Drawing Number
D-6188-2

Drawing Number
D-6190-2

Figure 15B. Transfer Line Details.

Drawing Number
D-6197

Figure 16B. Sub-Assembly J, K Vacuum Pumpout Valve.
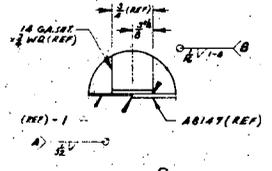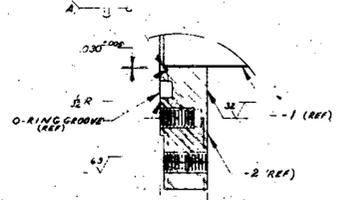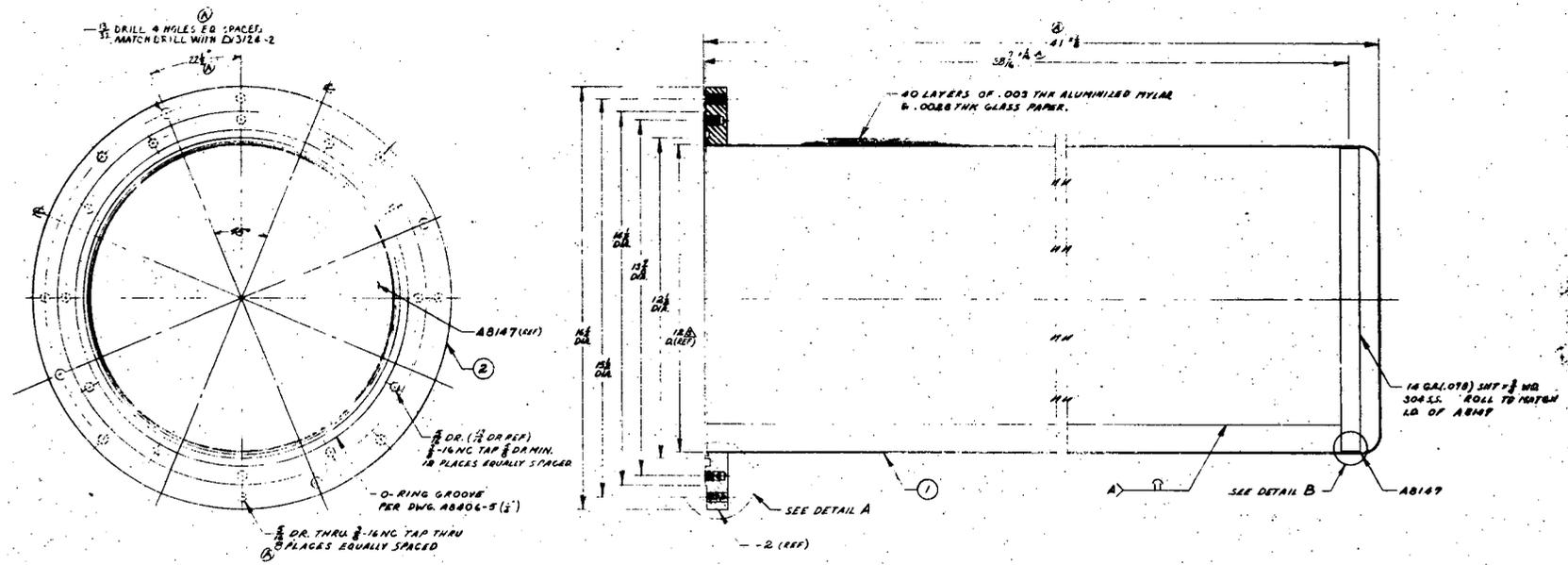
Drawing Number
D-13123A

Figure 17B.   DRS Dewar Details.

Drawing Number
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Figure 18B.   DRS Dewar Details.

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