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at Cryogenic Temperatures***

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ABSTRACT

This paper will describe the application of moderately high pressures to work at low temperatures either at or under the cognizance of the Los Alamos Scientific Laboratory. The problems involved in the merging of these two disciplines will be discussed as they relate to laboratory research as well as to large scale nuclear rocket testing facility usage.

The equipment used to determine some physical properties of liquid cryogens up to 50,000 lb./sq. in. will be described, but no new results will be reported. The methods of obtaining and applying the low temperature to the high pressure volume will be mentioned.

* Work done under the auspices of the U. S. Atomic Energy Commission.

The use of a reciprocating piston pump to pump cryogenic liquids to high pressures will be discussed. Some attention will be paid to the problems of cryogenic seals for large size vacuum jacketed cryogenic piping.

The safety requirements due to the danger of lack of purity and due to the high pressures that can be obtained when relief valves or vents plug are additional complications in the carrying out of work under combined high pressure and low temperatures.

The Use of Moderately High Pressures at Cryogenic Temperatures

INTRODUCTION

While the term "high pressure" usually brings to mind somewhat higher pressures than will be mentioned in this paper, it is true that most applications of high pressure are made at moderate or elevated temperatures. This paper will consider the use of moderately high pressure at low temperature. For the research that is discussed, the pressures extend up to 50,000 lb./sq. in., whereas for large scale applications in cryogenic test facilities, the pressures are usually no more than a few thousand lb./sq. in.

There is no universally accepted range of temperatures which defines cryogenics. Although the lower limit is clearly absolute zero, the upper limit has been considered to be anywhere from 220 to 400°R, depending on the interest of the investigator. Since interest in cryogenics is rapidly expanding and in order to avoid an upper temperature limit which varies with individual interest, it is proposed that this limit be defined as the lowest naturally-occurring terrestrial temperature (335°R).

There are two methods available for obtaining experimental low temperatures. One of these involves a bath or stream of cryogenic liquid which boils at or near the temperature of the experiment; the other utilizes a mechanical refrigerator which can, by means of a heat transfer medium such as helium gas, carry away the heat that enters the apparatus during the course of the experiment. Due to the high cost of refrigerators, the cryogen bath method is by far the more commonly used. It allows the creation of refrigeration at some remote point, where the cryogen is first liquefied, and subsequent transportation to the point of application.

One might properly ask what is different about the realm of low temperatures that justifies the discussion of, or the carrying out of experiments in this region. Originally low temperature experiments might have been justified on the basis of scientific curiosity. However, as is usually the case, the result of such well directed curiosity was a number of "surprises" which sooner or later become useful. We are now "cashing in" on previous low temperature research work. But in order to carry out any application of low temperature, it is necessary to understand the idiosyncrasies of such work. Yield and tensile strength, specific heat, thermal and electrical conductivity, and thermal expansion,

change in such a way as to make extrapolation of high temperature data unreliable. In some cases totally new phenomena, such as electrical superconductivity, may appear. Furthermore, as pointed out by Ruhemann,⁽¹⁾ refrigeration work requirements are proportional to $(T_{\text{warm}} - T_{\text{cold}})/T_{\text{cold}}$ and increase drastically as the temperature of the experiment is pushed lower and lower.

Prior to about 1950, research in cryogenics was devoted largely to the determination of the properties of cryogenic liquids. Critical pressures for all of the common cryogens are less than 800 lb./sq. in., hence the experimental pressures could not be classified as high. Since the early 1950's, interest in cryogenic high pressure research has increased although the scale of experiments has remained small. Such experiments routinely obtain pressures in excess of 50,000 lb./sq. in. which is considerably greater than presently required for cryogenic applications.

The principal uses of cryogens today involve the handling and storage of large quantities of cryogenic liquids for ultimate end use as gases. Such end uses can be as widely divergent as the use of oxygen for steelmaking, or the use of hydrogen as a propellant in rocket programs. All of these applications use pressures under 10,000 lb./sq. in. The flow rates involved vary from a few gallons per minute

to tens of thousands of gallons per minute. Our technology has relied on a backlog of basic research developed over the past seventy-five years. According to Vance⁽²⁾ it is somewhat questionable as to whether research is being carried on at a rate adequate to prevent delays in future technological development. Two problem areas receiving considerable attention today in the space program are heat transfer and two-phase flow of cryogenic fluids. Prior knowledge in these areas would have greatly facilitated cryogenic applications.

To emphasize the uses and potentialities of cryogenics, a brief summary of the cryogenic industry is presented in Table 1. The cryogenic industry is much newer than the large production capabilities listed would lead one to believe. Although commercial production of liquid nitrogen and liquid oxygen for distribution as a liquid in the United States dates to 1928, the liquid hydrogen production capability shown in the table has been developed in the past ten years whereas the liquid helium production capability has been developed only in the past three years.

One can consider a division of the fluids listed in Table 1 into two classes: special purpose fluids, such as liquid oxygen for use as a concentrated oxygen supply, and service fluids which are used only to provide specific

temperatures. It is tempting to restrict the service fluids to the inert liquids, He, Ne, N_2 , and A. However, because of availability, low cost, and low temperature range, liquid hydrogen can be added to the list of service fluids, granted the necessary safety precautions are taken in its handling. Because of their low heats of vaporization and low boiling points, liquid hydrogen and liquid helium are the most difficult cryogenics to transport. Nevertheless modern technology permits economical shipment of these liquids for thousands of miles in quantities of 25 to 25,000 gallons. Hollis-Hallett⁽³⁾ has estimated that the number of laboratories capable of doing research at liquid helium temperature has increased from fifteen in 1946 to over six hundred throughout the world today.

Rapid expansion in the applications of cryogenics give impetus to more extensive research. Such research is fostered by the increasing availability of cryogenic liquids throughout the world.

SMALL SCALE USES OF LOW TEMPERATURE AND HIGH PRESSURE

The small scale experiments discussed in this section cover pressures up to 50,000 lb./sq. in. and generally are concerned with research on the properties of the cryogens themselves or the properties of other materials at cryogenic temperatures. Generally such experiments are designed to fit into specially designed cryostats with a fluid capacity of not more than a few gallons. Refrigeration is provided from mobile supply dewars with a capacity of up to twenty-five gallons. Typical experiments are the determination of phase transition curves, equation of state relationships, and various thermodynamic quantities.

In 1926 Kamerlingh Onnes and Gulik⁽⁴⁾ at Leiden devised what has come to be known as the "blocked-capillary" technique for measuring the variation with pressure of melting temperatures. In essence a metal capillary tube is bent in the form of a V and the tip is held at some low temperature. The tube is filled with the high pressure gas or liquid to be measured and the onset of freezing is indicated when pressure increases introduced in one arm of the capillary are "blocked" by the solid and therefore not detected at the other arm.

At Los Alamos refinements of this technique have been used to measure melting curves for He^3 , He^4 , H_2 , D_2 , T_2 , Ne , O_2 , and N_2 up to 50,000 lb./sq. in.⁽⁵⁾ One form of the apparatus is shown in Figure 1. Pressures were produced hydraulically with an intensifier and measured with a controlled-clearance free-piston gauge. Hydraulic fluid was separated from the experimental gas by a mercury U-tube. Pressure variations at the far end of the capillary were detected with a small volume, highly sensitive gauge. A later apparatus used a manganin gauge.

Typical melting curves for He^3 and He^4 are shown in Figure 2. At moderate and high pressures the melting relationship for all materials is well expressed by the three-constant Simon melting formula,⁽⁵⁾ $P_m = a + bT_m^c$, in which P_m is melting pressure, T_m is melting temperature and a , b , and c are constants. This equation has been reliably extrapolated to high pressures but at low pressures some deviations are observed. Notable are minima in the melting curves of He^3 and He^4 which occur at about 0.6 and 1.4°R, respectively. The curve⁽⁶⁾ for He^3 is given in Figure 3. From theoretical entropy considerations these minima were predicted before they were found experimentally. Elaborate apparatus and methods were required to make melting point measurements at temperatures below the minima

because blocked capillary technique fails due to blockage higher up in the capillary at the warmer temperature of the minimum.

The usefulness of melting curve data can be appreciated from a consideration of the Clapeyron equation as applied to the melting transition, $dP_m/dT_m = \Delta H_m / (T_m \Delta V_m) = \Delta S_m / \Delta V_m$. If additional data are available on the change of molar volume with melting, $\Delta V_m = V_{\text{liquid}} - V_{\text{solid}}$, then the molar enthalpy change, ΔH_m , and the molar entropy change, ΔS_m , on melting can be determined.

Such volume measurements have been made on N_2 and on He^3 and He^4 . Figure 4 shows the apparatus used for the N_2 study.⁽⁷⁾ Solid N_2 was formed in the cell when the coolant bath level was slowly raised with a constant high pressure of N_2 maintained in the cell. The bath was then heated just above the N_2 melting point and excess cell pressure, indicated by a manganin gauge, was released to and determined quantitatively in the metering system. In this way ΔV_m was measured. Molar volumes of the liquid at melting were determined by releasing the entire contents of the calibrated cell to the metering system.

The ΔV_m data could be fitted to Tammann's expression,⁽⁸⁾

$$\Delta V_m = A - B \log (P_m + C).$$

At high pressure this equation extrapolates to zero for ΔV_m and may indicate that melting curves are terminated by critical points, analogous to the critical points in vaporization curves. Thus far, critical melting points have not been observed experimentally.

For He^3 and He^4 , as for N_2 , the ΔV_m measurements all proved to be positive, that is, the melting solid is denser than its liquid. According to the Clapeyron equation, at temperatures below the melting curve minima where dP_m/dT_m is negative then ΔH_m and ΔS_m must likewise be negative. This means that here the melting of solid He gives off heat and the entropy of the well ordered solid is greater than that of the randomly oriented liquid. This curious anomaly has been explained for He^3 in terms of the nuclear spins being aligned in the liquid but not in the solid.

The ΔV_m measurements for He^3 and He^4 also proved interesting from the standpoint that at certain temperatures, discontinuities appeared. Figure 5 shows the results.^(9, 10) These data were interpreted as indicating phase transitions in the solid, that is, transitions to new crystal structures. At high pressures a similar transition had been indicated for He^4 from discontinuities in warming curves⁽¹¹⁾ -- essentially heat capacity measurements, which are much more sensitive in pointing up transitions.

It now became of interest to determine the crystal structures of all the solid modifications of He^3 and He^4 . A cryostat was developed which permitted x-ray diffraction studies of the solid heliums.⁽¹²⁾ Figure 6 shows the x-ray cryostat that was used to take photographs of He^3 and He^4 . Here solid He is formed in a beryllium cell sealed to a steel filling capillary with a conical closure shown at the bottom center of the figure. Helium prefers to solidify in one or, at most, only a few large crystals rather than a powder. To determine the unit cell dimensions, it was necessary to oscillate the solid through an angle of forty-five degrees during the four-hour x-ray exposure. As shown in Figure 6, the cell was surrounded at each end by a small container of liquid helium which oscillated with the cell and which was kept supplied with liquid from the main stationary dewar through flexible metal bellows. Copper radiation shields cooled to liquid nitrogen and helium temperatures and equipped with thin aluminum windows enclosed the assembly.

The crystal structures are summarized in Figure 7 where it can be seen that a complete analogy exists between solid modifications of He^3 and He^4 . At low pressures the preferred structure is body centered cubic, BCC, at intermediate pressures hexagonal closest packed, HCP, and at

high pressures cubic closest packed, CCP. Note that the region for BCC He⁴ is quite restricted. All the other noble gases solidify only as cubic closest packed.

Apparently He can assume the less dense body centered cubic form at low pressures because of its very large zero point energy.

Currently experiments are underway which will attempt to probe the properties of solid helium at low temperatures and high pressures far above the equilibrium melting curves.

RESEARCH FLOW SYSTEMS

Experiments which involve flowing cryogens are not easily carried out in apparatus of the type just described. For the study of transient effects during cooldown, the determination of heat transfer coefficients, and the study of two-phase flow, small-flow test systems have been built. Such systems will generally involve a high pressure (up to 1,500 lb./sq. in.) cryogenic supply dewar, transfer lines, valves, instrumentation, and a test section.

The test sections vary from one experiment to the next, but the other components can serve for any number of experiments. Such systems are generally run remotely because of safety considerations. Figure 8 shows a typical system that has been used: to determine heat transfer coefficients to liquid, gaseous, and two-phase hydrogen; to verify machine

calculations of temperature-time profiles for various cooldown configurations; to investigate pressure oscillations during two-phase flow; and for instrumentation calibration. This system, now in use at Los Alamos, has a capacity of 75 gal. and a pressure rating of 300 lb./sq. in. A new system now under construction will extend these limits to 125 gal. and 1,500 lb./sq. in.

LARGE SCALE USES

For the transportation of large quantities of industrial gases, it is usually more economical to ship the materials as liquids with conversion to high pressure gases at the final destination.

In the case of hydrogen, for example, a given liquid shipment at atmospheric pressure will contain more than twenty-five times the material carried as high pressure gas. Putting it a different way, the ratio of pounds of shipping container per pound of hydrogen is less for liquid by a factor of several hundred.

At the final destination, the liquid is converted to gas by a pump and heat-exchanger combination (as shown in Figure 9) which first pumps the liquid to high pressure and then warms it to usable temperatures. Since the pressures involved are usually above the critical pressure, the term vaporization does not strictly apply. The pumps used are generally reciprocating piston pumps operating in a sump

filled with the cryogenic liquid. Because of the great volume expansion between the low and high temperatures, the liquid flow through these pumps is quite small (3-10 gal./min.). This requirement of low flow and high pressure dictates the use of a reciprocating pump. Converters of this type have been built for O_2 , N_2 , H_2 , A and He. Pressures up to 3,500 lb./sq. in. are obtained routinely, with pressures up to 10,000 lb./sq. in. not unknown. There have been problems in providing adequate sliding high-pressure low-temperature seals, tight inlet valves with low impedance, and in minimizing heat leak to the input fluid.

Several large scale flow facilities have been built in the United States in support of the national space program. An example is the large liquid hydrogen nuclear rocket test facility shown in Figure 10. This facility, now being enlarged, already contains two 50,000-gal. liquid hydrogen dewars, 8-in. and 10-in. I.D. vacuum jacketed transfer lines, and a centrifugal pump. The system is capable of flow rates up to 100 lb./sec. and pressures up to 1,200 lb./sq. in. Problem areas encountered in the checkout and operation of such systems must be capable of remote operation. Special attention is given to seals, valves, cooldown of transfer lines, and safety.

In cryogenic systems two levels of seal leakage are tolerable. For seals between a volume at elevated pressure and one at atmospheric pressure, bubble-tight leakage rates ($< 10^{-3}$ std. cm.³/sec.) are generally acceptable. For barriers between cryogenic liquids and a vacuum space, joints which are merely bubble tight are grossly inadequate. In this case leakage rates of 10^{-6} std. cm.³/sec. or less are required.

Figure 11 shows a typical joint used in Test Cell C. This kind of joint has been used where it is necessary to open the line for modifications and additions. It is important that the cold inner seal remain absolutely tight to prevent leakage into the vacuum space with consequent cooling of the outer pipe which would lead to much greater leakage of the outer warm seals. The cold seal is effected by means of an octagonal stainless steel ring which is forced into trapezoidal grooves on the mating flanges. Provided the proper tolerances are maintained, such joints have leakage rates of the order of 10^{-6} std. cm.³/sec.

For anticipated facilities utilizing larger pipes and higher pressures, the required flange becomes prohibitively large. The excess metal would lengthen the time to chill the system to its operating temperature and greatly increase

the amount of cryogenic fluid required for cooldown. This points up the desirability of using all-welded joints or specially designed lightweight joints, even though, in ground facilities, weight is not otherwise a consideration.

SAFETY

In addition to the normal safety procedures required in high pressure experiments, provisions must be made to prevent pressure increases above those normally expected where low temperatures are involved. Figure 12 shows schematically three areas where excess pressures could develop upon loss of refrigeration. In the experimental volume and the cryogenic bath fluid regions, a rise in pressure with temperature will occur if the fluid is not allowed to vent. In the case of trapped liquid H_2 , pressures up to 28,000 lb./sq. in. can be obtained by this mechanism alone.

A less obvious place for trouble to occur is in the annular vacuum space which insulates the experiment. Any leakage into the vacuum space during the course of the experiment might not be noticed either because of inadequate instrumentation or because of a phenomenon called "cryo-pumping." The latter involves the condensation or adsorption of the leakage gas on the cold inner surface of the vacuum space. At the low temperature of the cryogenic fluid the

vapor pressure of the cryopumped gas can be virtually zero. However upon warmup the evaporation of the trapped materials results in an elevated pressure in a space not designed for such pressures. Damage to the outer or inner shells can result.

To prevent such pressure buildup, relief valves should be installed at all three points. In Test Cell C all such areas are equipped with relief valves. Where the spaces to be relieved are located within rooms, the pressure relief is provided by spring-loaded relief valves which are connected to a common exhaust system vented outside.

Another frequent source of trouble in cryogenic systems is leaky valves. Cryogenic systems can usually be designed so that the valves are at ambient temperature. However valves can still leak when warm, even with small pressure differentials. One solution to the problem is shown in Figure 13. Here a valve in series downstream of the main shutoff valve permits the maintaining of a small section of line at a pressure greater than dewar pressure. This increased pressure is maintained with helium gas. The contents of the "helium block" are analyzed daily by gas chromatography for H_2 , O_2 and N_2 content. In this manner very small leaks can be detected and corrective measures taken before any dangerous concentrations result.

In conclusion it may be said that cryogenics is a rapidly expanding field which is being integrated into industrial applications at an increasingly rapid rate. Undoubtedly many cryogenic applications will involve the concurrent use of high pressure. To support industrial applications, continued low temperature research is necessary. Fortunately, the present easy access to liquid cryogens will help promote such research.

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- Table 1 - The Cryogens
- Figure 1 - Schematic Diagram of Blocked Capillary Apparatus
for Determining Melting Curves, P_m vs. T_m
- Figure 2 - Melting Curves of Helium Isotopes
- Figure 3 - Melting Curve of He^3 near the Minimum
- Figure 4 - Schematic Diagram of Apparatus for Determining
Volume Change on Melting, ΔV_m (Reprinted from
Phys. Rev., 105, No. 4 p. 1140.)
- Figure 5 - Volume Change on Melting of Helium Isotopes
- Figure 6 - X-ray Cryostat
- Figure 7 - Phase Diagram Showing Crystal Structures of
Helium Allotropes
- Figure 8 - Research Flow Facility
- Figure 9 - Schematic Drawing of Liquid Hydrogen Pump Vaporizer
- Figure 10 - Large Scale Cryogenic Flow Facility
- Figure 11 - High Pressure Cold Seal
- Figure 12 - Potential Pressure Build up Areas in Cryogenic
Systems
- Figure 13 - Helium Block

TABLE I: THE CRYOGENS

	Temperature Range °R	Critical Pressure psia	Critical Temperature °R	Liquid Density #/gal	Heat of Vaporization btu/lb	Production gal/day	Cost \$/gal	Remarks
He ³	0.5-6	17	6	0.5	3.6	0	--	Research Very scarce
He ⁴	1.3-9	33	9	1.0	8.8	1,850	25	Research Space program Easily transportable
H ₂	25-60	188	60	0.6	193	600,000	0.30	Space program Good supply and easily transportable
Ne	44-81	400	81	10	37	1.4	568	Space program and occasional substitute for H ₂
N ₂	114-228	492	228	6.7	85	1.2 x 10 ⁶	0.17	Refrigerant Many uses
A	151-271	705	271	11.7	70	26,000	5.10	Use as gas Inert atmos
O ₂	98-279	737	279	9.5	92	3.6 x 10 ⁶	0.24	Steel making Research Space programs
F ₂	97-260	808	260	12.6	74	--	--	Space program Research

Figure 1 - Schematic Diagram of Blocked Capillary Apparatus for Determining Melting Curves,
 P_m vs. T_m

Figure 2 - Melting Curves of Helium Isotopes

Figure 3 - Melting Curve of He^3 near the Minimum

Figure 4 - Schematic Diagram of Apparatus for Determining Volume Change on Melting, ΔV_m

Figure 5 - Volume Change on Melting of Helium Isotopes

Figure 6 - X-ray Cryostat

Figure 7 - Phase Diagram Showing Crystal Structures of Helium Allotropes

Figure 8 - Research Flow Facility

KIWI A HIGH PRESSURE LIQUID HYDROGEN PUMP-VAPORIZER

Figure 9

Figure 10 - Large Scale Cryogenic Flow Facility

HIGH PRESSURE COLD SEAL

Figure 11

LEGEND

<u>CRYOGENIC FLUID</u>	<u>PRESSURE TO MAINTAIN LIQUID DENSITY AT ROOM TEMPERATURE</u>
He	18,000 PSI
H ₂	28,000 PSI
N ₂	43,000 PSI

POTENTIAL PRESSURE BUILDUP AREAS IN CRYOGENIC SYSTEMS

Figure 12

HELIUM BLOCK

Figure 13