

105  
GEORGIA INSTITUTE OF TECHNOLOGY  
STATE ENGINEERING EXPERIMENT STATION  
ATLANTA, GEORGIA

REPORTS

PROJECT NO. 116-18

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF THE  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

BY

W. T. ZIEGLER

VOL. I

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

CONTRACT NO. N6-ori-192, TASK ORDER I

NOV. 27, 1946-DEC. 31, 1949

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**GEORGIA SCHOOL OF TECHNOLOGY**

**THE STATE ENGINEERING EXPERIMENT STATION**

**ATLANTA, GEORGIA**

**PROGRESS REPORT NO. 1**

**PROJECT NO. 116-18**

**NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH**

**CONTRACT NO. N6-ori-192, TASK ORDER I**

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**W. T. ZIEGLER**

**NOVEMBER 27, 1946**

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## I. ABSTRACT OF REPORT

After a statement of the problem being pursued under this contract a considerable amount of background material underlying the choice and methods for execution of the problem is presented. The major units of the experimental apparatus, such as the hydrogen liquefier, helium cryostat, helium cycle, etc., are briefly described. A summary of the work performed to date is presented which shows that the design of the major units is largely complete. Ordering of materials for these units is also well under way. Deliveries of materials have been slow, so that extensive construction on most units will not begin until after December 15, 1946. Construction of numerous accessory items, such as furnaces, glass apparatus for vacuum systems, etc., has already begun.

## II. STATEMENT OF THE PROBLEM

Task Order I of this contract reads as follows:

"The Contractor shall furnish the necessary personnel and facilities for and conduct, in accordance with any instructions issued by the Scientific Officer or his authorized representative, research at very low temperatures upon fundamental properties of the elements and their compounds including the rare earths with particular emphasis upon superconductivity."

More specifically, we have as our immediate objective the testing of certain rare earth metals and compounds for superconductivity by electrical and magnetic means. The metals selected for study are lanthanum, cerium, praseodymium, and neodymium. It is hoped that others may be added to this list later. The compounds to be studied are lanthanum hydride and nitride. The problem of handling the rare earth hydrides and nitrides is complicated by the fact that they must be handled in the absence of air and water vapor.

### III. BACKGROUND OF THE PROBLEM

#### A. The Rare Earth Metals

The rare earth metals have been chosen for study for several reasons. In the first place, apparently, only two of them, lanthanum and cerium, have ever been investigated in a pure state. McLennan, Allen, and Wilhelm (Phil. Mag. (7) 10, 500-11 (1930)) have measured the electrical resistance of these two metals as a function of temperature and have reported that neither became superconducting at the lowest temperature reached ( $1.9^{\circ}\text{K.}$ ).

McLennan, Howlett, and Wilhelm (Trans. Roy. Soc. Canada, Sect. III (3), 23, 287-306 (1930)) have studied the electrical conduction of misch metal down to  $2.3^{\circ}\text{K.}$  and found no evidence of superconductivity. The sample studied was free of iron and had the composition: cerium 35%, lanthanum 20%, neodymium 20%, samarium 10%, gadolinium 6%, praeaseodymium 5%, europium 2%, yttrium 2%. From this measurement, McLennan et al concluded that none of these elements were superconducting above  $2.3^{\circ}\text{K.}$

On the other hand, Mendelssohn and Daunt, (Nature 139, 473 (1937)), using a magnetic method, have reported that lanthanum is a superconductor with a transition temperature of  $4.71^{\circ}\text{K.}$  Confirmation of the superconductivity of lanthanum has been reported by Shoenberg, (Proc. Comb. Phil. Soc. 33, 577 (1937)).

These contradictory results can only be reconciled if the electrical and magnetic transition in lanthanum are separated by several degrees; this seems highly unlikely for a pure metal. It was felt, therefore, that the experimental proof of nonsuperconductivity in the rare earth metals at temperatures above  $1.9^{\circ}\text{K.}$  was not clear-cut and that a reinvestigation of these metals would be worthwhile.

The rare earth metals have certain other properties which make them interesting objects of study. Thus, both lanthanum and cerium exist in at least

two crystalline modifications (hexagonal close-packed and face centered cubic). It would be interesting to see if two different crystalline forms could be cooled to low temperatures and studied for superconductivity. Tin is the only substance obtainable in two crystalline forms at low temperatures which has been studied to date. White tin is a superconductor; gray tin is not a superconductor at 1.32°K. However, the two crystalline forms have very widely different normal properties and crystal structures.

Another unusual property of certain of the rare earth metals is that they are rather strongly paramagnetic. Some, such as gadolinium and dysprosium, have been found to be ferromagnetic. Thus, there is an interesting, though perhaps remote, possibility of finding a metal which is ferromagnetic in the normal state and perfectly diamagnetic in the superconducting state.

#### B. Rare Earth Metal Compounds

The recent studies of Horn and co-workers (F. H. Horn, Dissertation, Johns Hopkins University, Baltimore, Md., June 1942; E. H. Horn, W. F. Brucksch, Jr., W. T. Ziegler, and D. H. Andrews, Phys. Rev. 61, 738 (1942); paper to be published shortly in J. A. C. S.) and Aschermann et al (G. Aschermann, E. Friederich, E. Justi, and J. Kramer, Physik. Z. 42, 349 (1941)) have shown that the hydrides and nitrides of columbium and the hydrides of tantalum are superconducting. Studies of Horn of superconductivity in columbium-hydrogen and tantalum-hydrogen solid solutions showed that the expansion of the body centered cubic metal atom lattice, which occurs with increasing atomic per cent dissolved hydrogen, is accompanied by a corresponding decrease in transition temperature and increased transition range. The rare earth metals form both hydrides and nitrides which apparently are solid solutions. The hydrides, prepared by direct combination of the metal with hydrogen gas at 200-400°C., usually have a composition corresponding to  $MH_x$  where x ranges from 1.8 to 2.8. They are, in general, black,

friable materials which ignite spontaneously on exposure to air. The nitrides, prepared by direct combination of the metal with nitrogen at 800-900°C., have compositions ranging from  $MN_{0.80}$  to  $MN_{1.0}$ . These nitrides are very readily attacked by moist air, decomposing to liberate ammonia.

No magnetic or electrical studies of the rare earth hydrides and nitrides have been reported below 80°K. No systematic study has yet been made of the lanthanum-hydrogen or lanthanum-nitride system with a view to correlating the X-ray structure of the solid with nonmetal content of the solid solution. The hydride and nitride preparations studied to date have been reported to have a face centered cubic and NaCl structure, respectively.

We hope, therefore, to correlate any superconducting properties of these solid solutions with the lattice structure of the solid solutions.

#### IV. PROPOSED EXPERIMENTAL METHODS

The experimental method to be used in these studies is the measurement of the magnetic permeability of the metals and powdered compounds as a function of temperature down to about 2°K. These measurements will permit the detection of superconductivity by the change occurring in the induction of a coil in which the sample is placed when the material goes from its normal state, in which permeability is approximately unity, to the superconducting state in which the permeability is zero.

Electrical resistance measurements will be made as a function of temperature on such samples as may be obtained in a suitable form.

The use of these methods presupposes facilities for the production of liquid hydrogen and liquid helium in order to obtain the necessary low temperatures.

## V. APPARATUS AND AUXILIARY EQUIPMENT

The experimental apparatus to be constructed is shown in schematic fashion in Figure 1. The principal pieces of apparatus are: (1) the high pressure hydrogen purifier, (2) the hydrogen liquefier, (3) the helium cryostat, (4) the electrical measuring system, and (5) the helium gas cycle. It is planned at present to use commercial hydrogen gas purchased in standard cylinders at 2000 psi to operate the liquefier, instead of using a hydrogen compressor.

### A. The Hydrogen Purifier

This unit consists of two series of traps through which the high pressure hydrogen is passed. The first series is a single trap containing activated silica gel for removing water vapor; this trap operates at room temperature. After leaving this, the hydrogen gas passes through the second series of three traps containing activated charcoal; these charcoal traps are immersed in liquid air. At this temperature, all of the remaining noxious gas impurities are removed by adsorption on the charcoal.

### B. The Hydrogen Liquefier

The hydrogen liquefier operates on the purified high pressure hydrogen gas obtained from the purifier. After simple Joule-Thomson expansion and passage through a system of heat exchangers, the low pressure gaseous hydrogen is vented to the atmosphere. The liquefier to be built is similar in design to those built at Johns Hopkins University during the war, which in turn were modeled after a liquefier described by Ahlberg, Estermann, and Lundberg (Rev. Sci. Instruments 8, 422 (1937)). With pumping on the liquid nitrogen used as the precooling refrigerant for the hydrogen, it is expected that a production rate of 1.5 liters of liquid hydrogen per hour can be achieved.

The liquefier will be so arranged that it will deliver liquid hydrogen directly into hydrogen dewar vessel of the helium cryostat. It is also planned

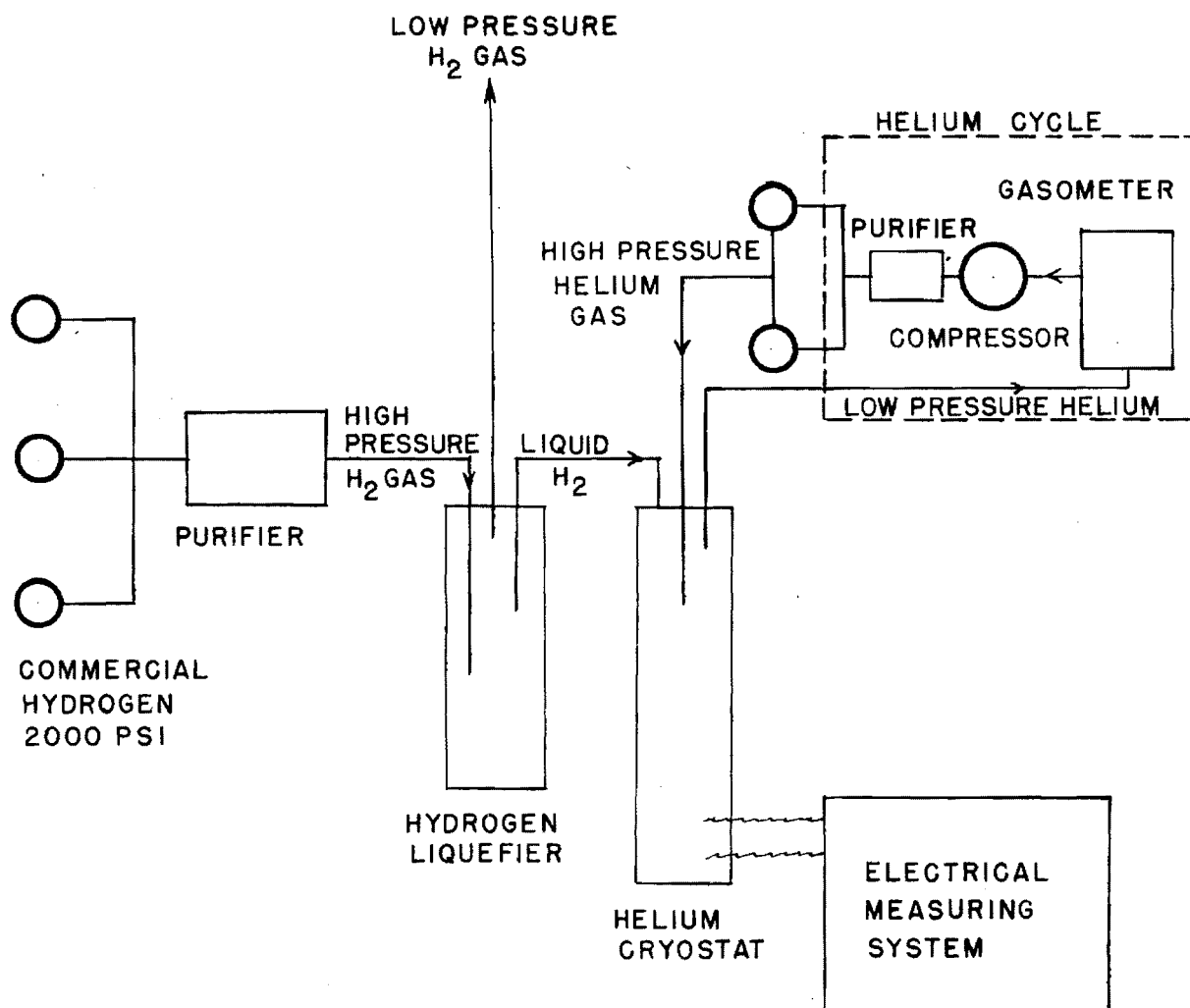


Figure 1. Latent heat measurement of low temperature apparatus and associated components.



to make the liquefier portable so that it may be used to deliver liquid hydrogen to more than one cryostat.

### C. The Helium Cryostat

The helium cryostat is modeled closely after one built by Dr. F. H. Horn (see reference under Section III B.) which, in turn, utilizes design features well tested in the very low temperature field. The liquid helium is produced in two separate processes. The main charge of liquid helium is produced by suddenly releasing the pressure of high pressure (2500 psi) helium gas previously cooled to about 12°K. by the use of solid hydrogen, contained in a thick-walled copper vessel. This vessel is suspended in an evacuated space to decrease heat leak to it. The work done by the helium gas, on expanding, results in sufficient cooling of the copper vessel and a portion of the helium so that considerable liquid helium is obtained in the copper vessel. Under the conditions mentioned, a copper vessel having a volume of 100 cc will be about 70 per cent filled with liquid helium.

The experimental chamber containing the samples to be investigated is suspended from the above-mentioned copper vessel. Liquid helium is condensed in the experimental chamber by passing helium gas at 15-30 psi through a tube wound about the copper vessel and connected at its lower end to the experimental chamber. This process results in the evaporation of an equivalent amount of liquid helium from the copper vessel. The advantages of this lower experimental chamber are twofold: (1) the experimental chamber, being suspended from the copper vessel whose temperature is 4.2°K. (normal boiling point of helium), is thermally protected so that a lower temperature may be reached, for a given pumping capacity, than would be possible if the copper vessel were used as the experimental chamber, and (2) the samples may be placed inside the experimental chamber and hence in direct contact with the cooling medium, a procedure which

is not possible with the heavy walled copper container.

The experimental chamber will be so constructed that measurements of magnetic induction may be made on powdered samples and electrical resistance measurements may be made on materials obtainable in wire form.

#### D. The Helium Cycle

Liquid helium can be made by the method outlined (the Simon expansion method) using helium pressures available in commercial tanks (i.e., 2000 psi). It is, however, desirable to have a helium cycle consisting of a compressor for recompressing the low pressure helium gas, which would otherwise be discarded and also for raising the pressure of the purified gas to about 2600-2800 psi, since the percentage filling of the copper vessel is considerably increased at these higher pressures.

Such a cycle is planned. It consists essentially of a 3000 psi, 6.5 cu. ft. free air, Ingersoll-Rand compressor (Model P-33-10-6), a purifier, and a gasometer for collecting the low pressure helium gas in addition to serving as a source of supply for the compressor intake.

#### E. Electrical Measuring System

The electrical measuring systems consist of (1) potentiometric means for measuring temperature using thermocouples and resistance thermometers and measurement of electrical resistance, and (2) a ballistic system for the magnetic measurement of induction.

#### F. Accessories

A large number of additional items such as vacuum systems, liquefied gas handling equipment, fittings, special glass apparatus, etc., are necessary adjuncts of the various units described above.

## VI. PREPARATION OF RARE EARTH METALS AND COMPOUNDS

### A. Rare Earth Metals

It is planned to procure these from three sources: (a) commercial concerns, (b) private loan of purified samples, and (c) electrolysis of molten purified salts which are available commercially. Chemical, X-ray, and spectroscopic analyses are planned whenever feasible.

### B. Rare Earth Metal Compounds

The preparation of the compounds requires a furnace, a gas measuring system, gas purification trains, and a high vacuum system. In addition, provisions must be made for the handling of samples in inert atmospheres.

## VII. DISCUSSION OF PROGRESS OF WORK

### A. Estimate of Progress on Construction of Equipment

The following table sums up the progress made on the various units outlined above during the period from October 1, 1946, to December 1, 1946. The estimated percentage completion figures are intended largely for comparative purposes and are not expressed in dollar values:

Estimated Per Cent Completed

| <u>Unit</u>   | <u>Design</u> | <u>Ordering of<br/>Materials</u> | <u>Materials<br/>on Hand</u> | <u>Construction</u> |
|---|---------------|----------------------------------|------------------------------|---------------------|
| Purifier  | 90%           | 80%                              | 20%                          | None                |
| Liquefier   | 90%           | 80%                              | 30%                          | None                |
| Cryostat  | 90%           | 80%                              | 20%                          | None                |
| Helium Cycle  | 20%           | 20%                              | 10%                          | None                |
| Electrical Measuring<br>System                                    | 80%           | 70%                              | 5%                           | None                |
| Accessories, such as<br>special fittings,<br>vacuum systems, etc. | 20%           | 20%                              | 10%                          | 5%                  |
| Equipment for compound<br>preparation                             | 60%           | 60%                              | 20%                          | 10%                 |

B. Comments on Progress to Date

The design work on the major units is largely finished. In general, the main features of the designs have been tested elsewhere and should therefore be sound and workable.

Because of the difficulty in obtaining reasonable delivery of much of the rather special or scarce material required for the construction of low temperature equipment, it is not expected that full-time construction will begin before about December 15, 1946. Actually, a number of orders for materials expected to be difficult to obtain were placed as early as August 15, 1946, and this material is only now beginning to arrive.

Assembly of one of the two Navy Torpedo Topping Compressors, which is to be used for the helium cycle, has already been begun.

The personnel working on the problem to date have been Dr. W. T. Ziegler (two-thirds time) and the part-time assistance of the machine shop and the drafting department of the Engineering Experiment Station.

Respectfully submitted,

W. T. Ziegler  
Project Director

Approved:

Gerald A. Rosselot  
Director

GEORGIA SCHOOL OF TECHNOLOGY  
THE STATE ENGINEERING EXPERIMENT STATION  
ATLANTA, GEORGIA

PROGRESS REPORT NO. 2

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

CONTRACT NO. N6-ori-192, TASK ORDER I

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
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By

W. T. ZIEGLER

JANUARY 28, 1947

## I. PROGRESS ON CONSTRUCTION OF EXPERIMENTAL APPARATUS

Considerable progress has been made during the past two months in the construction of the component parts of the high pressure hydrogen gas purifier, the hydrogen liquefier, and accessories such as high vacuum systems, furnaces, etc. These units were described briefly in Progress Report No. 1, dated November 27, 1946. Material deliveries are still slow. Efforts are being made to obtain certain special materials through loan or purchase from other low temperature laboratories.

## II. PERSONNEL

Efforts to procure additional research personnel are continuing. At the present time, one graduate student in chemical engineering is working part-time on this project. It is expected that one or two others will soon join in this work.

## III. SECOND CRYOGENICS CONFERENCE

The writer represented the project at the Second Cryogenics Conference sponsored by the Office of Naval Research at Johns Hopkins University in Baltimore, Maryland, on December 9, 1946. A resumé of the objectives and progress of the research under the present contract was presented at the conference. This resumé was largely a condensation of Progress Report No. 1, dated November 27, 1946.

This meeting afforded an opportunity for an informal discussion among Dr. Estermann (Carnegie Tech), Dr. Germann (University of Colorado, Boulder), and the writer on plans for converting the Badger and Linde liquid oxygen plants, which are being loaned by the Office of Naval Research, to liquid

nitrogen producing plants. It was agreed to keep each other informed of plans and progress in the matters. In this connection, we have recently been informed that the Linde plant, previously scheduled to be delivered to us from Clearfield, Utah, on about December 15, 1946, is not available at that point, but will be shipped in the near future from the Naval Shipyard, Norfolk.

Respectfully submitted,

W. T. Ziegler  
Project Director

Approved:

Gerald A. Rosselot  
Director

State Engineering Experiment Station  
GEORGIA SCHOOL OF TECHNOLOGY  
Atlanta, Georgia

PROGRESS REPORT NO. 3

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

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MARCH 31, 1947



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W. T. ZIEGLER

MARCH 31, 1947

## I. PROGRESS ON CONSTRUCTION OF EXPERIMENTAL APPARATUS

Considerable progress has been made during the past two months in the construction of the component parts of the high pressure hydrogen gas purifier, the hydrogen liquefier, the helium cryostat, and accessories for these units. A unit for hydraulic testing of pressure vessels up to 10,000 psi has been built and used for testing the purifier traps.

### A. Purifier

This unit is about 75 per cent complete, with all material for its completion now on hand. Assembly of this unit will be completed within 2-3 weeks.

### B. Hydrogen Liquefier

This unit is about 50 per cent complete, with all materials for its completion on hand. The large copper-nickel alloy tubing used in this unit and in the helium cryostat was obtained through the courtesy of Dr. D. H. Andrews of Johns Hopkins University.

### C. Helium Cryostat

Construction work on this unit is proceeding somewhat more slowly than on the other two units. Practically all materials for its completion are on hand, however, and a number of parts have been completed. Among these is the special pyrex glass dewar vessel used for holding the liquid hydrogen.

## II. LIQUID NITROGEN PLANT

On March 17 the following components of a Linde liquid oxygen generating plant were received from the Naval Supply Officer, Norfolk Shipyard,

Portsmouth, Virginia.

- (a) One (1) liquid oxygen generator.
- (b) One (1) Worthington air compressor.
- (c) One (1) 150 gal. liquid oxygen storage tank.
- (d) One (1) Vacuum pump for use with storage tank.

To date, no spare parts, tools, starter box for compressor motor, or piping have been received. Letters aimed at clarifying these points have been directed to Mr. L. M. McKenzie, Office of Naval Research, Navy Department, Washington, D. C., to Mr. R. T. Moore, Bureau of Ships, Navy Department, Washington, D. C., and to the Naval Supply Officer, Norfolk Shipyard, Portsmouth, Virginia.

It is planned to erect this plant in an addition to the Chemical Engineering Building. Specifications for the concrete foundations for the units and for associated electrical power and laboratory services have been completed. Grading of the site has been completed, and construction is scheduled to proceed at once.

It is planned to redesign the oxygen generating plant so as to produce liquid nitrogen.

### III. PERSONNEL

During the past two months, two candidates for the Master's degree in Chemical Engineering have begun work on various phases of this project. Both of these men are at present unpaid members of the group working on the contract. Their work will be used to satisfy the requirements for the Master's thesis. Mr. Oswald Newell will help with the design, construction, and testing of the hydrogen liquefier and its associated parts. Mr. L. R.

Daniel will help with the design, construction, and testing of the helium cryostat. In both cases, the design work was largely completed before these men became associated with their respective problems.

Each man spends about ten hours per week on the project at present. This will be increased considerably during the summer months.

Mr. Weller A. Phillips has been employed for full-time work on this project, effective April 1st. Mr. Phillips is a graduate in Chemical Engineering from Georgia Tech.

The project now has one full-time machinist working.

Respectfully submitted,

W. T. Ziegler  
Project Director

Approved:

Gerald A. Rosselot  
Director

State Engineering Experiment Station  
GEORGIA SCHOOL OF TECHNOLOGY  
Atlanta, Georgia

PROGRESS REPORT NO. 4

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

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W. T. ZIEGLER

May 31, 1947

**GEORGIA SCHOOL OF TECHNOLOGY**

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**PROGRESS REPORT NO. 4**

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**W. T. ZIEGLER**

**May 31, 1947**

## I. PROGRESS ON CONSTRUCTION OF EXPERIMENTAL APPARATUS

Construction of the high pressure unit for purifying the hydrogen gas is completed. The unit will be tested in conjunction with the hydrogen liquefier. A complete description of the unit will be made in a subsequent report.

Construction of the hydrogen liquefier is nearly complete. It is hoped that a test run of the liquefier can be made by about June 15.

Further progress on the helium cryostat has been made.

The new building in which these units will be set up is nearing completion. It is expected that occupancy will be obtained by about July 15. Figure 1 is a general view of the floor plan pertinent to the present work. The spaces marked helium compressor laboratory, experimental low temperature laboratory, instrument room, storage room, sample preparation laboratory, and offices are all to be used for the work being carried out under the present contract. The spaces marked thermodynamic properties laboratories provide space for an extension of our thermodynamic program.

## II. LIQUID NITROGEN PLANT

It is planned to install the Linde type liquid oxygen generating plant in an addition to the Chemical Engineering Building now under construction. The layout of the plant is shown in Figure 2. It is expected that this addition will be completed not later than September 1, 1947. A cooling tower and pumping system for supplying cooling water to the large compressor of the plant has been designed and ordered. The expense of the cooling system will be borne almost entirely by the School.

A shipment of missing and spare parts for the liquid oxygen generating plant and compressor was received on May 29. Examination showed that no tools

or operating supplies had been shipped. The missing starter control for the 100 H.P. motor was not included in the above shipment.

Mr. E. L. Bedroe of the Plant Facilities Section, ONR, is continuing his efforts to locate three single-phase transformers of the following description: 50 KVA, 2400/120/240.

### III. PERSONNEL

Dr. Elmer Rhodes of the Physics Department has joined the group working on this project. Dr. Rhodes, who is employed part-time, will aid in designing and setting up the electrical equipment to be used for making the magnetic measurements of superconductivity.

### IV. TRIPS

Dr. W. T. Ziegler attended the Low Temperature Physics Conference sponsored by ONR at the Bureau of Standards, April 30. He also attended the meetings of the American Physical Society held thereafter.

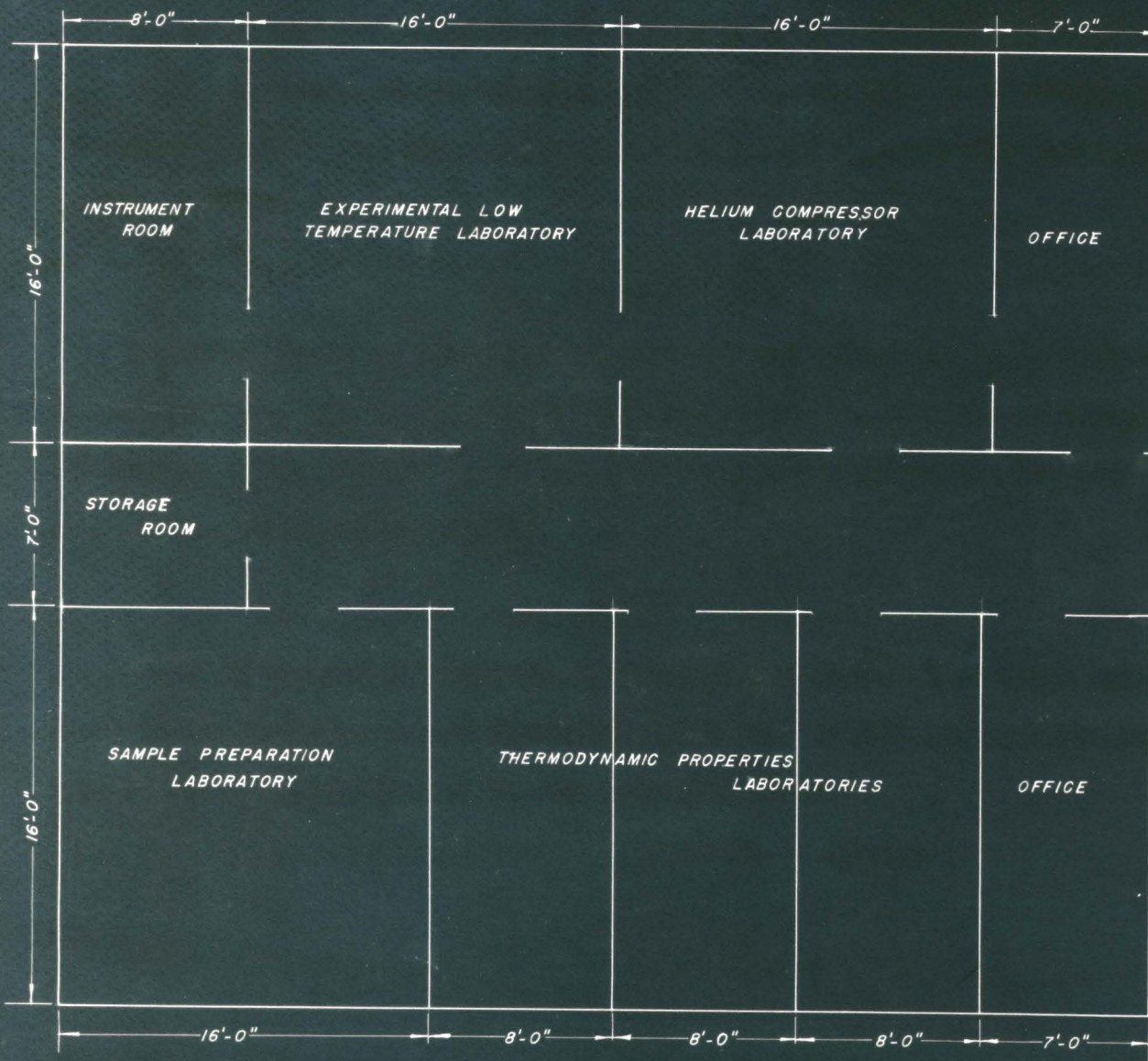
Respectfully submitted,

W. T. Ziegler  
Project Director

Approved:

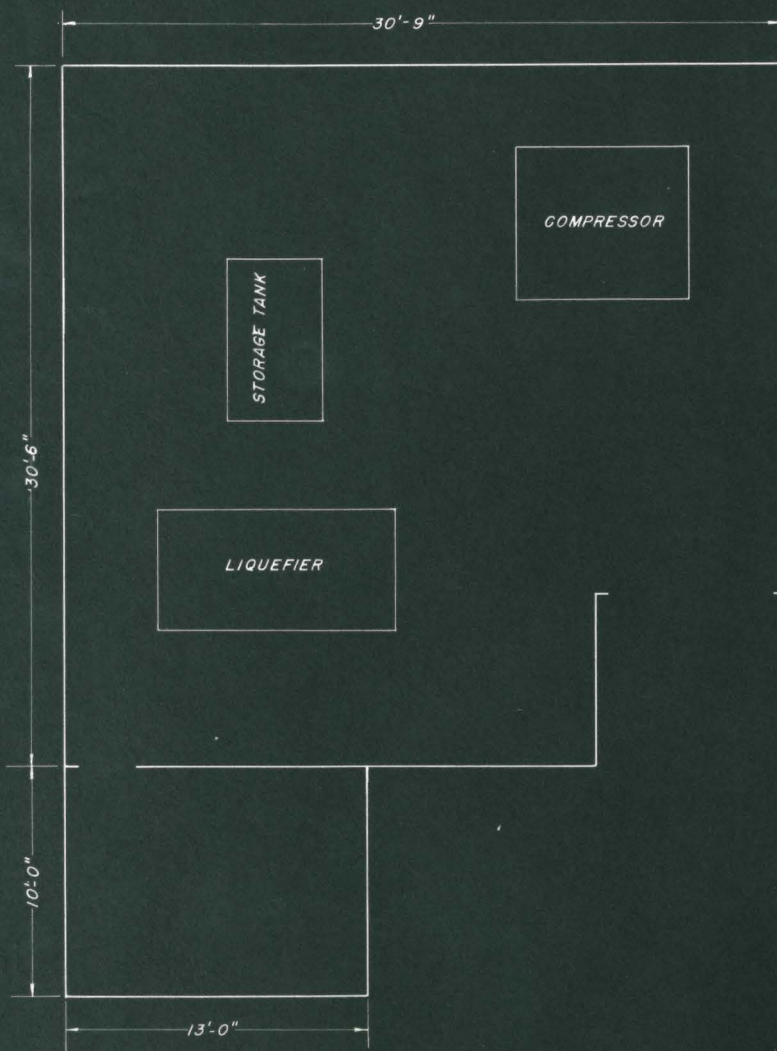
Gerald A. Rosselot  
Director





LAYOUT LOW TEMPERATURE LABORATORIES

FIG. 1



LIQUID OXYGEN PLANT LAYOUT

FIG. 2

State Engineering Experiment Station  
GEORGIA SCHOOL OF TECHNOLOGY  
Atlanta, Georgia

PROGRESS REPORT NO. 5

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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

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W. T. ZIEGLER

AUGUST 1, 1947

**GEORGIA SCHOOL OF TECHNOLOGY**  
**THE STATE ENGINEERING EXPERIMENT STATION**  
**ATLANTA, GEORGIA**

PROGRESS REPORT NO. 5

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

CONTRACT NO. N6-ori-192, TASK ORDER I

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF THE  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

By

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AUGUST 1, 1947

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## I. ABSTRACT OF REPORT

During the past two months the principal efforts have resulted in the completion of the hydrogen liquefier and its accessories. Liquid hydrogen has been successfully produced but with a lower efficiency than was hoped for. It is expected that the installation of a new heat interchanger will increase the efficiency of liquefaction considerably.

Progress has been made on the construction of the helium cryostat for the superconductivity studies and on the high pressure helium compression cycle.

A number of rare earth metals and their compounds have been procured and have been analyzed spectrographically.

The liquid nitrogen generating plant and its compressor have been placed on their bases in the new addition to the Chemical Engineering Building now under construction. Installation of the plant will begin about September 1 when possession of the new building can be expected. The installation of a cooling tower for supplying cool water to the compressor is nearing completion.

New quarters for this project in the addition to the Experiment Station Building now under construction will be ready about September 1. Considerable work has been done in designing and building various items for use in these new quarters.

## II. PROGRESS ON CONSTRUCTION OF EXPERIMENTAL APPARATUS

During the past two months principal efforts have been directed toward the completion and preliminary testing of the hydrogen liquefier and its accessories. This objective has been largely met. Mr. Oswald Newell, Jr., a graduate student in Chemical Engineering, has been working closely with this phase of the project, and will use a considerable portion of this work in satisfying the thesis requirement for the Master's Degree in Chemical Engineering. Figure 1 shows the liquefier assembly arranged for a run, with

the compressed hydrogen gas cylinders at the extreme left, the high pressure hydrogen purifier in the left center, and the liquefier proper in the right center. More detailed views of the liquefier and purifier are shown in Figures 2 and 3, and Figures 4 and 5, respectively.

The general designs of the purifier and liquefier which have been built are similar to the apparatus described by DeSorbo, Milton and Andrews<sup>1</sup>, which the writer helped design. The design of that liquefier was modeled after one described by Ahlberg, Estermann, and Lundberg<sup>2</sup>. The liquefier will be described more fully in a subsequent report.

#### A. Hydrogen Liquefier

The Georgia Tech liquefier differs in one important aspect from that described by DeSorbo et al. in that provision is made for cooling the incoming high pressure hydrogen to 65°K. instead of only to 77°K. (the normal boiling point of liquid nitrogen) by passing through a cooling coil immersed in liquid nitrogen boiling under reduced pressure. This has the effect of increasing the theoretical liquefaction efficiency from about 17.5% to a value of 26% at pressures of 1500-2000 psi. A second difference of a more practical nature lies in the construction of the main heat exchanger between the high pressure and low pressure hydrogen gases. This interchanger operates in the range between 65°K. and about 20°K. In the Georgia Tech liquefier this is constructed of a flattened 1/8" O.D. x 0.010" wall annealed copper-nickel alloy tube, soft-soldered between two round tubes of the same dimensions and material, whereas the liquefier of DeSorbo et al. used a so-called "twisted tube" interchanger which insures a high degree of turbulence<sup>3</sup>.

To date three runs have been made with the liquefier. Liquid hydrogen

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- (1) Chemical Review 39, 403 (1946).
- (2) Review of Scientific Instruments 8, 422 (1937).
- (3) Loc. cit. (1) and (2).

was produced on July 3, July 25, and August 1. The run of July 3 was made primarily to study the effect of cooling the system to liquid nitrogen and hydrogen temperatures. The runs of July 25 and August 1 were made to obtain an estimate of the operating efficiency and to further test the operational characteristics of the entire assembly.

The preliminary tests of the liquefaction efficiency showed that only about 5% of the hydrogen gas is being liquified when a flow rate of 5 CFM is used. This amounts to a production rate of about 450 cm<sup>3</sup> of liquid hydrogen per hour. An actual liquefaction efficiency of about 15 to 20% had been expected, compared with a theoretical efficiency of about 26%. Analysis of the performance suggests that the efficiency of the heat interchanger described above is low. Examination of this interchanger after the July 25 run showed that the cross section of the flattened high pressure tube has increased considerably, due to the high internal pressure. It is planned to replace this interchanger with one of another design. The various control and liquid hydrogen transfer features worked very well. No difficulty was experienced with control of the expansion throttling valve, indicating that the removal of impurities by the purifier was adequate.

#### B. The High Pressure Hydrogen Gas Purifier

Compressed electrolytic hydrogen as supplied in commerce is usually about 99.5% pure, the chief impurities being oil, water vapor, nitrogen, and oxygen. The removal of these impurities is essential for trouble-free operation of liquefiers of the type built to operate using commercial hydrogen in cylinders as a source of high pressure gas. The purifier which has been built is designed to remove these impurities by passing the impure gas first over activated silica gel maintained at room temperature and then over activated charcoal cooled to 77°K. by means of a bath of liquid nitrogen. In tests to date



approximately 1200 cubic feet of hydrogen (measured at 25°C and one atmosphere pressure) have been passed through the purifier without any noticeable difference in the behavior of the liquefier.

The complete purifier is shown in Figure 4. A more detailed view of the charcoal traps and interchanger is shown in Figure 5. Figure 6 gives a detailed view of the design of the silica gel and charcoal traps proper.

Referring to Figure 4, the impure high pressure hydrogen gas enters the purifier from the commercial cylinders at "a", passes through the silica gel trap "S" where most of the oil and water vapor are removed, and emerges at "b". The gas then passes to "c" by means of a jumper (not shown) where it enters the first of three series-connected charcoal-filled traps "M" which remove practically all of the remaining water and oil vapor, oxygen, and most of the nitrogen. These traps are immersed in a bath of liquid nitrogen contained in the metal Dewar vessel "D", which is sufficiently long so that it extends about one inch above the topmost coil of the interchanger "I". The purified gas which emerges at "d" then passes directly to the liquefier. The warm gas entering the charcoal traps at "c" is interchanged with the cold purified gas leaving the third trap in the heat interchanger "I". In practice the gas emerges at "d" at about 15 C° below room temperature when flows of 4 to 5 ft.<sup>3</sup> min.<sup>-1</sup> (CFM) are used.

#### 1. Details of Construction

All tubing used, unless otherwise noted, was 3/16" O.D. x 0.035" wall dead-soft temper copper tubing, using either standard SAE flare fittings or brazed (Easy-Flo) joints for connections. The interchanger "I" consisted of twelve (12) turns of this copper tubing 11.5 ft. long, constructed by soft-soldering two lengths side by side. The interchanger was wound on a 3-7/16" mandrel.

The cylindrical metal Dewar vessel "D" is 23-1/2" deep and has an inside diameter of 4-1/4". It was specially constructed for this project by the Hofman Laboratories, 212 Wright Street, Newark, N. J. It shows an evaporation rate of 0.125 lb. of liquid nitrogen per hour when somewhat over half filled.

The detailed design of the charcoal and silica gel traps is shown in Figures 5 and 6. The only difference between the two types of traps is that the silica gel trap is 32" long instead of 12" long. All parts of the trap, with the exception of the copper inlet and exit tubes "A" and the brass screens "ST" and "SB", are of monel. All joints were brazed using "Easy-Flo" silver brazing alloy. The tube "L" was constructed of 1.75" x 0.22" wall (No. 5 gauge) normalized cold-drawn seamless monel tubing. The threaded monel plugs, "ET" and "EB" (24 threads per inch), were made of hot rolled monel. The screens "ST" and "SB" were constructed of 1/32" brass sheet drilled with numerous 1/64" diameter holes. They are held in place by peening over the edge of the recess provided in the plugs "ET" and "EB", respectively. The screens are intended to prevent the charcoal (or silica gel) from leaving the trap, while permitting free passage of gas.

After brazing, each trap was hydraulically tested to 5000 psi using oil. The average increase in diameter at 5000 psi was 0.0005". No permanent set was observed. No oil leaks appeared. After the test the cap "C" was cut off the filling tube "T" (3/8" O.D. x 0.065" monel), and the trap was thoroughly cleaned with carbon tetrachloride. The trap was then filled either with 119 grams of activated charcoal (Columbia Activated Carbon, Grade 6G, 8/14 mesh, obtained from Carbide and Carbon Chemicals Corp., New York, N. Y.) or, 522 grams of activated silica gel (Commercial grade, Type 3, obtained from the Davison Chemical Corporation, Baltimore, Maryland). This material was introduced through the filling tube "T" which passes through the screen "ST". The

cap "C" was then replaced using Easy-Flo.

The silica gel trap "S" (Figure 4) is provided with a 44 ohm bare nichrome wire (No. 22) heater, "E1" and "E2", wound onto a thin-walled brass tube but separated from it by a layer of electrically insulating cement (Sauereisen Insa-lute Cement No. 1). The heater tube fits over the trap. The heater is then thermally lagged with asbestos.

## 2. Activation of Adsorbents

Activation of the silica gel and charcoal is carried out by simultaneously pumping at "b" and "c" using a small vacuum pump, protected by a trap cooled with liquid nitrogen or other refrigerant. Both the silica gel and charcoal traps are heated to 140-150°C for several hours at a pressure of about  $10^{-1}$  to  $10^{-2}$  mm. Hg (absolute). The charcoal traps are heated by a removable furnace into which the trap assembly slips. After the traps have cooled to room temperature again, the vacuum is broken by admitting hydrogen gas.

## C. Helium Cryostat

Steady progress is being made on the helium cryostat proper with most of the parts now having been completed. The installation of the cryostat and its associated controls and vacuum systems in our new quarters in the addition to the Research Building is scheduled to begin in September.

## D. Helium Compression Cycle

Considerable progress has been made on the helium compression cycle for obtaining purified helium gas at 3000 psi. The Ingersoll-Rand Model P 33 10 G three-stage air compressor, which was a component part of a Navy Torpedo Topping Compressor supplied to us, has been set up, fitted with a 10 H. P. electric motor, and instrumented for use with helium. A fifty cubic foot rubberized fabric gas bag has been ordered for use as a low pressure helium reservoir.

The helium purifying traps, similar in design to the charcoal traps used on the hydrogen purifier, are largely completed. Further progress on this cycle will be made when this phase of the work is moved into new quarters in September. Experiments requiring high pressure helium will be made using commercially available compressed helium.

### III. LIQUID NITROGEN PLANT

The new addition to the Chemical Engineering Building in which the liquid nitrogen plant will be housed is rapidly approaching completion, with a promise that possession of the building will be gained about September 1, 1947. The two major units of the plant, namely, the compressor and the nitrogen generator, have already been mounted on their bases.

Work on the erection of the cooling tower and associated piping to supply cooling water to the 100 H. P. compressor is well under way. All materials for this installation are now on hand.

Word has been received of the impending arrival of three 50 KVA 2300/2400-120/240, 60 cycle single phase transformers for use in supplying power to the plant.

### IV. RARE EARTH METALS AND COMPOUNDS

Progress in the procurement and preparation of rare earth metals and compounds have to date been directed largely toward procurement and spectrographic analysis of the materials obtained. Dr. W. M. Spicer, Professor of Chemistry, has undertaken the work of making these analyses, using an ARL-Dietert grating spectrograph with a dispersion of  $7\text{\AA}^{\circ}$  per mm. The instrument used is an improved model of that described by Hasler and Lindhurst<sup>4</sup>. The

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(4) Metal Progress 30, 59-63 (1936).

copper spark method<sup>5</sup> was employed. The wave length range covered in these tests was 2250-4350 Å°.

Samples of lanthanum, cerium, neodymium, and praseodymium metals, obtained from Cooper Metallurgical Laboratory, Division Acme Aluminum Alloys, Inc., 2135 Columbus Road, Cleveland 13, Ohio, are being analysed. Preliminary studies of the neodymium metal, using 99.75% pure neodymium oxide, Nd<sub>2</sub>O<sub>3</sub>, obtained from the Jarrell-Ash Company, 165 Newbury Street, Boston 16, Massachusetts (Hilger's spectroscopically standardized material) as a standard, show that somewhat over 0.5% lanthanum is present in this material in addition to the 2.7% iron reported by the vendor. Samarium, gadolinium, yttrium and praseodymium are present in amounts greater than 0.1% but less than 0.5%.

The starting materials for the preparation of the pure metals are being analysed as received.

#### V. PERSONNEL

Since the last report several persons have been added to the project staff. Dr. W. M. Spicer, Professor of Chemistry, has begun spectrographic analyses of rare earth materials (part-time). Mr. W. C. Giegold, a senior in Chemical Engineering, and Mr. J. M. Ziegler, a junior in Mechanical Engineering, are serving as technical assistants for the summer.

#### VI. NEW RESEARCH QUARTERS

The last bimonthly report (No. 4, dated May 31, 1947) contains a layout of the space set aside for the new Low Temperature and Thermodynamic Properties Laboratories in the addition to the Engineering Experiment Station now under construction. The present expectation is that occupancy will be gained by September 1, 1947.

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(5) Fred, Nachtrieb and Tomkins, Journal of the Optical Society of America 37, 279-281 (1947).

Considerable effort is being directed toward plans for setting up in these new quarters the equipment which has been built. These includes the designing of special fixtures such as: (1) tables, galvanometer supports, optical systems, etc., for the instrument room; (2) liquefier and cryostat supports, and ventilation system for the experimental room where the liquid hydrogen will be used. Provision is being made for approximately one change of air per minute in this room which has a volume of 3000 cubic feet. Heating of this room in winter presents a problem because our proposed movement of air (3000 CFM) greatly exceeds the air brought into the room through the hot air heating system to be installed. It was therefore necessary to plan for the installation of a special heating unit, using steam coils and thermostatic control for this room which will bring in fresh air from outside the building. The necessary heating and ventilating units and accessories have been ordered.

Respectfully submitted,

W. T. Ziegler  
Project Director

Approved:

Gerald A. Rosselot  
Director

## VII. APPENDIX

Figure 1. View of Hydrogen Liquefier

Figure 2. Front View of Operating Controls of Hydrogen Liquefier

Figure 3. Rear View of Hydrogen Liquefier

Figure 4. Front View of High Pressure Hydrogen Gas Purifier

Figure 5. Close-up of Charcoal Traps and Interchanger of Purifier

Figure 6. Detail of High Pressure Purifier Traps

State Engineering Experiment Station  
GEORGIA SCHOOL OF TECHNOLOGY  
Atlanta, Georgia

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## I. ABSTRACT OF REPORT

During the past two months efforts have been concentrated on the hydrogen liquefier. A new main heat exchanger has been installed and found to increase the efficiency of liquefaction so that a production rate of 0.75 to 1.0 liter of liquid hydrogen per hour has been attained. This rate is considered satisfactory. A complete description of the liquefier is included in the present report.

The installation of a cooling tower for supplying cool water to the compressor of the liquid nitrogen producing plant is now complete. The space to house the plant is completed. Power installations will be completed by October 15.

Work on the helium cryostat has continued with good progress.

The new quarters for this project in the addition to the Experiment Station Building are now scheduled for occupancy by October 15.

Dr. W. T. Ziegler attended the national meeting of the American Chemical Society held in New York, N. Y. September 15-19, and obtained much helpful information at the Symposium on Ion-Exchange Separations, which dealt principally with new methods of preparation of rare earth compounds.

## II. PROGRESS ON CONSTRUCTION AND TESTING OF EXPERIMENTAL APPARATUS

During the past two months, further progress has been made on the helium cryostat and a new main heat exchanger has been installed in the hydrogen liquefier.

The hydrogen liquefier has been operated three times since the installation of the new heat exchanger, on September 5, 11, and 22. The runs of September 5 and 11 resulted in only qualitative information, due to severe plugging of the throttle valve. This was traced to a shipment of impure hydrogen gas which had been received. Arrangements were made with the National Cylinder Gas Company of Atlanta for special handling of cylinders to insure that hydrogen of a purity of 99.8<sup>+</sup> % was supplied. The run of September 22, in which this gas was used, showed no plugging troubles. We have been assured that we will be supplied with hydrogen gas of comparable purity in the future.

The results of these three runs, especially the run of September 22, showed that the new "twisted tube" heat exchanger has increased the efficiency of liquefaction considerably.

A detailed description of the liquefier and its operation follows.

### A. The Hydrogen Liquefier.

#### 1. General Description

The hydrogen liquefier is a compact, relatively portable unit so designed that its principal parts are readily accessible for inspection and repair. The assembled liquefier occupies a floor space 14" x 23" and is 48" tall. Figures 1, 2, and 3 show

respectively, the assembled liquefier (rear view), the liquefier proper mounted in the brass tube which contains the Dewar vessel for collecting the liquid hydrogen, and the liquefier proper.

Figure 4 presents a schematic detail of the liquefier.

Briefly, the liquefier consists of two pots, N1 and N2, for the liquid nitrogen which is used as the refrigerant; four heat exchangers E1, E2, E3, and X; two cooling coils, F1 and F2; and the expansion valve V. The liquid hydrogen produced is collected in the glass Dewar vessel J and can be removed therefrom through the vacuum-jacketed transfer system HT which extends to the bottom of this vessel.

The two nitrogen pots operate at different temperature levels. Pot N1, which is filled through K and has a vent R, operates at  $77^{\circ}$  K., the normal boiling point of nitrogen at one atmosphere pressure. The liquid nitrogen in Pot N2, which is admitted to Pot N2 from Pot N1 by means of the needle valve NV operated by the valve stem O, is made to boil under reduced pressure at  $65^{\circ}$  K. by means of a vacuum pump (Welch Duo-Seal No. 1400B) connected at L.

The liquid level in Pot N1 is controlled by means of the thermocouples T1 and T2 so that it falls between these two couples. The cooling coil F1 is thus always immersed in the refrigerant. The space between T1 and T2 has a volume of 350 cc.

The liquid level in Pot N2 is not directly measurable but can be regulated sufficiently well by means of the thermocouple T3 and the behavior of the vacuum pump. This pot has a volume of 300 cc.

and needs to be filled only about twice during a run.

Compressed electrolytic hydrogen gas, 99.8 <sup>+</sup>% pure, at 2000 psi, commercially available in standard 1.528 cubic foot cylinders, is used as the source of high pressure gas. This gas is first passed through a purifier consisting of an activated silica gel trap followed by three series connected activated charcoal traps immersed in liquid nitrogen. (For a description of this purifier see Progress Report No. 5, August 1, 1947). The high pressure hydrogen gas from the purifier enters the liquefier at HP, passing in turn through the external heat exchanger E1, the heat exchanger E2, the cooling coil F1, the heat exchanger E3, and the cooling coil F2. The high pressure gas then enters the main heat exchanger X at a temperature of 65-77° K., depending on the efficiency of the cooling and operating temperature of Pot N2. After passing through the exchanger X the cold, high pressure gas then reaches the expansion valve V where its pressure falls to about 10-15 psig and a part of the gas is liquefied. A thermocouple T4, soldered to the body of the expansion valve V, permits the temperature of V to be followed. About one liter of liquid hydrogen can be collected in J before the liquid level reaches the expansion valve.

The cold low pressure gas passes in countercurrent flow through the various exchangers outlined above, emerging from E1 at LP. This gas is passed through a flow meter before being discarded.

The space between the bottom of Pot N2 and the lowest coil of the exchanger X was packed loosely with woolen blanket cloth. Insulation here is important since otherwise the cold, low pressure

hydrogen gas may become heated up before entering X, with the result that the efficiency of liquefaction is greatly reduced.<sup>1</sup> The spaces (a) between the bottom of N1 and the top of N2, (b) between the brass dome W, and the outside surface of N1 in the region of the heat exchanger E2, and (c) the space surrounding the heat exchanger E1 were all packed with this same material. The importance of insulating the outside surface of the upper part of Pot N1 is considerable since the Dewar vessel does not extend into the brass dome. Even so, a large amount of moisture condenses on the outside surface of the brass dome.

The exposed high and low pressure lines connecting E1 and E2 were also wrapped with this material. During operation these lines become heavily frosted if not insulated. With these lines insulated the low pressure hydrogen leaving E1 is only about 5-10° C. below room temperature. These facts show the importance of this external exchanger.

A number of controls for operating the liquefier, as well as for diagnosing troubles, are provided. Measurements of high pressure are made at the entrance to the heat exchanger E1 and at a point G2 just before the cold gas enters the expansion valve. At flow rates of 3-5 cfm no appreciable pressure drop exists across these points. A third gage G3 measures the hydrogen pressure after expansion, which in normal operation is 10-15 psig. The Dewar vessel

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(1) Alhberg, J. E., Estermann, I., and Lundberg, W. O.,  
Rev. Sci. Instruments 8, 422 (1937).

is protected by a safety valve (not shown) connected to G3 which is set to blow at 50 psi.

A bourdon type vacuum gage in the pumping line L to Pot N2 permits the pressure in Pot N2 to be measured. A Kerotest diaphragm type valve in the pumping line allows the pressure in this pot to be maintained at the desired value.

Four copper-constantan thermocouple junctions (B&S No. 36 double nylon enameled wire) T1, T2, T3, and T4 permit the temperatures in various parts of the liquefier to be measured. Junctions T1 and T2 are soldered to the 1/8" O.D. x 0.035" wall copper tube which serves as the high pressure line in Pot N1. When the nitrogen level in N1 falls below the first turn of the cooling coil F1, a temperature rise is indicated by T2 due to the fact that the incoming high pressure gas is considerably warmer than 77° K. The liquid level in this pot may therefore be maintained by means of these two thermocouples.

Provision has been made for thawing out both the expansion valve V and the heat exchanger X. This is accomplished by directing a stream of warm hydrogen gas against the body of the expansion valve. This gas is admitted to the liquefier through a 0.040" O.D x 0.010" wall Cupro-nickel capillary tube (visible in Figure 3, but not shown in Figure 4) which passes along the outside surface of both Pots N1 and N2. This device is of great help in rapidly warming up the expansion valve and heat exchanger X, an almost immediate response being indicated by thermocouple T4. The small heat capacity of the



parts involved permits a rapid return to hydrogen liquefaction conditions when expansion is resumed.

## 2. Construction Details.

A more detailed description of the materials and method of construction may be of interest. Certain of these details have been collected and shown in Tables I and II of the Appendix.

The materials of construction consist primarily of Cupro-nickel<sup>2</sup> (30% Ni, 70% Cu), copper and brass tubing. All tubes passing through the brass end plates A-A, B-B, C-C, and D-D, with the exception of the copper high and low pressure hydrogen lines, are Cupro-nickel. The two nitrogen pots N1 and N2 were made of the 30% copper-nickel alloy material<sup>3</sup>. Longitudinal strains were thus minimized, and the low thermal conductivity of this alloy was used to advantage.

All joints and seals were made using either 60 Pb-40 Sn solder or "Easy-Flo" silver brazing alloy. All joints at sections A-A, B-B, C-C, and D-D were soft-soldered, with the exception of the joint between plate D-D and N2 which was brazed. All joints in the high pressure hydrogen circuit were brazed and tested for leaks at 2000 psi before final assembly. The joints in the low pressure hydrogen line are for the most part made with soft solder.

The joint between the brass tube which surrounds the Dewar vessel and the plate which supports the liquefier (compare Figures 1 and 3)

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(2) Obtained from Superior Tube Co., Norristown, Pa.

(3) Made available to us by Dr. D. H. Andrews, The Johns Hopkins University, to whom we wish to express our thanks.

is a soft-solder seal. This seal can be broken quite easily, when necessary, by heating the joint simultaneously with two small air-gas hand torches.

The main heat exchanger X was modeled after the so-called Nelson "twisted tube" heat exchanger<sup>4</sup>, which has been used successfully by others. The present design is modeled after one proposed by Mr. William Asher of The Johns Hopkins University Low Temperature Laboratory. The twisted tube, which constitutes the high pressure side of the exchanger, was made by first flattening a 1/8" O.D. x 0.010" wall well-annealed Cupro-nickel tube to a thickness of 0.088" for a length of 30 inches by passing through a set of hand rolls. About 3 inches was left round at either end and the ends were soft-soldered to brass plugs. The plugs were then clamped between the head and tail stocks of a lathe. The flattened portion of the tube was then twisted, with the tail stock locked in position, until the entire flattened portion had assumed a spiral form. A pitch of 20 turns per foot was obtained in this manner. The effective diameter of the finished spiral was 0.164 inches. This fitted easily into a 3/16" O.D. x 0.010" wall well-annealed Cupro-nickel tube (I.D. = 0.167") which was to serve as the outside wall of the exchanger.

Pieces of 1/32" 50-50 solder wire were wrapped in the grooves of the spiral, a light coat of flux applied, and the whole slipped into the 3/16" tube. The length of the 3/16" tube was such that the spiral portion protruded about 1/4" on each end. This was done

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(4) Bichowsky, F. R. J. Ind. Eng. Chem. 14, 62 (1922).

to reduce the pressure drop which might otherwise be present if the round section of the  $1/8$ " tube came at the ends. The assembly was then heated in a tube furnace to about  $220^{\circ}$  C., turned in a vertical position, and the excess flux and solder forced out by the application of nitrogen gas under low pressure.

When the soldering was complete, the exchanger was thoroughly washed with carbon tetrachloride, water, and acetone to remove all flux. The assembly was then wound on a  $2-1/8$ " mandrel without any difficulty.

This twisted tube heat exchanger has proved to be considerably more efficient than the earlier one (See Progress Report No. 5, August 1, 1947) made by soft-soldering a flattened  $1/8$ " O.D. x 0.010" wall Cupro-nickel tube 30 inches long, (thickness after flattening was 0.061"), between two round tubes of the same kind. After three runs the flattened high pressure tube was found to have become more nearly round, having a thickness of 0.066". This latter construction was used for the two-turn exchanger E3.

The liquid hydrogen transfer system is shown in schematic detail in Figure 5. It consists essentially of a Cupro-nickel tube "a" surrounded by a vacuum jacket formed by the tubes "b" and "d". The materials used have been listed in Table III of the Appendix. Flow of liquid hydrogen is controlled by the valve V, actuated by the stem S. The valve body is made of brass, the needle of monel. All joints in the liquid hydrogen line are brazed with "Easy-Flo"; with a few exceptions, all joints in the vacuum jacket were soft-soldered.

### 3. Operating Characteristics of the Liquefier

Six runs of varying duration have been made with the hydrogen liquefier to date. The runs of July 3, July 25, and August 1 were made with the flattened tube heat exchanger, while those of September 5, 11 and 22 were made with the twisted tube exchanger. Unfortunately, the runs of September 5 and 11 yielded only incomplete information, due to the use of unsuspectedly impure hydrogen gas which resulted in plugging difficulties in the liquefier. The run of September 22 yielded very good results.

The liquefier has given trouble-free performance except when impure gas was used. The expansion valve needed only occasional adjustment as the pressure in the cylinders fell. The hydrogen transfer system worked smoothly. The consumption of nitrogen was not found to be excessive. After liquefaction began, the upper nitrogen pot N1 required filling about once every 12-15 minutes; the lower pot N2 required filling about once an hour.

From an analysis of all the runs to date, the composite run given in Table IV has been drawn up. The production rate is essentially that observed in the run of September 22. It is believed that this table represents a fairly accurate evaluation of the performance of the liquefier.

The rate of production of liquid hydrogen was measured as follows: The liquefier was first drained of all liquid hydrogen and then allowed to run for a period of 20-30 minutes. At the end of this time the liquid hydrogen was transferred from the liquefier to a deep Dewar vessel which already contained liquid hydrogen from a previous transfer.

The increase in height of the liquid level was measured by means of a thermocouple probe surrounded by an electrical heater. This method permitted measurement of the level to an accuracy of about  $1/8$ ". The production rate quoted in the summary of Table IV of the Appendix was measured in this fashion. The actual production rate in the liquefier is somewhat greater than that measured by this collection procedure since losses are experienced due to transfer and to the pressure drop at the transfer valve.

A calculation of the efficiency of liquefaction has been made from the volume of liquid hydrogen collected and the drop in pressure of the cylinders during the same period. In this calculation the volume of the standard hydrogen cylinder was taken as 1.528 ft.<sup>3</sup> The actual average efficiency in the range 1900 to 1200 psi was found to be 10%. If transfer losses, etc., are taken into account, this may be raised to perhaps 12 or 15%. In this run the temperature of the lower nitrogen was about 66° K. as determined from the vapor pressure of the nitrogen measured with the pump shut off. The average theoretical efficiency of liquefaction in this pressure range is 22% at  $T = 66^{\circ}$  K. and 16.5% at  $T = 77.3^{\circ}$  K.<sup>5</sup>

It remains to be seen how the efficiency of liquefaction is affected by flow rate.

### III. LIQUID NITROGEN PLANT

Construction work on the new addition to the Chemical Engineering Building in which the liquid nitrogen plant will be housed is essentially complete. Three 50 KVA 2300/2400-120/240, 60 cycle single phase

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(5) Keyes, F. G., Gerry, H. T., and Hicks, Jr., J. F. G., J. Am. Chem. Soc., 59, 1426 (1937); Johnston, H. L., Bezman, I. I., and Hood, C. B., Ibid., 68, 2367 (1946).

transformers have been received (August 4, 1947) from the Naval Air Station, Anacostia, D. C., for powering this plant. These transformers have been reconditioned and are scheduled for installation within the next two weeks.

Formal request has been made of the Office of Naval Research through Mr. L. M. McKenzie (letter of August 21, 1947) for another Linde-type Liquid Oxygen Plant to replace the incomplete plant (Linde Model SM-LO-P270) now on hand. This request was based on the condition of the plant as it stands at present. This plant, as received at Georgia Tech, was found to be stripped of many parts essential to its operation. Efforts on the part of the Plant Facilities Section of ONR succeeded in locating some of the missing parts, but many other parts proved to be no longer available. In addition, the condition of the plant suggested that considerable work would have to be done to get it into running shape.

An analysis of the overall situation suggested that it would greatly expedite the work under this contract, by the saving in research time, money and the greater certainty of successful operation of the plant, if a complete plant, as originally contemplated, could be obtained for the project.

Informal assurances have been received that another plant will be made available to the project, but as yet, no notice of its shipment has been received.

The installation of a cooling tower and associated piping to supply cooling water to the 100 H.P. air compressor has been completed. This installation has been largely the responsibility of Mr. W. A.

Phillips. The component parts of the cooling system and most of the labor of installation have been supplied by the Department of Chemical Engineering. The system has been designed so that in addition to cooling the compressor, its operation can also be studied as a laboratory experiment in chemical engineering.

#### IV. NEW RESEARCH QUARTERS

Completion of the new research addition to the Engineering Experiment Station, which will house the new low temperature and thermodynamics properties laboratories, is scheduled for mid October, and occupancy of the project's new quarters will be gained before November 1.

#### V. PERSONNEL

During the past two months, several members of the group have left or have been away on vacation from the School. Mr. W. C. Giegold, a senior in Chemical Engineering, has graduated and left the project. Mr. Oswald Newell, Jr., and Mr. L. R. Daniel, who are doing their Master's thesis problems in Chemical Engineering in connection with the hydrogen liquefier and helium cryostat, respectively, have been away on vacation. Mr. Newell's work with the liquefier is nearly completed. Mr. Daniel will resume his work with the project on October 1. Mr. J. M. Ziegler and Mr. F. A. Peedo, students, are working part-time as technical assistants.

## VI. TRIPS

Dr. W. T. Ziegler attended the national meeting of the American Chemical Society held in New York, N. Y., September 15-19. A great deal of helpful information was obtained at the Symposium on Ion-Exchange Separations which dealt principally with new methods of preparation of pure rare earth compounds.

Respectfully submitted,

W. T. Ziegler  
Project Director

Approved:     )     /     /

Gerald A. Rossélet, Director



VII. APPENDIX

- Table I. Details of Construction of Cooling Coils and Heat Exchangers of Hydrogen Liquefier.
- Table II. Specifications for Parts of Hydrogen Liquefier.
- Table III. Construction Materials for Hydrogen Transfer Valve.
- Table IV. Composite Run of Hydrogen Liquefier.
- Figure 1. Rear View of Hydrogen Liquefier.
- Figure 2. View of Hydrogen Liquefier.
- Figure 3. Hydrogen Liquefier Proper.
- Figure 4. Schematic Detail of Hydrogen Liquefier.
- Figure 5. Liquid Hydrogen Transfer Valve.

TABLE I  
DETAILS OF CONSTRUCTION OF COOLING COILS AND HEAT EXCHANGERS  
OF HYDROGEN LIQUEFIER

| mbol          | Descrip-<br>tion | Material* | Tubing                              |  | Length<br>in<br>Feet | Number<br>of<br>Turns | Diameter<br>of Man-<br>drel used<br>for Wind-<br>ing in<br>Inches | Final<br>I.D. of<br>Coil<br>in<br>Inches |
|---------------|------------------|-----------|-------------------------------------|--|----------------------|-----------------------|---|--|
|               |                  |           | Outside<br>Diameter<br>in<br>Inches | Wall<br>Thick-<br>ness<br>in<br>Inches |                      |                       |   |  |
| oling<br>ils  |                  |           |                                     |  |                      |                       |   |  |
| F1            | H.P. gas         | copper    | 1/8                                 | 0.032                                  | 14                   | 21                    | 2-1/4   | 2-5/16                                   |
| F2            | H.P. gas         | copper    | 1/8                                 | 0.032                                  | 5.3                  | 8                     | 2-1/4   | 2-5/16                                   |
| at<br>hangers |                  |           |                                     |  |                      |                       |   |  |
| E1            | H.P. gas         | copper    | 3/16                                | 0.035                                  | 10                   | 16                    | 2-1/4   | 2-5/16                                   |
|               | L.P. gas         | copper    | 1/4                                 | 0.032                                  |                      |                       |   |  |
| E2            | H.P. gas         | copper    | 1/8                                 | 0.032                                  | 9.5                  | 14.5                  | 2-1/4   | 2-5/16                                   |
|               | L.P. gas         | copper    | 1/4                                 | 0.032                                  |                      |                       |   |  |
| E3            | H.P. gas         | Cu-Ni     | 1/8**                               | 0.010                                  | 1.3                  | 2                     | 2-1/4   | 2-3/8                                    |
|               | L.P. gas(2)      | Cu-Ni     | 1/8                                 | 0.010                                  |                      |                       |   |  |
| X             | H.P. gas         | Cu-Ni     | 1/8***                              | 0.010                                  | 2.5                  | 4                     | 2-1/8   | 2-9/32                                   |
|               | L.P. gas         | Cu-Ni     | 3/16                                | 0.010                                  |                      |                       |   |  |

\* All tubing was of "dead-soft" temper.

\*\* Before flattening.

\*\*\* Before twisting.

TABLE II  
SPECIFICATIONS FOR PARTS OF HYDROGEN LIQUEFIER

| Symbol      | Description               | Material   | Tubing            |                                    | Length in<br>Inches |
|-------------|---------------------------|------------|-------------------|------------------------------------|---------------------|
|             |                           |            | O.D. in<br>Inches | Wall Thick-<br>ness in In-<br>ches |                     |
| N1          | Upper pot                 | Cu-Ni (h)* | 3                 | 0.042                              | 15                  |
| N2          | Lower pot                 | Cu-Ni (h)  | 3                 | 0.042                              | 3                   |
| K           | N1 filling tube           | Monel (h)  | 1/2               | 0.010                              | 8                   |
| L           | N2 vacuum line            | Cu-Ni (h)  | 3/8               | 0.010                              | 18-1/2              |
| M           | Expansion valve<br>stem   | Cu-Ni (h)  | 5/32              | 0.020                              | 26                  |
|             | Sleeve tube<br>for stem   | Cu-Ni (h)  | 3/16              | 0.010                              | 25-1/4              |
| O           | Stem for NV               | Cu-Ni (h)  | 5/32              | 0.020                              | 16-1/2              |
|             | Sleeve tube<br>for stem   | Cu-Ni (h)  | 3/16              | 0.010                              | 16-1/2              |
|             | Tube between N1<br>and NV | Cu-Ni (h)  | 1/4               | 0.010                              | 1                   |
|             | Tube between NV<br>and N2 | Cu-Ni (h)  | 1/8               | 0.010                              | 1-1/2               |
| HT          | Hydrogen transfer<br>tube |            |                   |                                    |                     |
|             | Vacuum jacket             | Cu-Ni (h)  | 3/8               | 0.010                              | 23-1/2              |
|             | Inner tube                | Cu-Ni (h)  | 3/16              | 0.010                              | 33-1/2              |
| R           | N1 exhaust                | Cu-Ni (h)  | 3/8               | 0.010                              |                     |
| G3          | Dewar vessel<br>pressure  | Copper (a) | 3/16              | 0.032                              | 2                   |
| (Continued) |                           |            |                   |                                    |                     |

\* The letters (a) and (h) refer to "dead-soft" and "hard-drawn" temper, respectively.

TABLE II (Cont'd)

SPECIFICATIONS FOR PARTS OF HYDROGEN LIQUEFIER

| <u>Symbol</u> | <u>Description</u>           | <u>Material</u> | <u>Tubing</u>             |   | <u>Length in<br/>Inches</u> |
|---------------|------------------------------|-----------------|---------------------------|---|-----------------------------|
|               |                              |                 | <u>O.D. in<br/>Inches</u> | <u>Wall Thick-<br/>ness in In-<br/>ches</u> |                             |
| W             | Brass dome                   | Brass           | 4                         | 0.065                                       | 4-3/8                       |
| None          | Conduit for T1 and<br>T2     | Cu-Ni (h)       | 1/16                      | 0.010                                       | 12                          |
| None          | Conduit for T3 and<br>and T4 | Cu-Ni (h)       | 1/16                      | 0.010                                       | 17                          |
| J             | Dewar vessel                 | Pyrex           |                           |   |                             |
|               | Outer tube                   |                 | 100 (mm)                  | 2.4 (mm)                                    | 30                          |
|               | Inner tube                   |                 | 85 (mm)                   | 2.4 (mm)                                    | 29                          |
|               |                              |                 | I.D. = 3-1/8 In.          |   |                             |

\*The letters (a) and (h) refer to "dead-soft" and "hard-drawn" temper, respectively.

TABLE III

CONSTRUCTION MATERIALS FOR HYDROGEN TRANSFER VALVE

| <u>Symbol</u> | <u>Material</u>          | <u>Dimensions</u>        |
|---------------|--------------------------|--------------------------|
| a             | Cupro-nickel             | 3/16" O.D. x 0.010" wall |
| b             | Cupro-nickel             | 3/8" O.D. x 0.010" wall  |
| c             | Cupro-nickel             | 1/4" O.D. x 0.010" wall  |
| d             | Brass                    | 7/8" O.D. x 0.035" wall  |
| e             | Copper (evacuation line) |                          |
| f             | Bakelite (spacers)       |                          |
| i             | Monel insert             |                          |
| s             | Cupro-nickel             | 5/32" O.D. x 0.020" wall |
| v             | Brass                    |                          |

TABLE IV  
COMPOSITE RUN OF HYDROGEN LIQUEFIER

| TIME (hours) | OPERATION  |
|--------------|--|
| 0.00         | Three tanks on at 1900 psi. Began cooling charcoal traps of purifier with liquid nitrogen.                                   |
| 0.25         | Charcoal traps at liquid nitrogen temperature (6.2 liters required to cool and fill metal Dewar surrounding charcoal traps). |
| 0.27         | Began slow flow of hydrogen through liquefier. (1 cfm).  |
| 0.33         | Began transfer of liquid N <sub>2</sub> to Pot N1.   |
| 0.50         | Began transfer of liquid N <sub>2</sub> to Pot N2.   |
| 0.75         | Both pots full (2.0 liters liquid N <sub>2</sub> required). T4 reads 0.3 millivolt.  |
| 0.77         | H <sub>2</sub> flow increased to 4 cfm.  |
| 1.22         | T4 reads 6.7 millivolts liquefaction of hydrogen began. Tank pressure = 1500 psi. Flow rate: 3 to 4 cfm.                     |
| 1.9          | Tank pressure at 800 psi. Tanks replaced by three full cylinders at 1900 psi.  |
| 3.2          | Pressure in tanks at 700 psi. Run stopped.   |

SUMMARY

Total volume liquid hydrogen produced = 1.5 liters.  
Production rate = 0.75 liter per hour at 3-4 cfm.  
Liquid hydrogen produced per set of three cylinders (1900 to 700 psi) = 0.9 liter.  
Consumption of liquid nitrogen:  
    (1) To cool charcoal traps = 6.2 liters.  
    (2) To cool liquefier to hydrogen liquefaction temperature = 3.0 liters.  
    (3) To produce 1.5 liters liquid hydrogen:  
        a. Purifier = 4.7 liters.  
        b. Liquefier = 4.4 liters.  
Total nitrogen consumption = 18.3 liters.

Figure 5. Hydrogen Liquefier Pro



Figure 1 - Rear View of Hydrogen Liquefier



Figure 2 - View of Hydrogen Liquefier



Figure 3 - Hydrogen Liquefier Proper



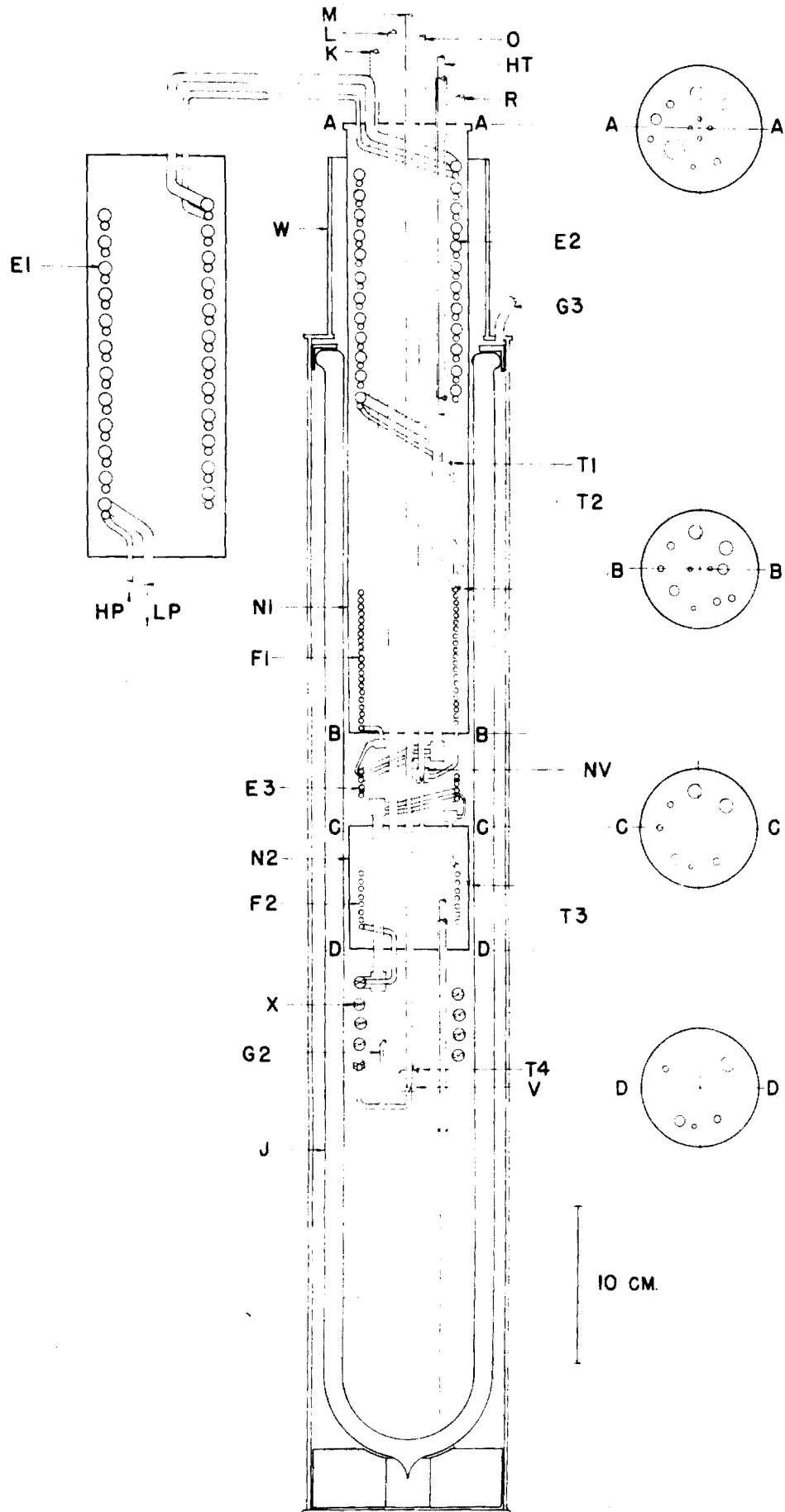


Figure 4

SCHEMATIC DETAIL OF HYDROGEN LIQUEFIER

Georgia School of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

ANNUAL REPORT FOR THE PERIOD  
OCTOBER 1, 1946 THROUGH SEPTEMBER 30, 1947

PROJECT 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH  
CONTRACT NO. N6-ori-192, TASK ORDER I

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF THE  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES,  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

By

W. T. ZIEGLER

JANUARY 2, 1948

**GEORGIA SCHOOL OF TECHNOLOGY**  
THE STATE ENGINEERING EXPERIMENT STATION  
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## I. SUMMARY OF REPORT

During the period October 1, 1946, through September 30, 1947, work on the project has been carried on under Contract No. N6-ori-192, Task Order I. The general intent of this contract was for the contractor to carry out "research at very low temperatures upon the fundamental properties of the elements and their compounds including the rare earths, with particular emphasis upon superconductivity." A list of the bi-monthly progress reports upon which the present report is based is given in Appendix B.

The first phase of this work was to assemble and build the necessary low temperature equipment. Indeed, due to procurement and building construction delays, this constituted the major effort during the past year.

A high pressure hydrogen gas purifier has been built and is operating.

A small hydrogen liquefier having a capacity of approximately one liter of liquid hydrogen per hour has been built and tested. Liquid hydrogen was first produced on July 3, 1947.

The helium cryostat, in which liquid helium will be produced, is nearing completion.

The precision electrical equipment for carrying out the necessary measurements of electrical resistance and magnetic induction has been assembled.

A helium purification and compression cycle for delivering helium gas at 3000 psi has been partially completed.

Numerous pieces of accessory equipment such as furnaces, vacuum systems, etc., have been constructed.

A large liquid-oxygen-producing plant which is to be converted to the production of liquid nitrogen has been received. This plant is now partially installed. A cooling system for supplying water to the 100 H.P. air compressor has been designed and installed.

The procurement of the spectrographic analysis and rare earth materials has been carried on. Some of the necessary equipment for preparing the pure starting materials has been constructed or assembled.

Preparations for the housing of the project in new research quarters of the Low Temperature Laboratory have been carried forward.

Three graduate students in chemical engineering have worked on their master's thesis problems as part of the project.

## II. FUTURE PLANS

A proposal for extending the contract under which the project has been carried out (Contract No. N6-on-192, Task Order I) from October 1, 1947, to March 31, 1949, has been submitted to the Office of Naval Research for discussion. The following research problems have been proposed as objectives for the period indicated; in each case, particular emphasis would be placed on evidence for possible superconductivity of each substance investigated:

- (1) Completion of any unfinished work on praseodymium and neodymium metals and lanthanum hydride or nitride.
- (2) Reinvestigation of lanthanum and cerium metals for superconductivity.
- (3) Investigation of gadolinium metal for possible superconductivity.
- (4) Investigation of cerium hydride and nitride for possible superconductivity.
- (5) Investigation of such other rare earth metals as may be obtainable for possible superconductivity.

These research objectives are a continuation of the general intent of Task Order I of the above contract.

During the past year, construction has been under way for a new Research Annex in which space for the setting up of the Low Temperature Laboratory in a permanent fashion was to be provided. This space became

available on October 21, 1947. It consists of 1,600 square feet, most of which is laboratory space. Hereafter, the Project's research activities will be centered in this space, to which the transfer of equipment has been completed. The setting up of the chemical equipment for the preparation of rare earth metals and the low temperature apparatus and accessory devices is well under way, along with the installation of special service lines. Considerable work remains to be done, however, before all phases of actual experimentation can begin. It is hoped that experiments at temperatures at which helium is liquid will be under way by the spring of 1948.

It is planned that some studies of the new synthetic resin ion-exchange technique for separating the rare earth ions will be undertaken. The preparation of rare earth metals and their compounds should be well under way by the summer of 1948.



### III. SURVEY OF THE PROBLEM

Task Order I of this contract reads as follows:

"The Contractor shall furnish the necessary personnel and facilities for and conduct, in accordance with any instructions issued by the Scientific Officer or his authorized representative, research at very low temperatures upon fundamental properties of the elements and their compounds including the rare earths, with particular emphasis upon superconductivity."

More specifically, the experimental objective of this work is the testing, by electrical and magnetic means, of certain rare earth metals and compounds for superconductivity. The reasons underlying this objective are given in Section IV of this report. The metals selected for study are lanthanum, cerium, praseodymium, and neodymium. It is hoped that others may be added to this list later. The compounds to be studied first are lanthanum hydride and nitride. The problem of handling the rare earth hydrides and nitrides is complicated by the fact that they must be handled in the absence of air and water vapor.

The experimental method to be used in these studies is the measurement of the magnetic permeability of the metals and powdered compounds as a function of temperature down to about 2° K. These measurements will permit the detection of superconductivity by the change occurring in the induction of a coil in which the sample has been placed when the material goes from its normal state, in which permeability is unity or larger, to the superconducting state in which the permeability is zero. This method has been used before by others.<sup>1</sup>

- - - - -

(1) Kurti, N. and Simon, F. Proc. Roy. Soc. (London) A151, 610 (1935).

Electrical resistance measurements will be made as a function of temperature on such samples as may be obtained in a suitable form.

The study of materials at very low temperatures obviously presupposes the availability of low temperature producing equipment. This equipment was, in fact, not available at the outset of this project, but plans for setting up facilities for modest experimentation in this field were already under way when the assistance of the Office of Naval Research was obtained. The construction of this equipment, therefore, constituted a necessary first step in providing the facilities for carrying out the proposed low temperature experiments. Unfortunately, due to difficulties of procurement and delays in the construction of the new building, all of which were beyond our control, the construction of the low temperature equipment consumed almost the entire year with no actual experiments having been carried out on the rare earth materials. However, it is expected that with the impending completion of this equipment actual experiments can be begun shortly.

#### IV. BACKGROUND OF THE PROBLEM

##### A. The Rare Earth Metals.

The rare earth metals have been chosen for study for several reasons. In the first place, apparently only two of them, lanthanum and cerium, have ever been investigated in a pure state. McLennan, Allen, and Wilhelm<sup>2</sup> have measured the electrical resistance of these two metals as a function of temperature and have reported that neither became superconducting at the lowest temperature reached ( $1.9^{\circ}$  K.).

McLennan, Howlett, and Wilhelm<sup>3</sup> have studied the electrical conductivity of misch metal down to  $2.3^{\circ}$  K. and found no evidence of superconductivity. The sample studied was free of iron and had the composition: cerium 35%, lanthanum 20%, neodymium 20%, samarium 10%, gadolinium 6%, praseodymium 5%, europium 2%, yttrium 2%. From this measurement, McLennan, et al., concluded that none of these elements were superconducting above  $2.3^{\circ}$  K.

On the other hand, Mendelssohn<sup>4</sup> and Daunt, using a magnetic method, have reported that lanthanum is a superconductor with a transition temperature of  $4.71^{\circ}$  K. Confirmation<sup>5</sup> of the superconductivity of lanthanum has been reported by Shoenberg.

These contradictory results can only be reconciled if the electrical and magnetic transition in lanthanum are separated by several degrees; this seems highly unlikely for a pure metal. It was felt, therefore,

- - - - -

- (2) McLennan, Allen, and Wilhelm, Phil. Mag. (7) 10, 500 (1930).
- (3) McLennan, Howlett, and Wilhelm, Trans. Roy. Soc. Canada.  
Sect. III 23, No. 3, 287 (1930).
- (4) Mendelssohn and Daunt, Nature 139, 473 (1937).
- (5) Shoenberg, Proc. Camb. Phil. Soc. 33, 577 (1937).

that the experimental proof of non-superconductivity in the rare earth metals at temperatures above  $1.9^{\circ}$  K. was not clear-cut and that a re-investigation of these metals would be worthwhile.

The rare earth metals have certain other properties which make them interesting objects of study. Both lanthanum and cerium exist in at least two crystalline modifications (hexagonal close-packed and face-centered cubic). It would be interesting to determine whether two closely similar crystalline forms could be cooled to low temperatures and studied for superconductivity. Tin is the only substance, obtainable in two crystalline forms at low temperatures, whose electrical conductivity has been studied to date. White tin is a superconductor ( $3.7^{\circ}$  K.); gray tin is not a superconductor at the lowest temperature studied so far ( $1.32^{\circ}$  K.). However, the two crystalline forms have very widely different normal properties and crystal structures.

Another unusual property of certain of the rare earth metals is that they are rather strongly paramagnetic. Some, such as gadolinium and dysprosium, have been found to be ferromagnetic. Thus, there is an interesting, though perhaps remote, possibility of finding a metal which is ferromagnetic in the normal state but which exhibits zero permeability in the superconducting state.

#### B. Rare Earth Metal Compounds.

Recent studies of Horn<sup>6,7,8</sup> and co-workers, Socolor,<sup>9</sup> Aschermann, et al.,<sup>10</sup> have shown that the hydrides and nitrides of columbium and the

- -- --
- (6) Horn, F. H., Dissertation. Johns Hopkins University, Baltimore Md., June, 1942.
  - (7) Horn, F. H., Brucksch, W. F., Jr., Ziegler, W. T., and Andrews, D. H., Phys. Rev. 61, 738 (1942).
  - (8) Horn, F. H. and Ziegler, W. T., J. Am. Chem. Soc. 69, 2762 (1947).
  - (9) Socolor, S. J., "New Preparations and Superconductivity Studies on Columbium Nitride." Presented at the 109th Meeting of the American Chemical Society, Atlantic City, N. J., April, 1946.
  - (10) Aschermann, G., Friederich, E., Justi, E., and Kramer, J., Physik. Z. 42, 349 (1941).

hydrides of tantalum are superconducting. The studies by Horn, et al., of superconductivity in columbium-hydrogen and tantalum-hydrogen solid solutions showed that the expansion of the body-centered cubic metal atom lattice, which occurs as the atomic per cent dissolved hydrogen increases, is accompanied by a corresponding decrease in transition temperature and an increased transition range. The rare earth metals form both hydrides and nitrides which apparently are solid solutions. The hydrides, prepared by direct combination of the metal with hydrogen gas 200-400° C., usually have a composition corresponding to  $MH_x$ , where  $x$  ranges from 1.8 to 2.8. They are, in general, black, friable materials which ignite spontaneously on exposure to air. The nitrides prepared by direct combination of the metal with nitrogen at 800-900° C., have compositions ranging from  $MN_{0.80}$  to  $MN_{1.0}$ . These nitrides are very readily attacked by moist air, reacting to liberate ammonia.

No magnetic or electrical studies of the rare earth hydrides and nitrides have been reported below 80° K. No systematic study has been published of the lanthanum-hydrogen or lanthanum-nitrogen system with a view to correlating the X-ray structure of the solid with the nonmetallic content of the solid solution. The hydride and nitride preparations studied to date have been reported to have a face-centered cubic and a NaCl structure, respectively.

Our aim is, therefore, to be able to correlate any superconducting properties of these solid solutions with the lattice structure of the solid solutions.

## V. LOW TEMPERATURE APPARATUS AND AUXILIARY EQUIPMENT

The apparatus to be constructed or assembled for carrying out the low temperature experiments is shown in schematic fashion in Figure 1 (See Appendix A). The principal pieces of apparatus are: (1) the high pressure hydrogen purifier, (2) the hydrogen liquefier, (3) the helium cryostat, (4) the helium gas cycle, and (5) the electrical measuring system. It is planned at present to use commercial hydrogen gas purchased in standard cylinders at 2000 psi to operate the liquefier, instead of using a hydrogen compressor.

In addition to this equipment, a Linde Type Portable Oxygen Producing Plant, Linde Model SM-LO-P270, is to be converted to a liquid nitrogen producing plant, so that an adequate supply of liquid nitrogen will be available at all times.

The production of liquid helium is to be accomplished by the so-called Simon adiabatic expansion method and will be carried out directly in the cryostat in which the materials are to be studied. The production of liquid helium by this method presupposes the availability of liquid hydrogen, which in turn requires the use of liquid air, oxygen, or nitrogen as a refrigerant. Liquid nitrogen, due to its inertness, has been chosen as the refrigerant for producing liquid hydrogen.

Briefly, the production of liquid hydrogen is accomplished by using hydrogen gas which is commercially available compressed to 2000 psi in standard cylinders. The high pressure gas, after passing through a purifier to remove all condensable impurities, is passed directly to the liquefier where a portion of it is liquefied. The portion of the gas not

liquefied<sup>11</sup> is discarded. The liquid hydrogen is then transferred directly into the helium cryostat.

A fairly detailed description of the progress to date on each of the above-mentioned units is presented below.

A. The High Pressure Hydrogen Gas Purifier.

The hydrogen gas purifier which has been built is similar in design and construction to one<sup>12</sup> described by DeSorbo, Milton, and Andrews, which the writer helped to design.

Compressed electrolytic hydrogen as supplied in commerce is usually about 99.7% pure, the chief impurities being oil, water vapor, nitrogen, and oxygen. The removal of these impurities is essential for trouble-free operation of liquefiers using commercial hydrogen in cylinders as a source of the high pressure gas. The purifier which has been built is designed to remove these impurities by passing the impure gas first over activated silica gel maintained at room temperature, and then over activated charcoal cooled to about 80° K. by means of a bath of liquid nitrogen. In tests to date approximately 1200 cubic feet of hydrogen (measured at 25° C. and one atmosphere pressure) have been passed through the purifier after activation, without any noticeable plugging of the liquefier.

The complete purifier is shown in Figure 2 (Appendix A.) Figure 3 (Appendix A) gives a detailed sketch of the design of the silica gel and charcoal traps proper.

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- (11) The use of commercial cylinders as a source of compressed gas has been shown to be more economical than the conventional compressor-gasometer system, when moderate quantities of liquid hydrogen are needed. Keyes, F. G., Gerry, H. T., and Hicks, J. F. G., J. Am. Chem. Soc. 59, 1426 (1937).
- (12) DeSorbo, W., Milton, R. M., and Andrews, D. H., Chemical Rev. 39, 403 (1946).

Referring to Figure 2, the impure high pressure hydrogen gas enters the purifier from the commercial cylinders at "a", passes through the silica gel trap "S" where most of the oil and water vapor are removed, and emerges at "b". The gas then passes to "c" by means of a jumper (not shown) where it enters the first of three series-connected charcoal-filled traps "M" which remove practically all of the remaining water and oil vapor, oxygen, and most of the nitrogen. These traps are immersed in a bath of liquid nitrogen contained in the metal Dewar vessel "D", which is sufficiently long so that it extends about one inch above the topmost coil of the interchanger "I". The purified gas which emerges at "d" then passes directly to the liquefier. The warm gas entering the charcoal traps at "c" is interchanged with the cold purified gas leaving the third trap in the heat interchanger "I". In practice the gas emerges at "d" at about 15° C. below room temperature when flows of 4 to 5 ft<sup>3</sup> min.<sup>-1</sup> (CFM) are used.

#### 1. Details of Construction.

All tubing used, unless otherwise noted, was 3/16" O.D. x 0.035" wall dead-soft temper copper tubing, using either standard SAE flare fittings or brazed (Easy-Flo) joints for connections. The interchanger "I" consisted of twelve (12) turns of this copper tubing 11.5 ft. long, constructed by soft-soldering two lengths side by side. The interchanger was wound on a 3-7/16" mandrel.

The cylindrical metal Dewar vessel "D" is 23-1/2" deep and has an inside diameter of 4-1/4". It was specially constructed for this project by the Hofman Laboratories, 212 Wright Street, Newark, N. J. It shows an evaporation rate of 0.125 lb. of liquid nitrogen per hour when somewhat over half filled.



The detailed design of the charcoal and silica gel traps is shown in Figure 3. The only difference between the two types of traps is that the silica gel trap is 32" long and the charcoal one 12" long. All parts of the trap, with the exception of the copper inlet and exit tubes "A" and the brass screens "ST" and "SB" are of monel. All joints were brazed using "Easy-Flo" silver brazing alloy. The tube "M" was constructed of 1.75" x 0.22" wall (No. 5 gauge) normalized cold-drawn seamless monel tubing. The threaded monel plugs, "ET" and "EE" (24 threads per inch), were made of hot-rolled monel. The screens "ST" and "SB" were constructed of 1/32" brass sheet drilled with numerous 1/64" diameter holes. They are held in place by peening over the edge of the recess provided in the plugs "ET" and "EB" respectively. The screens are intended to prevent the charcoal (or the silica gel) from leaving the trap, while permitting free passage of gas.

After brazing, each trap was hydraulically tested to 5000 psi using oil. The average increase in diameter at 5000 psi was 0.0005". No permanent set was observed. No oil leaks appeared. After the test the cap "C" was cut off the filling tube "T" (3/8" O.D. x 0.065" monel), and the trap was thoroughly cleaned with carbon tetrachloride. The trap was then filled either with 119 grams of activated charcoal (Columbia Activated Carbon, Grade 6G, 8/14 mesh, obtained from Carbide and Carbon Chemicals Corp., New York, N. Y.) or, 522 grams of activated silica gel (Commercial grade, Type 3, obtained from the Davidson Chemical Corporation, Baltimore, Maryland). This material was introduced through the filling tube "T" which passes through the screen "ST". The cap "C" was then replaced using

Easy-Flo.

The silica gel trap "S" (Figure 2) is provided with a 44-ohm bare nichrome wire (No. 22) heater, "E1" and "E2", wound onto a thin-walled brass tube but separated from it by a layer of electrically insulating cement (Sauereisen Insa-lute Cement No. 1). The heater tube fits over the trap. The heater is then thermally lagged with asbestos.

## 2. Activation of Adsorbents.

Activation of the silica gel and charcoal is carried out by simultaneously pumping at "b" and "c", using a small vacuum pump protected by a trap cooled with liquid nitrogen or other refrigerant. Both the silica gel and the charcoal traps are heated to 140-150° C. for several hours at a pressure of about  $10^{-1}$  to  $10^{-2}$  mm. Hg (absolute). The charcoal traps are heated by a removable furnace into which the trap assembly slips. After the traps have cooled to room temperature again, the vacuum is broken by admitting hydrogen gas.

## B. The Hydrogen Liquefier.

The production of liquid hydrogen on a small scale can be carried out quite expeditiously using commercially available cylinders of compressed electrolytic hydrogen gas of high purity as a source of high pressure gas, in place of the conventional compressor-gasometer arrangement. Small liquefiers employing this method have been described<sup>12, 13, 14, 15, 16</sup> by a number of experimenters.

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- (12) DeSorbo, W., Milton, R. M., and Andrews, D. H., Chem. Rev., 39 403 (1946).
- (13) Latimer, W. M., J. Am. Chem. Soc. 44, 90 (1922).
- (14) Latimer, W. M., Buffington, R. M., and Hoenshel, H. D., ibid. 47, 1571 (1925).
- (15) Keyes, F. G., Gerry, H. T., and Hicks, J. F. G., Jr., loc. cit.
- (16) Ahlberg, J. E., Estermann, I., and Lundberg, W. O., Rev. Sci. Instruments 8, 422 (1937).

A major factor in achieving compactness of design and simplicity of construction has been the development of the Nelson "twisted tube" heat exchanger described by Bichowsky<sup>17</sup> for use as the main heat exchanger.

### 1. General Description

The general design of the liquefier which has been built is similar to the apparatus described by DeSorbo, Milton, and Andrews<sup>18</sup> which the writer helped design. The design of that liquefier was modeled after an apparatus described<sup>19</sup> by Ahlberg, Estermann, and Lundberg.

The Georgia Tech liquefier differs in one important respect from that described by DeSorbo, et al., in that provision has been made within the liquefier for cooling the incoming high pressure hydrogen to 65° K. instead of only to 77° K. (the normal boiling point of liquid nitrogen), by passing it through a cooling coil immersed in liquid nitrogen boiling under reduced pressure. This has the effect of increasing the average theoretical liquefaction efficiency from about 17.5% to a value of 26% at operating pressures of 1500-2000 psi.

A second difference of a more practical nature lies in the construction of the twisted tube main heat exchanger between the high pressure and low pressure hydrogen gases. This interchanger operates in the range between 65° K. and about 20° K. In the Georgia Tech liquefier this is constructed of a flattened 1/8" O.D. x 0.010" wall annealed copper-nickel alloy tube, which, after twisting, was soft-soldered inside a

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(17) Bichowsky, F. R., J. Ind. Eng. Chem. 14, 62 (1922).

(18) DeSorbo, Milton, and Andrews, loc. cit.

(19) Ahlberg, Estermann, and Lundberg, loc. cit.

3/16" O.D. x 0.010" wall annealed copper-nickel alloy tube in a manner suggested by Mr. William Asher of the Johns Hopkins University Low Temperature Laboratory.

The hydrogen liquefier is a compact, relatively portable unit, so designed that its principal parts are readily accessible for inspection and repair. The assembled liquefier occupies a floor space 14" x 23" and is 48" tall. Figures 4 and 5 of Appendix A show respectively, the assembled liquefier (rear view) and the liquefier proper. Figure 6 presents a schematic detail of the liquefier.

Briefly, the liquefier consists of two pots, N1 and N2, for the liquid nitrogen which is used as the refrigerant; four heat exchangers E1, E2, E3, and X; two cooling coils, F1 and F2; and the expansion valve V. The liquid hydrogen produced is collected in the glass Dewar vessel J and can be removed therefrom through the vacuum-jacketed transfer system HT which extends to the bottom of this vessel.

The two nitrogen pots operate at different temperature levels. Pot N1, which is filled through K and has a vent R, operates at 77° K., the normal boiling point of nitrogen at one atmosphere pressure. The liquid nitrogen in Pot N2, which is admitted to Pot N2 from Pot N1 by means of the needle valve NV operated by the valve stem O, is made to boil under reduced pressure at 65° K. by means of a vacuum pump (Welch Duo-Seal No. 1400B) connected at L.

The liquid level in Pot N1 is controlled by means of the thermocouples T1 and T2 so that it falls between these two couples. The cooling coil F1 is thus always immersed in the refrigerant. The space between T1

and T2 has a volume of 350 cc.

The liquid level in Pot N2 is not directly measurable, but can be regulated sufficiently well by means of the thermocouple T3 and the behavior of the vacuum pump. This pot has a volume of 300 cc. and needs to be filled only about once an hour during a run.

Compressed electrolytic hydrogen gas, 99.8<sup>+</sup>% pure, at 2000 psi, commercially available in standard 1.528-cubic foot cylinders, is used as the source of high pressure gas. This gas is first passed through a purifier consisting of an activated silica gel trap followed by three series connected activated charcoal traps immersed in liquid nitrogen. The high pressure hydrogen gas from the purifier enters the liquefier at HP, passing in turn through the external heat exchanger E1, the heat exchanger E2, the cooling coil F1, the heat exchanger E3, and the cooling coil F2. The high pressure gas then enters the main heat exchanger X at a temperature of 65-77° K., depending on the efficiency of the cooling and operating temperatures of Pot N2. After passing through the exchanger X the cold, high pressure gas then reaches the expansion valve V where its pressure falls to about 10-15 psig and a part of the gas is liquefied. A thermocouple T4, soldered to the body of the expansion valve V, permits the temperature of V to be followed. About one liter of liquid hydrogen can be collected in J before the liquid level reaches the expansion valve.

The cold low pressure gas passes in countercurrent flow through the various exchangers outlined above, emerging from E1 at LP. This gas is passed through a flow meter before being discarded.

The space between the bottom of Pot N2 and the lowest coil of

the exchanger X was packed loosely with woolen blanket cloth. Insulation here is important since otherwise the cold, low pressure hydrogen gas may become heated before entering X, with the result that the efficiency of liquefaction is greatly reduced.<sup>20</sup> The spaces (a) between the bottom of N1 and the top of N2, (b) between the brass dome W and the outside surface of N1 in the region of the heat exchanger E2, and (c) the space surrounding the heat exchanger E1 were all packed with this same material. The importance of insulating the outside surface of the upper part of Pot N1 is considerable since the Dewar vessel does not extend into the brass dome. Even so, a large amount of moisture condenses on the outside surface of the brass dome.

The exposed high and low pressure lines connecting E1 and E2 were also wrapped with woolen blanket cloth. During operation these lines become heavily frosted if not insulated. With these lines insulated the low pressure hydrogen leaving E1 is only about 5-10° C. below room temperature. These facts show the importance of this external exchanger.

A number of controls for operating the liquefier, as well as for diagnosing troubles, are provided. Measurements of high pressure are made at the entrance to the heat exchanger E1 and at a point G2 just before the cold gas enters the expansion valve. At flow rates of 3-5 cfm no appreciable pressure drop exists across these points. A third gauge G3 measures the hydrogen pressure after expansion, which in normal operation is 10-15 nsig. The Dewar vessel is protected by a safety valve (not

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(20) Ahlberg, J. E. Estermann, I., and Lundberg, W. O., Rev. Sci. Instruments 8, 422 (1937).

shown) connected to G3 which is set to blow at 50 psi.

A bourdon-type vacuum gauge in the pumping line L to Pot N2 permits the pressure in Pot N2 to be measured. A Kerotest diaphragm-type valve in the pumping line allows the pressure in this pot to be maintained at the desired value.

Four copper-constantan thermocouple junctions (B&S No. 36 double nylon enameled wire) T1, T2, T3, and T4 permit the temperatures in various parts of the liquefier to be measured. Junctions T1 and T2 are soldered to the 1/8" O.D. x 0.035" wall copper tube which serves as the high pressure line in Pot N1. When the nitrogen level in N1 falls below the first turn of the cooling coil F1, a temperature rise is indicated by T2 due to the fact that the incoming high pressure gas is considerably warmer than 77° K. The liquid level in this pot may therefore be maintained by means of these two thermocouples.

Provision has been made for thawing out both the expansion valve V and the heat exchanger X. This is accomplished by directing a stream of warm hydrogen gas against the body of the expansion valve. This gas is admitted to the liquefier through a 0.040" O.D. x 0.010" wall Cupro-nickel capillary tube (visible in Figure 5, but not shown in Figure 6) which passes along the outside surface of both Pots N1 and N2. This device is of great help in rapidly warming up the expansion valve and heat exchanger X, an almost immediate response being indicated by thermocouple T4. The small heat capacity of the parts involved permits a rapid return to hydrogen liquefaction conditions when expansion is resumed.

## 2. Construction Details.

A more detailed description of the materials and the method of construction may be of interest. Certain of these details are shown in Table I, II, and III of Appendix B.

The materials of construction consist primarily of Cupro-nickel<sup>21</sup> (30% Ni, 70% Cu), copper, and brass tubing. All tubes passing through the brass and plates A-A, B-B, C-C, and D-D, with the exception of the copper high and low pressure hydrogen lines, are Cupro-nickel. The two nitrogen pots N1 and N2 were made of the 30% copper-nickel alloy material<sup>22</sup>. Longitudinal strains were thus minimized, and the low thermal conductivity of this alloy was used to advantage.

All joints and seals were made using either 60 Pb-40 Sn solder or "Easy-Flo" silver brazing alloy. All joints at sections A-A, B-B, C-C, and D-D were soft-soldered, with the exception of the joint between plate D-D and N2 which was brazed. All joints in the high pressure hydrogen circuit were brazed and tested for leaks at 2000 psi before final assembly. The joints in the low pressure hydrogen line are for the most part made with soft solder.

The joint between the brass tube which surrounds the Dewar vessel and the plate which supports the liquefier (compare Figures 4 and 5) is a soft-solder seal. This seal can be broken quite easily, when necessary, by heating the joint simultaneously with two small air-gas hand torches.

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(21) Obtained from Superior Tube Co., Norristown, Pa.

(22) Made available to us by Dr. D. H. Andrews, The Johns Hopkins University, to whom we wish to express our thanks.



The main heat exchanger was modeled after the so-called Nelson "twisted tube" heat exchanger<sup>23</sup>, which has been used successfully by others. The present design, as stated in the general description, is modeled after one proposed by Mr. William Asher of The Johns Hopkins University Low Temperature Laboratory. The twisted tube, which constitutes the high pressure side of the exchanger, was made by first flattening a 1/8" O.D. x 0.010" wall well-annealed Cupro-nickel tube to a thickness of 0.088" for a length of 30 inches by passing through a set of hand rolls. About 3 inches was left round at either end and the ends were soft-soldered to brass plugs. The plugs were then clamped between the head and tail stocks of a lathe. The flattened portion of the tube was then twisted, with the tail stock locked in position, until the entire flattened portion had assumed a spiral form. A pitch of 20 turns per foot was obtained in this manner. The effective diameter of the finished spiral was 0.164 inches. This fitted easily into a 3/16" O.D. x 0.010" wall well-annealed Cupro-nickel tube (I.D. = 0.167") which was to serve as the outside wall of the exchanger.

Pieces of 1/32" 50-50 solder wire were wrapped in the grooves of the spiral, a light coat of flux applied, and the whole slipped into the 3/16" tube. The length of the 3/16" tube was such that the spiral portion protruded about 1/4" on each end. This was done to reduce the pressure drop which might otherwise be present if the round section of the 1/8" tube came at the ends. The assembly was then heated in a tube furnace to about 220° C., turned in a vertical position, and the excess flux and solder forced out by the application of nitrogen gas under low

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(23) Bichowsky, F. R., loc. cit.

pressure.

When the soldering was complete, the exchanger was thoroughly washed with carbon tetrachloride, water, and acetone to remove all flux. The assembly was then wound on a 2-1/8" mandrel without any difficulty.

This twisted tube heat exchanger has proved to be considerably more efficient than an earlier one (See Progress Report No. 5, August 1, 1947) made by soft-soldering a flattened 1/8" O.D. x 0.010" wall Cupro-nickel tube 30 inches long, (thickness after flattening was 0.061"), between two round tubes of the same kind. After three runs the flattened high pressure tube was found to have become more nearly round, having a thickness of 0.066". This latter construction was used for the two-turn exchanger, E3, however.

The liquid hydrogen transfer system is shown in schematic detail in Figure 7 of Appendix A. It consists essentially of a Cupro-nickel tube "a" surrounded by a vacuum jacket formed by the tubes "b" and "d". The materials used have been listed in Table III of Appendix B. Flow of liquid hydrogen is controlled by the valve V, actuated by the stem S. The valve body is made of brass, the needle of monel. All joints in the liquid hydrogen line are brazed with "Easy-Flo"; with a few exceptions, all joints in the vacuum jacket were soft-soldered.

### 3. Operating Characteristics of the Liquefier.

Six runs of varying duration have been made with the hydrogen liquefier. The runs of July 3, July 25, and August 1 were made with the flattened tube heat exchanger, while those of September 5, 11, and 22 were made with the twisted tube exchanger. Unfortunately, the runs of September 5 and 11 yielded only incomplete information, due to the use of unsuspectedly impure hydrogen gas which resulted in plugging difficulties in the

liquefier. The run of September 22 yielded very good results.

The liquefier has given trouble-free performance except when insufficiently pure gas was used. The expansion valve needed only occasional adjustment as the pressure in the cylinders fell. The hydrogen transfer system worked smoothly. The consumption of nitrogen was not found to be excessive. After liquefaction began, the upper nitrogen pot N1 required filling about once every 12-15 minutes; the lower pot N2 required filling about once per hour.

From an analysis of all the runs to date, the composite run given in Table IV of Appendix B has been prepared. The production rate is essentially that observed in the run of September 22. It is believed that this table represents a fairly accurate evaluation of the performance of the liquefier.

The rate of production of liquid hydrogen was measured as follows: The liquefier was first drained of all liquid hydrogen and then allowed to run for a period of 20-30 minutes. At the end of this time, the liquid hydrogen was transferred from the liquefier to a deep Dewar vessel which already contained liquid hydrogen from a previous transfer. The increase in height of the liquid level was measured by means of a thermocouple probe surrounded by an electrical heater. This method permitted measurement of the level to an accuracy of about 1/8". The production rate quoted in the summary of Table IV of Appendix B was measured in this fashion. The actual production rate in the liquefier is somewhat greater than that measured by this collection procedure since losses are experienced due to transfer and to the pressure drop at the transfer valve.

A calculation of the efficiency of liquefaction has been made from the volume of liquid hydrogen collected and the drop in pressure of the cylinders during the same period. In this calculation the volume of the standard hydrogen cylinder was taken as 1.528 ft.<sup>3</sup> The actual average efficiency in the range 1900 to 1200 psi was found to be 10%. If transfer losses, etc., are taken into account, this may be raised to perhaps 12 or 13%. In this run the temperature of the lower nitrogen was about 66° K. as determined from the vapor pressure of the nitrogen measured when the pump was shut off. The average theoretical efficiency of liquefaction<sup>24,25</sup> in this pressure range is 22% at  $T = 66^{\circ}$  K. and 16.5% at  $T = 77.3^{\circ}$  K.

It remains to be seen how the efficiency of liquefaction is affected by flow rate.

### C. The Helium Cryostat.

The helium cryostat which is being built (and is now nearing completion) is modeled after one built by Dr. F. H. Horn<sup>26, 27</sup> and the writer. This cryostat utilizes design features well-tested in the very low temperature field.<sup>28</sup>

The liquid helium is produced within the cryostat in two separate processes. The main charge of liquid helium is produced by suddenly releasing the pressure of high pressure (say 2500 psi) helium gas, previously cooled to about 12° K. by the use of solid hydrogen, contained in a thick-walled copper vessel. This vessel is suspended in an evacuated space to decrease heat leak to it. The work done by the helium gas on expanding results in sufficient cooling so that a considerable amount of liquid

(24) Johnston, H. L., Bezman, I. I., and Hood, C. B., J. Am. Chem. Soc., 68, 2367 (1946).

(25) Keyes, Gerry, and Hicks, loc. cit.

(26) Horn, F. H., loc. cit.

(27) Horn and Ziegler, loc. cit.

(28) Simon, F., Actes du VII<sup>e</sup> Congres International du Froid, Vol. II, p. 367 (1937).

helium is obtained in the copper vessel. Under the conditions mentioned, a copper vessel having a volume of 100 cc. will be about 70 per cent filled with liquid helium.

The experimental chamber containing the samples to be investigated is suspended from the above-mentioned copper vessel. Liquid helium is condensed in the experimental chamber by passing helium gas at 15-30 psi through a tube wound about the copper vessel and connected at its lower end to the experimental chamber. This process results in the evaporation of an equivalent amount of liquid helium from the copper vessel. The advantages of this lower experimental chamber are twofold: (1) the experimental chamber, being suspended from the copper vessel whose temperature is  $4.2^{\circ}$  K. (the normal boiling point of helium), is thermally protected so that a lower temperature may be reached for a given pumping capacity than would be possible if the copper vessel were used as the experimental chamber, and (2) the samples may be placed inside the experimental chamber and hence in direct contact with the cooling medium, a procedure which is not feasible with the heavy-walled copper container.

The experimental chamber is so constructed that measurements of magnetic induction may be made on powdered samples and electrical resistance measurements can be made on materials obtainable in wire form.

#### D. The Helium Cycle.

Liquid helium can be made by the method outlined above (the Simon expansion method) using helium pressures available in commercial tanks (i.e., 2000 psi). However, the percentage yield of liquid helium increases

considerably with increasing pressure. It is, therefore, desirable to have a helium compression system for raising the pressure of the purified helium gas to about 2800-3000 psi. Such a compression cycle, consisting of a compressor and gasometer, can also be used for recompressing low pressure helium gas not liquefied in the cryostat.

Considerable progress has been made in setting up such a helium compression cycle for obtaining purified helium gas at 3000 psi. The Ingersoll-Rand Model P 33 10 G three-stage air compressor, which was a component part of a Navy Torpedo Topping Compressor supplied to us, has been set up, fitted with a 10 H.P. electric motor, and instrumented for use with helium. A fifty-cubic foot rubberized fabric gas bag for use as a low pressure helium reservoir has been received. The helium purifying traps, similar in design to the charcoal traps used on the hydrogen purifier, are largely completed. Cylinders for the storage of the purified high pressure gas have been obtained.

#### E. The Electrical Measuring System.

The electrical measuring systems consist of (1) potentiometric means for measuring temperature using thermocouples and resistance thermometers and for the measurement of electrical resistance, and (2) a ballistic system for the measurement of magnetic induction. The electrical equipment for carrying out these measurements is now on hand. The equipment includes a Leeds and Northrup 100,000 microvolt White double potentiometer.

#### F. The Liquid Nitrogen Plant.

Considerable quantities of liquid air or nitrogen are required for carrying out very low temperature research on even a modest scale. Liquid

nitrogen is greatly to be preferred, due to its inertness and the resulting elimination of possible explosion hazards encountered with liquid air and, particularly, with liquid oxygen.

On October 1, 1946, when this project started, there was no source of liquid nitrogen in the Atlanta area, and liquid air could be obtained only in very limited amounts. The nearest sources of liquid nitrogen were in Birmingham, Alabama and Chattanooga, Tennessee--each somewhat over one hundred miles distant.

In view of these facts, the Office of Naval Research made available to the project a Linde Type Liquid Oxygen Generating Plant (Linde Model SM-LO-P270) for conversion to a liquid nitrogen producing plant. The major components of this plant arrived from the Norfolk Naval Shipyard on March 17, 1947. The plant, which had been used, was found to lack many parts essential to its initial operation. Subsequently, a considerable number of the missing and necessary spare parts peculiar to the plant were received.(May 29, 1947). Further efforts by the Plant Facilities Section of the Office of Naval Research to locate the remainder of the missing and necessary spare parts was without avail. It was finally decided to send to us another used plant of the same description, so that by combining the two used plants one complete plant could be obtained. At the present time this second plant has not yet arrived.

While efforts to locate the missing parts were proceeding, the plant was set up in space provided in a new addition to the Chemical Engineering Building. Figure 8 of Appendix 1 shows the floor plan of this space, which amounts to more than 1000 square feet. The two major units of the plant, namely, the compressor--100 H.P. motor combination unit--and the

liquid oxygen generator, have been mounted on their bases. Three 50-KVA 2300/2400 - 120/240, 60 cycle single phase transformers for supplying power to the plant were obtained through the efforts of the Plant Facilities Section. These have been installed.

A small cooling system for supplying cooling water at the rate of 30 gallons per minute to the compressor was designed and installed. The cost of this cooling system, other than design and supervision, was borne by the Chemical Engineering Department. The system was so designed that it could be used by the Unit Operations Laboratory in the Chemical Engineering Department when it was not being used by the liquid nitrogen plant. Figure 9 (Appendix A) gives a schematic view of the cooling system. Figure 10 (Appendix A) is a photograph of the Marley #105W redwood atmospheric cooling tower which was mounted on the roof of the Chemical Engineering Building.



## VI. RARE EARTH METALS AND COMPOUNDS

Progress to date in the procurement and preparation of rare earth metals and compounds has been directed largely toward procurement and spectrographic analysis of the materials obtained. Dr. W. M. Spicer, Professor of Chemistry, has undertaken the work of making these analyses, using the ARL-Dietert grating spectrograph with a dispersion of  $7 \text{ \AA}$  per mm. The instrument used is an improved model of that described by Hasler<sup>29</sup> and Lindhurst. The copper spark method<sup>30</sup> was employed. The wave length range covered in these tests was 2250-4350  $\text{\AA}$ .

Samples of lanthanum, cerium, neodymium, and praseodymium metals, obtained from the Cooper Metallurgical Laboratory, Division Acme Aluminum Alloys, Inc., 2135 Columbus Road, Cleveland 13, Ohio, are being analyzed. Preliminary studies of the neodymium metal, using 99.75% pure neodymium oxide,  $\text{Nd}_2\text{O}_3$ , obtained from the Jarrell-Ash Company, 165 Newbury Street, Boston 16, Massachusetts (Hilger's spectroscopically standardized material) as a standard, show that somewhat over 0.5% lanthanum is present in this material in addition to the 2.7% iron reported by the vendor. Samarium, gadolinium, yttrium, and praseodymium are present in amounts greater than 0.1%, but less than 0.5%.

Apparatus and equipment for preparing the pure rare earth metals and compounds are being assembled. Efforts to obtain pure rare earth materials through the Atomic Energy Commission are contemplated.

- - - -

(29) Hasler and Lindhurst, Metal Progress 30, 59-63 (1936).

(30) Fred, Nachtrieb, and Tomkins, Journal of the Optical Society of America 37, 279-288 (1947).

## VII. NEW RESEARCH QUARTERS

In July, 1946, ground was broken for a new addition to the research facilities of the Engineering Experiment Station. About 1600 square feet of space, most of it laboratory space, was set aside for a Low Temperature Laboratory. At that time it was hoped that occupancy of the building could be obtained about March, 1947. Circumstances beyond our control prevented this, with the result that the space did not become available until October 21, 1947.

Figure 11 of Appendix A shows a floor plan of the new laboratory. The low temperature work will be carried out primarily in the two rooms marked "Experimental Low Temperature Laboratory" and the "Helium Compressor Laboratory". All electrical measurements pertaining to the cryostats will be made in a central instrument room. Provision is made for connecting apparatus in any room to the central instrument room. The rare earth work will be carried out in the chemical laboratory designated "Sample Preparation Room".

Considerable effort has been directed toward plans for setting up in these new quarters the equipment which has been built. These include the designing of special fixtures such as: (1) tables, galvanometer supports, optical systems, etc., for the instrument room; (2) liquefier and cryostat supports, and (3) a ventilation system for the experimental room where the liquid hydrogen will be used. Provision is being made for approximately one change of air per minute in this room, which has a volume of 3000 cubic feet. Heating of this room in winter presents a problem because our proposed movement of air (3000 CFM) greatly exceeds

the air brought into the room through the hot air heating system. It was therefore necessary to plan for the installation of a special heating unit, using steam coils and thermostatic control for this room which will bring in fresh air from outside the building. The necessary heating and ventilating units and accessories have been ordered.

### VIII. PERSONNEL

During the past year the following individuals have been associated with the project on either a part-time or full-time basis:

| <u>Name</u>            | <u>Position</u>        | <u>Time</u> |
|------------------------|------------------------|-------------|
| Dr. W. T. Ziegler      | Director               | 2/3 time    |
| Mr. W. A. Phillips     | Research Assistant     | full-time   |
| Dr. W. M. Spicer       | Professor of Chemistry | part-time   |
| Dr. J. E. Rhodes       | Asst. Prof. of Physics | part-time   |
| Mr. Oswald Newell, Jr. | Graduate Student       | part-time   |
| Mr. L. R. Daniel       | Graduate Student       | part-time   |
| Mr. W. C. Giegold      | Student                | part-time   |
| Mr. J. M. Ziegler      | Student                | part-time   |
| Mr. George Cook        | Machinist              | part-time   |
| Mr. F. A. Peede        | Student                | part-time   |

Dr. W. M. Spicer of the Chemistry Department has carried out the spectrographic analyses of the rare earth materials. Dr. J. E. Rhodes of the Physics Department has aided in the design of the electrical equipment to be used for making the magnetic measurements for detecting superconductivity.

Messrs. Newell and Daniel are graduate students working towards the Master's degree in Chemical Engineering. They are doing their thesis work in helping with the construction of the hydrogen liquefier and helium cryostat, respectively. Mr. Phillips is doing his Master's thesis work in Chemical Engineering on the project by setting up the liquid oxygen plant and its associated controls.

Respectfully submitted:

W. T. Ziegler  
Project Director

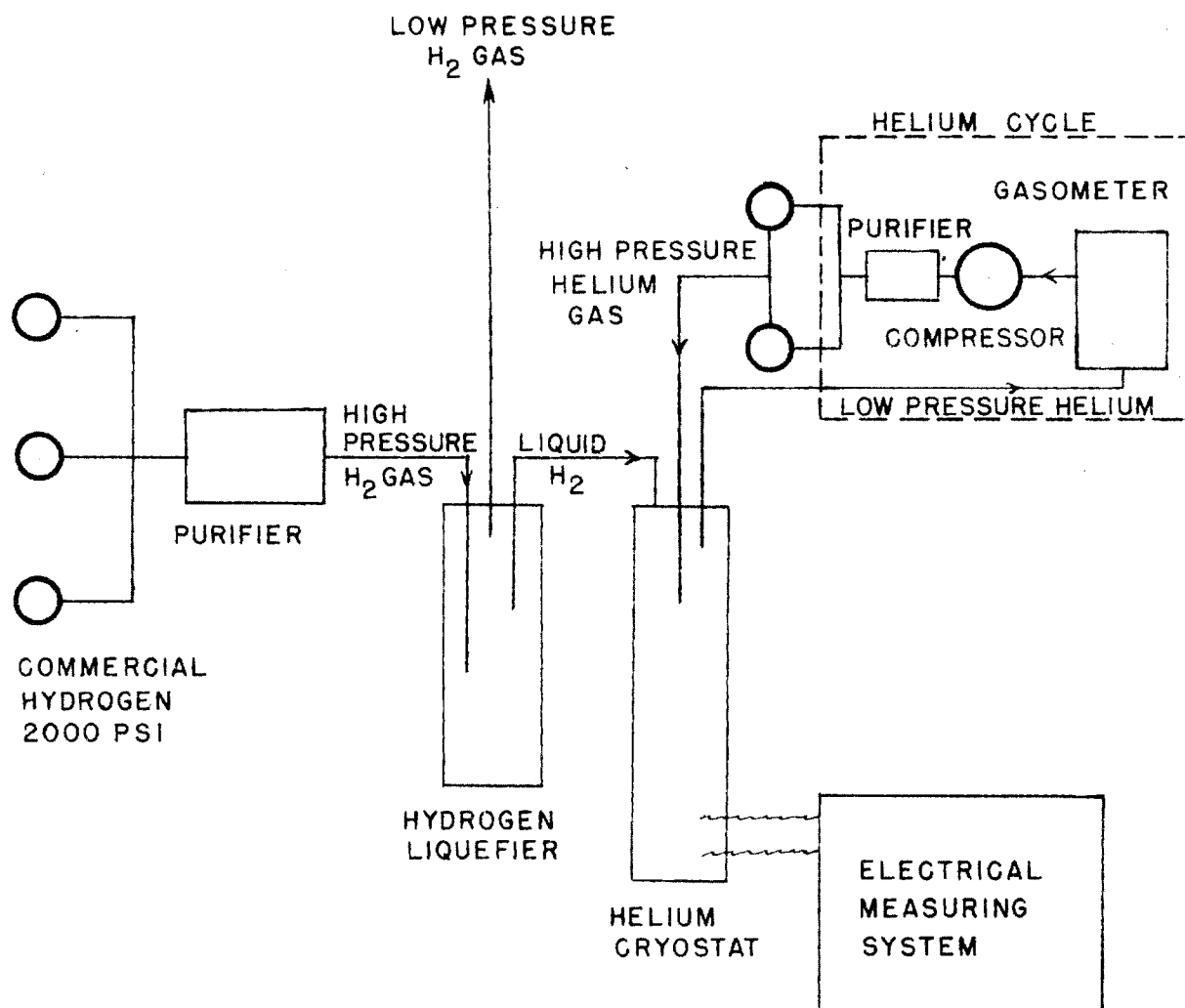
Approved:

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Gerald A. Rosselot  
Director

IX. APPENDIX A

- Figure 1. Schematic Arrangement of Low Temperature Apparatus and Associated Equipment
- Figure 2. Front View of High Pressure Hydrogen Gas Purifier
- Figure 3. Detail of High Pressure Purifier Traps
- Figure 4. Rear View of Hydrogen Liquefier
- Figure 5. Hydrogen Liquefier Proper
- Figure 6. Schematic Detail of Hydrogen Liquefier
- Figure 7. Liquid Hydrogen Transfer Valve
- Figure 8. Liquid Oxygen Plant Layout
- Figure 9. Diagram of Cooling Water System for Air Compressor of Liquid Oxygen Plant
- Figure 10. View of Cooling Tower for Cooling Water System
- Figure 11. Layout of Low Temperature Laboratories



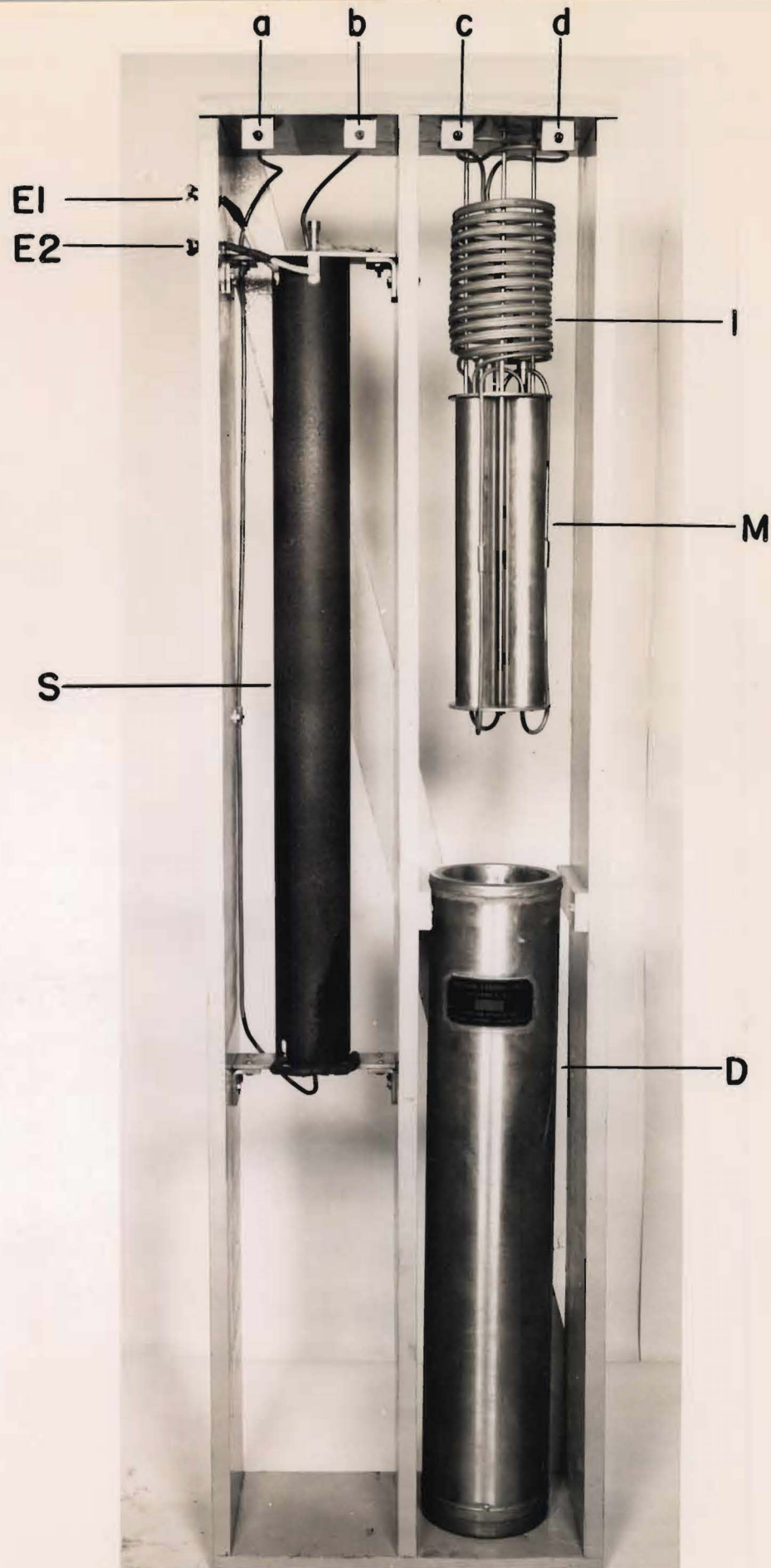


Figure 2. Front View of High Pressure Hydrogen Gas Purifier

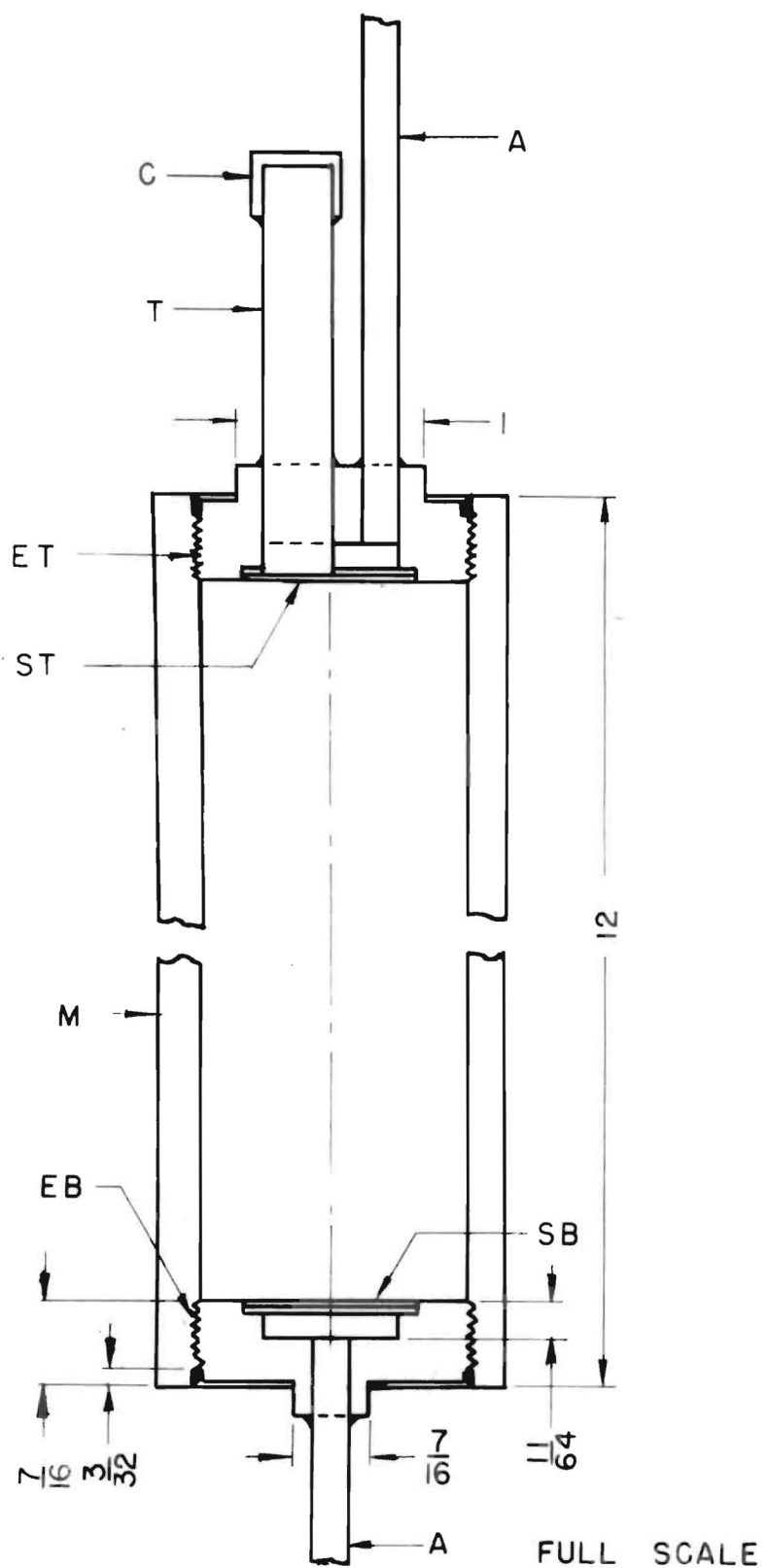


FIGURE 3 DETAIL OF HIGH PRESSURE PURIFIER TRAPS



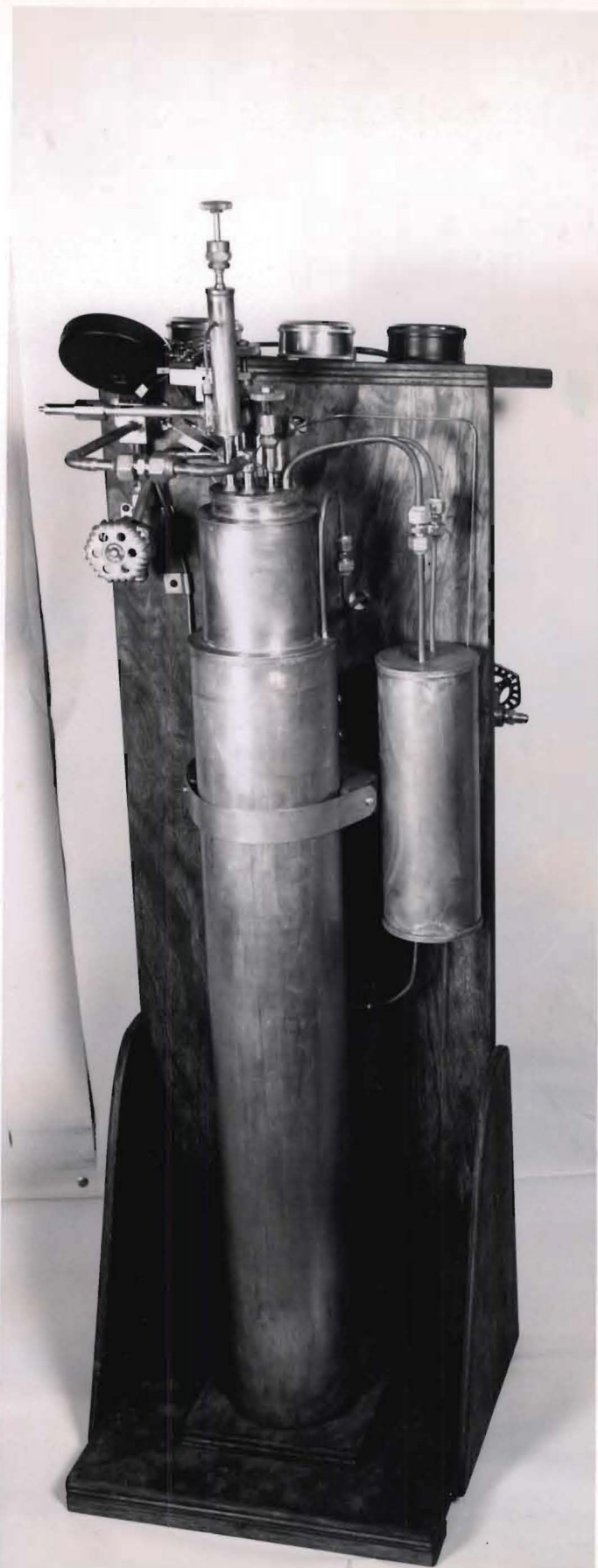


Figure 4. Rear View of Hydrogen Liquefier

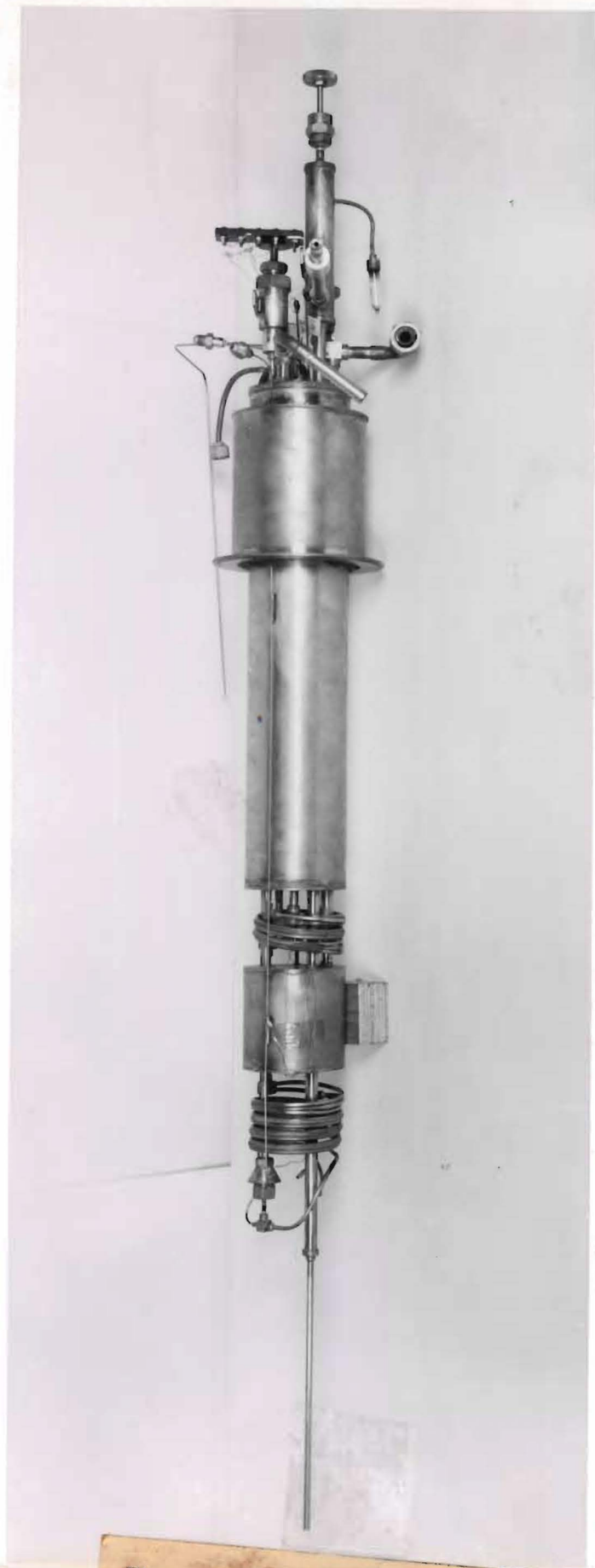


Figure 5. Hydrogen Liquefier Proper

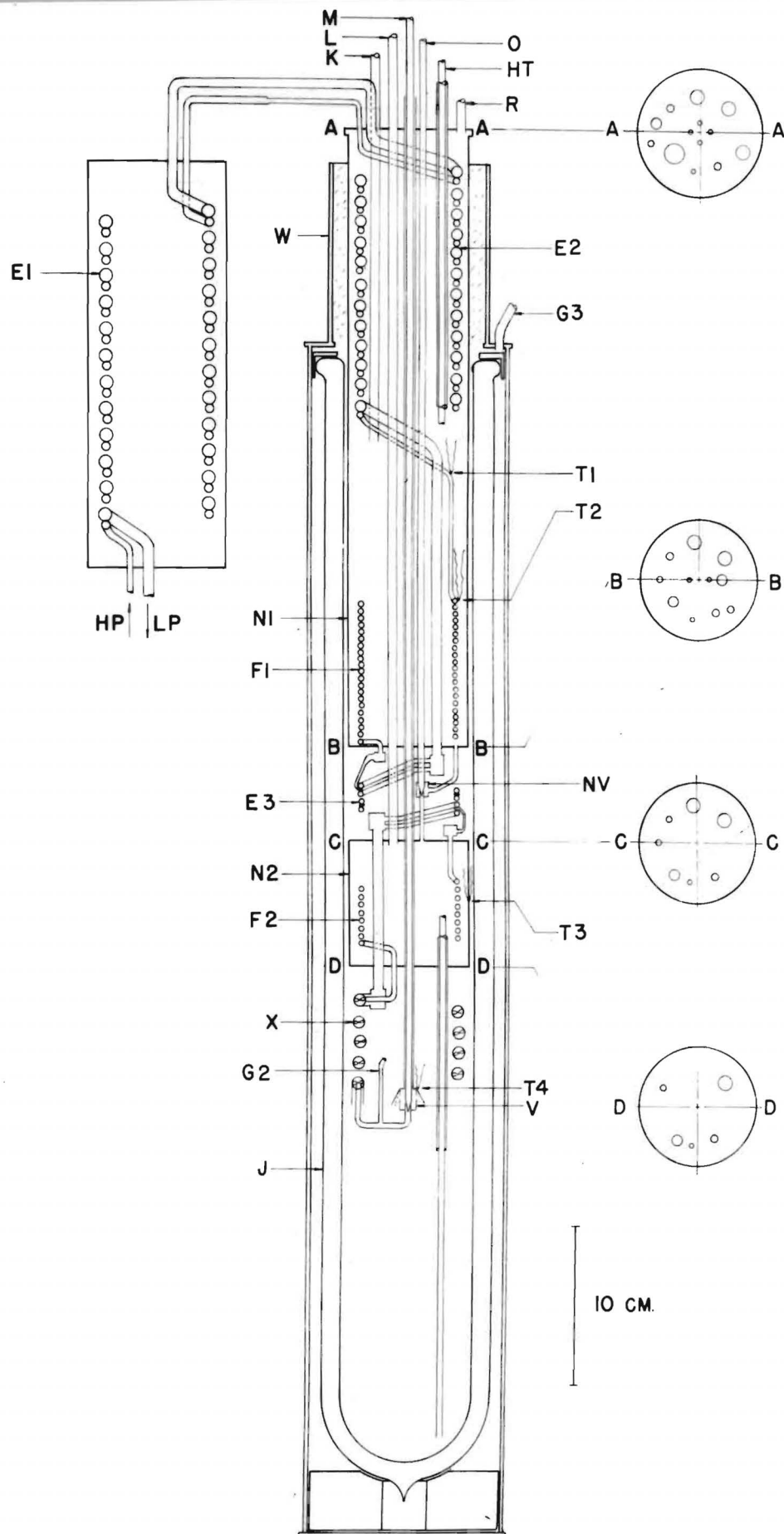


Figure 6

SCHEMATIC DETAIL OF HYDROGEN LIQUEFIER

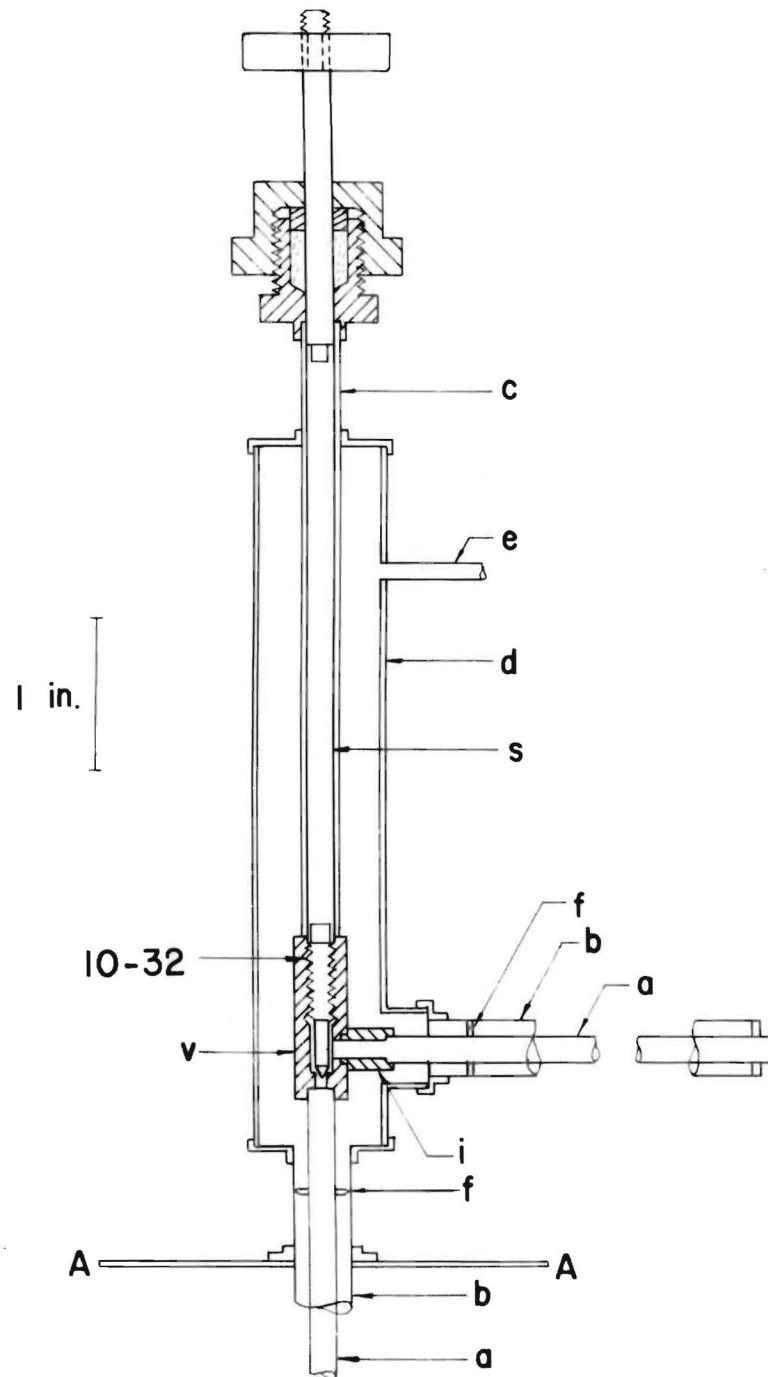
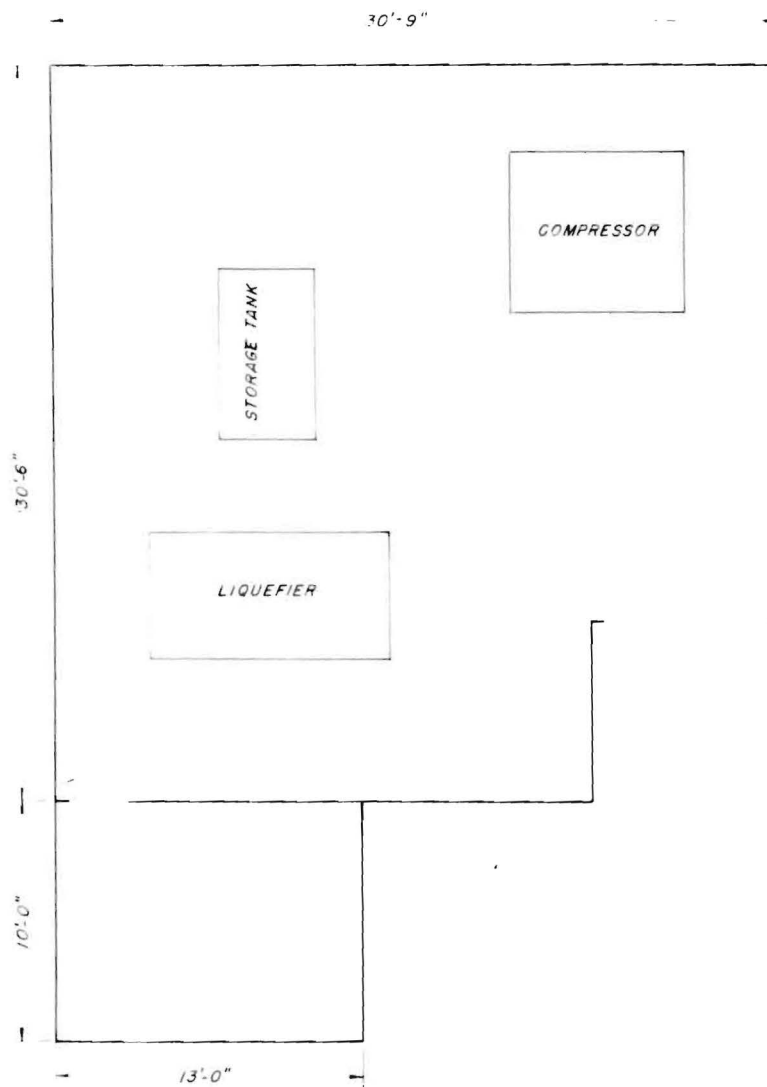


FIGURE 7 LIQUID HYDROGEN TRANSFER VALVE



LIQUID OXYGEN PLANT LAYOUT

Figure 8

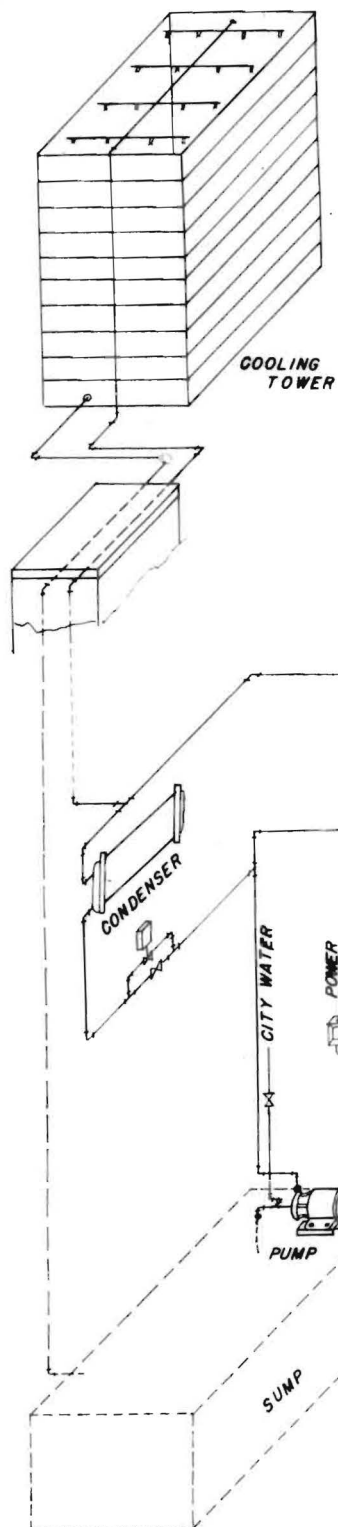
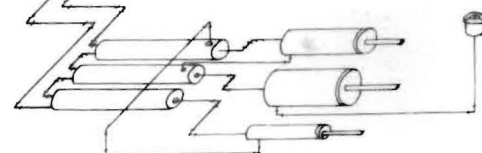


Figure 9

DIAGRAM COOLING WATER SYSTEM  
FOR CHEM. ENG. BUILDING

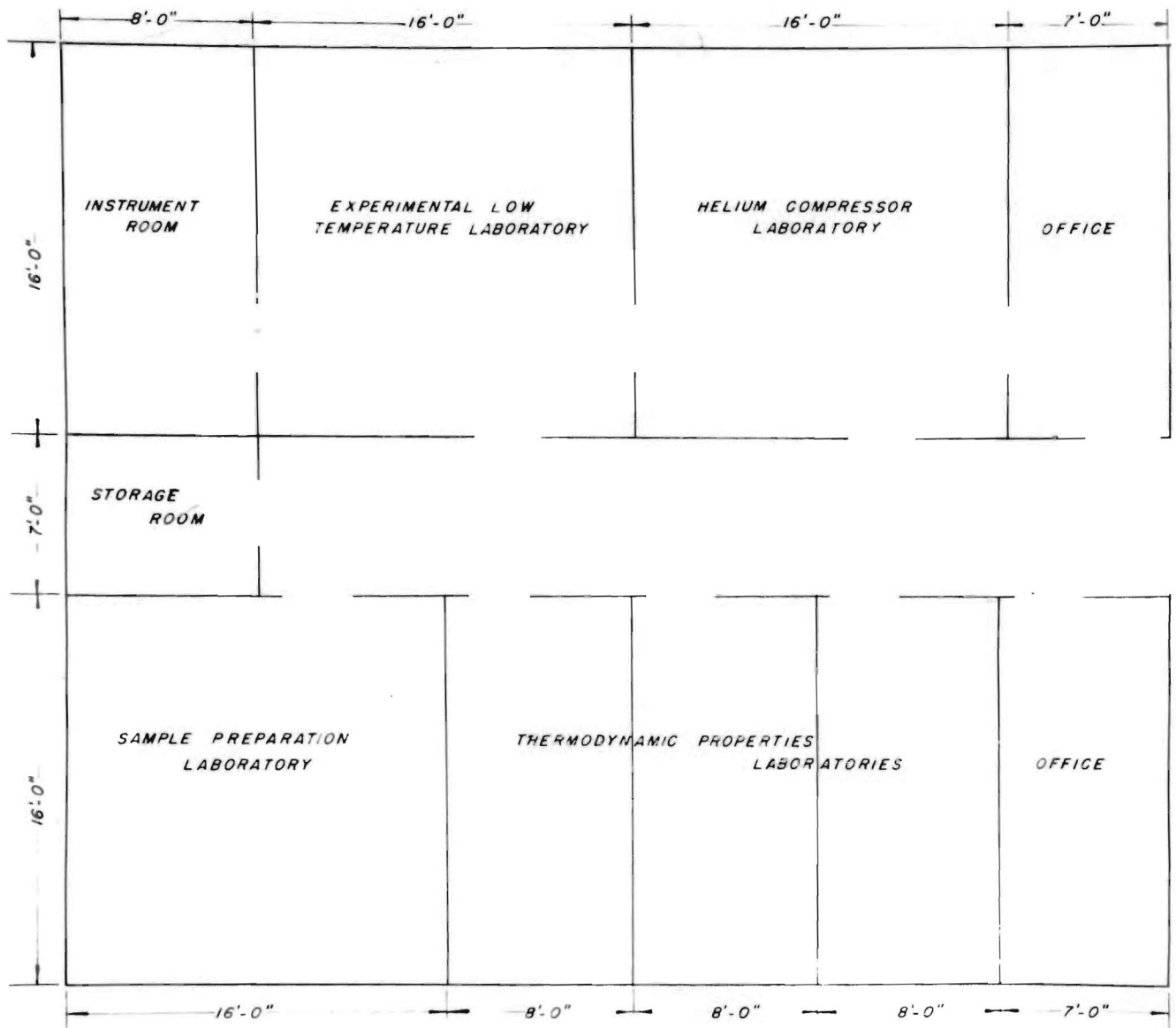


AIR COMPRESSOR LIQUID NITROGEN PLANT



Figure 10. View of Cooling Tower for Cooling Water System





LAYOUT LOW TEMPERATURE LABORATORIES

Figure 11



X. APPENDIX B

List of Progress Reports

- |            |  |
|------------|--|
| Table I.   | Details of Construction of Cooling Coils and Heat Exchangers of Hydrogen Liquefier |
| Table II.  | Specifications for Parts of Hydrogen Liquefier                                     |
| Table III. | Construction Materials for Hydrogen Transfer Valve.                                |
| Table IV.  | Composite Run of Hydrogen Liquefier  |

X. APPENDIX B

A List of Progress Reports

Progress Reports on Project No. 116-18, Navy Department, Office of Naval Research, Contract N6-ori-192, Task Order I. Investigation of Fundamental Properties of the Elements and Their Compounds Including the Rare Earths at Very Low Temperatures with Particular Emphasis upon Superconductivity, by W. T. Ziegler.

1. Progress Report No. 1, November 27, 1946.
2. Progress Report No. 2, January 28, 1947.
3. Progress Report No. 3, March 31, 1947.
4. Progress Report No. 4, May 31, 1947.
5. Progress Report No. 5, August 1, 1947.
6. Progress Report No. 6, September 30, 1947.

TABLE I  
DETAILS OF CONSTRUCTION OF COOLING COILS AND HEAT EXCHANGERS  
OF HYDROGEN LIQUEFIER

| Symbol             | Description  | Material* | Tubing                              |  | Length<br>in<br>Feet | Number<br>of<br>Turns | Diameter<br>of Man-<br>drel used<br>for Wind-<br>ing in<br>Inches | Final<br>I.D. of<br>Coil<br>in<br>Inches |
|--------------------|--------------|-----------|-------------------------------------|--|----------------------|-----------------------|---|--|
|                    |              |           | Outside<br>Diameter<br>in<br>Inches | Wall<br>Thick-<br>ness<br>in<br>Inches |                      |                       |   |  |
| Cooling<br>coils   | F1 H.P. gas  | copper    | 1/8                                 | 0.032                                  | 14                   | 21                    | 2-1/4   | 2-5/16                                   |
|                    | F2 H.P. gas  | copper    | 1/8                                 | 0.032                                  | 5.3                  | 8                     | 2-1/4   | 2-5/16                                   |
| Heat<br>exchangers | E1 H.P. gas  | copper    | 3/16                                | 0.035                                  | 10                   | 16                    | 2-1/4   | 2-5/16                                   |
|                    | L.P. gas     | copper    | 1/4                                 | 0.032                                  |                      |                       |   |  |
|                    | E2 H.P. gas  | copper    | 1/8                                 | 0.032                                  | 9.5                  | 14.5                  | 2-1/4   | 2-5/16                                   |
|                    | L.P. gas     | copper    | 1/4                                 | 0.032                                  |                      |                       |   |  |
|                    | E3 H.P. gas  | Cu-Ni     | 1/8**                               | 0.010                                  | 1.3                  | 2                     | 2-1/4   | 2-3/8                                    |
|                    | L.P. gas (2) | Cu-Ni     | 1/8                                 | 0.010                                  |                      |                       |   |  |
| X                  | H.P. gas     | Cu-Ni     | 1/8***                              | 0.010                                  | 2.5                  | 4                     | 2-1/8   | 2-9/32                                   |
|                    | L.P. gas     | Cu-Ni     | 3/16                                | 0.010                                  |                      |                       |   |  |

\* All tubing was of "dead-soft" temper.

\*\* Before flattening.

\*\*\* Before twisting.

TABLE II  
SPECIFICATIONS FOR PARTS OF HYDROGEN LIQUEFIER

| <u>Symbol</u> | <u>Description</u>     | <u>Material</u> | <u>Tubing</u>         |                                 | <u>Length in Inches</u> |
|---------------|------------------------|-----------------|-----------------------|---------------------------------|-------------------------|
|               |                        |                 | <u>O.D. in Inches</u> | <u>Wall Thickness in Inches</u> |                         |
| N1            | Upper pot              | Cu-Ni (h)*      | 3                     | 0.042                           | 15                      |
| N2            | Lower pot              | Cu-Ni (h)       | 3                     | 0.042                           | 3                       |
| K             | N1 filling tube        | Monel (h)       | 1/2                   | 0.010                           | 8                       |
| L             | N2 vacuum line         | Cu-Ni (h)       | 3/8                   | 0.010                           | 18-1/2                  |
| M             | Expansion valve stem   | Cu-Ni (h)       | 5/32                  | 0.020                           | 26                      |
|               | Sleeve tube for stem   | Cu-Ni (h)       | 3/16                  | 0.010                           | 25-1/4                  |
| O             | Stem for NV            | Cu-Ni (h)       | 5/32                  | 0.020                           | 16-1/2                  |
|               | Sleeve tube for stem   | Cu-Ni (h)       | 3/16                  | 0.010                           | 16-1/2                  |
|               | Tube between N1 and NV | Cu-Ni (h)       | 1/4                   | 0.010                           | 1                       |
|               | Tube between NV and N2 | Cu-Ni (h)       | 1/8                   | 0.010                           | 1-1/2                   |
| HT            | Hydrogen transfer tube |                 |                       |                                 |                         |
|               | Vacuum jacket          | Cu-Ni (h)       | 3/8                   | 0.010                           | 28-1/2                  |
|               | Inner tube             | Cu-Ni (h)       | 3/16                  | 0.010                           | 36-1/2                  |
| R             | N1 exhaust             | Cu-Ni (h)       | 3/8                   | 0.010                           |                         |
| G3            | Dewar vessel pressure  | Copper (a)      | 3/16                  | 0.032                           | 2                       |
|               |                        | (Continued)     |                       |                                 |                         |

\*The letters (a) and (h) refer to "dead-soft" and "hard-drawn" temper, respectively.

TABLE II (Cont'd)  
SPECIFICATIONS FOR PARTS OF HYDROGEN LIQUEFIER

| <u>Symbol</u> | <u>Description</u>    | <u>Material</u> | <u>Tubing</u>         |                                 | <u>Length in Inches</u> |
|---------------|-----------------------|-----------------|-----------------------|---------------------------------|-------------------------|
|               |                       |                 | <u>O.D. in Inches</u> | <u>Wall Thickness in Inches</u> |                         |
| W             | Brass dome            | Brass           | 4                     | 0.065                           | 4-3/8                   |
| None          | Circuit for T1 and T2 | Cu-Ni (h)       | 1/16                  | 0.010                           | 12                      |
| None          | Conduit for T3 and T4 | Cu-Ni (h)       | 1/16                  | 0.010                           | 17                      |
| J             | Dewar vessel          | Pyrex           |                       |                                 |                         |
|               | Outer tube            |                 | 100 (mm)              | 2.4 (mm)                        | 30                      |
|               | Inner tube            |                 | 85 (mm)               | 2.4 (mm)                        | 29                      |

\*The letters (a) and (h) refer to "dead-soft" and "hard-drawn" temper, respectively.

TABLE III  
CONSTRUCTION MATERIALS FOR HYDROGEN TRANSFER VALVE

| <u>Symbol</u> | <u>Material</u>          | <u>Dimensions</u>        |
|---------------|--------------------------|--------------------------|
| a             | Cupro-nickel             | 3/16" O.D. x 0.010" wall |
| b             | Cupro-nickel             | 3/8" O.D. x 0.010" wall  |
| c             | Cupro-nickel             | 1/4" O.D. x 0.010" wall  |
| d             | Brass                    | 7/8" O.D. x 0.035" wall  |
| e             | Copper (evacuation line) |                          |
| f             | Bakelite (spacers)       |                          |
| i             | Monel insert             |                          |
| s             | Cupro-nickel             | 5/32" O.D. x 0.020" wall |
| v             | Brass                    |                          |

TABLE IV  
COMPOSITE RUN OF HYDROGEN LIQUEFIER

| TIME (hours) | OPERATION  |
|--------------|--|
| 0.00         | Three tanks on at 1900 psi. Began cooling charcoal traps of purifier with liquid nitrogen.                                   |
| 0.25         | Charcoal traps at liquid nitrogen temperature (6.2 liters required to cool and fill metal Dewar surrounding charcoal traps). |
| 0.27         | Began slow flow of hydrogen through liquefier. (1 cfm).  |
| 0.33         | Began transfer of liquid N <sub>2</sub> to Pot N1.   |
| 0.50         | Began transfer of liquid N <sub>2</sub> to Pot N2.   |
| 0.75         | Both pots full (2.0 liters liquid N <sub>2</sub> required). T4 reads 0.8 millivolt.  |
| 0.77         | H <sub>2</sub> flow increased to 4 cfm.  |
| 1.22         | T4 reads 6.7 millivolts liquefaction of hydrogen began. Tank pressure = 1500 psi. Flow rate: 3 to 4 cfm.                     |
| 1.9          | Tank pressure at 800 psi. Tanks replaced by three full cylinders at 1900 psi.  |
| 3.2          | Pressure in tanks at 700 psi. Run stopped.   |

#### SUMMARY

Total volume liquid hydrogen produced = 1.5 liters.  
Collection rate in external Dewar = 0.75 liter per hour at 3-4 cfm.  
Liquid hydrogen produced per set of three cylinders (1900 to 700 psi) = 0.9 liter.

Consumption of liquid nitrogen:

- (1) To cool charcoal traps = 6.2 liters.
- (2) To cool liquefier to hydrogen liquefaction temperature = 3.0 liters.
- (3) To produce 1.5 liters liquid hydrogen:
  - a. Purifier = 4.7 liters.
  - b. Liquefier = 4.4 liters.

Total nitrogen consumption = 18.3 liters.



Georgia School of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

PROGRESS REPORT NO. 7

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

CONTRACT NO. N6-ori-192, TASK ORDER I

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF THE  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

By

W. T. ZIEGLER

NOVEMBER 30, 1947

**GEORGIA SCHOOL OF TECHNOLOGY**

**THE STATE ENGINEERING EXPERIMENT STATION**

**ATLANTA, GEORGIA**

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NOVEMBER 30, 1947



## I. PROPOSAL FOR EXTENSION OF CONTRACT

A proposal for extending the contract under which the project is being carried out (Contract No. N6-ori-192, Task Order I) from October 1, 1947, to March 31, 1949, has been submitted to the Office of Naval Research. The following research problems have been proposed as objectives for the period indicated; in each case, particular emphasis will be placed on evidence for possible superconductivity of each substance investigated:

- (1) Completion of any unfinished work on praseodymium and neodymium metals and lanthanum hydride or nitride.
- (2) Reinvestigation of lanthanum and cerium metals for superconductivity.
- (3) Investigation of gadolinium metal for possible superconductivity.
- (4) Investigation of cerium hydride and nitride for possible superconductivity.
- (5) Investigation of such other rare earth metals as may be obtainable for possible superconductivity.

These research objectives are a continuation of the general intent of Task Order I of the above contract; namely, that the contractor shall carry out "research at very low temperatures upon the fundamental properties of the elements and their compounds including the rare earths, with particular emphasis upon superconductivity."

## II. NEW RESEARCH QUARTERS

During the past year, the construction of a new Research Annex has been under way, in which space for the setting up of the Low Temperature Laboratory in a permanent fashion was to be provided.

This space became available on October 21, 1947. It consists of 1,600 square feet, most of which is laboratory space. Hereafter the Project's research activities will be centered in this space, to which the transfer of equipment has been completed. The setting up of the chemical equipment for preparation of rare earth metals and the low temperature apparatus and accessory devices is well underway, along with the installation of special service lines. Considerable work remains to be done, however, before all phases of actual experimentation can begin.

### III. LIQUID NITROGEN PLANT

Work on the setting up of the liquid oxygen plant (Linde Model SM-LO-P270), which is to be converted to a liquid nitrogen producing plant, was continued. The three 50 kva 2300/2400 - 120/240, 60 cycle single phase transformers, for powering the 100 h.p. motor of the compressor, have been installed.

A shipping notice has not, as yet, been received for the parts still missing from this plant. However, notification was received (November 26, 1947) that such a shipment was being requested of the Bureau of Ships by the Office of Naval Research, Plant Facilities Section.

### IV. TRIPS

Dr. W. T. Ziegler attended the Third Cryogenic Conference, which was held under the sponsorship of the Office of Naval Research at Ohio State University on October 27 and 28, and reported upon the program of work at Georgia Tech. This report included a detailed description of the small hydrogen liquefier described in the last Progress Report (dated September 30, 1947).

Papers describing this hydrogen liquefier were also presented by Dr. Ziegler before recent meetings of the local sections of the American Chemical Society held in Chattanooga, Tennessee and Atlanta, Georgia.

Respectfully submitted:

W. T. Ziegler  
Project Director

Approved:

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Gerald A. Rosselot  
Director

Georgia School of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

PROGRESS REPORT NO. 8

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

CONTRACT NO. N6-ori-192, TASK ORDER I

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W. T. ZIEGLER

MAY 7, 1948

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## I. SUMMARY

A cryostat for carrying out experiments at liquid helium temperatures has been completed, and liquid helium has been produced.

Measurements have been made which make it appear that the sample of lanthanum metal tested underwent a superconducting transition at  $4.85 \pm 0.15^{\circ}\text{K}$ . in a field of 10-20 gauss.

The large liquid oxygen plant received for use on this project has been converted, for the time being, to a liquid air producing plant. This plant has been operated twice, once on April 27 and again on May 4. Certain adjustments in the plant were indicated. These preliminary tests were considered satisfactory even though the yield of liquid air was observed to be considerably below the rated yield of the plant.



## II. PROGRESS IN LOW TEMPERATURE RESEARCH

### A. Low Temperature Apparatus.

Considerable progress has been made on the construction and assembly of the low temperature apparatus since the last progress report (Progress Report No. 7, November 30, 1947) was issued.

The component parts of the helium cryostat, namely, the hydrogen liquefier, the helium cryostat proper and its accessories, and the electrical measuring systems have been completed and tested. The hydrogen liquefier has been described in a previous report (Progress Report No. 6, September 30, 1947). The helium cryostat, which contains apparatus for producing liquid helium by the Simon expansion method, will be described in a subsequent technical report. It is very similar in design and construction to one described by Horn and Ziegler<sup>1</sup>.

Figures 1 and 2 of the Appendix give two views of the low temperature assembly. In Figure 1 the hydrogen liquefier can be seen in the left center, with the helium cryostat (with case removed) in the lower center. The various controls for operating the liquefier and helium cryostat are located on the two

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(1) Horn, F. H. and Ziegler, W. T., Jour. Am. Chem. Soc. 69, 2762 (1947).



panel boards. The entire assembly is mounted on a raised platform (about four feet above floor level) to facilitate removal of the long glass Dewar vessel which surrounds the cryostat during operation.

Figure 2 gives a view of the high vacuum system used for evacuating the cryostat.

Figure 3 gives a view of the switchboard in the instrument room which is adjacent to the room containing the experimental apparatus. All electrical measurements relating to the cryostat are controlled from this switchboard.

Liquid helium was produced in the first test run on April 20 and again on April 29. All parts of the apparatus operated satisfactorily. Briefly, the expansion method for producing liquid helium works as follows. Helium gas is compressed and cooled in a container to the temperature of solid hydrogen. The container is then thermally isolated by means of an evacuated space. The cold high-pressure helium gas is then allowed to discharge through a small-bore tube to a low-pressure (1 atm.) space outside the cryostat. In so doing, the helium gas in the container does work, thereby reducing its temperature with the result that a considerable portion of the helium may remain behind in the container as a liquid.

The main helium reservoir in which the liquid helium is produced has a volume of  $101 \text{ cm}^3$ . In the run of April 20th,  $45 \text{ cm}^3$  of liquid helium was produced; in the run of April 29th,  $69 \text{ cm}^3$  was produced. These yields compare favorably with yields reported by Simon using the same temperature and pressure conditions.<sup>2</sup>

The yield of liquid helium produced in this expansion process is a major factor in determining the length of time available for experimentation in the range  $4.2^\circ\text{K}$  (normal boiling point of helium) and below. In the experiments of April 20th and April 29th, liquid helium temperatures were maintained for 1.4 and 2.5 hours, respectively. These proved adequate for carrying out a number of experimental tests for superconductivity.

The helium gasometer-compressor cycle for compressing and purifying helium gas to 3000 psi is nearly finished, and awaits only the installation of a relay before its final testing. The use of this higher pressure gas will enable still higher yields of liquid helium to be produced in the expansion process.

- - - - -  
(2) Keesom, W. H., Helium, Elsevier Publishing Company, Amsterdam, Holland, 1942. P. 160.

B. Superconductivity Studies.

Samples of pure lead and tin metals, together with a sample of lanthanum metal, labeled as containing 0.8% iron, were studied on April 20th and April 29th. Transitions into superconductivity were observed for all three metals. The lanthanum metal was obtained from the Cooper Metallurgical Laboratory, Acme Aluminum Alloys, Inc., Cleveland, Ohio.

The method of measurement is similar to that described by Horn and Ziegler<sup>3</sup>. In this method a d.c. pulse is sent through a primary coil, wound in the form of a solenoid, along the axis of which are located the samples. Each sample is surrounded by a secondary coil. In addition, there is an empty or standard secondary coil. The standard coil is connected to each sample in turn in such a manner that the e.m.f. induced in the coil surrounding a given sample opposes the e.m.f. induced in the standard coil. A variable inductance in the standard coil circuit outside the cryostat permits the e.m.f. in the standard coil circuit to be varied, with the result that a sensitive galvanometer in the secondary circuit can be made to show zero deflection. If such a balance is made for the sample in its normal

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(3) Horn and Ziegler, loc. cit.

state, then, when a sample becomes superconducting, the large change in permeability accompanying the transition causes an unbalance of the coils which is observed as a galvanometer deflection.

At the present time the calibration of the temperature scale is not complete. However, it appears that the sample of lanthanum metal tested undergoes a superconducting transition at  $4.85 \pm 0.15^{\circ}\text{K}$  in a field of 10-20 gauss. The transition appeared to be quite sharp, probably occurring over a range of less than  $0.1^{\circ}\text{K}$ .

Mendelssohn and Daunt<sup>4</sup> reported a transition temperature of  $4.71^{\circ}\text{K}$  for a sample of lanthanum containing 1% iron. Shoenberg<sup>5</sup> reported a superconducting transition in lanthanum, Hilger (7259), at a temperature above  $4.2^{\circ}\text{K}$ .

In addition to further studies on lanthanum metal, samples of cerium, neodymium, and praseodymium are on hand and will be tested for superconductivity in the near future.

- - - - -
- (4) Mendelssohn, K. and Daunt, J. G., Nature 139, 473, (1937).
  - (5) Shoenberg, D., Proc. Camb. Phil. Soc. 33, 577 (1937).

### III. LIQUID NITROGEN PLANT

On February 29, 1948, certain components of a second liquid oxygen producing plant (Linde Model SM-LC-P270) were received from Clearfield, Ogden, Utah, Naval Supply Depot under Buships Shipment Order No. 100510. These components were used to obtain parts necessary to complete an incomplete plant of the same type already on hand.

The original liquid oxygen plant has now been completely set up for operation as a liquid oxygen or liquid air producing unit, with the exception that a vacuum pump is still needed for the 150-gallon liquefied gas storage container. The lack of this pump will not hamper operations for the present.

Figures 4, 5, and 6 give three views of the liquid oxygen plant. Figure 4 is a view of the large air compressor which is powered by a 100 H.P. motor. Figure 5 is a view of the control panel of the liquefaction unit. Figure 6 is a rear view of the liquefaction unit. In Figure 6, the 150-gallon storage tank can be seen on the extreme left, while the temporary liquid transfer line can be seen extending into a 25-liter metal liquid air storage can. The expansion engine which produces the major portion of the refrigeration in this liquefaction cycle can be seen at the right center.



The plant has been operated twice as a liquid air producing plant, once on April 27th and again on May 4th. Both of these runs were made for the purpose of testing the plant and training the operators, rather than to obtain a large supply of liquid air. During the second run a production rate of at least 10 liters of liquid air per hour was achieved. Further experience with the idiosyncrasies of the plant, together with some additional mechanical work, is expected to increase the yield considerably.

Mr. W. A. Phillips has been largely responsible for the installation and testing of the plant. Mr. Phillips, who is employed full-time on the Project, is also enrolled as a graduate student in Chemical Engineering. He has selected as his thesis problem "The Erection of a Liquid Oxygen Producing Plant and Re-Design of This Plant to Produce Liquid Nitrogen." The design of the column which will be required will be finished about June 1st. It has not yet been decided whether this work of Mr. Phillips will be used as a basis for building the nitrogen column at Georgia Tech or whether an attempt will be made to have the column built elsewhere.

#### IV. PERSONNEL

At the present time the following individuals are employed by the project:

| <u>Name</u>        | <u>Position</u>    | <u>Time</u> |
|--------------------|--------------------|-------------|
| Dr. W. T. Ziegler  | Director           | 2/3 time    |
| Mr. W. A. Phillips | Research Assistant | full-time   |
| Mr. B. F. Smith    | Student            | part-time   |
| Mr. G. S. Baird    | Student            | part-time   |
| Mr. J. M. Ziegler  | Student            | part-time   |
| Mr. George Cook    | Machinist          | part-time   |


Mr. Oswald Newell, Jr. and Mr. L. R. Daniel, graduate students in Chemical Engineering, have helped with certain phases of the work. Mr. F. A. Peedo has graduated and left for other employment.

Two graduate students, one in chemistry and one in physics, will be added to the group for the summer months to aid in the research on the preparation of pure rare earth metals and compounds, as well as to assist in the low temperature program.

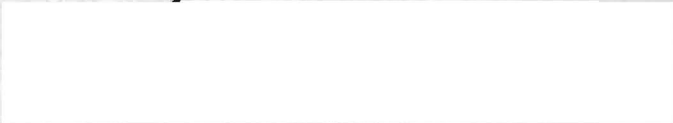
V. TRIPS

Dr. W. T. Ziegler attended the Cryogenics Conference, which was held under the sponsorship of the Office of Naval Research at Yale University on April 5 and 6, where he reported upon the work being carried out at Georgia Tech.

Respectfully submitted;

  
W. T. Ziegler,  
Project Director

Approved:

  
Gerald A. Rosselot,  
Director



VI. APPENDIX

- Figure 1. View of Helium Cryostat and Associated Apparatus
- Figure 2. View of High Vacuum System for Helium Cryostat
- Figure 3. View of Switchboard in Instrument Room for the Low Temperature Laboratory
- Figure 4. View of Air Compressor of Liquid Nitrogen Plant
- Figure 5. View of Control Panel of Liquefier of Liquid Nitrogen Plant
- Figure 6. Rear View of Liquefier of Liquid Nitrogen Plant

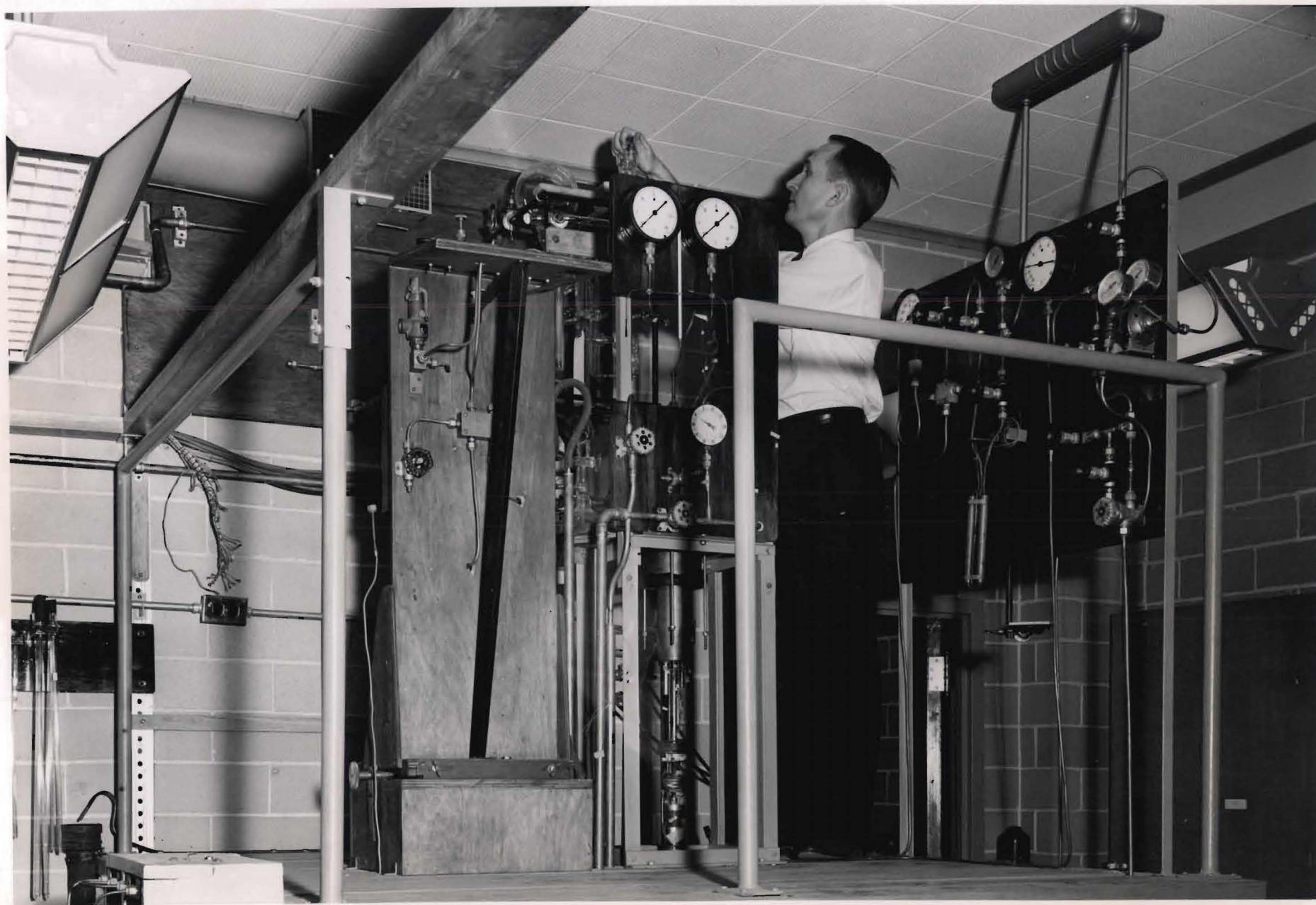


Figure 1. View of Helium Cryostat and Associated Apparatus



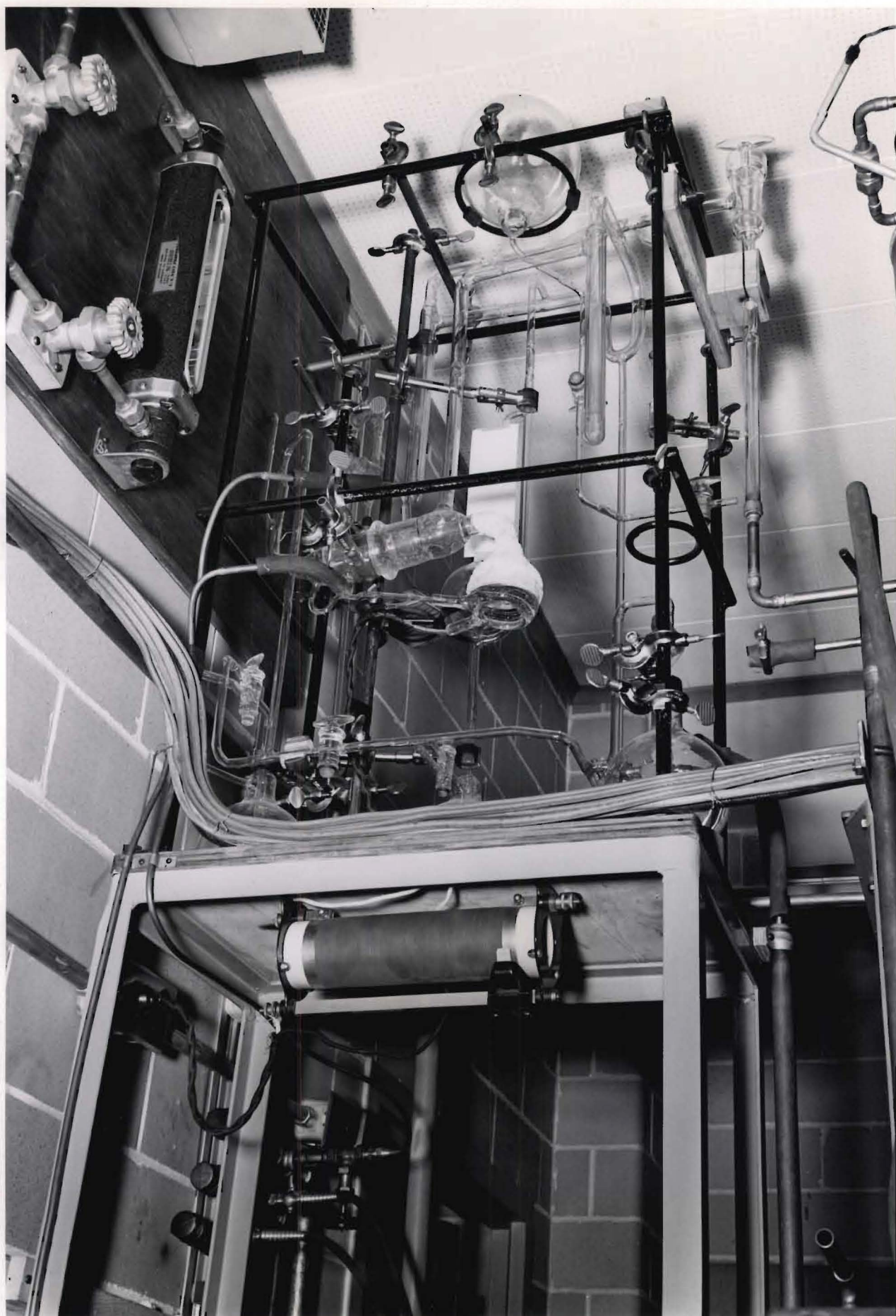


Figure 2. View of High Vacuum System for Helium Cryostat

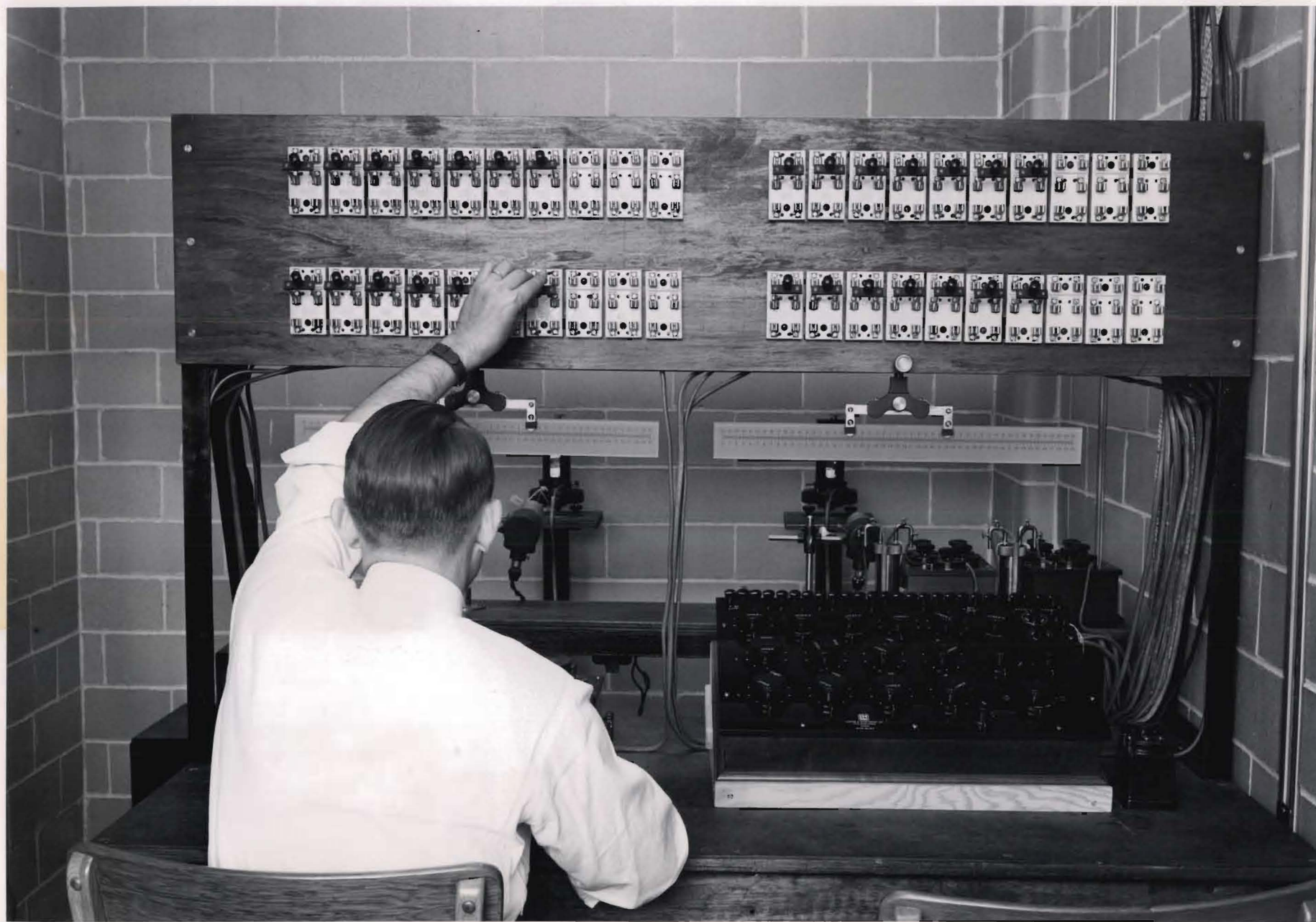


Figure 3. View of Switchboard in Instrument Room for the  
Low Temperature Laboratory



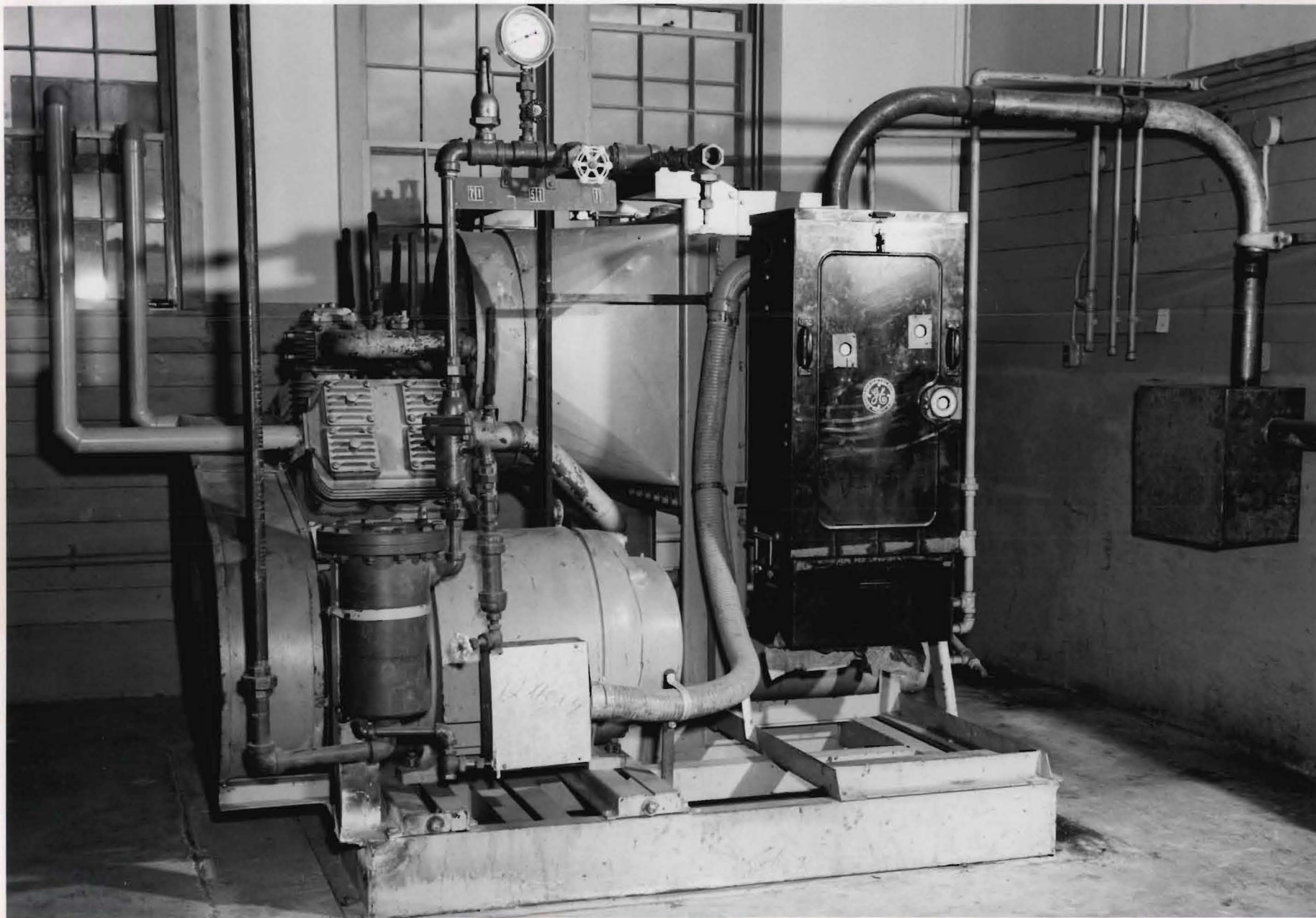


Figure 4. View of Air Compressor of Liquid Nitrogen Plant

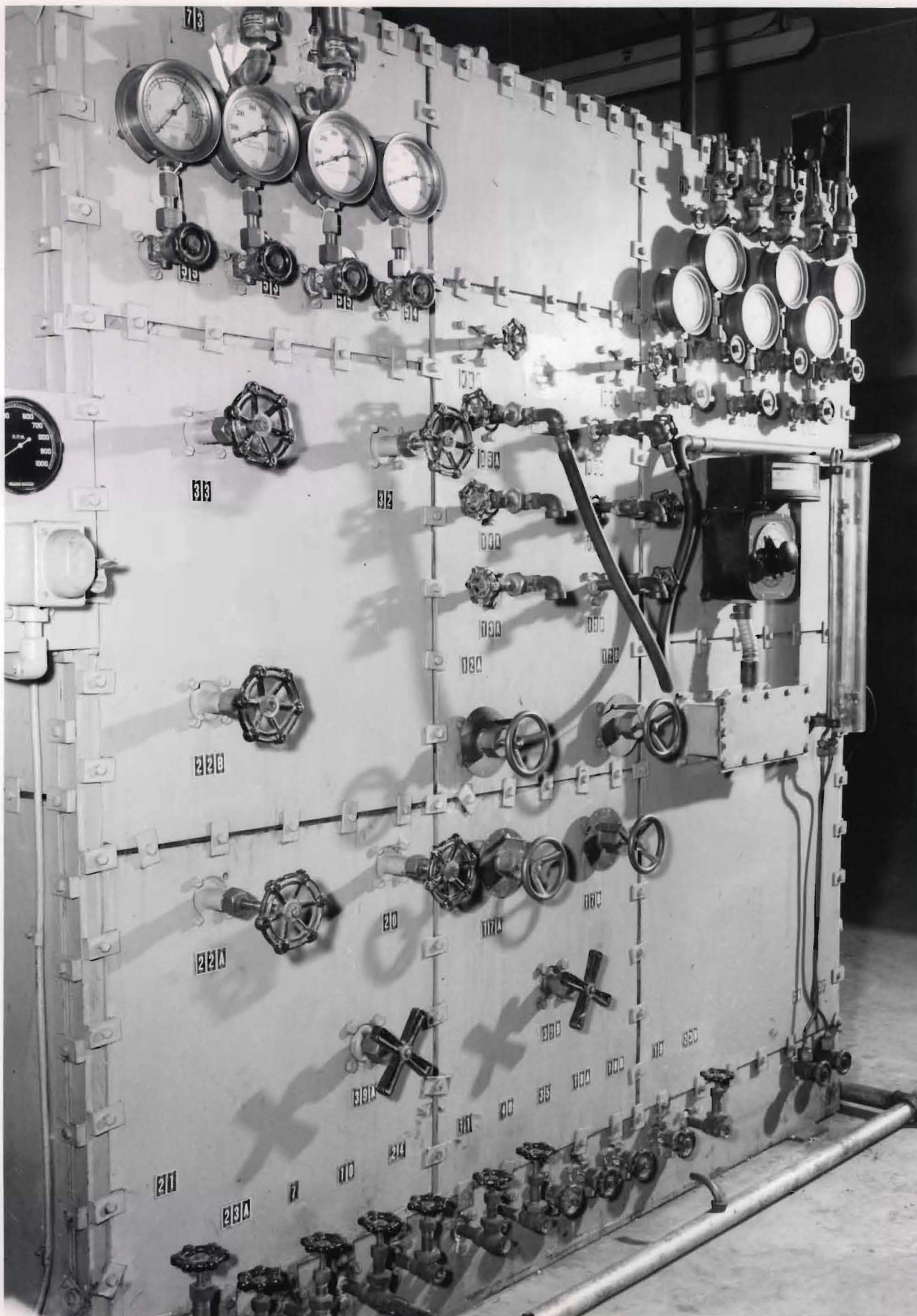


Figure 5. View of Control Panel of Liquefier of Liquid Nitrogen Plant



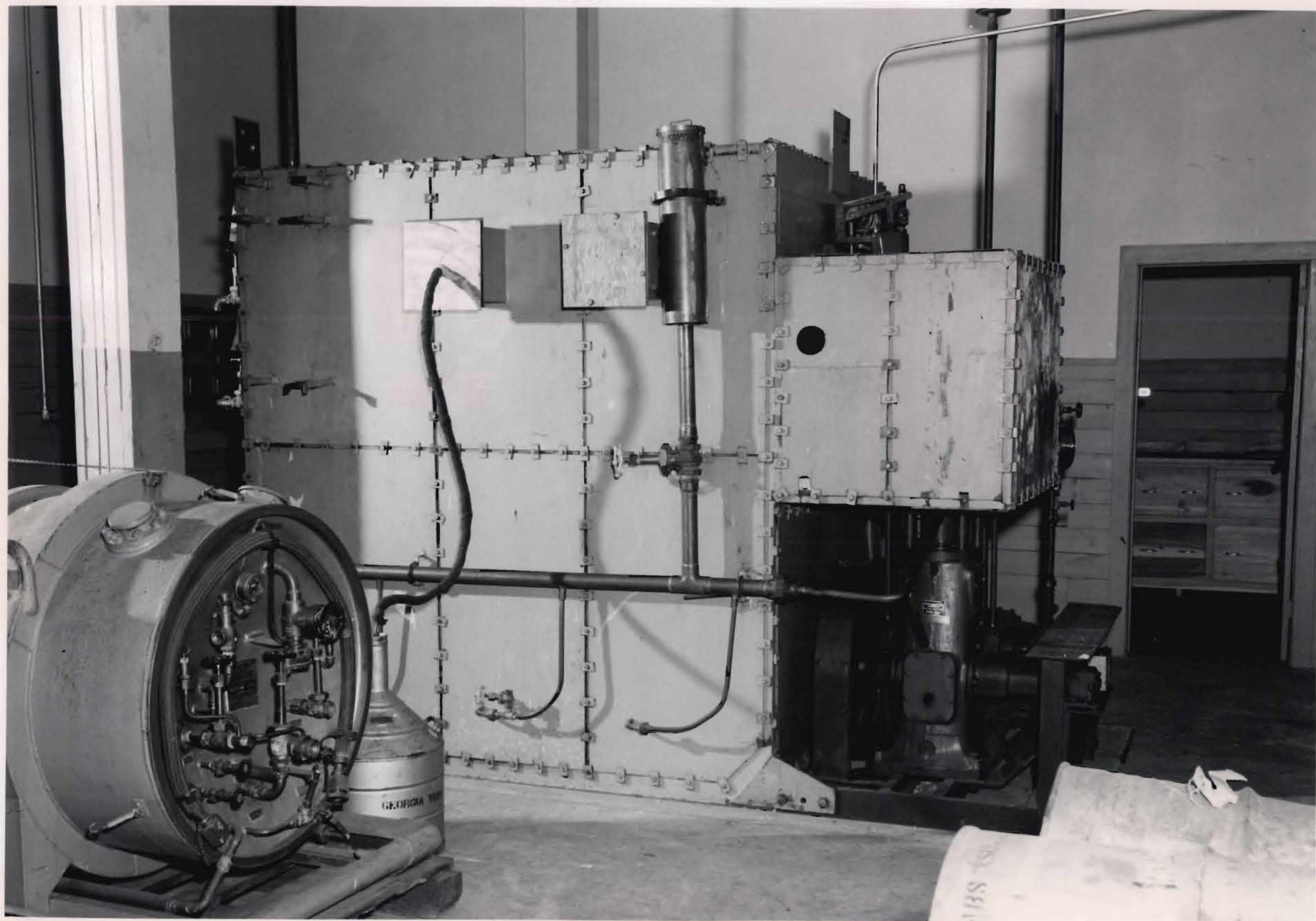


Figure 6. Rear View of Liquefier of Liquid Nitrogen Plant

Georgia Institute of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

PROGRESS REPORT NO. 9

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

CONTRACT NO. N6-ori-192, TASK ORDER I

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF THE  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

By

W. T. ZIEGLER

JULY 9, 1948



**GEORGIA SCHOOL OF TECHNOLOGY**

**THE STATE ENGINEERING EXPERIMENT STATION**

**ATLANTA, GEORGIA**

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## I. SUMMARY

Magnetic measurements have been carried out on commercially available samples of lanthanum, cerium, praseodymium, and neodymium metals from 300° to 2°K. in order to determine if these metals exhibit the phenomenon of superconductivity. Only lanthanum metal was found to exhibit a magnetic transition into superconductivity.

The study and development of methods of analysis of rare earth materials are being actively pursued. These studies include spectrophotometric, spectrographic, and X-ray diffraction methods. A high vacuum apparatus for the preparation of metal hydrides and nitrides is nearing completion.

A liquid nitrogen column for separating liquid nitrogen from air has been designed. Engineering drawings are being prepared for constructing the column in the shops of the Georgia Tech Experiment Station.

## II. LOW TEMPERATURE RESEARCH

In the last progress report (Progress Report No. 8, May 7, 1948) a report was made on the first two liquid helium runs made with the new helium cryostat. In these runs a sample of lanthanum metal was found to undergo a magnetic transition into superconductivity at  $4.85 \pm 0.15^\circ\text{K}$ . in a field of 10-20 gauss. Since that time two further runs have been made, one on May 27 (Run No. 3) and another on July 2 (Run No. 4).

In Run No. 3 two samples of lanthanum metal,<sup>1</sup> La2 and La3 (Hilger,<sup>2</sup> Lab. No. 7259), and one sample of cerium metal<sup>1</sup> <sup>Cel</sup> were studied down to about  $2^\circ\text{K}$ . using the magnetic technique described in the last progress report. The samples La2 and Cel were in the form of cylinders approximately 20 mm. long and 4.8 mm. in diameter. The sample La3 was 11.5 mm. long and had a rectangular cross section 2.6 mm. x 4 mm. Sample La2 was observed to undergo a magnetic transition into superconductivity at  $4.85 \pm 0.15^\circ\text{K}$ . while Sample La3 underwent a similar transition at  $4.45 \pm 0.10^\circ\text{K}$ . In each instance the transition range was less than  $0.1^\circ$ .

Cerium metal did not become superconducting down

- - - - -
- (1) Obtained from Cooper Metallurgical Laboratory, 2135 Columbus Road, Cleveland 13, Ohio.
  - (2) Obtained from Jarrell-Ash Company, 165 Newbury St., Boston 16, Mass.

to about  $2^{\circ}\text{K.}$ , the lowest temperature obtained in these studies. It is estimated that a transition of 10% of the cerium from the normal to the superconducting state could have been detected. A letter describing these results has been accepted for publication by the Editor of the Journal of Chemical Physics.

Lanthanum metal has previously been studied by Mendelssohn and Daunt<sup>3</sup> using a magnetic method. These investigators reported a transition temperature of  $4.71^{\circ}\text{K.}$  for a sample containing about 1% iron. Shoenberg,<sup>4</sup> also using a magnetic method, reported that a lanthanum sample (Hilger, Lab. No. 7259), presumably identical with our Sample La3, was superconducting at  $4.2^{\circ}\text{K.}$  On the other hand, McLennan, Allen, and Wilhelm<sup>5</sup> have measured the electrical conductivity of "pure" samples of lanthanum and cerium from 300 to  $1.9^{\circ}\text{K.}$  and reported that neither substance became superconducting.

In Run No. 4, samples of praseodymium,<sup>1</sup> Pr1, neodymium,<sup>2</sup> Nd2, and lanthanum, La1, were studied down to  $2^{\circ}\text{K.}$  using the same techniques. Neither praseodymium

-- -- --  
(3) Mendelssohn, K., and Daunt, J. G., Nature 139, 473 (1937).

(4) Shoenberg, D., Proc. Camb. Phil. Soc. 33, 577 (1937).

(5) McLennan, J. C., Allen, J. F., and Wilhelm, J. O. Phil. Mag. (7) 10, 500 (1930).

nor neodymium exhibited any magnetic anomaly down to 2° K. The lanthanum sample, Lal, was found to undergo a transition at  $4.85 \pm 0.15$  K., a result which had previously been obtained for this sample in Runs No. 1 and 2.

The purity of the metal samples which have been studied is not high. Tentative analytical results obtained so far for the metals obtained from the Cooper Metallurgical Laboratories are summarized in Table I.

TABLE I  
APPROXIMATE ANALYSIS OF RARE EARTH METALS

| Impurity          | Metal     |              |              |              |
|-------------------|-----------|--------------|--------------|--------------|
|                   | Lanthanum | Cerium       | Praseodymium | Neodymium    |
| Iron(%)*          | 0.8       | 2.5          | 1.3          | 2.7          |
| Neodymium(%)      |           | ?            | 3            |              |
| Other rare earths | trace     | small amount | small amount | small amount |
| Silicon, aluminum | present   | present      | present      | present      |

\*Analysis supplied by Cooper Metallurgical Laboratories.

The Hilger sample (Lab. No. 7259) was reported to contain between 0.5 and 1% aluminum, silicon, and tungsten, with the rare earths other than lanthanum virtually absent.

Further quantitative analysis of these materials is being carried out.

### III. STUDIES IN THE CHEMISTRY OF THE RARE EARTHS

Work on the chemistry of the rare earths is proceeding along several lines. Mr. J. B. Downs, Jr., a graduate student in chemistry, has joined the project to carry out quantitative analyses of rare earth materials. Spectrophotometric methods of analysis are being worked out using a quartz Beckman spectrophotometer. Spectrographic methods, as well as more conventional methods of analysis, also are being studied.

A high vacuum apparatus for the preparation of rare earth hydrides and nitrides is nearing completion. It is anticipated that the preparation of several rare earth metal hydrides will begin shortly.



#### IV. X-RAY DIFFRACTION STUDIES

Mr. A. L. Floyd, a graduate student in physics, has joined the project for the summer to carry out X-ray studies of the structure of rare earth materials. A General Electric Company "XRD" Unit located in the Physics Department is being used for this work. Powder diffraction pictures have been taken of a number of substances chosen to give a familiarity with the structures likely to be encountered. X-ray diffraction studies of the rare earth metal samples used in the low temperature work will be started shortly.

An additional diffraction camera has been ordered which will nearly double the number of exposures possible per unit time.



#### V. LIQUID NITROGEN PLANT

The completion of the erection of the liquid oxygen plant (Linde Model SM-LO-P270) and the results of two trial runs were reported in the last progress report (Progress Report No. 8, May 7, 1948). These tests indicated a need for a partial overhaul of the compressor. This work has now been completed.

The design of a "packed tower" liquid nitrogen column for use with this plant has been completed. It has been decided to construct this column in the Experiment Station shops. Engineering drawings are now being prepared, and bids on materials are being obtained. It is planned to begin construction about July 19.

## VI. PERSONNEL

At the present time the following individuals are employed on the project.

| <u>Name</u>          | <u>Position</u>     | <u>Time</u> |
|----------------------|---------------------|-------------|
| Dr. W. T. Ziegler    | Director            | 2/3 time    |
| Dr. W. M. Spicer     | Research Associate  | part-time   |
| Mr. W. A. Phillips   | Research Assistant  | full-time   |
| Mr. A. L. Floyd      | Research Assistant  | full-time   |
| Mr. J. B. Downs, Jr. | Research Assistant  | full-time   |
| Mr. Hugh D. Ivey     | Research Assistant  | part-time   |
| Mr. J. M. Ziegler    | Technical Assistant | full-time   |

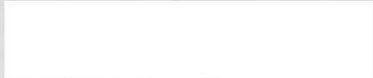
Mr. Floyd and Mr. Ivey are graduate students in physics, while Mr. Downs is a graduate student in chemistry. It is hoped that all three men will decide to carry out research for their Master's theses while associated with the project.

Mr. W. A. Phillips and Mr. Oswald Newell, Jr. received the M.S. degree in Chemical Engineering in June, 1948. Their thesis research was carried out as part of the work of this project. Mr. Phillips' thesis problem was "The Erection of a Liquid Oxygen Producing Plant and the Re-Design of This Plant to Produce Liquid Nitrogen." This design will serve as a basis for the nitrogen column to be constructed for the present oxygen plant. Mr. Newell's thesis problem was "The Construction and Testing of a Hydrogen Liquefier."

This liquefier is being used to produce the liquid hydrogen used in the low temperature experiments of this project.

Mr. Newell has left the School for other work. Mr. G. S. Baird and Mr. B. F. Smith, seniors in chemical engineering who helped part-time on the project, have also graduated and left for other work.

Respectfully submitted:

  
W. T. Ziegler,  
Project Director

Approved:

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Gerald A. Rosselot,  
Director

Georgia Institute of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

ANNUAL REPORT FOR THE PERIOD  
OCTOBER 1, 1947 THROUGH SEPTEMBER 30, 1948

PROJECT NO. 116-18

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH  
CONTRACT NO. N6-ori-192, TASK ORDER I

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FEBRUARY 28, 1949

GEORGIA INSTITUTE OF TECHNOLOGY

THE STATE ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

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FEBRUARY 28, 1949



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I. SUMMARY OF REPORT

This is the second annual report describing progress on the project being carried out under Contract No. N6-ori-192, Task Order I. It covers the period October 1, 1947, through September 30, 1948. The general intent of this contract has been to carry out "research at very low temperatures upon the fundamental properties of the elements and their compounds including the rare earths, with particular emphasis upon superconductivity." The more specific immediate objectives have been to set up a laboratory in which such work could be carried out, to investigate the metals lanthanum, cerium, praseodymium, and neodymium for superconductivity, and to set up a chemical laboratory for the preparation and analysis of rare earth metals and compounds.

Facilities necessary to carry out tests for superconductivity by magnetic means down to 2°K have been completed and are now in operation. Equipment which has been constructed or assembled includes a hydrogen liquefier, a helium cryostat, a helium gas cycle, and the necessary electrical measuring systems. This equipment, together with the chemical laboratory, is housed in a new addition to the Research Building where about 1,600 square feet of office and laboratory space has been assigned the project. The space became available October 21, 1947.

A Linde Liquid Oxygen Producing Plant, Linde Model Sm-LO-P270, Portable, which has been supplied by the Navy Department



for use on this project, has been installed. Conversion of this plant to a liquid nitrogen producing plant is nearing completion.

Research at low temperature has been carried out on commercially available specimens of lanthanum, cerium, praseodymium, and neodymium. Of these metals only lanthanum was found to become a superconductor above 2°K, the lowest temperature reached in our experiments.

Facilities are at hand and have been used for determining the crystal structures of the above rare earth metals by means of X-ray diffraction techniques.

A chemical laboratory has been set up with facilities for carrying out chemical and spectrophotometric analyses of rare earth materials. Spectrographic analyses have been made of a number of these materials, utilizing facilities located in the Department of Chemistry.

Research has been carried out on the preparation of pure rare earth materials, particularly praseodymium and neodymium, using the technique of ion-exchange, with a view to obtaining adequate amounts of materials of high purity for use in the preparation of the pure metals and for analytical purposes.

Two graduate students who received their Master's Degree in Chemical Engineering in June, 1948, submitted as their Master's theses research carried on by them on the project.

II. INTRODUCTION TO THE PROBLEM

Task Order I of this contract reads as follows:

"The Contractor shall furnish the necessary personnel and facilities for and conduct, in accordance with any instructions issued by the Scientific Officer or his authorized representative, research at very low temperatures upon fundamental properties of the elements and their compounds including the rare earths, with particular emphasis upon superconductivity."

More specifically, the experimental objective of this work has been the testing, by electrical and magnetic means, of certain rare earth metals and compounds for superconductivity. The reasons underlying this research have been discussed in considerable detail in previous reports.<sup>21,22</sup> Briefly, these reasons may be summarized as follows: (1) none of these metals have been studied previously more than superficially, if at all, at very low temperatures; (2) lanthanum, cerium, praseodymium, and neodymium (and perhaps other rare earth metals) exhibit two or more crystalline structures which may be stable at low temperatures, thus permitting a possible study of the effect of structure on superconductivity; (3) the hydrides and nitrides of some superconductors (e.g., columbium) are themselves superconductors, the transition temperature varying with the hydrogen and nitrogen content. Similar relations may also be true for a superconductor such as lanthanum.

Annual Report, Project No. 116-18

The prosecution of this research program has, in its first phase, been largely devoted to the design, construction, assembly, and testing of the necessary low temperature facilities. These facilities are now sufficiently complete so that experimentation down to 2°K can be carried on. The first liquid helium was produced on April 20, 1948.

Simultaneously, with the construction of the low temperature facilities, it was necessary to equip and instrument a chemical laboratory for the preparation and analyses of rare earth metals and compounds. The chemical laboratories are now sufficiently complete so that spectrophotometric and conventional chemical analyses can be performed. In addition, research on the preparation of pure rare earth compounds by the use of synthetic ion-exchange resins is proceeding in order that the metals themselves may be produced. The analytical facilities are of great importance in characterizing the materials being studied at low temperatures, as well as in analysing the materials being purified.

Both the low temperature facilities and the chemical facilities are housed on the second floor of a new addition to the Research Building, where 1,600 square feet of laboratory and office space has been allotted the project. This space became available on October 21, 1947.

Progress for the period October 1, 1947 to September 30, 1948 is reviewed in the present report. A technical report

covering in greater detail the low temperature results presented in the present report will be issued shortly. A more detailed description of some of the subjects discussed may be found in the quarterly progress reports listed in the Bibliography.<sup>22, 23, 24, 25</sup>

### III. LOW TEMPERATURE RESEARCH FACILITIES

Research at temperatures in the neighborhood of 2°K necessarily implies the availability of considerable specialized equipment. The principal pieces of apparatus which have been constructed, or assembled from commercially available component parts, are: (1) a high pressure hydrogen gas purifier, (2) a hydrogen liquefier, (3) a helium cryostat, (4) a helium gas cycle, and (5) an electrical measuring system.

The production of liquid helium is accomplished by the so-called Simon adiabatic expansion method and is carried out directly in the cryostat in which the samples are studied. The production of liquid helium by this method presupposes the availability of liquid hydrogen, the production of which, in turn, requires the use of a refrigerant such as liquid nitrogen or air. The above mentioned pieces of apparatus are now all in use.

In the present section, a brief description of the facilities will be given. These facilities have been used to obtain the results on superconductivity discussed in Section VI of this report. Figure 1 gives a view of the low temperature



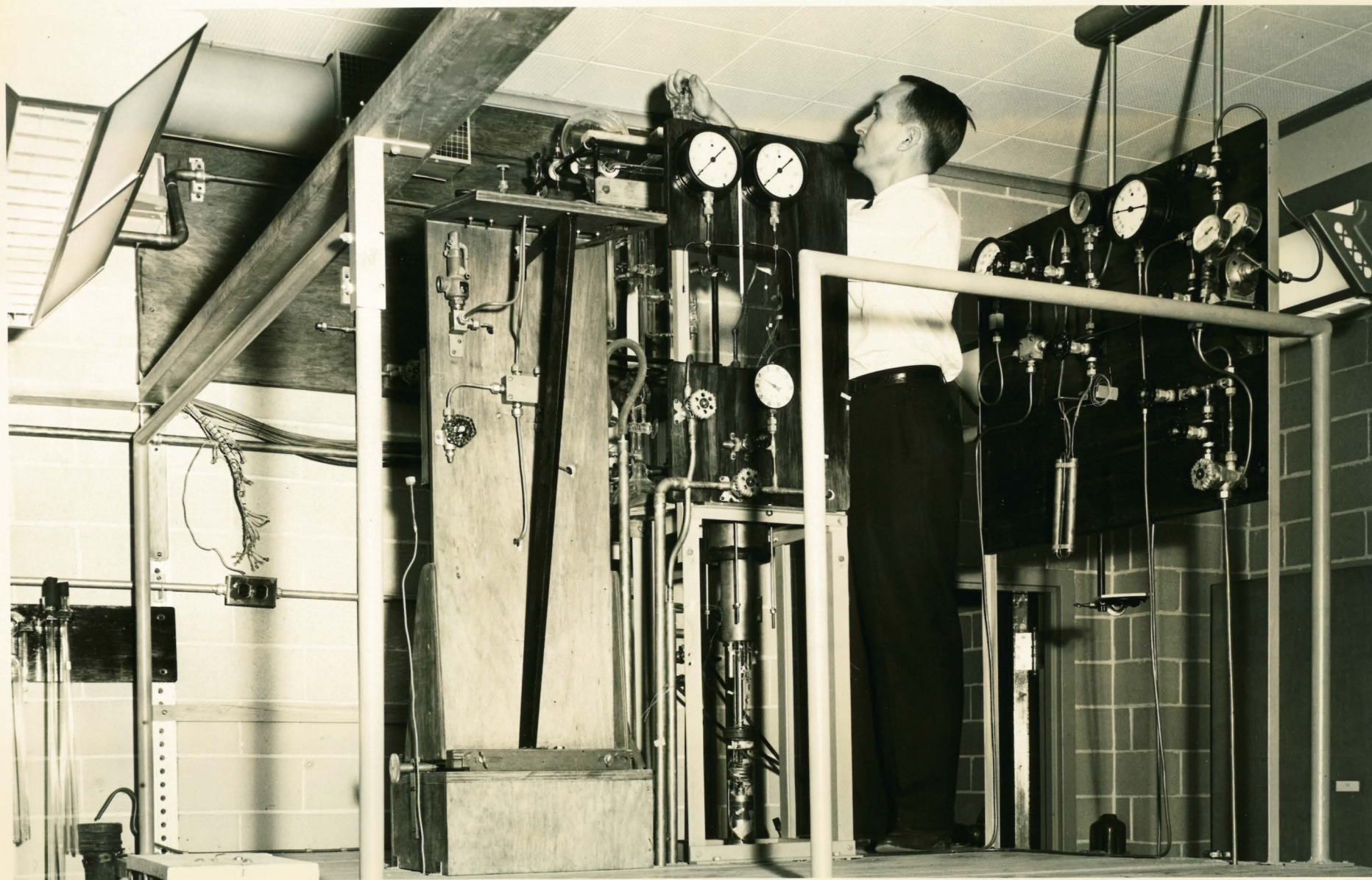


FIGURE 1. VIEW OF HELIUM CRYOSTAT AND ASSOCIATED APPARATUS.

assembly. The hydrogen liquefier can be seen in the left center, with the helium cryostat in the lower center. The various controls are located on the two panel boards. The entire assembly is mounted on a raised platform (about four feet above floor level) to facilitate removal of the long glass Dewar vessel which surrounds the cryostat during operation. A short paper describing the low temperature facilities of the laboratory has been accepted for publication in the November, 1948, issue of Refrigerating Engineering.

A. High Pressure Hydrogen Gas Purifier and Hydrogen Liquefier

These units have been described in detail in the last annual report<sup>22</sup> and will not be discussed in detail here. The hydrogen liquefier has been altered somewhat so as to permit the level of liquid hydrogen in the liquefier to be observed visually. With a flow rate of about five cubic feet per minute (N.T.P.) a liquefaction rate of 1.5 liters per hour is currently being obtained.

B. Helium Cryostat

1. General Description

The helium cryostat which has been constructed is shown schematically in Figure 2. It differs only in detail from one described by Horn<sup>3</sup> and Horn and Ziegler.<sup>4</sup> Liquid helium is produced within the cryostat in two separate processes, the helium produced in one reservoir serving as the thermal dam for the experimental helium chamber.<sup>16</sup> Briefly, the apparatus consists of a heavy-walled copper vessel, A, in which the main



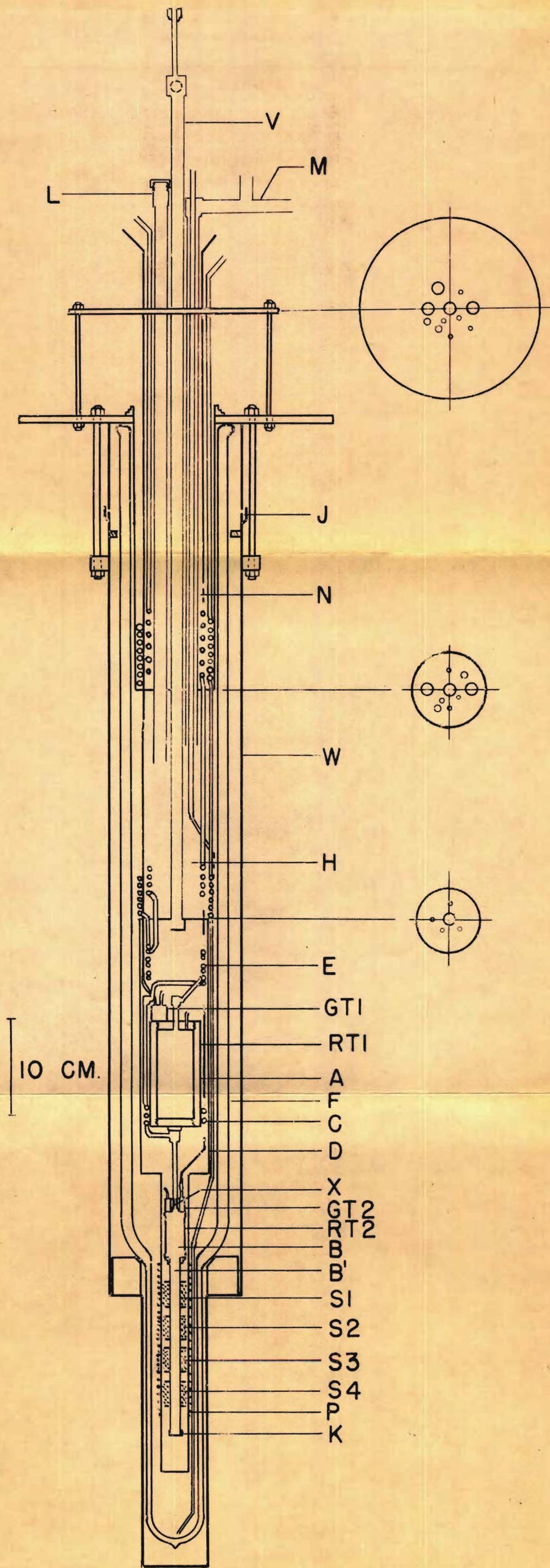


FIGURE 2. SCHEMATIC DIAGRAM OF HELIUM CRYOSTAT



charge of liquid helium is produced. Suspended from A is the experimental chamber, consisting of the sections B and B', in which the samples to be studied are located. The experimental chamber and helium reservoir are surrounded by a case, D, which can be evacuated at will. All tubes and wires leading to the helium reservoir and experimental chamber pass first through a liquid nitrogen bath, N, and then through a liquid hydrogen bath, H, which serve as thermal dams. The entire apparatus is surrounded by a glass Dewar vessel, F, supported in the brass case, W. A vacuum tight seal is formed at the joint, J, by means of Apiezon Q putty.

The main charge of liquid helium is produced in the helium reservoir, A, by the Simon expansion method. This reservoir has a volume of 101 cubic centimeters. Starting from a temperature of  $11.5^{\circ}\text{K}$ , and a pressure of 2,300 psi, a filling of 70-80% can be achieved. The yields obtained thus far are in good agreement with those reported by Simon for similar starting conditions.<sup>16</sup> The yield of liquid helium produced in this expansion process is the major factor governing the length of time available for experimentation below  $11^{\circ}\text{K}$ . Seventy-five cubic centimeters of liquid helium provide about 2.5 hours time for experimentation.

Helium is condensed into the experimental chamber, B and B', by bringing gas at about 20 psi into contact with A in the condensing coil, C. This condensation results in the loss of



an equivalent amount of liquid helium from A. The cold gas from A passes through the heat exchanger, E, thus cooling the incoming low pressure helium before it reaches C.

The temperature of the reservoir, A, is measured by means of the gas thermometer, GT1, and the constantan resistance thermometer, RT1.

## 2. The Experimental Chamber

The all-copper experimental chamber consists of two parts, an upper section, B, having a volume of 12 cubic centimeters, and a lower section, B', having a volume of nine cubic centimeters, in which the samples are placed. The section, B', was constructed by boring and machining a single piece of copper rod. It has an inside diameter of 5/16 in. (eight mm) and a wall thickness of 0.047 in. On the outside of B' are wound four secondary coils which are used in the magnetic measurements. It is closed at the bottom end by a cap, K, sealed on with Wood's metal.

The temperature of the experimental chamber is measured by means of the constantan resistance thermometer, RT2, and the gas thermometer, GT2.

The pumping line leading to B contains a constriction, X, 0.50 in. long and 0.029 in. in inside diameter, which is introduced to reduce the "creep" of liquid helium.<sup>1</sup>

## 3. Temperature Measurement and Control

The temperature of the experimental chamber was measured using a gas thermometer of the type described by

Mendelssohn,<sup>11</sup> the bulb of which is attached by means of a supernickel capillary (one mm i.d.) to a bourdon gauge and a closed-end mercury manometer made of two mm capillary glass tubing. The volume of the gas thermometer bulb is 1.67 cubic centimeters, and the external volume (bourdon gauge and manometer) at room temperature is approximately 20 cubic centimeters. The thermometer system was filled with helium gas at one atmosphere pressure while at room temperature and then sealed off.

This system was quite sensitive in the range 3.2 to 8°K, a change of 0.1° being detectable. Below 3°K the gas thermometer acted as a vapor pressure thermometer.

The pressure measurements made with this system were converted to temperatures by assuming that the connecting capillary had a negligible volume. If this be done, it can then be shown that the temperature of the bulb is given by an expression of the form

$$T = \frac{1}{\left[ \frac{P_0}{PT_0} (1 + a) - \frac{a}{T'} \right] c}$$

where

T = temperature of the bulb in °K

P = observed pressure in mm

P<sub>0</sub> = filling pressure in mm

T<sub>0</sub> = filling temperature in °K

T' = temperature of external volume at time of experiment in °K

$a$  = ratio of external volume,  $V_e$ , to volume of bulb,  $V_b$

$c$  = the compressibility factor  $c = P_v/RT$ .

For practical purposes,  $a$  can be taken as a parameter to be determined at a known temperature. In our experiment this parameter was found to be 12.2, using the normal boiling point of helium as a fixed point.

Gas imperfection was taken into account by utilizing P-V-T data from which values of the compressibility factor,  $c$ , were either calculated or estimated.<sup>7</sup>

Comparisons of this temperature scale were made against the vapor pressure of helium in the experimental chamber in the range 4.2 to 3.2°K and agreement to  $\pm 0.1^\circ$  was found. Samples of pure lead and tin were run in the apparatus in the manner described later and were found to undergo magnetic transitions at 3.6° and about 7°K, respectively. The generally accepted values for these transition temperatures are 3.69 and 7.26°K, respectively.<sup>15</sup> The transition range in each case was less than  $0.1^\circ$ .

The resistance thermometer, RT2, was constructed of No. 40 B and S constantan wire. It had a resistance of 1,069 ohms at 4°K, a  $dR/dT$  of 0.96 ohm per degree, and could be read to  $0.05^\circ$ . It was useful for interpolation purposes and for judging the sharpness of transitions.

The main helium reservoir is fitted with a similar temperature measuring system except that pressures were read with a

bourdon gauge only. In this instance the boiling point and triple point of hydrogen were used to fix the parameter of the gas thermometer.

More detailed descriptions of the magnetic circuits are given in Section IV where the experimental measurements are discussed.

#### C. Electrical Measuring Systems

The electrical measuring systems consist of (1) standard potentiometric means for measuring temperature using thermocouples and resistance thermometers and for the measurement of electrical resistance and (2) a null-point system for measurement of magnetic induction. This system is described in greater detail in Section IV B. The equipment includes Leeds and Northrop Company Type K-2 and White potentiometers. Figure 3 gives a view of the switchboard which is adjacent to the room containing the low temperature apparatus.

#### D. Helium Gas Cycle

The production of liquid helium by the method outlined above requires the use of high pressure helium gas, the percentage yield of liquid helium increasing considerably with the use of pressures above 2,000 psi. It was desirable, therefore, to have available a compression system for raising the pressure of purified helium gas to about 2,800 psi. Such a cycle, consisting of a high pressure helium purifier, a gasometer for storing low pressure gas, a compressor and three



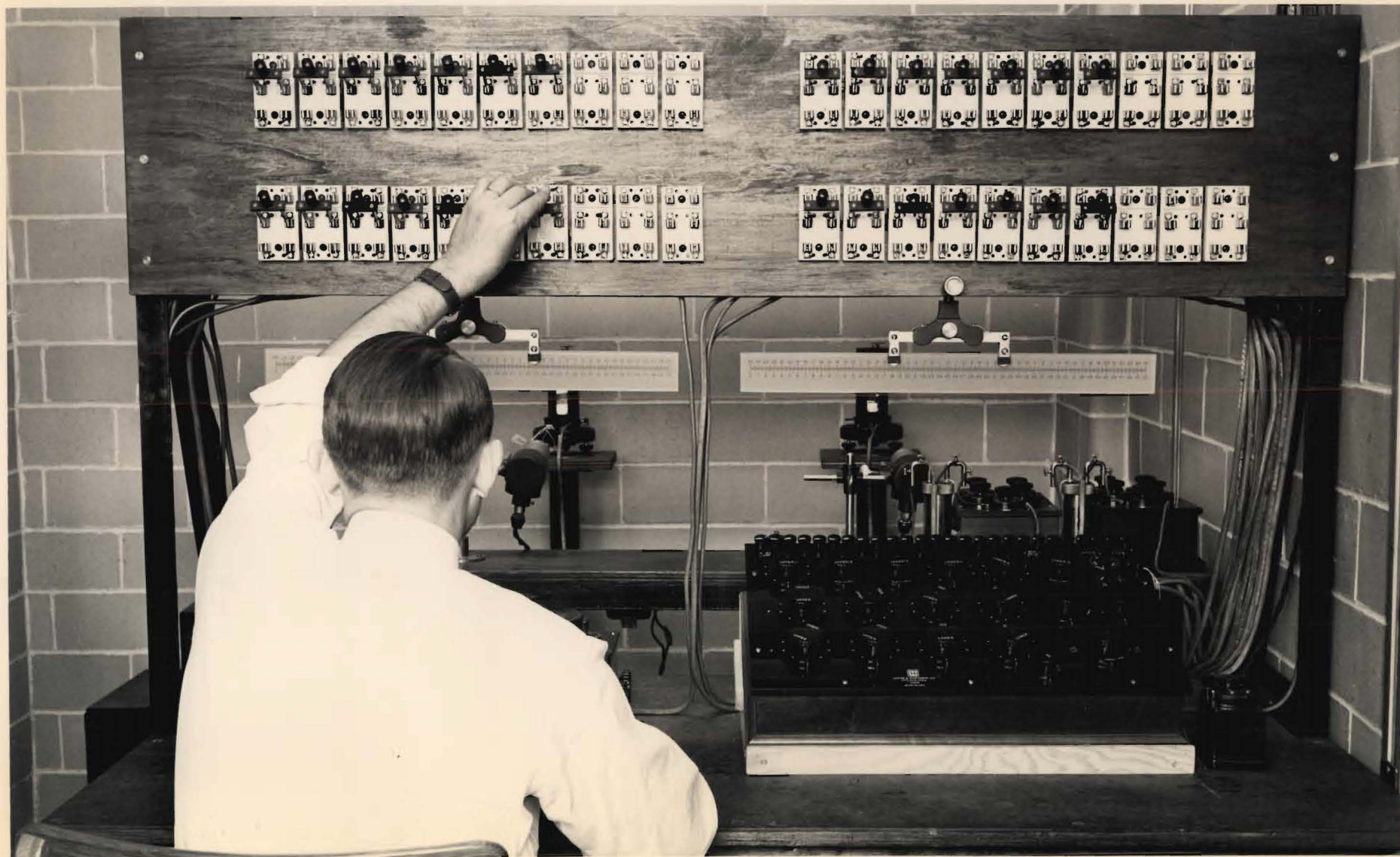


FIGURE 3. VIEW OF SWITCHBOARD IN INSTRUMENT ROOM FOR THE  
LOW TEMPERATURE LABORATORY.

storage cylinders has been completed and put into use. The compressor is an Ingersoll-Rand Model P-33-10-G three-stage air compressor, having a pumping capacity of seven CFM, which was a component part of a Navy Torpedo Topping Compressor. The compressor has been instrumented for its present use with helium. Figure 4 is a view of the completed cycle.

#### IV. LOW TEMPERATURE RESEARCH

Liquid helium was first produced in the helium cryostat (see previous section) on April 20, 1948. The apparatus was found to function satisfactorily, permitting studies for possible superconductivity to be made down to 2°K. During the period to September 30, 1948, commercially available samples of lanthanum (from two sources), cerium, praseodymium, and neodymium metals have been studied by magnetic means down to 2°K. Samples of lead and tin of high purity were also studied to check the operations of the apparatus, since these metals are known to become superconductors, having well-established transition temperatures of 7.26 and 3.69°K, respectively.<sup>15</sup>

##### A. Sources and Purity of Materials

Samples of lanthanum, cerium, praseodymium, and neodymium were obtained from Cooper Metallurgical Laboratory (now Cooper Metallurgical Associates), Cleveland, Ohio, in the form of irregular pieces from which small cylinders having the approximate dimensions 5 mm x 20 mm were cut.



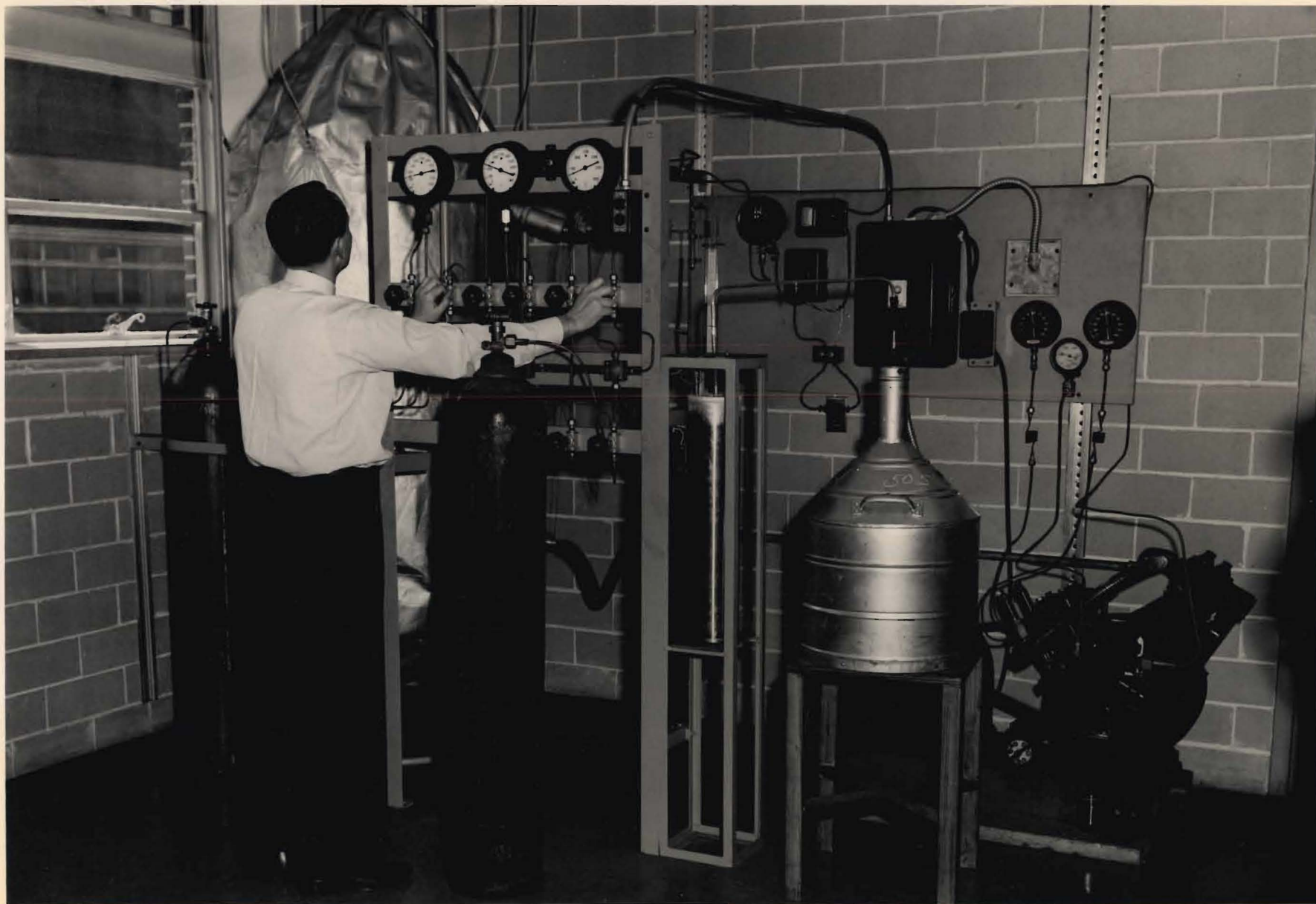


FIGURE 4. HIGH PRESSURE HELIUM CYCLE.

A second sample of lanthanum, obtained from Adam Hilger, Ltd., London, England, and designated by them as Lab. No. 7359, was reported to contain a total of between one-half and one per cent of aluminum, silicon, and tungsten and to be substantially free of other rare earth metals.

The rare earth metals obtained from the Cooper Metallurgical Laboratory were analyzed qualitatively using a spectrographic method employing the copper spark technique.<sup>2</sup> Using the spectrographic results as a guide, the metals were then analysed quantitatively by spectrophotometric and chemical methods for insoluble matter (reported as silicon), iron, praseodymium, neodymium, and in some instances, lanthanum and cerium. Calcium, magnesium, aluminum, and traces of other rare earths, which also were shown to be present in all samples by spectrographic analysis, were not determined quantitatively. The results of these analyses are shown in Table I.

#### B. Magnetic Method of Detecting Superconductivity

The system for carrying out the magnetic measurements will be described briefly by referring to Figure 5. It consisted of a primary coil, P, wound upon the lower end of the vacuum case, D, and four equally spaced secondary coils S1, S2, S3, and S4, wound on the outside of the experimental chamber, B', co-axial with the primary. Figure 5 also includes a diagram of the superconduction detection circuit used.



TABLE I  
ANALYSES OF COMMERCIAL RARE EARTH METALS<sup>a</sup>

|                    | <u>Lanthanum</u> | <u>Cerium</u>    | <u>Praseodymium</u> | <u>Neodymium</u> |
|--------------------|------------------|------------------|---------------------|------------------|
| La, %              | 95.5             | b                | 37.0                | ca 5             |
| Ce, %              | b                | 88.4             | b                   | b                |
| Pr, %              | (<1)             | 0.4              | 54.8                | 15               |
| Nd, %              | (<1.5)           | 1.4              | 3.5                 | 78.7             |
| Fe, %              | 0.8              | 2.5              | 1.6                 | 2.8              |
| Si, %              | 0.7              | 0.5              | 0.9                 | 1.2              |
| Total              | 97.0             | 93.2             | 97.8                | 102.7            |
| Unaccounted<br>for | 3.0 <sup>c</sup> | 6.8 <sup>c</sup> | 2.2                 | -2.7             |

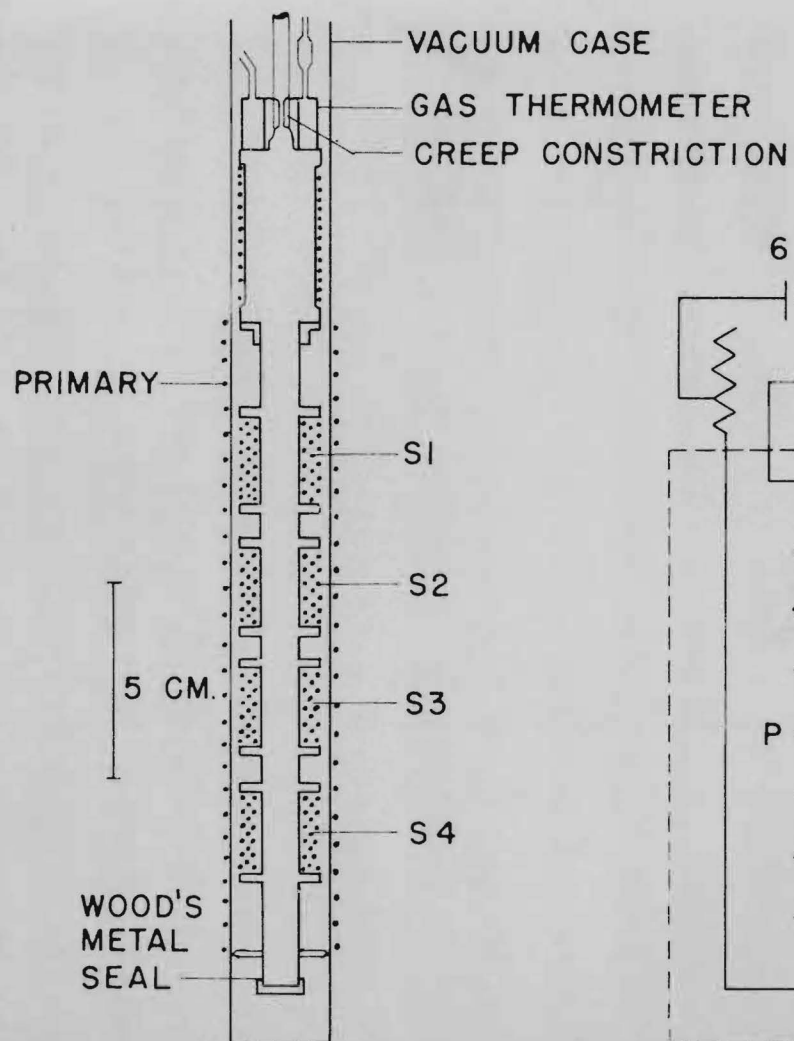
(a) Obtained from Cooper Metallurgical Laboratory, Cleveland, Ohio.

(b) Not determined.

(c) It is possible that a portion of the unaccounted for balance may have been the parent metal, in which case the lanthanum and cerium contents may have been as high as 98 and 95 per cent, respectively.

In all experiments described in this paper, coil S1 was always empty, with the samples to be studied contained in coils S2, S3, and S4. In order to prevent air-oxidation of the rare earth metals all samples were sealed in small glass capsules, made of seven mm o. d. Pyrex glass tubing, under helium gas at ten cm Hg pressure. Three capsules were then separated by

-19-



A. EXPERIMENTAL CHAMBER

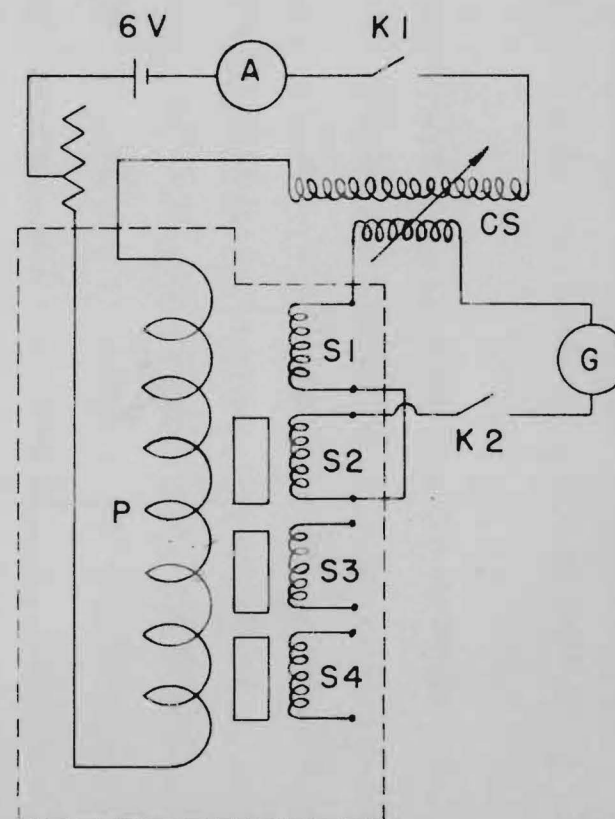
B. SUPERCONDUCTIVITY  
DETECTION CIRCUITS

FIGURE 5. MAGNETIC MEASUREMENTS SYSTEM

lucite spacers and the entire assembly held together with cellulose acetate cement. This assembly was then slipped into the experimental chamber, B', after which the cap, K, was soldered on with Wood's metal. The spacers were so made that each sample was properly positioned in the center of its secondary coil.

The experimental procedure was as follows. With the samples in place and at a fixed temperature coil S1 and another coil, for example, coil S2, were connected by means of a suitable switching arrangement outside the cryostat in such a manner that the voltages induced in them when the tap key, K1, in the primary circuit was closed opposed each other. With the tap key, K2, closed, the galvanometer, G, usually showed a deflection when the primary was energized, due to some unbalance between S1 and S2. (Opening K2 prior to de-energizing the primary was found to be helpful in restoring the galvanometer to its zero position quickly.) This unbalance was removed by adjusting the variable external compensating coil, CS, until the galvanometer showed no deflection. The temperature of the experimental chamber was then lowered (or raised) slowly. With K2 closed, K1 was tapped every few seconds and any unbalance of the coils observed as a galvanometer deflection. In passing from room temperature to a temperature just above the transition, a single setting of the external compensating coil, CS, usually sufficed, an unbalance corresponding to only

one or two mm galvanometer deflection being observed. The transition of a sample from the normal to the superconducting state was easily recognized by the appearance of a sudden large unbalance. In these experiments a galvanometer deflection of three to seven cm was observed, depending upon the sample being studied and the magnitude of the current in the primary circuit. For instance, a deflection of 5.0 cm, using a primary current of 260 milliamperes, was obtained when a sample of lanthanum (La 1, Run No. 4) underwent a transition from the normal to the superconducting state.

In a given experiment time-temperature and time-galvanometer deflection measurements were made from which temperature vs. galvanometer deflection data were obtained. Such measurements were made both on warming and cooling through the transition range, though cooling was usually preferred since this process was controllable. Measurements were made on warming by allowing the experimental chamber to warm up due to the heat leaks present.

Controlled cooling in the temperature range  $8^{\circ}$  to  $4.2^{\circ}\text{K}$  was achieved by increasing the pressure of the helium gas in the experimental chamber. This resulted in the condensation of some helium in the condenser coil in contact with the main helium reservoir, with the result that the liquid helium so formed flowed down to the experimental chamber where it re-evaporated, thus cooling the samples. Cooling rates of 0.2

to  $0.3^{\circ}$  per minute were obtained, and no difficulty was encountered in making deflection measurements once every ten seconds. However, this method of cooling is not wholly satisfactory, since much depends upon the skill of the operator.

### C. Magnetic Measurements

Specimens of tin, lead, lanthanum, cerium, praseodymium, and neodymium have been studied by means of the technique outlined above, the last four metals down to  $2^{\circ}\text{K}$ . Of these, only tin, lead, and lanthanum were found to undergo a magnetic transition into superconductivity, the transition taking place in a range of  $0.1^{\circ}$  or less in each instance. Tin and lead were studied, primarily, to observe the behavior of the magnetic circuits, since the transition temperatures of these metals are well established. Table II summarizes the results obtained, together with other pertinent data. A brief report of the results obtained for lanthanum and cerium has already appeared.<sup>20</sup>

The experimental results obtained show that the two different lanthanum metal samples studied underwent magnetic transitions in the neighborhood of  $4.7^{\circ}\text{K}$ . The transition temperature of the samples obtained from the Cooper Metallurgical Laboratory (La 1 and La 2) was definitely higher than that of the Hilger sample (La 3). While it is possible to ascribe the observed difference to the existence of a temperature gradient along the experimental chamber, it is felt that the actual experimental conditions largely obviate this possibility.

Furthermore, the good agreement obtained from samples La 1 and La 2 in Runs 2 and 3 in which coils S4 and S2, respectively, were used indicate that the temperature gradient was probably too small to be entirely responsible for the observed difference in transition temperatures for the two different samples.

TABLE II

## SUMMARY OF RESULTS OF MAGNETIC MEASUREMENTS

| Run | Sample            | Source | Dimensions   |                | Coil<br>Used | Transition<br>Temp. |
|-----|-------------------|--------|--------------|----------------|--------------|---------------------|
|     |                   |        | Dia.<br>(mm) | Length<br>(mm) |              |                     |
| 1   | Sn 1              | a      | 6.9          | 22.5           | S2           | $3.6 \pm 0.05$      |
|     | Pb 1              | b      | 6.6          | 22.4           | S3           | $7.0 \pm 0.2$       |
|     | La 1              | c      | 4.4          | 19.0           | S4           | $4.6-5.1$           |
| 2   | Sn 1              | a      | 6.9          | 22.5           | S2           | —                   |
|     | Pb 1              | b      | 6.6          | 22.4           | S3           | —                   |
|     | La 1              | c      | 4.4          | 19.0           | S4           | $4.85 \pm 0.15$     |
| 3   | La 2 <sup>d</sup> | c      | 4.8          | 20.3           | S2           | $4.75 \pm 0.15$     |
|     | Ce 1              | c      | 4.8          | 21.2           | S3           | $< 2.0^e$           |
|     | La 3              | f      | g            |                | S4           | $4.45 \pm 0.10$     |
| 4   | Nd 1              | c      | 4.8          | 20.0           | S2           | $< 2.0^e$           |
|     | Pr 1              | c      | 4.8          | 17.8           | S3           | $< 2.0^e$           |
|     | La 1              | c      | 4.4          | 19.0           | S4           | $4.9 \pm 0.15$      |

(a) Bureau of Standards, Standard Freezing Point Sample No. 42d.

(b) Johnson, Matthey and Co., Ltd., London, England.

(c) Cooper Metallurgical Laboratory, Cleveland, Ohio.

(d) La 1 and La 2 were both cut from same piece of metal.

(e) Lowest temperature reached in these experiments.

(f) Adam Hilger, Ltd., London, England.

(g) A roughly rectangular piece 4 x 11.5 x 2.6 mm



Lanthanum sample La 2 was studied down to 2°K. No further changes were noted in its magnetic behavior once it had become superconducting.

The samples of cerium, praseodymium, and neodymium studied did not exhibit any detectable magnetic anomaly down to 2°K, the lowest temperature reached in these experiments.

#### D. Comparison with Work of Other Investigators

The superconductivity of lanthanum metal has previously been studied by Mendelssohn and Daunt,<sup>12</sup> using a magnetic method. These investigators reported a transition temperature of 4.71°K for a sample containing one per cent iron. Shoenberg,<sup>14</sup> also using a magnetic method, has reported that a lanthanum sample (Hilger, Lab. No. 7259), presumably identical with our sample La 3 (which will be discussed below), was superconducting at 4.2°K. On the other hand, McLennan, Allen, and Wilhelm<sup>9</sup> have measured the electrical conductivity of "pure" samples of lanthanum and cerium from 300 to 1.9°K and reported that neither substance became superconducting. Cerium has been reported to remain in the normal state down to 1.43°K.<sup>6</sup>

McLennan, Howlett, and Wilhelm<sup>10</sup> have studied the electrical conductivity of "misch" metal down to 2.3°K and found no evidence of superconductivity. The sample was free of iron and had the following composition: cerium-35%, lanthanum-20%, neodymium-20%, samarium-10%, gadolinium-6%, praseodymium-5%, europium-2%, and yttrium-2%.

Our results are in substantial agreement with the work of previous investigators where comparison is possible, with the exception of the work of McLennan, et al.<sup>9</sup> It is of interest to note that lanthanum, cerium, praseodymium, and neodymium all exhibit both hexagonal close-packed and face-centered cubic structures.<sup>19,26</sup>

There is some evidence that lanthanum may exist in three allotropic modifications<sup>5</sup> and cerium in four modifications.<sup>5,18</sup> The rates of transition between the various allotropic modifications are only imperfectly known. In view of this multiplicity of structures, there would seem to be some uncertainty as to the actual allotropic modifications of the metals which have been investigated for superconductivity.

#### V. CHEMISTRY OF THE RARE EARTH METALS AND THEIR COMPOUNDS

During the past year considerable effort has been devoted to a study of the chemistry of the rare earth metals and their compounds. This effort has been directed along several lines, including (1) development and testing of methods of analysis, (2) the preparation of pure rare earth salts from which the pure metal may be subsequently obtained, and (3) construction of a high vacuum system for heat-treating the metals at about 1,000° C and for preparing the hydrides and nitrides of several of the metals.

##### A. Analytical Methods

The necessity for analysing the lanthanum, cerium, neodymium,



and praseodymium samples which were studied for superconductivity required that a considerable amount of time be spent in investigating the analytical methods to be used. The methods which have been employed to date include spectrographic, spectrophotometric, and conventional chemical procedures. Both qualitative and quantitative analyses have been made using these techniques.

The spectrographic method used here made use of the copper spark technique,<sup>2</sup> already applied to similar problems. A new application of this technique to the determination of lanthanum in impure praseodymium has been worked out. A brief description of this new application has been submitted for publication in Analytical Chemistry.

Spectrophotometric methods of analysis have been carried out using a Beckman Model DU quartz spectrophotometer which permits the absorption spectrum of a solution to be studied in the range 380 to 1,000 millimicrons. The methods used have generally followed the techniques described by Rodden<sup>13</sup> and Spedding, et al,<sup>17</sup> with certain modifications peculiar to our own problems.

#### B. Preparation of Pure Rare Earth Salts

A considerable effort has been devoted to the preparation of pure neodymium and praseodymium salts from crude concentrates, utilizing the methods of ion-exchange on synthetic resins.<sup>17</sup> These methods provide a powerful new technique for separating the rare earth metal ions from each other. So far,

our experiments have been confined to the purification of neodymium and praseodymium, using the resin Dowex 50.<sup>17</sup> Further work along these lines is planned.

The technique of ion-exchange also permits the development of new analytical methods. Thus, certain experiments which have been carried out indicate that it is possible to separate lanthanum quantitatively from praseodymium and neodymium using Dowex 50 as the ion-exchange resin.

Experiments to prepare the pure metals are planned but have not yet begun.

#### C. Preparation of Hydrides and Nitrides

A high vacuum system for preparing these materials has been completed. It has been used so far to study the effect of heat treatment on the crystal structure of the lanthanum, cerium, praseodymium, and neodymium samples described in Section VI of this report. It is hoped that experiments on lanthanum hydride and nitride can be started shortly.

### VI. X-RAY DIFFRACTION STUDIES

As was pointed out in Section IV, the rare earth metals (La, Ce, Pr, Nd) each exhibit two or more crystalline structures. In order to provide information as to the structure of the materials being studied for superconductivity, X-ray diffraction methods of analysis have been used.

The equipment available consists of a General Electric "XRD" unit, a copper and a molybdenum tube, and two cameras

for this unit. The equipment is located in the School of Physics.

Early studies included the taking of powder diffraction pictures of a number of substances of known structure to obtain a familiarity with the structures likely to be encountered among the rare earth metals and their compounds.

The chief result of the work during the past summer has been the determination of the crystal structures of specimens of lanthanum, cerium, praseodymium, and neodymium. These specimens had previously been studied for superconductivity as described in Section IV of this report. Powder diffraction pictures of the specimens, both in the "as received" state and after heat treatment in a vacuum furnace at 350° C, were taken using copper K-alpha radiation. The results of these investigations are shown in Table III.

These experiments indicate that both lanthanum and cerium can be converted by heat treatment from the hexagonal close-packed to the face-centered cubic structure. The results for praseodymium and neodymium were inconclusive.

Experiments to study the effect on crystal structure of cooling the lanthanum and cerium samples to liquid helium temperatures are planned. It is also planned to examine the heat treated samples for superconductivity. It will be noted that the lanthanum sample which became superconducting at  $4.85 \pm 0.15^{\circ}\text{K}$  had a predominantly hexagonal close-packed

TABLE III

## STRUCTURES OF RARE EARTH SAMPLES AS SHOWN BY X-RAY DIFFRACTION

| Metal                     | Purity<br>(Per Cent) | Major Impurity<br>(Per Cent) | Structure  |  |
|---------------------------|----------------------|------------------------------|--|--|
|                           |                      |                              | As Received  | After Heating at 350° C<br>for 96 Hours          |
| Lanthanum <sup>a</sup>    | 95.5-98              |                              | h.c.p., lines diffuse  | f.c.c., lines sharp                              |
| Cerium <sup>a</sup>       | 88.4-95              |                              | f.c.c., <sup>b</sup> lines diffuse<br>h.c.p., <sup>b</sup> lines diffuse | f.c.c., lines sharp                              |
| Praseodymium <sup>a</sup> | 54.8                 | 37.0 (La)                    | Only a few diffuse lines<br>obtained                                     | Many sharp lines of<br>unidentified<br>structure |
| Neodymium <sup>a</sup>    | 78.7                 | 15 (Pr)                      | Similar to Pr  | Similar to Pr                                    |

(a) Obtained from Cooper Metallurgical Laboratory, Cleveland, Ohio.

(b) Approximately three parts f.c.c. to one part h.c.p.

h.c.p. = hexagonal close-packed; f.c.c. = face-centered cubic

structure, whereas the cerium, which did not become superconducting down to 2°K, was predominantly face-centered cubic. Whether these structural relations apply to the metals in question at low temperatures remains to be seen.

#### VII. LIQUID NITROGEN PLANT

Considerable quantities of liquid air or nitrogen are required for carrying out research at low temperatures on even a modest scale. Liquid nitrogen is greatly to be preferred, due to its inertness, lower boiling point, and the resulting elimination of possible explosion hazards encountered with the use of liquid air and, particularly, with liquid oxygen.

On October 1, 1946, when the project was started, there was no source of liquid nitrogen in the Atlanta area, and liquid air could be obtained only in very limited amounts. The nearest sources of liquid nitrogen were in Birmingham, Alabama, and Chattanooga, Tennessee--each somewhat over one hundred miles distant.\*

In view of these facts, the Office of Naval Research made available to the project a used Linde Type Liquid Oxygen Generating Plant (Linde Model SM-LO-P270) for conversion to a liquid nitrogen producing plant. This plant has a rated production of 50 lb. of liquid oxygen per hour.

- - - - -

\* Liquid nitrogen has now become available in Atlanta in moderate quantities.

During the period covered by this report, the installation of the oxygen producing plant was completed. Final erection of the plant was considerably delayed due to the fact that the original plant lacked a number of parts essential to its operation. On February 28, 1948, certain components of a second liquid oxygen producing plant of the same type were received from which the parts necessary to complete the original plant were obtained.

The plant was first operated (as a liquid air producer) on April 2, 1948, and again on May 4, 1948. Both of these runs were made for the purpose of testing the plant and familiarizing personnel with its operation. During the second run, a production rate of at least ten liters of liquid air per hour was achieved.

With the information gained from operating the plant, together with a thermodynamic and mass flow analysis of the plant, a distillation column for producing liquid nitrogen was designed. Construction of the column was begun in the shops of the Experiment Station on July 19, 1948, and the work of installation was well along by September 30, 1948.

The design of the distillation column was based on the most recent data available.<sup>8</sup> The column is of the "packed" rather than "tray" type, the distillation section consisting of four parallel copper tubes, 3-5/8 inch o.d. and 32 inches long, packed with aluminum shoe eyelets. The overall length of the



column is about 5-1/2 feet. It is expected that the column will produce about 20 liters of liquid nitrogen per hour, having a purity of 99.5+, provided the liquefaction efficiency of the original oxygen plant is as great as 50 lb. of liquid oxygen per hour (its rated capacity).

Figure 6 gives a view of the nearly completed column installation. Figure 7 is a flow diagram of the present plant, showing the relation of the column to the plant.

A more detailed description of the plant will be given after operating tests of the column, scheduled in the next few months, have been completed.

#### VIII. PERSONNEL

During the period covered by this report the following individuals have been employed by the project in a scientific or technical capacity.

| <u>Name</u>          | <u>Position</u>     | <u>Time</u> |
|----------------------|---------------------|-------------|
| Dr. W. T. Ziegler    | Director            | 2/3-time    |
| Dr. W. M. Spicer     | Research Associate  | Part-time   |
| Mr. W. A. Phillips   | Research Assistant  | Full-time   |
| Mr. J. B. Downs, Jr. | Research Assistant  | Part-time   |
| Mr. A. L. Floyd      | Research Assistant  | Part-time   |
| Mr. B. F. Smith      | Technical Assistant | Part-time   |
| Mr. G. S. Baird      | Technical Assistant | Part-time   |
| Mr. J. M. Ziegler    | Technical Assistant | Part-time   |
| Mr. George Cook      | Machinist           | Part-time   |

Dr. Spicer, Professor of Chemistry, has been responsible for the spectrographic analyses.

Mr. Phillips has had charge of the erection of the liquid nitrogen plant, as well as the design of the liquid nitrogen

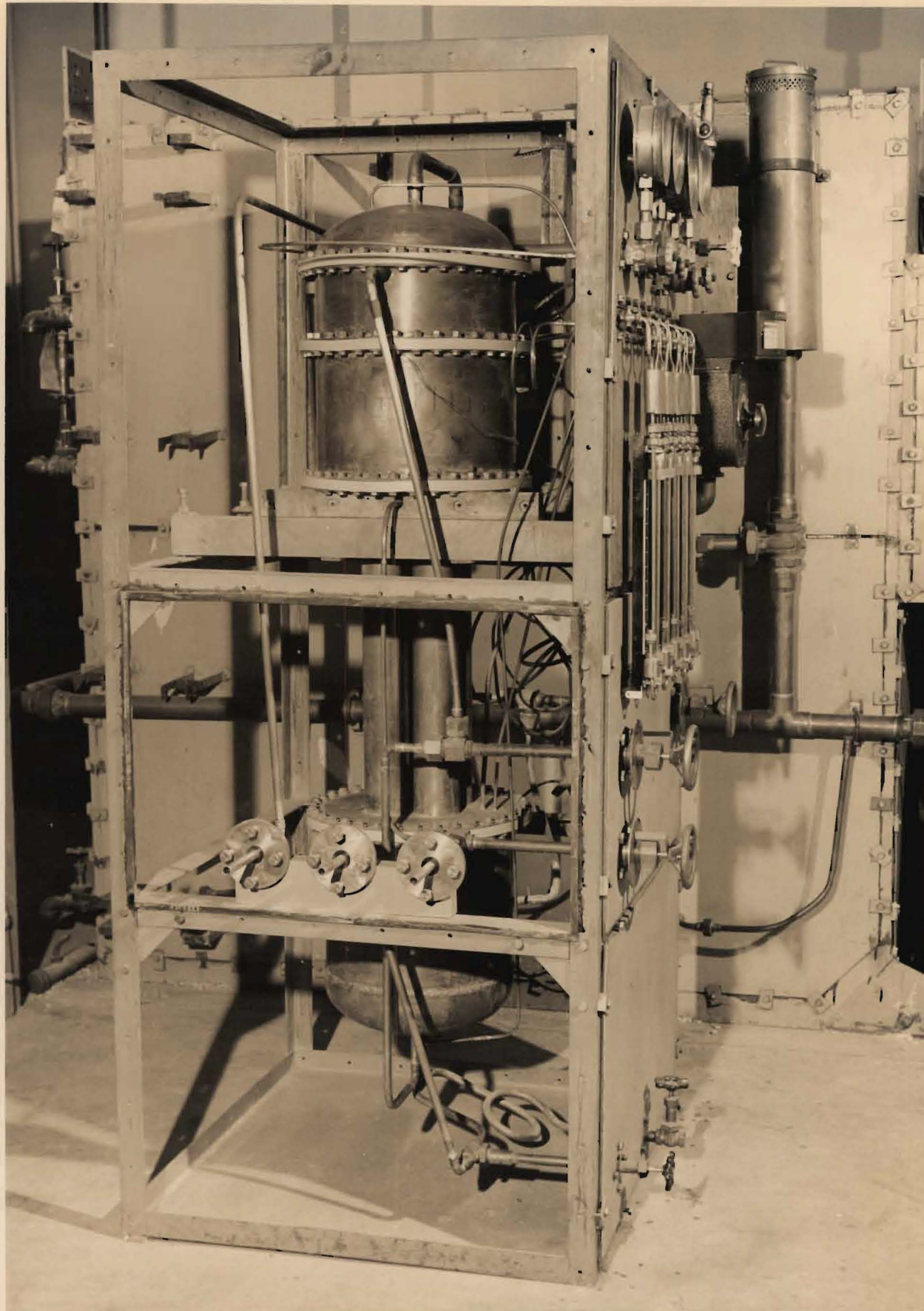
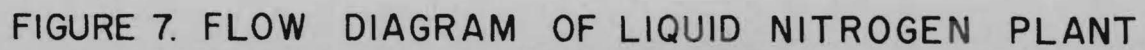


FIGURE 6. VIEW OF NEARLY COMPLETED DISTILLATION COLUMN  
FOR PRODUCING LIQUID NITROGEN.





column and the supervision of its construction in the shops of the Experiment Station. Mr. Phillips received his M. S. degree in Chemical Engineering in June, 1948, using as his thesis problem some of the work which he has carried out on the project.

Mr. Downs, a B. S. graduate in Chemistry, was with the project full-time during the summer of 1948 and carried out most of the chemical and spectrophotometric analyses of the rare earths. He plans to leave the project in October for other work.

Mr. A. L. Floyd, a graduate student in Physics, has carried out the X-ray diffraction studies on the rare earth metals and related substances. Mr. Floyd plans to continue this work as his thesis problem for the M. S. degree in Physics.

Messrs. Smith, Baird, and J. M. Ziegler are undergraduate engineering students who have contributed to various phases of the program, including help with measurements.

Mr. George Cook has been responsible for much of the mechanical construction and assembly of the various pieces of low temperature equipment.

Mr. Oswald Newell, Jr., a graduate student in the Department of Chemical Engineering, but not employed by the project, received his M. S. in Chemical Engineering in June, 1948, his thesis problem being "The Construction and Testing of a Hydrogen Liquefier." This liquefier with certain modifications is the one now being used to produce liquid hydrogen for the project.

## IX. CONFERENCES

During the year Dr. W. T. Ziegler attended Cryogenics Conferences, held under the sponsorship of the Office of Naval Research, at Ohio State University on October 27 and 28, 1947, and at Yale University, April 5 and 6, 1948. At both these meetings a report of work in progress was given. He also attended the Conference on Low Temperature and Nuclear Physics held at Oak Ridge, Tennessee, on August 7 and 8, 1948.

## X. FUTURE PLANS

The design, construction, assembly, and testing of the very considerable amount of equipment necessary to carry out research at low temperatures and to perform satisfactorily the chemical analyses described has been a more time-consuming operation than was anticipated. Certain objectives, such as the preparation and study of the hydrides and nitrides of lanthanum and cerium have scarcely been begun. However, with most of the facilities in a reasonably complete state, present plans are to pursue the preparation of these materials with great vigor. Efforts to prepare and obtain from other sources, by loan or purchase, purer specimens of lanthanum, cerium, neodymium, and praseodymium will be continued.

A study of the relation of superconductivity to crystal structure, work which is now in its preliminary stage, will be continued. During the next year it is hoped that it will be possible to prepare both lanthanum and cerium in face-centered

cubic and hexagonal close-packed structure and to compare the two forms of each metal as regards superconducting properties.

Plans are also being made to investigate the electrical conductivity of the samples studied so that the change in this property with temperature may be correlated with any magnetic transition into superconductivity.

Further research on the separation and purification of rare earth salts is also planned.

Respectfully submitted:

[REDACTED]  
W. T. Ziegler,  
Project Director

Approved:

[REDACTED]  
Gerald A. Rossetot, Director /  
State Engineering Experiment Station

XI. APPENDIX

Annual Report, Project No. 116-18

- (1) Blaisse, B. S., Cooke, H. H., and Hull, P. A., Physica 6, 231 (1934).
- (2) Fred, M., Nachtrieb, N. H., and Tomkins, F. S., J. Optical Soc. Am. 37, 279 (1947).
- (3) Horn, F. H., Dissertation, The Johns Hopkins University, Baltimore (1941).
- (4) Horn, F. H., and Ziegler, W. T., J. Am. Chem. Soc. 69, 2762 (1947).
- (5) Jaeger, F. M., Bottema, J. A., and Rosenbohm, R., Rec. Trav. Chim. des Pays-Bas 57, 1137 (1938).
- (6) Justi, E., and Koch, K. M., photostatic copy of unpublished article entitled "Superleitfähigkeit," p. 121 (captured document).
- (7) Landolt-Bornstein Tabellen, Erg. I, 59 (1929).
- (8) Lobo, W. E., and Williams, B., Liquid Air Fractionation, O. S. R. D. Report No. 3768, M. W. Kellogg Company, 1944.
- (9) McLennan, J. C., Allen, J. F., and Wilhelm, J. O., Phil. Mag. 10 (7), 500 (1930).
- (10) McLennan, J. C., Howlett, L. E., and Wilhelm, J. O., Trans. Roy. Soc., Canada, Sect. III 23, (3) 287 (1930).
- (11) Mendelssohn, K., Z. Physik 73, 482 (1931).
- (12) Mendelssohn, K., and Daunt, J. G., Nature 139, 473 (1937).
- (13) Rodden, C. J., Bur. Stds. J. Research 26, 557 (1941).
- (14) Shoenberg, D., Proc. Camb. Phil. Soc. 33, 577 (1937).
- (15) Shoenberg, D., Superconductivity, Cambridge Univ. Press, 1938, p 106.
- (16) Simon, F., Actes du VIIe Congres. intern. du Froid I, 367 (1937).
- (17) Symposium on The Separation of Rare Earth, Fission Product and Other Metal Ions and Anions by Adsorption on Ion-Exchange Resins, J. Am. Chem. Soc. 69, 2769-2881 (1947).
- (18) Trombe, F., and Foex, M., Ann. Chim. 19, 417 (1944).

- (19) Yost, D. M., Russell, H. R. Jr., and Garner, C. S., The Rare Earth Elements and Their Compounds, John Wiley and Sons, Inc., New York, 1947, p. 52.
- (20) Ziegler, W. T., J. Chem. Phys. 16, 838 (1948).
- (21) Ziegler, W. T., Investigation of Fundamental Properties of Elements and Their Compounds Including the Rare Earths at Very Low Temperatures with Particular Emphasis Upon Superconductivity, Project No. 116-18, Navy Department Office of Naval Research Contract No. N6-ori-192, Task Order I, Progress Report No. 1, November 27, 1946.
- (22) Ibid., Annual Report No. 1, January 2, 1947.
- (23) Ibid., Progress Report No. 7, November 30, 1947.
- (24) Ibid., Progress Report No. 8, May 7, 1948.
- (25) Ibid., Progress Report No. 9, July 9, 1948.
- (26) Zintl, E., and Neumayr, S., Z. Elektrochem. 39, 84 (1933).



Georgia Institute of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

PROGRESS REPORT NO. 10

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

CONTRACT NO. N6-ori-192, TASK ORDER I

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF THE  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

By

W. T. ZIEGLER

NOVEMBER 1, 1948



GEORGIA INSTITUTE OF TECHNOLOGY

THE STATE ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

PROGRESS REPORT NO. 10

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

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## I. SUMMARY

Chemical analyses of the lanthanum, cerium, praseodymium, and neodymium metal specimens which have already been studied for superconductivity, have been largely completed. These show that the commercially available metal specimens were not very pure. The purities were as follows: lanthanum, 95.5%; cerium, 88.4%; praseodymium, 54.8%; and neodymium, 78.7%.

Considerable progress has been made in the preparation of praseodymium and neodymium oxides of high purity (99.5+%) for use in the preparation of the pure metals.

Powder X-ray diffraction studies of the metal specimens referred to above have been made both before and after heat treatment in a vacuum furnace at 350° C. These studies indicate that it may be possible to prepare lanthanum and cerium metals in both hexagonal close-packed and face-centered cubic structures for study at low temperatures.

A distilling column for separating liquid nitrogen from liquid air has been built for use with the large liquid air plant supplied for use on the project.

## II. LOW TEMPERATURE RESEARCH

During the past three months no additional low temperature experiments have been made, pending chemical analysis of the metal samples already studied, namely, lanthanum, cerium, praseodymium, and neodymium. A short

paper reporting the results obtained for lanthanum and cerium appeared recently in the Journal of Chemical Physics 16, 828, 1948. Reprints of this paper have not yet become available.

Further experiments on heat-treated samples of lanthanum and cerium are planned in the near future. These are described briefly in Section IV.

A short paper describing the low temperature facilities of the laboratory has been accepted for publication in the November, 1948, issue of Refrigerating Engineering.

### III. STUDIES IN THE CHEMISTRY OF THE RARE EARTHS

During the past four months intensive work on chemical, spectrographic, and spectrophotometric methods of analysis of rare earth materials have been carried on. This work has had a two-fold objective: (1) to permit the chemical analysis to be made of the metal samples already subjected to low temperature studies, and (2) to aid in the purification of rare earth salts from which pure metals are to be prepared. Good progress has been made. A paper covering some of this work, entitled "Spectrochemical Determination of Lanthanum in Praseodymium Metal" by W. M. Spicer and W. T. Ziegler, has been submitted for publication in Analytical Chemistry.

The chemical analyses of the rare earth metal samples already studied at low temperatures are now essentially complete, and the results, to date, are shown in Table I.

These analyses reveal that the materials which have been studied were, unfortunately, not particularly pure. This was especially true of the praseodymium and neodymium. It seems quite possible that the nonappearance of superconductivity in the cerium, praseodymium, and neodymium samples studied may have been due to the large amounts of impurities present. The nonappearance of superconductivity in the praseodymium sample, which contained about 37% lanthanum, shows that one must be cautious about deducing the properties of the pure metal from the alloy, since, if the lanthanum in this sample had become superconducting above 2° K., this effect could have been detected.

TABLE I  
ANALYSES OF COMMERCIAL RARE EARTH METALS\*

|                    | <u>Lanthanum</u><br><u>Per Cent</u> | <u>Cerium</u><br><u>Per Cent</u> | <u>Praseodymium</u><br><u>Per Cent</u> | <u>Neodymium</u><br><u>Per Cent</u> |
|--------------------|-------------------------------------|----------------------------------|--|-------------------------------------|
| La                 | 95.5                                | —                                | 37.6**                                 | ca 5**                              |
| Ce                 | —                                   | 88.4                             | —                                      | —                                   |
| Pr                 | (41)                                | 0.4                              | 54.8                                   | 15                                  |
| Nd                 | (1.5)                               | 1.4                              | 3.5                                    | 78.7                                |
| Fe                 | 0.8                                 | 2.5                              | 1.6                                    | 2.8                                 |
| Si                 | <u>0.7</u>                          | <u>0.5</u>                       | <u>0.9</u>                             | <u>1.2</u>                          |
| Total              | 97.0                                | 93.2                             | 98.4                                   | 102.7                               |
| Unaccounted<br>for | 3.0                                 | 6.8                              | 1.6                                    | -2.7                                |

\* Obtained from Cooper Metallurgical Laboratory, Cleveland, Ohio.

\*\* Spectrographic determination.

Exploratory experiments leading to the production of moderate amounts (about 50 gm) of highly pure (99.5+%) neodymium and praseodymium oxides for use in the preparation of the pure metals have been carried out. The methods employed involved the use of the new ion-exchange techniques developed for this purpose during the war on the Manhattan Project.<sup>1</sup> So far the following materials have been produced:  $\text{Pr}_6\text{O}_{11}$ , 3.5 gm, 99.9+% pure, 7 gm, 98% pure; and  $\text{Nd}_2\text{O}_3$ , 12 gm, 99.5% pure. These separation methods have also proven useful as methods of analysis of commercial materials of dubious purity.

#### IV. X-RAY DIFFRACTION STUDIES

Powder X-ray diffraction studies (using copper K  $\alpha$  radiation) of the metals already studied for superconductivity have been carried out by Mr. A. L. Floyd, a graduate student in physics. An X-ray tube having a molybdenum target has been purchased to give shorter wave length radiation.

The work done to date has been summarized in Table II. Powder X-ray diffraction studies have been made of lanthanum, cerium, neodymium, and praseodymium metals both in the "as received" state and after heat treatment in a vacuum at 350° C. These experiments indicated that both lanthanum and cerium can be converted by heat treatment

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(1) "Symposium on the Separation of Rare Earth, Fission Product, and Other Metal Ions and Anions by Adsorption on Ion-Exchange Resins," Jour. Am. Chem. Soc. 69, 2769-2881 (1947).



TABLE II

| Metal*       | Purity<br>Per Cent | Major Impurity<br>Per Cent | Structure  |  |
|--------------|--------------------|----------------------------|--|--|
|              |                    |                            | As Received  | After Heated at 350° C<br>for 96 Hours   |
| Lanthanum    | 95.5               | —                          | h.c.p., lines diffuse                              | f.c.c., lines sharp                      |
| Cerium       | 88.4               | —                          | f.c.c.,** lines diffuse<br>h.c.p.,** lines diffuse | f.c.c., lines sharp                      |
| Praseodymium | 54.8               | 37.6 (La)                  | Only a few diffuse lines<br>obtained               | Many sharp lines of<br>unknown structure |
| Neodymium    | 78.7               | 15 (Pr)                    | Similar to Pr                                      | Similar to Pr                            |

\* Metals obtained from Cooper Metallurgical Laboratory, Cleveland, Ohio.

\*\* Approximately 3 parts f.c.c. to 1 part h.c.p.

from the hexagonal close-packed to the face-centered cubic structure. The results for praseodymium and neodymium were inconclusive.

Experiments to study the effect on crystal structure of cooling the lanthanum and cerium samples to liquid helium temperatures are planned. It is also planned to examine the heat-treated samples for superconductivity. It will be noted that the lanthanum sample which became superconducting had a predominantly hexagonal close-packed structure whereas the cerium, which did not become superconducting down to 2° K., was predominantly face-centered cubic. Whether these structural relationships apply to the metals in question at low temperatures remains to be seen.

#### V. LIQUID NITROGEN PLANT

Construction and installation of a large liquid nitrogen distilling column for use with the liquid oxygen plant (Linde Model SM-LO-P270) have been essentially completed. This column was designed by Mr. W. A. Phillips, who also supervised its construction in the Experiment Station shops. The column was designed to produce liquid nitrogen at 99.5+% purity at a rate of approximately 20 liters per hour. This column is of the "packed" type, employing aluminum shoe-eyelets for packing. A complete description of the installation will be given after operating tests are completed.



## VI. PERSONNEL

At the present time the following individuals are employed on the project.

| <u>Name</u>        | <u>Position</u>    | <u>Time</u> |
|--------------------|--------------------|-------------|
| Dr. W. T. Ziegler  | Director           | 2/3 time    |
| Dr. W. M. Spicer   | Research Associate | Part-time   |
| Mr. W. A. Phillips | Research Assistant | Full-time   |
| Mr. A. L. Floyd    | Research Assistant | Part-time   |
| Mr. J. O. Blomeke  | Research Assistant | Part-time   |
| Mr. N. M. Hallman  | Research Assistant | Part-time   |
| Mr. J. M. Ziegler  | Research Assistant | Part-time   |

Mr. J. B. Downs, Jr., who very ably carried out much of the analytical work on the rare earth metals this summer, has left the Project for other work.

## VII. CONFERENCES

W. T. Ziegler attended the Conference on Low Temperatures and Nuclear Physics held at Oak Ridge, Tennessee, on August 7 and 8, 1948.

Respectfully submitted:

W. T. Ziegler,  
Project Director

Approved:

Gerald A. Rossetot,  
Director

Georgia Institute of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

PROGRESS REPORT NO. 11

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

CONTRACT NO. N6-ori-192, TASK ORDER I

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF THE  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

By

W. T. ZIEGLER

DECEMBER 31, 1948

GEORGIA INSTITUTE OF TECHNOLOGY

THE STATE ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

PROGRESS REPORT NO. 11

PROJECT NO. 116-18

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH

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By

W. T. ZIEGLER

DECEMBER 31, 1948:

## I. GENERAL ACTIVITIES

During the past two months some minor changes have been made in the hydrogen liquefier which will increase its ease of operation.

Several operational tests on the liquid air separation column for producing liquid nitrogen, which has been built for use with the liquid oxygen plant, have been made. The results of these tests have been encouraging insofar as the operation of the column has been concerned, but have revealed a low overall efficiency for the plant, arising from poor performance of the compressor and low temperature expansion engine. These units have since been overhauled and further tests planned.

Further work on the preparation and analysis of rare earth materials has been carried out. Work on the preparation of lanthanum metal from its chloride is in progress. Studies of means of producing, by heat treatment, lanthanum and cerium having a desired crystal structure are continuing. The heat treated samples will be subjected to tests for superconductivity.

A very considerable effort has been devoted to the examination of much of the work done during the past six months. A technical paper summarizing the low temperature researches on lanthanum, cerium, praseodymium, and neodymium has been completed and will be released shortly. An annual

report covering the work from October 1, 1947 to October 1, 1948 is in preparation.

A brief description of the low Temperature Laboratory was published in the November, 1948 issue of REFRIGERATING ENGINEERING. Two research papers covering work done in connection with some analytical aspects of rare earth chemistry were presented at a "Meeting-in-Miniature" of the Georgia Section of the American Chemical Society held in Atlanta, Georgia, on November 19, 1948. The titles of these papers were "Spectrochemical Determination of Lanthanum in Praseodymium Metal" by W. M. Spicer and W. T. Ziegler and "Spectrophotometric Determination of Praseodymium and Neodymium" by W. T. Ziegler and J. B. Downs, Jr.

## II. PERSONNEL

At the present time the following individuals are employed on the project:

| <u>Name</u>       | <u>Position</u>    | <u>Time</u> |
|-------------------|--------------------|-------------|
| Dr. W. T. Ziegler | Director           | 2/3-time    |
| Dr. W. M. Spicer  | Research Associate | Part-time   |
| Mr. J. O. Blomeke | Research Assistant | Part-time   |
| Mr. A. L. Floyd   | Research Assistant | Part-time   |
| Mr. N. M. Hallman | Research Assistant | Part-time   |
| Mr. J. M. Ziegler | Research Assistant | Part-time   |

Mr. Blomeke is a candidate for the Ph.D. degree in Chemical Engineering and will probably do research on a problem related to the project for his doctorate thesis.





Mr. A. L. Floyd, a graduate student in physics, will carry out X-ray diffraction studies of the rare earth metals for his M. S. thesis problem.


Messrs. M. A. Turner and R. I. Tarver, graduate students in Chemical Engineering, have undertaken M. S. thesis problems involving the concentration and purification of samarium and scandium, respectively; work which is closely related to that being carried out on the present project.

Mr. W. A. Phillips, who has contributed much to the engineering aspects of the project to date, especially the setting up and operation of the liquid oxygen plant, and the design and construction of the nitrogen column, has left the project for other work.

Respectfully submitted:

  
W. T. Ziegler,  
Project Director

Approved: 

  
Gerald A. Rosselot,  
Director

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STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

PROGRESS REPORT NO. 12

PROJECT NO. 116-18

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH  
CONTRACT NO. N6-ori-192 , TASK ORDER I

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MARCH 31, 1949



GEORGIA INSTITUTE OF TECHNOLOGY

THE STATE ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH  
CONTRACT NO. N6-ori-192 , TASK ORDER I

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MARCH 31, 1949

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## I. SUMMARY

The present report presents a brief summary of the activities of the Project during the past three months (January 1, 1949 to March 31, 1949). Work during this period has been directed primarily toward a study of the relation between the crystal structure and superconductivity of lanthanum. The experiments are not yet sufficiently complete to warrant a detailed description and discussion of them.

## II. LOW TEMPERATURE RESEARCH

Previous work<sup>1, 2</sup> has shown that two test pieces (designation La 1 and La 2) cut from a sample of lanthanum metal having the composition\* 97.1% La, 0.8% Fe, 0.7% Si underwent a magnetic transition into superconductivity at  $4.85 \pm 0.15^{\circ}\text{K}$ . Filings taken from this sample gave an X-ray powder diffraction photograph with copper K-alpha radiation corresponding to a hexagonal close-packed structure. A second sample of lanthanum, obtained from a different source (designation La 3, and reported to contain a total of between one-half and one per cent of aluminum, silicon, and tungsten and to be substantially free of other rare earth metals) has been found to undergo a similar magnetic transition into superconductivity

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\* A redetermination of the lanthanum content of this sample has shown that it contained 97.1% La instead of the 95.5-98% previously reported.<sup>1,2</sup>

at  $4.45 \pm 0.10^{\circ}\text{K}$ . This sample now has also been found to have a hexagonal close-packed structure.

Previous work<sup>1, 2</sup> has also shown that it was possible to convert lanthanum filings from the hexagonal close-packed to the face-centered cubic structure by heat treatment in a furnace at  $350^{\circ}\text{C}$  for 96 hours.

During the past three months, sample La 1, heat treated under the above-mentioned conditions, has been tested down to  $2^{\circ}\text{K}$  and found not to be superconducting, whereas sample La 2 which had not been heat treated in the same experiments was found to be superconducting, as before, at about  $4.8^{\circ}\text{K}$ . The presumption is that face-centered cubic lanthanum is not a superconductor above  $2^{\circ}\text{K}$ , whereas lanthanum having a hexagonal close-packed structure is a superconductor below approximately  $4.8^{\circ}\text{K}$ . Considerable effort has been made to convert lanthanum from the face-centered cubic to the hexagonal close-packed structure, so far without success.

Similar experiments are being conducted with cerium. At the present time it appears that cerium, having the face-centered cubic structure, is not superconducting down to  $2^{\circ}\text{K}$ . Efforts to convert cerium to the hexagonal close-packed structure have not, as yet, been successful.

A technical report<sup>2</sup> covering low temperature work carried out to December 31, 1948, has been distributed.

### III. CHEMISTRY OF THE RARE EARTHS

Work on the preparation of pure neodymium, praseodymium, and samarium oxides has been continued. A new Beckman quartz spectrophotometer, Model DU, has been purchased by the Experiment Station for use in this project.

A note on analytical procedures entitled "Spectrochemical Determination of Lanthanum in Praseodymium Metal" by W. M. Spicer and W. T. Ziegler has been accepted for publication in Analytical Chemistry.

The annual report for the period October 1, 1947, to September 1, 1948, has been completed and will be distributed about April 15.

### IV. FUTURE PROGRAM

During the next year it is planned to conduct further work on the preparation of pure rare earth metals, particularly lanthanum, cerium, praseodymium, and neodymium, and to prepare nitrides and hydrides of some of these metals. These metals and compounds will be tested for superconductivity.

Experimental studies of the relationship between crystal structure and superconducting transition temperature for lanthanum will be continued.


It is also planned to redetermine, by the magnetic method previously described,<sup>2</sup> the superconducting transition temperature of a number of substances, such as lead sulfide, which have heretofore been studied only by the measurement of change in electrical resistance.

V. CONFERENCES

Dr. W. T. Ziegler attended the Cryogenics Conference sponsored by the Office of Naval Research at the University of California on February 1 and 2, 1949, and gave a report of low temperature work in progress under Contract No. N6-ori-192, Task Order I.

Respectfully submitted:

[REDACTED]  
W. T. Ziegler,  
Project Director

Approved: 

[REDACTED]  
Gerald A. Rosselot, Director  
State Engineering Experiment Station



VI. BIBLIOGRAPHY

- (1) Ziegler, W. T., Investigation of Fundamental Properties of Elements and Their Compounds Including the Rare Earths at Very Low Temperatures with Particular Emphasis Upon Superconductivity, Project No. 116-18, Navy Department, Office of Naval Research Contract No. N6-ori-192, Task Order I, Progress Report No. 10, November 1, 1948.
- (2) Ziegler, W. T., Superconductivity of Lanthanum, Cerium, Praseodymium and Neodymium, Project No. 116-18, Navy Department, Office of Naval Research, Contract No. N6-ori-192, Task Order I, Technical Report No. 1, January 20, 1949.



Georgia Institute of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

STATUS REPORT NO. 13

PROJECT NO. 116-18

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
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BY

W. T. ZIEGLER

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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH  
CONTRACT NO. N6-ori-192, TASK ORDER I  
NR 016-406

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JUNE 30, 1949

Georgia Institute of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

STATUS REPORT NO. 13

PROJECT NO. 116-18

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

BY

W. T. ZIEGLER

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JUNE 30, 1949

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## I. SUMMARY

The study of the relation between crystal structure and superconductivity for lanthanum metal has continued. In the last Progress Report<sup>1</sup> it was tentatively reported that whereas lanthanum in the hexagonal close-packed structure was a superconductor at  $4.85 \pm 0.15^{\circ}\text{K}$ , lanthanum in the face-centered cubic structure was not a superconductor at temperatures down to  $2^{\circ}\text{K}$ . These conclusions were based on samples of lanthanum from two different sources. During the past three months additional experiments on these same samples have been carried out with conflicting results. These experiments, while by no means conclusive, cause some doubt as to the correctness of the conclusion that lanthanum having a face-centered cubic structure is not a superconductor above  $2^{\circ}\text{K}$ . Explanations which account for these discrepancies in terms of poor heat transfer do not appear to be convincing. A hypothesis is presented which attempts to explain the observed results in terms of a third (unknown) structure of lanthanum which may exist at low temperatures. Further work designed to elucidate questions raised by these experiments is planned.

Work on the purification of neodymium and praseodymium oxides has continued and approximately 15 grams of each material have been obtained in a very pure form.

## II. LOW TEMPERATURE RESEARCH

The study of the relation between crystal structure and superconductivity of lanthanum metal has continued.



A. Previous Work

Previously it was reported<sup>2</sup> that lanthanum metal in the hexagonal close-packed structure became a superconductor in the range 4.5-5°K. These conclusions were based on experiments carried out with samples of lanthanum metal obtained from two different sources.<sup>1, 2</sup> One of these samples, obtained from the Cooper Metallurgical Laboratory (now Cooper Metallurgical Associates) Cleveland, Ohio, had been found to have the following composition: 97.1 per cent, La, 0.7 per cent Si, 0.8 per cent Fe, aluminum, calcium, and traces of other rare earths.<sup>1, 2</sup> The second sample, obtained from Adam Hilger, Ltd., London, England, was reported by the supplier to contain a total of between one half and one per cent of aluminum, silicon, and tungsten, and to be substantially free of other rare earths.<sup>2</sup>

Examination of these samples in the "as received" condition by X-ray powder diffraction techniques has shown them to have a hexagonal close-packed structure. It has also been shown that lanthanum metal filings having a hexagonal close-packed structure could be converted to the face-centered cubic structure by heat treatment in a vacuum furnace at  $350 \pm 20^\circ \text{C}$  for 96 hours.<sup>2</sup>

In the last Progress Report<sup>1</sup> it was tentatively reported that lanthanum metal having a face-centered cubic structure showed no magnetic transition into superconductivity down to 2°K, the lowest temperature reached. The method of measurement

used was the same as that employed in previous magnetic studies.<sup>2</sup>

The conclusions relative to the nonsuperconducting properties of the face-centered cubic structure were based on two separate experiments carried out on January 26, 1949 (Run No. 5) and February 16, 1949 (Run No. 6) on a single specimen (designated as La 1) cut from the Cooper material. This specimen, a cylinder having the dimensions 4.4 x 19.0 mm, was heat treated while sealed in a pyrex capsule containing helium gas at approximately ten cm (Hg) pressure according to the above-mentioned schedule. La 1 had previously<sup>2</sup> been used in the "as received" (hexagonal close-packed) structure for low temperature studies and found to exhibit a magnetic transition into superconductivity at  $5.0 \pm 0.1^{\circ}\text{K}.$ \* (Run No. 4).

The capsule was not actually opened after the heat treatment so that no filings were taken from it. However, filings from the original Cooper sample in the hexagonal close-packed structure, which were heated in the furnace at the same time as the capsule containing La 1, were found to have been transformed to the face-centered cubic structure. It was on this basis that the Cooper specimen used in the low temperature studies was assumed to be in the face-centered cubic structure. In one instance (Run No. 5) La 1 was kept for 29 minutes at

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\* This transition was reported in earlier work as being at  $4.85 \pm 0.15^{\circ}\text{K}.$  More recent work has indicated that the temperature scale in use in Runs No. 1-4 was somewhat in error, and that the midpoint of the magnetic transition for the Cooper material is nearer  $5.0 \pm 0.1^{\circ}\text{K}.$

4.2°K or below without any detectable magnetic anomaly, whereas an untreated specimen La 2 (cut from the original Cooper material and hence in the hexagonal close-packed structure) showed a sharp magnetic transition into superconductivity at  $5.05 \pm 0.1^\circ\text{K}$  with no noticeable hysteresis.

In these low temperature experiments separate, sealed glass capillary tubes containing Cooper lanthanum metal filings in the hexagonal and face-centered cubic structures were also cooled to 2°K. After warming to room temperature again the samples were re-examined by means of X-ray diffraction and found to have the same structures as prior to cooling. It was concluded, therefore, that transition between these two structures did not occur in the bulk specimens due to cooling alone.

Other tests showed that Cooper lanthanum metal filings which had been converted to the face-centered cubic structure by heat treatment at 350° C did not show any detectable amount of the hexagonal close-packed structure after three weeks at room temperature.

#### B. Recent Work

During the past three months additional low temperature experiments have been carried out with a view to further examining the apparent nonsuperconductivity of the face-centered cubic form of lanthanum. Further work has also been carried out on the X-ray structure of lanthanum metal. The results obtained have not been conclusive and in some instances appear to contradict the previous conclusions relative to the nonsuperconductivity of lanthanum in the face-centered structure.



Table I gives a condensed summary of the low temperature experiments which have been made during the past three months (Runs 7 through 9), together with several previous experiments which are pertinent to the present discussion. These experiments are discussed in greater detail in the following paragraphs. All experiments have been conducted using the cryostat and methods previously described.<sup>2</sup> The measurement of the transition is based upon the change in induction occurring when a specimen passes from the normal to the superconducting state or vice versa. This unbalance appears experimentally as a galvanometer deflection. The difference in galvanometer deflections obtained when the specimen is in these two states is taken as 100 per cent. On this basis the transition temperature is reported as the temperature at which 50 per cent of this difference has been reached.

An approximately rectangular (4 x 11.5 x 2.6 mm) specimen (La 3) cut from the Hilger sample which had previously been shown to have the hexagonal close-packed structure<sup>1</sup> and to undergo a magnetic transition into superconductivity<sup>2</sup> at  $4.6 \pm 0.1^\circ$  (Run No. 3)\* was heat treated in a vacuum furnace at  $350^\circ \text{C}$  for four days. The specimen had been sealed in a pyrex capsule under nine cm (Hg) pressure of helium gas for the original low temperature experiments and was not opened

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\* In the light of later runs in which the temperature scale was known more accurately it is believed that this temperature is more nearly correct than the temperature previously reported, namely,  $4.45 \pm 0.10^\circ \text{K}$ .

TABLE I

## CONDENSED SUMMARY OF LOW TEMPERATURE RUNS ON LANTHANUM METAL SPECIMENS

| Run No. | Specimen | Source | Structure                          | Warming Rate deg./min.   | Transition Temp., °K | Transition Range, deg. | Comments   |
|---------|----------|--------|------------------------------------|--|----------------------|------------------------|--|
| 4       | La 1     | Cooper | h.c.p. <sup>a</sup>                | 0.15   | 5.03                 |                        | Specimen in "as received" condition  |
| 5       | La 1     | Cooper | f.c.c. <sup>b</sup>                | Not superconducting down to 2°K                                  |                      |                        | Run made ten days after heat treatment of specimen for 96 hours at 350° C    |
|         | La 2     | Cooper | h.c.p. <sup>a</sup>                |  | 5.04                 | 0.15                   | Specimen in "as received" condition  |
| 6       | La 2     | Cooper | h.c.p. <sup>a</sup>                | 0.3<br>0.22  | 5.04<br>4.95         | 0.18                   | Same specimen as in Run 5  |
|         | La 1     | Cooper | f.c.c. <sup>c</sup>                | Not superconducting down to 2.27°K                               |                      |                        | Same specimen as in Run 5. Run made 21 days after original heat treatment.   |
| 7       | La 3     | Hilger | f.c.c. <sup>b</sup>                | Not superconducting down to 2.25°K                               |                      |                        | Run made 12 days after heat treatment of specimen for 96 hours at 350° C     |
|         | La 1     | Cooper | h.c.p. <sup>a</sup><br>some f.c.c. | Superconducting below approximately 5.5°K with strong hysteresis |                      |                        | Between Run 6 and 7 La 1 was treated so as to convert it to h.c.p. structure |

(Continued on page 7)

Superscripts are explained on page 8.

TABLE I (continued)

## CONDENSED SUMMARY OF LOW TEMPERATURE RUNS ON LANTHANUM METAL SPECIMENS

| Run No. | specimen | Source | Structure                           | Warming Rate deg./min.                             | Transition Temp., °K | Transition Range, deg. | Comments   |
|---------|----------|--------|-------------------------------------|--|----------------------|------------------------|--|
| 7       | La 1     |        |                                     |  |                      |                        | Treatment was judged unsuccessful on basis of simultaneous tests on filings having f.c.c. structure. On completion of Run 7 filings taken from specimen were found to be mixture of h.c.p. and f.c.c. structures. Elapsed time since original heat treatment (prior to Run 5) was 60 days. |
| 8       | La 3     | Hilger | h.c.p. <sup>a</sup><br>trace f.c.c. | 0.12   | 5.45                 | 0.16                   | Both La 1 and La 3 were resealed in capsules at ten cm pressure (Hg) of helium gas just prior to Run 8. No hysteresis observed.  |
|         | La 1     | Cooper | h.c.p. <sup>a</sup><br>some f.c.c.  | 0.07<br>0.065                                      | 5.16<br>4.99         | 0.16<br>0.17           |  |
|         | La 4     | Cooper | h.c.p. <sup>a</sup>                 | Superconducting below 5.5°K with small hysteresis. |                      |                        | "As received" condition. Specimen sealed in capsule under high vacuum.   |

(Continued on page 8)

Superscripts are explained on page 8.

TABLE I (continued)

## CONDENSED SUMMARY OF LOW TEMPERATURE RUNS ON LANTHANUM METAL SPECIMENS

| Run No. | Specimen | Source | Structure           | Warming Rate deg./min. | Transition Temp., °K | Transition Range, deg. | Comments   |
|---------|----------|--------|---------------------|------------------------|----------------------|------------------------|--|
| 9       | La 3     | Hilger | f.c.c. <sup>b</sup> | 0.18                   | 5.45                 | 0.07                   | Following Run 8 both La 1 and La 3 were again heat treated for 96 hours at 350° C to convert them to f.c.c. structure. After heat treatment capsules were resealed under ten cm pressure (Hg) of helium gas. |
|         |          |        |                     | 0.08                   | 5.45                 | 0.14                   |  |
|         |          |        |                     | 0.09                   | 5.51                 | 0.13                   |  |
|         | La 1     | Cooper | f.c.c. <sup>b</sup> | 0.15                   | 5.22                 | 0.10                   |  |
|         |          |        |                     | 0.16                   | 5.22                 | 0.12                   |  |
|         |          |        |                     | 0.16                   | 5.22                 | 0.12                   |  |

<sup>a</sup> Structure based on filings taken from specimen.

<sup>b</sup> Structure of specimen inferred from observations made on filings which were heat treated simultaneously with specimen.

<sup>c</sup> Structure of specimen assumed to be the same as in Run 5.



prior to or after heat treatment. A thin wedge of the original material was heat treated at the same time and was found to be converted from the hexagonal close-packed to the face-centered cubic structure. It was, therefore, assumed that the specimen La 3 also had been converted to the face-centered cubic structure.

Specimen La 3 was cooled to 2.25°K on April 6, 1949 (Run No. 7) twelve days after it had been heat treated. Although the specimen was kept at or below 4.2°K for at least 20 minutes, no magnetic transition into superconductivity could be detected. This result was in agreement with those previously found for the Cooper specimen in the face-centered cubic structure.

Between Runs No. 6 and 7 the specimen La 1 (capsule unopened since heat treatment of the specimen on January 11-17) was subjected to a number of treatments designed to convert it from the face-centered cubic to the hexagonal close-packed structure. These treatments consisted primarily in repeated cooling and warming between room temperature and 80°K. In one series of experiments the specimen was held in a vacuum furnace at 100° C for four days after which it was cycled between liquid nitrogen temperature and 85° C. Each specific treatment was carried out simultaneously on capillary tubes containing Cooper lanthanum filings known to be in the face-centered cubic structure. After each treatment the capillary tubes were examined by means of X-ray diffraction. In no case was there an observable change to the hexagonal close-packed structure. However, when La 1 was tested for superconductivity in Run No.

7 a magnetic transition was observed which exhibited a very strong hysteresis. This hysteresis was so marked that no satisfactory measurement of the transition temperature was possible. Thus, the specimen was tested magnetically at 10-15 second intervals as the temperature of the cryostat was lowered from 4.2 to 2.3°K over a ten minute period. Superconductivity was observed to begin only at the lowest temperature. A similar temperature lag was observed on warming.

The unexpected hysteresis encountered suggested a possible lack of thermal equilibrium between the sample and the cryostat, due to the loss of helium by diffusion from the pyrex glass capsule during heat treatment at 350° C. This possibility was examined as follows:

- (1) The lanthanum specimen, La 1, was removed from its capsule, resealed in a new capsule under ten cm pressure (Hg) of helium, and again examined for superconductivity (Run No. 8, April 15, 1949). The sample was found to undergo a magnetic transition into superconductivity at  $5.05 \pm 0.1^{\circ}\text{K}$  with a transition range of  $0.16^{\circ}$ . Similarly the La 3 (Hilger) specimen, which was found not to be superconducting in Run 7, was resealed under ten cm pressure (Hg) of helium gas and re-examined for superconductivity in Run No. 8. This specimen now exhibited a magnetic transition into superconductivity at  $5.4 \pm 0.1^{\circ}\text{K}$  with a transition range of  $0.16^{\circ}$ . This later temperature was  $0.8^{\circ}$

higher than that previously observed for this specimen in the hexagonal close-packed structure (Run No. 3).

Filings were taken from specimens La 1 and La 3 immediately following Run No. 7 and analysed by means of X-ray diffraction. These analyses showed that both La 1 and La 3 consisted of both hexagonal close-packed and face-centered cubic structure.

- (2) A new specimen, La 4, in the form of a cylinder having the dimensions 4.4 x 13.8 mm, was cut from the original lump of Cooper lanthanum. This specimen was sealed in a pyrex capsule under air at a pressure of  $10^{-5}$  mm Hg. When cooled to helium temperatures in Run No. 8 this specimen also was found to exhibit a hysteresis. Thus, the sample, on cooling, remained in the normal state for three minutes with the cryostat at  $4.2^{\circ}$  (i.e.,  $0.8^{\circ}$  below the transition temperature usually observed) before the transition occurred. A similar behavior was observed on warming. These observations are explainable as thermal lag resulting from the absence of an exchange gas in the capsule, the cooling of the specimen being accomplished by the metal-to-glass contact points only.
- (3) Calculations were made of the loss of helium to be expected at  $350^{\circ}$  C because of diffusion through the walls of the pyrex capsule. These capsules were all



constructed from seven mm O.D. pyrex tubing having a wall thickness of approximately one mm. The calculations were made using the data of Urry<sup>3</sup> and required an extrapolation of his results from 283° C to 350° C. The calculations indicated that only about ten per cent of the helium gas present would be lost by diffusion.

The experiments listed in (2) and the calculations outlined in (3) above both make it seem doubtful that the failure to observe superconductivity in La 1 and La 3 in Run Nos. 5, 6, and 7 was because of the loss of helium as an exchange gas from the capsules. The observation of superconductivity of La 1 in Run Nos. 7 and 8 and of La 3 in Run No. 8 could be explained by the presence of some of the hexagonal close-packed structure in each specimen. The hysteresis in the transition of La 1 in Run No. 7 is not explained nor is the much higher transition temperature of La 3 in Run No. 8.

A fact which has some bearing on this problem involves the rate of transition of La 1 and La 3 from the face-centered cubic to the hexagonal close-packed structure when stored at room temperature. Previous experiments had shown that filings, taken from the original Cooper sample, which had been converted to the face-centered cubic structure showed no detectable transition to the hexagonal close-packed structure when examined by X-ray diffraction after three weeks storage at room temperature. On the other hand, a thin wedge cut from the original Hilger

sample and converted to the face-centered cubic structure did give evidence of the presence of the hexagonal close-packed structure after about three weeks at room temperature. The presence of the hexagonal close-packed structure in La 3 (Hilger) sample used in Run No. 7 can therefore be explained as the result of slow transition occurring over the 21 days which had lapsed since the sample was originally heat treated. The appearance of the hexagonal close-packed structure in the La 1 (Cooper) sample used in Run No. 7 probably is caused by a similar, but still slower, transition which had occurred during storage since Run No. 6, a lapse of 60 days. This transition may have been hastened by the cooling cycles to which La 1 was subjected between Run Nos. 6 and 7.

The slow transition of the face-centered cubic structure to the hexagonal close-packed structure has previously been observed by Zintl and Neumayr,<sup>4</sup> who noticed that in a pure sample of lanthanum the transition was detectable after several days storage at room temperature. It seems reasonable to suppose that the observed differences in the rate of phase transition is caused by the differing purities of the Cooper and Hilger samples. Mahn<sup>5</sup> has observed that as little as 0.08 per cent magnesium will greatly retard this phase transition in cerium, an otherwise quite similar metal. A similar retardation is produced in cerium by calcium impurity.<sup>6</sup> Both calcium and magnesium were shown by spectrographic analysis to be present in small amounts in the Cooper sample.

The results obtained in Run Nos. 7 and 8 suggested that specimens La 1 and La 3 be reconverted to the face-centered cubic structure, the capsules containing them being filled with helium gas at ten cm pressure (Hg) following heat treatment, and the specimens immediately subjected to tests for superconductivity. Accordingly, these two specimens, along with the filings taken from them after Run No. 7, were heat treated for four days at 350° C. After heat treatment X-ray diffraction photographs showed the filings to have the face-centered cubic structure. After removal from the vacuum furnace the specimens La 1 and La 3 were resealed under ten cm pressure (Hg) of helium gas and tested for superconductivity in Run No. 9 (April 21, 1949). Both specimens were found to undergo a magnetic transition into superconductivity. The Hilger specimen, La 3, was studied carefully over the range 4.5-5.6°K and a single magnetic transition found at  $5.45 \pm 0.1^\circ\text{K}$ . The Cooper specimen, La 1, was studied over the range 4.9-5.3°K and exhibited a single transition at  $5.22 \pm 0.1^\circ\text{K}$ . In both cases the transition range was approximately 0.15°.

The results of Run No. 9 were unexpected because it had been supposed that in view of the results of Run Nos. 5, 6, and 7 no transitions would be observed in these samples. The fact that the heat treatment used in preparing these specimens for Run Nos. 5, 6, and 7 was identical with that used in their preparation for Run No. 9 makes it seem unlikely that there

was any essential difference between these samples at the start of their respective low temperature runs. It is conceivable that these bulk samples were primarily in hexagonal close-packed structure even though the filings, which were treated simultaneously, were known to have been transformed to the face-centered cubic structure. If the bulk specimens had actually remained in the hexagonal close-packed structure, then the explanation for their failure to exhibit superconductivity in Run Nos. 5, 6, and 7 must lie in extremely poor thermal contact between the cryostat and the sample. However, explanations which account for these discrepancies in terms of poor heat transfer do not appear to be very convincing.

It is possible to advance the following working hypothesis which will explain the results. This hypothesis is based upon a survey of the literature dealing with phase changes in lanthanum and cerium.<sup>7</sup> Briefly the hypothesis assumes that: (a) lanthanum having a hexagonal close-packed,  $\beta$ , structure is a superconductor at  $5.0 \pm 0.1^\circ\text{K}$ ; (b) lanthanum having a face-centered cubic,  $\gamma$ , structure is not a superconductor down to  $2^\circ\text{K}$ ; (c) under certain conditions (not clearly defined)  $\gamma$ -lanthanum can transform to  $\alpha$ -lanthanum (structure unknown) at low temperatures; (d)  $\alpha$ -lanthanum is stable only at low temperatures; and (e)  $\alpha$ -lanthanum exhibits a magnetic transition into superconductivity in the range  $5.1$ - $5.4^\circ\text{K}$ .

The results of most of these studies have been used by Mr. A. L. Floyd as part of his thesis for the degree of Master



of Science in Physics.<sup>8</sup> Mr. Floyd carried out the X-ray structure studies and the heat treatments, and assisted with the low temperature experiments.

### C. Future Work

Much work remains before the seeming inconsistencies in these experiments are removed. Future work will include a more detailed examination of the rate of transition of the bulk samples from the hexagonal close-packed to the face-centered cubic structure, further experiments on the problem of thermal lag because of possible loss of helium gas, and an attempt to measure the electrical resistivity of lanthanum as a function of temperature down to 2°K in order to see if any evidence can be found for the occurrence of an anomalous phase transition.

## III. THE CHEMISTRY OF THE RARE EARTHS

During the past three months work on the preparation of pure neodymium and praseodymium oxides by means of ion exchange techniques has continued. Approximately 12 and 15 grams, of extremely pure praseodymium and neodymium oxides, respectively, have been prepared. Final spectrophotometric and spectrographic analyses of these materials are now in progress.

It is hoped that preliminary experiments on the production of lanthanum and its hydrides can be started in the near future.

Mr. M. A. Turner, a graduate student in Chemical Engineering, has carried out as his Master's thesis problem<sup>9</sup> an attempt to prepare pure samarium oxide from a mixture rich in gadolinium using Dowex-50 as the ion exchange resin. The eluting

solution used was a five per cent citric solution, adjusted to pH = 2.85-3.0 with concentrated ammonium hydroxide. Mr. Turner found that under these conditions the separation of samarium from gadolinium was not accomplished. This result was in agreement with a similar experiment using the resin Amberlite IR-100 carried out by Spedding et al., J. Am. Chem. Soc. 69, 2812 (1947).

#### IV. PERSONNEL

At the present time the following individuals are employed on the Project:

| <u>Name</u>              | <u>Position</u>    | <u>Time</u> |
|--------------------------|--------------------|-------------|
| Dr. W. T. Ziegler        | Director           | 2/3 time    |
| Dr. W. M. Spicer         | Research Associate | Part-time   |
| Mr. J. O. Blomeke        | Research Assistant | Part-time   |
| Mr. B. R. Willeford, Jr. | Research Assistant | Full-time*  |
| Mr. J. T. Roberts, Jr.   | Research Assistant | Full-time*  |
| Mr. R. A. Young          | Research Assistant | Part-time   |
| Mr. George Cook          | Machinist          | Part-time   |

Messrs. A. L. Floyd, N. M. Hallman, and J. M. Ziegler have graduated from the Institute and left the Project for other work.

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\* For the summer

V. TRIPS

Dr. W. T. Ziegler visited the Oak Ridge National Laboratory on June 10, 1949 to examine the low temperature facilities being set up there under the direction of Dr. L. E. Roberts. He also visited the chemical laboratories where Dr. B. H. Ketelle is carrying out rare earth separations using ion exchange techniques.

Respectfully submitted:

[REDACTED]  
W. T. Ziegler,  
Project Director

Approved:

[REDACTED]  
Gerald A. Rosselot, Director  
State Engineering Experiment Station



VI. BIBLIOGRAPHY

- (1) Ziegler, W. T., Investigation of Fundamental Properties of Elements and Their Compounds Including the Rare Earths at Very Low Temperatures with Particular Emphasis Upon Superconductivity, Project No. 116-18, Navy Department, Office of Naval Research Contract No. N6-ori-192, Task Order I, Progress Report No. 12, March 31, 1949.
- (2) Ziegler, W. T., Superconductivity of Lanthanum, Cerium, Praseodymium and Neodymium, Project No. 116-18, Navy Department, Office of Naval Research, Contract No. N6-ori-192, Task Order I, Technical Report No. 1, January 20, 1949.
- (3) Urry, W. D., J. Am. Chem. Soc. 54, 3887 (1932).
- (4) Zintl, E. and Neumayr, S., Z. Elektrochem. 39, 814 (1933).
- (5) Mahn, F., Compt. Rend. 223, 78 (1946).
- (6) Trombe, F. and Foex, M., Compt. Rend. 223, 949 (1946).
- (7) Vide: (a) Trombe, F. and Foex, M., Ann. Chim. 19, 417 (1944); (b) Trombe, F. and Foex, M., Compt. Rend. 217, 501 (1943).
- (8) Floyd, A. L., Thesis, Effect of Temperature on the Crystal Structure of Lanthanum, Cerium, Neodymium and Praseodymium. The Relation Between Crystal Structure and Superconductivity. Georgia Institute of Technology, Atlanta, 1949.
- (9) Turner, M. A., Thesis, The Separation of Samarium From Rare Earth Mixtures by Means of Ion Exchange, Georgia Institute of Technology, Atlanta, 1949.

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This Report Contains 25 Pages

## I. SUMMARY

Further studies have been made of the conditions under which the transition of lanthanum metal from the hexagonal close-packed ( $\alpha$ ) to the face-centered cubic ( $\beta$ ) structure occurs. It has been found that, whereas it is possible to convert lanthanum metal filings from the  $\alpha$  to the  $\beta$  structure at temperatures varying from 250 to 400° C., this has not proven possible, as yet, with bulk specimens. These observations have thrown considerable doubt on the tentative conclusion reached earlier, namely, that lanthanum metal in the face-centered cubic modification is not a superconductor down to about 2°K, since there is now some doubt that the bulk specimens tested for superconductivity had the face-centered cubic structure as was believed at that time.

A brief review of the large amount of chemical work carried out during the past fifteen months is presented and related to the work of the past three months. This work has been concerned with (1) the preparation and analysis of highly pure rare earth oxides, particularly neodymium and praseodymium oxides, from commercially available concentrates, and (2) the preparation of rare earth metals from the oxides.

The separation experiments have yielded about 30 grams of  $\text{Nd}_2\text{O}_3$  and 20 grams of  $\text{Pr}_6\text{O}_{11}$  having a purity estimated to be greater than 99.5 per cent, as well as 20 grams of  $\text{Nd}_2\text{O}_3$  and 100 grams of  $\text{Pr}_6\text{O}_{11}$  having a purity greater than 95 per cent.

Preliminary experiments to produce rare earth metals from



their salts have been carried out. So far only the problem of producing lanthanum metal has been studied. While a few tenths of a gram of lanthanum metal has been produced, considerably more research will be necessary before the method can be considered satisfactory.

The liquid oxygen plant assigned to the Project has been converted to a liquid nitrogen producing plant. This plant has been found to have a low production rate (about 40 per cent of rated capacity).

A list of the personnel currently associated with the Project is given.

## II. X-RAY STRUCTURE STUDIES OF LANTHANUM METAL

As has already been indicated in previous reports<sup>14,15,16,17,18</sup> a study is being made of the phase transition of lanthanum metal from the hexagonal close-packed structure (stable at room temperature) to the face-centered cubic structure (apparently stable above about 250° C.). It is the purpose of these experiments to prepare bulk specimens of both structures, so that these two structures may be tested for superconductivity. As indicated in the last status report<sup>18</sup> the structure of all heat-treated bulk specimens used in the previous low temperature studies was inferred from the structure of filings heat treated simultaneously with the bulk specimens.

During the past three months further heat treatment experiments designed to convert bulk samples of lanthanum from hexagonal close-packed to face-centered cubic have been carried

out. Heat treatments were carried out for about four days at 350 and 400° C., conditions previously found satisfactory for the conversion of filings by Zintl and Neumayr.<sup>19</sup> Filings taken from the bulk specimens before heat treatment were heat-treated simultaneously with the bulk specimens. These filings were examined by means of the X-ray diffraction powder technique, both before and after heat treatment and were found to have been converted from the hexagonal close-packed to the face-centered cubic structure. Filings taken from the bulk samples after heat treatment were found still to have the hexagonal close-packed structure.

It was thought that perhaps the strains set up in the operation of obtaining the filings from the heat-treated bulk sample might have altered the structure of the filings so as to convert the originally face-centered cubic structure to the observed hexagonal close-packed structure. Experiments to test this point were made by taking X-ray diffraction pictures of a thin bulk sample directly without filing. The results of these tests, while not conclusive, indicated that the structure of the heat-treated sample was primarily hexagonal close-packed.

Thus, it seems that the heat treatment experiments so far carried out by us on lanthanum samples\* obtained from three different sources successfully converted filings from the hexagonal

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\* These samples contained 97 to 98 per cent lanthanum.<sup>15, 17</sup>



close-packed to the face-centered cubic structure, but that there is no evidence that more than a small per cent of a bulk sample has been made to undergo this transition.

Careful measurements have been made on filings to obtain the crystal parameters of the face-centered cubic and hexagonal close-packed structure. The results are shown in Table I.

TABLE I  
CRYSTAL PARAMETERS OF LANTHANUM METAL

| Structure              | $a_0$       | Parameters        | $c/a_0$   | Reference                       |
|------------------------|-------------|-------------------|-----------|---------------------------------|
|                        | kx units    | $a_0$<br>kx units | kx units  |                                 |
| Face-centered cubic    | 5.285+0.005 |                   |           | This re-search                  |
|                        | 5.296+0.002 |                   |           | Zintl and Neumayr <sup>19</sup> |
| Hexagonal close-packed |             | 3.74+0.01         | 1.62+0.01 | This re-search                  |
|                        |             | 3.72              | 1.63      | McLennan and McKay <sup>5</sup> |
|                        |             | 3.757             | 1.61      | Rossi <sup>7</sup>              |

It will be seen that the results obtained in our research agree reasonably well with results obtained by other investigators. It is possible that the differences which exist may arise from the differing purities of the samples used by different investigators.

Further attempts to obtain bulk specimens of lanthanum having the face-centered cubic structure are planned.

### III. LOW TEMPERATURE RESEARCH

One of the objectives of the low temperature research being carried out under this contract has been to study the relation between crystal structure and superconductivity in the rare earth metals. To date most of our experiments have been carried out using lanthanum metal, primarily because of its availability. Experiments previously reported indicated that, whereas lanthanum having a hexagonal close-packed structure was a superconductor, the face-centered cubic structure was not.<sup>17, 18</sup>

During the past three months further experiments on the X-ray structure of lanthanum metal have indicated that bulk samples previously inferred to be in the face-centered cubic structure might not have been. Thus, the nonsuperconductivity previously reported may not have been associated with a change in structure but rather with some other factor such as lack of thermal equilibrium in the low temperature experiments.<sup>18</sup> Studies to elucidate these discrepancies are continuing.

One further low temperature experiment was carried out on a specimen of lanthanum metal (La I), previously heat-treated for 96 hours at 350° C. This specimen had been found (Run No. 9) to exhibit a transition into superconductivity at 5.22°K. After heat treatment for 96 hours at 400° C. the specimen exhibited a transition into superconductivity at 5.31<sub>±</sub>0.02°K.

This latter result probably agrees within experimental error with the previous result, indicating that heat treatment at this higher temperature had no significant effect on the transition temperature. The transition occurred in each instance over a range of about  $0.1^{\circ}$ . X-ray structure studies of filings taken from the bulk specimen both before and after this heat treatment showed that the structure of the specimen was predominantly hexagonal close-packed.

#### IV. CHEMISTRY OF THE RARE EARTH ELEMENTS

When the present investigation of the properties of the rare earth metals and their compounds was begun in October, 1946, it was fully realized that no adequate sources of highly pure materials of this kind were available. Furthermore, it was obvious that facilities must be at hand for the identification and analysis of the various rare earths. These two facts have resulted in a very considerable effort along several lines of purely chemical work.

One of these lines of study has been the development and testing of methods of preparing in a pure form the rare earth oxides which serve as the starting materials from which the rare earth metals are prepared, and, from which metals, in turn, the rare earth hydrides and nitrides are to be prepared.

A second series of studies has been concerned with the problem of preparing anhydrous chlorides from which the metal could be prepared by electrolysis.

A third series of studies has been concerned with the

preparation of the metals themselves.

A fourth line of endeavor has been the calibration and testing of spectrophotometric and spectrographic methods of analysis of the rare earths, and the use of these methods in following the separation and purification of the rare earth oxides mentioned above. These methods of analysis have also been used to determine the composition of such rare earth metals and compounds as were suitable for the present investigation.

The progress of these problems has been discussed in earlier reports<sup>14, 15, 16, 17, 18</sup> only briefly, largely because of the incomplete character of many of the experiments. It seems appropriate to give in the present report a somewhat more detailed picture of the results obtained to date, with a resumé of the work carried out during the period July 1 to October 1, 1949.

#### A. The Separation of the Rare Earth Elements

The separation of the rare earth elements from one another has always been recognized as an extremely difficult chemical problem. The great similarity in the chemical behavior of these elements has made the preparation of pure compounds difficult and expensive. In September, 1947, a new method of separating the rare earths was described<sup>11</sup> which was the result of research work carried out on the Manhattan Project. This method of separation, known as the "ion-exchange method," takes advantage of the ion-exchange properties of certain synthetic



resins, together with the ability of the tripositive rare earth ions to form complex ions with citric acid solution. This method has proved to be much more rapid in operation than older separation methods and yields highly pure products.

An important aspect of the problem was the use of radioactive tracers as a means of following the course of the separation. Indeed, much of the work reported upon dealt with the separation of milligram and microgram quantities of radioactive materials, while only a few papers dealt with the separation of multigram quantities of the rare earths.<sup>10, 11</sup>

With this background, work was initiated here in June, 1948, with a view to gaining experience in the use of the ion-exchange method for the preparation of multigram (20-200 grams) quantities of the pure rare earth oxides necessary to serve as starting materials for the preparation of the metals. At the same time work was begun on setting up methods of analysis. The methods of analysis will be discussed in another place in this report.

Up to the present time this study has been concerned primarily with the separation, by means of ion-exchange, of neodymium, praseodymium, and lanthanum from commercially available rare earth concentrates. Some work has also been carried out on the separation of samarium and gadolinium. The choice of the conditions employed for carrying out these separations was based, in part, upon the results obtained by Spedding and his co-workers<sup>8, 9, 10</sup> using the Amberlite resins IR-1 and IR-100

and upon the results of Harris and Tompkins<sup>3</sup> and Ketelle and Boyd<sup>4</sup> using the resin Dowex-50.

### 1. Previous Work

The method used for the separation of rare earths by means of ion-exchange resins may be described briefly by referring to Figure 1, which is a schematic diagram of the apparatus used for this purpose at Georgia Tech. The essential features of this apparatus are identical with those used by other investigators.<sup>11</sup> The apparatus consists of a cylindrical pyrex glass tube, A, in which the resin bed, B, is supported at F by a fritted glass plate. The resin employed, which has been "conditioned" so as to remove all interfering substances, is in a wet form and covered by a layer of liquid, H (usually distilled water). A solution of the chlorides of the rare earths, approximately 0.2 M in HCl, is added to the top of the column and the solution allowed to flow through slowly by controlling the setting of a pinch clamp at C2. In this process, the rare earth ions are quantitatively adsorbed onto the resin. The actual separation process is then begun by passing the complex-ion-forming solution from the reservoir, E, through the column at a slow rate, the flow being adjusted by controlling the setting of the pinch clamps at C1 and C2. The effluent solution is caught in various fractions at R. The rare earth ions present in the fractions may be precipitated as oxalates, the oxalates removed by filtration and ignited to the oxides.

It has been shown experimentally<sup>11</sup> that, in general, the

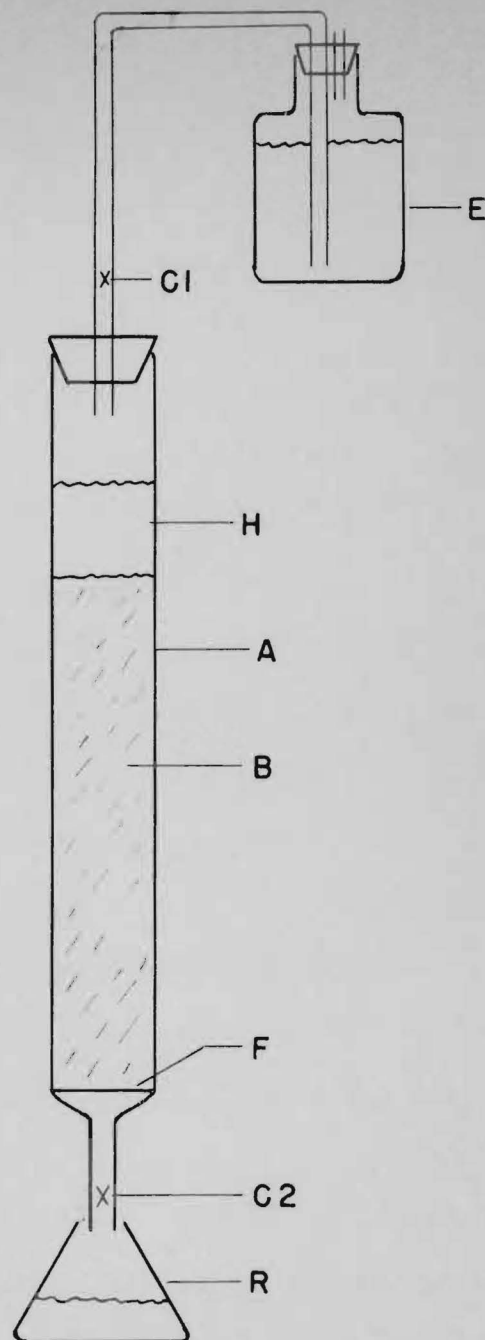


FIGURE 1. RESIN COLUMN USED IN  
SEPARATING RARE EARTHS



rare earths appear in the effluent fractions in their order of decreasing atomic number when ammonia-citric acid mixtures of controlled pH are used as the eluting solution. Furthermore, under optimum conditions, complete separation of mixtures containing certain of the rare earths may be achieved in one pass through a column.

Many factors combine to determine the optimum conditions for column operation. Among these are (1) nature and particle size of the resin employed, (2) the nature, concentration, and pH of the complexing agent, (3) the composition of the starting rare earth mixture, (4) the ratio of starting weight of oxide to cross-sectional area of the resin bed, (5) the geometry of the resin bed, (6) the flow rate of the eluting solution, and (7) the temperature. The choice of conditions for column operation is made, essentially, by balancing these factors, which determine optimum separation (i.e., longer columns, slower flow rates, small cation-to-resin ratios), against the desire for reasonable speed, yield, and economy of materials.

During the period June 1, 1948, to June 30, 1949, eleven ion-exchange separation runs were carried out on rare earth materials. All of these runs, except the first, employed the resin Dowex-50 as the exchange resin. In these experiments columns of two different sizes were used. The smaller columns contained a resin bed having a diameter of 2.1 cm. and a length of 81 cm. The larger columns contained a resin bed having a

diameter of 4.7 cm. and a length of  $73 \pm 2$  cm. In these experiments the weight of crude oxide used varied from four to six grams for the small columns and 16 to 24 grams for the large columns.

Two types of experiments have been carried out. Type I separation experiments were performed with a crude mixture of rare earth oxides having the approximate composition: 9 per cent  $\text{Nd}_2\text{O}_3$ , 43 per cent  $\text{Pr}_6\text{O}_{11}$ , and 48 per cent  $\text{La}_2\text{O}_3$ . This oxide mixture was prepared from a special grade of praseodymium ammonium nitrate obtained from the Lindsay Light and Chemical Company, West Chicago, Illinois. The purpose of these experiments was to obtain relatively pure  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  and at the same time to study to some extent the variables controlling the separation process.

Type II separation experiments were performed with relatively pure starting oxides used, such as those obtained from Type I experiments and from commercial sources, with a view to obtaining high purity ( $99.5^+$  per cent) oxides.

As a result of these two types of experiments, considerable information and experience was gained concerning the problem of rare earth separation, and sizable amounts (12 to 15 grams) of neodymium and praseodymium oxides having a purity of  $99.5$  to  $99.8^+$  per cent were prepared.

## 2. Work During the Period July 1, 1949, to October 1, 1949

During this period additional Type I and Type II separation experiments were carried out. Of twelve experiments nine

were of Type I (Runs 14, 15, 16, 17, 20, 21, 22, 23, 24) and three were of Type II (Runs 12, 13, 18). Dowex-50 (60-80 mesh) in the acid or ammonium form and the large-size column already referred to were used in all experiments. The starting weight of oxide used in each Run was about 30 grams.

The Type I experiments carried out were designed so as to give a better understanding of the effect of pH, flow rate, and weight of starting rare earth oxide on the separation of neodymium and praseodymium, while at the same time increasing the laboratory stock of praseodymium oxide of relatively high purity. These Type I experiments produced approximately 20 grams of  $\text{Nd}_2\text{O}_3$  and 100 grams of  $\text{Pr}_6\text{O}_{11}$  having a purity greater than 95 per cent.

The Type II experiments performed were carried out with a view to producing additional quantities of high purity neodymium and praseodymium oxides. The Type II experiments yielded about 30 grams of  $\text{Nd}_2\text{O}_3$  and 20 grams of  $\text{Pr}_6\text{O}_{11}$  having a purity estimated to be greater than 99.5 per cent.

#### B. Development and Testing of Methods for Analysing Rare Earth Mixtures

The problem of the analysis of rare earth mixtures is a moderately difficult one since in most instances simple chemical procedures do not exist for carrying out such analyses. In the course of the present work it has been necessary to utilize spectrophotometric and spectrographic, as well as conventional chemical methods of analysis. Also, the ion-exchange techniques already described have proven useful in the analysis

of certain materials. These various methods have been applied not only to the study of the separation and purification of rare earth oxides referred to in the previous section, but also to the analysis of the commercially available rare earth metals, lanthanum, cerium, praseodymium, and neodymium, which have been tested for superconductivity.<sup>15</sup>

The spectrophotometric and spectrographic methods of analysis both require pure substances for the calibration of the instruments used. While small amounts of lanthanum, cerium, praseodymium, neodymium, and samarium oxides presumably of high purity were purchased early in the work, the highly pure materials prepared in the ion-exchange separation experiments have served to establish confidence in these commercial products, as well as in the methods of analysis.

#### 1. Spectrophotometric Methods of Analysis

a. Previous Work. Recent work by Rodden<sup>6</sup> and Spedding et al.<sup>9</sup> suggested to us that the spectrophotometric method of analysis should prove a satisfactory method for the analysis of rare earth mixtures, particularly those containing praseodymium, neodymium, and samarium. Rodden, using the absorption bands of neodymium nitrate at 521 and 798 m $\mu$  has shown that for concentration up to about 10 mg. of neodymium metal per ml. (0.07 M) Beer's law holds, while above this concentration the extinction coefficient begins to be dependent upon concentration. On the other hand, he found that praseodymium nitrate solutions exhibited marked deviations from Beer's law throughout



the range 0.25 mg. (0.018 M) to 25 mg. (0.18 M) of praseodymium per ml. for the band at 446  $\mu$ . In our studies it was planned to analyze solutions of the rare earths in the form of chlorides and sulfates, by means of a different type of spectrophotometer than that used by Rodden. It was, therefore, necessary to re-investigate the dependence of extinction coefficient on concentration for these solutions.

The spectrophotometric methods of analysis used have all employed the measurement of the absorption spectra of water solutions of the rare earth chlorides in the range 380 to 1000 millimicrons.<sup>13</sup> All measurements have been made with the Beckman Model DU quartz spectrophotometer equipped with quartz cells having a  $1.000 \pm 0.002$  cm. light path. Analyses have been carried out for praseodymium, neodymium, and samarium. The absorption bands used for analysis were: (1) neodymium, 794 and 739  $\mu$ ; (2) praseodymium, 444  $\mu$ ; samarium, 401  $\mu$ . The effect of concentration of these ions on the extinction coefficient has been studied for the absorption bands used for analysis. In addition the effect of interfering substances such as chlorine, hypochlorous acid, hydrochloric acid, ceric, cerous and ferric ions has also been studied.

Experiments were also carried out to determine the effect of slit width on the optical density of a given solution for each absorption band used. The results of these tests showed conclusively that a standard slit width must be used in all measurements with a given absorption band.

During the course of this work it was necessary to use two different instruments. This fact complicated the work somewhat, since the magnitude of the extinction coefficient was found to be dependent upon the particular instrument used. The wave length scales of the two instruments were also found to be somewhat different. This latter fact did not result in any difficulties in operation, since in practice the maximum of an absorption band was always located by a manual scanning technique. The use of such a scanning technique was almost obligatory because of the extreme sharpness of the absorption bands used.

b. Work During the Period July 1, 1949, to October 1, 1949. During this period further work on the calibration of spectrophotometer No. 3204 was carried out in which were used as standard materials the highly pure praseodymium and neodymium oxides prepared in ion-exchange Runs No. 11 and 12, respectively. The purpose of the calibrations was to permit the analysis of mixtures of praseodymium and neodymium oxides ranging from 0 to 100 per cent  $\text{Nd}_2\text{O}_3$ . (These mixtures resulted from separation Runs No. 20 through 24.) Accordingly, synthetic mixtures containing these two oxides in known amounts were prepared in the form of chloride solutions, and the extinction coefficients of the solutions determined.

The results of these studies are shown in Table II. The extinction coefficients are reproducible to 0.1 units at the lowest concentration and about 0.06 units at the highest

concentration studied. Several facts are evident. First, the extinction coefficient for the praseodymium band at about 446  $m\mu$  is independent of concentration over the range studied. Comparison with data obtained with spectrophotometer No. 1513 shows that the magnitude found for the extinction coefficient for this band is the same for both instruments and is independent of the presence of neodymium.

TABLE II

## VARIATION OF EXTINCTION COEFFICIENT WITH CONCENTRATION

| Solution | Composition <sup>a</sup>                 |   | Molar Extinction Coefficient |            |            |
|----------|--|---|------------------------------|------------|------------|
|          | Pr <sub>6</sub> O <sub>11</sub><br>(gm.) | Nd <sub>2</sub> O <sub>3</sub><br>(gm.) | Nd                           |            | Pr         |
|          |  |   | 746 $m\mu$                   | 799 $m\mu$ | 446 $m\mu$ |
| A        | 0.1000 <sup>b</sup>                      | 0                                       |                              |            | 10.08      |
| 1        | 0.0800                                   | 0.0200                                  | 6.97                         | 10.40      | 9.95       |
| 2        | 0.0600                                   | 0.0400                                  | 6.88                         | 10.35      | 10.00      |
| 3        | 0.0400                                   | 0.0600                                  | 6.83                         | 10.20      | 10.05      |
| 4        | 0.0200                                   | 0.0800                                  | 6.88                         | 10.00      | 10.15      |
| B        | 0  | 0.1000 <sup>c</sup>                     | 6.90                         | 9.96       |            |

a. Each solution contained 0.1000 gm. of total oxide per 10 ml. of solution.

b. 0.0586 M PrCl<sub>3</sub>.

c. 0.0594 M NdCl<sub>3</sub>.

The extinction coefficients found for the 746- $m\mu$  and 799- $m\mu$  neodymium bands were about 10 per cent and 19 per cent larger, respectively, than those previously found with Instrument No. 1513. The extinction coefficient for the 799  $m\mu$  band was found to vary considerably with concentration, as had previously been observed for pure NdCl<sub>3</sub> solutions. The extinction coefficient for the 746  $m\mu$  band was constant within



experimental error over the range studied. From these results it was concluded that the extinction coefficients of the praseodymium and neodymium absorption bands studied were independent of each other within the experimental error of the measurements.

As a check on the method of analysis when a large amount of lanthanum oxide was present a known solution was analysed. This solution contained 0.0450 gm.  $\text{La}_2\text{O}_3$ , 0.0450 gm.  $\text{Pr}_6\text{O}_{11}$ , 0.0100 gm.  $\text{Nd}_2\text{O}_3$  as chlorides per 10 ml. of solution. The  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  used were portions of the same pure oxides used in the preparation of the solution referred to in Table II. The lanthanum oxide was a very pure material obtained from Adam Hilger, Ltd. (Lab. No. 6781). The results of the analysis are shown in Table III. In each instance the extinction coefficient in Table II appropriate to the concentration range has been used. It will be seen that the analysis is satisfactory within the limits of error of the measurements.

TABLE III  
ANALYSIS OF SYNTHETIC KNOWN MIXTURE

| $\text{Pr}_6\text{O}_{11}$ , Per Cent |                   | $\text{Nd}_2\text{O}_3$ , Per Cent |                   |                   |
|---------------------------------------|-------------------|------------------------------------|-------------------|-------------------|
|                                       | 446 $\text{m}\mu$ |                                    | 746 $\text{m}\mu$ | 799 $\text{m}\mu$ |
| Present                               | Found             | Present                            | Found             | Found             |
| 45.0                                  | 44.5+0.7*         | 10.0                               | 9.4+0.5*          | 9.7+0.3*          |
|                                       | 44.6 $\pm$ 0.7    |                                    | 10.0 $\pm$ 0.5    | 10.1 $\pm$ 0.3    |
| Mean                                  | 44.6 $\pm$ 0.7    |                                    | 9.7 $\pm$ 0.5     | 9.9 $\pm$ 0.3     |

\* Errors are calculated on the assumption that the optical density can be reproduced to  $\pm 0.002$  units.

The calibration data reported in Table II have been used in the analysis of a large number of the rare earth mixtures obtained in separation experiments designated as Runs 20 through 24.

## 2. Spectrographic Methods of Analysis

A very considerable effort has been spent in developing facility in carrying out both qualitative and quantitative spectrographic analyses of rare earth mixtures. The copper spark method<sup>2</sup> of analysis has been used in all analyses to date. This method was chosen because it requires a very small sample and avoids the formation of cyanogen bands which mask many important rare earth lines.

The spectrographic equipment used included a grating spectrograph, multisource unit, and comparator-densitometer, equipped with a voltage regulator, all supplied by the Applied Research Laboratories.

Analyses were carried out by evaporating a drop of the sample solution upon the ends of freshly cut 1/4 in. diameter copper rods. The spectra were recorded on Eastman spectrum analysis No. 2 film and processed in an ARL-Dietert film developing machine maintained at 70° F.

a. Previous Work. The spectrographic method has been used to carry out qualitative analyses of rare earth metals and rare earth mixtures. These analyses have been particularly helpful in elucidating some of the results obtained in the rare earth separation experiments, especially

when the ions in question exhibit no absorption spectra in solution. Some quantitative analyses have also been carried out. One of these, dealing with a new application of copper spark technique to the determination of lanthanum in impure praseodymium metal, has been accepted for publication in the November, 1949, issue of Analytical Chemistry.

b. Work During the Period July 1, 1949, to October 1, 1949. During this period quantitative analyses were carried out on sixteen rare earth mixtures obtained as fractions in separation Runs No. 9, 10, and 11.

C. Preparation of Rare Earth Metals

Early in the present program it was felt that in all probability it would be necessary to prepare certain of the rare earth metals from their pure salts. Efforts to procure rare earth metals of high purity were largely unsuccessful, as was shown when commercially available specimens were subjected to analysis during the summer of 1948. These analyses showed that only lanthanum metal could be obtained commercially in purity as great as 97-98 per cent.<sup>15, 17</sup> Accordingly, ion-exchange separation experiments were undertaken in the summer and fall of 1948 to prepare pure rare earth oxides, particularly praseodymium and neodymium oxides, from which to prepare the metals.

Three general methods have been described in the literature for the preparation of the rare earth metals. These methods are (1) the electrolysis of the anhydrous chloride in an absolute ethyl alcohol solution, with the use of a mercury cathode,

followed by removal of the mercury by vacuum distillation from the amalgam so formed; (2) the electrolysis at elevated temperatures (600-900° C.) of a fused salt or mixture of salts; (3) the reduction of an anhydrous salt at elevated temperatures by means of an alkali or alkaline earth metal. Since the metals are easily oxidized in air and readily react with nitrogen, water vapor, and silicates, at elevated temperatures their preparation presents a considerable problem. Furthermore, the preparation of the anhydrous halide (usually chloride) used was in itself a technique which had to be mastered.

Since lanthanum oxide can be obtained commercially in a high degree of purity relatively cheaply, this material has been employed as a starting point in attempts to prepare a rare earth metal. Thus, all experiments to date have been concerned with the preparation of lanthanum metal by the reduction of anhydrous lanthanum chloride.

#### 1. Previous Work

Several preliminary experiments were carried out during the fall and winter of 1948-1949 in which an attempt was made to prepare lanthanum metal by the formation of a lanthanum amalgam as a product of the electrolysis of anhydrous  $\text{LaCl}_3$  in anhydrous ethyl alcohol, the mercury being subsequently removed from the amalgam by vacuum distillation. The electrolysis was conducted according to the procedure of Jukkola, Audrieth, and Hopkins.<sup>1</sup> These experiments gave very low yields of lanthanum and were temporarily abandoned.



2. Work During the Period July 1, 1949, to October 1, 1949

During this period work on the problem of producing metallic lanthanum has continued. A furnace for carrying out the electrolysis of fused salts at elevated temperatures (600-900° C.) was designed and construction largely completed. It is proposed to study the electrolysis of fused lanthanum chloride using various electrode and crucible materials. The method being used is quite similar to that described by Trombe.<sup>12</sup>

V. LIQUID NITROGEN PLANT

The liquid oxygen plant originally supplied for use on this project has been redesigned to produce liquid nitrogen. A distillation column of the "packed" type has been constructed to produce liquid nitrogen having a purity of 99.5 mole per cent. During the past three months a considerable effort has been expended to determine the reason for the poor operating performance of the plant, with some success. However, even when operating as a liquid-air producing plant (i.e., in its original flow circuit) the maximum production rate so far achieved has been only about 18 pounds of liquid air per hour, which is 40 per cent of the plant's rated capacity. When operated so as to produce liquid nitrogen the production rate is also about 18 pounds (ten liters) per hour of liquid nitrogen containing less than one per cent oxygen.

The results with the plant to date suggest that the low yield is probably associated with the expansion engine and the heat exchangers rather than the compressor, loss of gas from

leaks, or the nitrogen column. The search for a remedy for these conditions is continuing.

## VI. CONFERENCES

Dr. W. T. Ziegler attended the International Conference on the Physics of Very Low Temperatures held at the Massachusetts Institute of Technology, September 6 through 10, 1949.

## VII. PERSONNEL


The following individuals have been associated with the project during the period covered by this report.

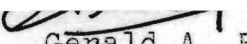
| <u>Name</u>              | <u>Position</u>     | <u>Time</u> |
|--------------------------|---------------------|-------------|
| Dr. W. T. Ziegler        | Director            | Full-time   |
| Dr. W. M. Spicer         | Research Associate  | Part-time   |
| Mr. J. O. Blomeke        | Research Assistant  | Part-time   |
| Mr. B. R. Willeford, Jr. | Research Assistant  | Part-time   |
| Mr. J. T. Roberts        | Research Assistant  | Part-time   |
| Mr. R. A. Young          | Research Assistant  | Part-time   |
| Mr. George Cook          | Technical Assistant | Part-time   |

Mr. Willeford left the project in August to resume his graduate work in Chemistry at the University of Wisconsin.

Respectfully submitted:

W. T. Ziegler,  
Project Director

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VIII. BIBLIOGRAPHY

- (1) Booth, H. S. (Editor-in-chief) Inorganic Synthesis I. McGraw-Hill Book Co., New York, 1949, p. 15.
- (2) Fred, M., Nachtrieb, N. H., and Tomkins, F. S., J. Optical Soc. Am. 37, 279 (1947).
- (3) Harris, D. H. and Tompkins, E.R., J. Am. Chem. Soc. 69, 2792 (1947).
- (4) Ketelle, B. H. and Boyd, G.E., J. Am. Chem. Soc. 69, 2800 (1947).
- (5) McLennan, J. C. and McKay, R. W., Trans. Roy. Soc. Canada (III), 24, 33 (1930).
- (6) Rodden, C. J., Bur. Stds. J. Research 26, 557 (1941).
- (7) Rossi, A., Nature 133, 174 (1934).
- (8) Spedding, F. H., Voigt, A.F., Gladrow, E. M., and Sleight, N. R., J. Am. Chem. Soc. 69, 2777 (1947).
- (9) Spedding, F. H., et al., ibid. 69, 2786 (1947).
- (10) Spedding, F. H., et al., J. Am. Chem. Soc. 69, 2812 (1947).
- (11) Symposium: The Separation of Rare Earth, Fission Product and Other Metal Ions and Anions by Adsorption on Ion-Exchange Resins. J. Am. Chem. Soc. 69, 2769-2881 (1947).
- (12) Trombe, F., Trans. Electrochem. Soc. 66, 57 (1934).
- (13) Yost, D. M., Russell, Jr., H. R., and Garner, C.S., The Rare-Earth Elements and Their Compounds. John Wiley and Sons, Inc., New York, 1947, pp. 22-23.
- (14) Ziegler, W. T., Investigation of Fundamental Properties of Elements and Their Compounds Including the Rare Earths at Very Low Temperatures with Particular Emphasis Upon Superconductivity, Project No. 116-18, Navy Department, Office of Naval Research Contract No. N6-ori-192, Task Order I. Progress Report No. 10, November 1, 1948.
- (15) Ibid., Technical Report No. 1, January 20, 1949.
- (16) Ibid., Annual Report for 1947-48, February 28, 1949.
- (17) Ibid., Progress Report No. 12, March 31, 1949.
- (18) Ibid., Status Report No. 13, June 30, 1949.



(19) Zintl, E. and Neumayr, S., Z. Elektrochem. 39, 814 (1933).

Georgia Institute of Technology  
STATE ENGINEERING EXPERIMENT STATION  
Atlanta, Georgia

STATUS REPORT NO. 15

PROJECT NO. 116-18

INVESTIGATION OF FUNDAMENTAL PROPERTIES  
OF  
ELEMENTS AND THEIR COMPOUNDS  
INCLUDING  
THE RARE EARTHS AT VERY LOW TEMPERATURES  
WITH  
PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

By

W. T. ZIEGLER

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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH  
CONTRACT NO. N6-ori-192, TASK ORDER I  
NR 016-406

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DECEMBER 31, 1949

Georgia Institute of Technology  
STATE ENGINEERING EXPERIMENT STATION  
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## I. SUMMARY

The present status report covers work carried out during the period October 1, 1949, through December 31, 1949. During this period a study has been made of the problem of converting bulk lanthanum specimens from the hexagonal close-packed to the face-centered cubic structure.

The rate of diffusion of helium gas through pyrex glass tubing has been measured at 350° and 400° C. The rate of diffusion of helium has been found to be of such magnitude that loss of helium from sealed pyrex capsules heated at these temperatures for several days must be taken into account in planning low temperature experiments in which helium is used as a heat transfer medium.

Exploratory work has been carried out on the preparation of lanthanum metal by electrolysis of fused  $\text{LaCl}_3\text{-KCl-CaF}_2$  mixtures at 700° to 900° C.

## II. X-RAY STRUCTURE STUDIES OF LANTHANUM METAL

Further experiments have been carried out in an attempt to convert bulk lanthanum metal from the hexagonal close-packed (h.c.p.) to the face-centered cubic (f.c.c.) structure. In one of these experiments the bulk material was heated in a vacuum furnace for two days at 722° C. X-ray examination of filings taken from the specimen before and after heat treatment showed them to have primarily the h.c.p. structure. On the other hand, the heat treatment of filings at 350° C. for two days has been shown to be sufficient to convert the filings

primarily to the f.c.c. structure, with the filings retaining the structure for more than six months after the heat treatment.

Further work on this problem is under way.

### III. LOW TEMPERATURE EXPERIMENTS

No low temperature experiments were carried out during the three months covered by this report. Rather, attention was directed toward finding ways of preparing bulk lanthanum in the f.c.c. structure so that this structure modification could be tested for superconductivity.

A second problem which was studied is that of the diffusion of helium gas through pyrex glass using heat treatment of the bulk lanthanum specimens at 350° to 400° C. This has a direct bearing on certain low temperature experiments carried out earlier in that the loss of helium from sealed pyrex capsules containing the metal specimens under test may have resulted in lack of thermal equilibrium between the metal specimens and the liquid helium bath.<sup>5, 6</sup> Results of the helium diffusion experiments are discussed in the next section.

### IV. DIFFUSION OF HELIUM THROUGH PYREX GLASS

Taylor and Rast<sup>4</sup> have measured the diffusion of helium through chemically resistant pyrex glass at 355° and 460° C. and have found that rate of diffusion is directly proportional to the pressure in the range 15 to 80 cm. Hg pressure. These investigators reported that the rate of diffusion,  $R$ , in gm.



He per cm.<sup>2</sup> per sec. per mm. wall thickness per atmosphere pressure difference was  $2.9 \times 10^{-12}$  at 355° C. and  $6.1 \times 10^{-12}$  at 460° C.

Smith and Taylor<sup>3</sup> have made similar measurements on pyrex and reported diffusion rates of  $2.8 \times 10^{-11}$  and  $4 \times 10^{-11}$  gm. He per cm.<sup>2</sup> per sec. per mm. wall thickness per atmosphere pressure difference at 350° and 400° C., respectively. The observed rates depended somewhat on the previous thermal history of the pyrex tube being investigated. Smith and Taylor compared their results with those of Taylor and Rast in a plot, in which the rates of Taylor and Rast are ten times greater than those actually given in the original article of Taylor and Rast. It would seem, therefore, that the data of Taylor and Rast given above probably should be converted to these higher rates, namely  $2.9 \times 10^{-11}$  and  $6.1 \times 10^{-11}$  gm. He per cm.<sup>2</sup> per mm. wall thickness per atmosphere pressure difference.

The rate of diffusion of helium through a 7 mm. o.d. x 1.1 mm. wall pyrex tube at approximately 350° C. and 400° C. has been measured in the Georgia Tech laboratory, and diffusion rates of  $2.9 \times 10^{-11}$  and  $4.9 \times 10^{-11}$  gm. He per cm.<sup>2</sup> per sec. per mm. wall thickness per atmosphere pressure difference have been found. These rates are about ten times larger than those reported by Taylor and Rast,<sup>4</sup> but agree quite well with those reported by Smith and Taylor.<sup>3</sup> The diffusion rate of helium through pyrex tubing of this size was measured by observing

the decrease in helium pressure in the tube manometrically while the tube was maintained at constant temperature in a vacuum furnace. When the helium gas in this apparatus was replaced by nitrogen gas no decrease in pressure was observed over a period of four days, the approximate duration of a helium diffusion experiment.

These results are of particular interest to this project because of the bearing they have on the possible loss of helium gas from sealed capsules during heat treatments previously carried out on lanthanum metal. Such sealed capsules containing about 10 cm. Hg of helium gas, together with a specimen of lanthanum metal, were subjected to tests for superconductivity at 4.2° K, after heat treatment in a vacuum furnace for four days at 350° C. No indication of a magnetic transition into superconductivity was observed even after 10 to 20 minutes exposure to a temperature of 4.2° K or less, although prior to heat treatment the specimens showed a sharp transition at about 5° K.

The possibility that the helium gas used for heat transfer at the low temperature had diffused out of the capsule during the heat treatment was considered. Calculations made by using our measured diffusion rate at 350° C., together with the assumption that the rate was directly proportional to the helium pressure, indicate that approximately 90 per cent of the helium would have been lost from the capsule by diffusion during heat treatment.

For a capsule originally filled with helium at room

temperature and 100 mm. Hg pressure, this calculation indicates a residual helium pressure at 4° K of 0.1 mm., as compared with 1.3 mm. obtained if no diffusion had taken place. These calculations assume that no adsorption of helium occurred. Since an initial gas pressure of 100 mm. had proved to give very rapid thermal response (i.e., lag in magnetic transition of less than 20 seconds) for a specimen before heat treatment, it is difficult to believe that the failure to observe superconductivity in the specimen after heat treatment arose because of the thirteen-fold decrease in helium pressure alone. It is possible, however, that diffusion and adsorption may have combined to give poor heat transfer.

In all low temperature experiments subsequent to those under discussion here the capsules have been opened after heat treatment and refilled with helium.

#### V. CHEMISTRY OF THE RARE EARTH ELEMENTS

Apparatus for the preparation of anhydrous rare earth chlorides has been set up, and anhydrous lanthanum chloride has been prepared for use in the preparation of the metal by electrolysis of the fused lanthanum chloride. The method used, which is similar to that employed by Kleinheksel and Kremers<sup>2</sup> and by Jantsch, Grubitsch, Hoffman, and Alber<sup>1</sup> consists in passing dry HCl gas over the hydrated chloride at successively higher temperatures up to about 350° C. Analysis of the product so obtained indicated essentially complete removal of water from the hydrated chloride.

Preliminary experiments have been carried out on the production of lanthanum metal by electrolysis of fused  $\text{LaCl}_3$ - $\text{KCl}$ - $\text{CaF}_2$  mixtures at 700-900° C. A number of different refractory materials have been tried with only moderate success. Further work on this problem is planned.

Some additional work on the separation of the rare earths by ion exchange has been carried out, and more studies are planned.

Two papers dealing with the chemistry of the rare earths were presented by project personnel before the Meeting-in-Miniature of the Georgia Section, American Chemical Society, held in Atlanta, November 18, 1949. These were "The Separation of Neodymium, Praseodymium, and Lanthanum by Ion Exchange" by J. O. Blomeke, J. T. Roberts, Jr., and W. T. Ziegler and "The Chemistry of the Rare Earth Elements" by W. T. Ziegler.

Two publications by project personnel have appeared during the past three months. These were "Separation of the Rare Earth Elements, Particularly Praseodymium and Neodymium" by W. T. Ziegler, The Research Engineer, November, 1949, and "Spectrochemical Determination of Lanthanum in Praseodymium Metal" by W. M. Spicer and W. T. Ziegler, Analytical Chemistry 21, 1422 (1949).

## VI. CONFERENCE

Dr. W. T. Ziegler visited the Physics Section of the Office of Naval Research on December 16 for the purpose of discussing plans for the ONR sponsored Cryogenics Conference to

be held at the Georgia Institute of Technology, March 20 and 21, 1950.

VII. PERSONNEL

The following individuals have been associated with the project during the period covered by this report.

| <u>Name</u>       | <u>Position</u>     | <u>Time</u> |
|-------------------|---------------------|-------------|
| Dr. W. T. Ziegler | Director            | Part-time   |
| Dr. W. M. Spicer  | Research Associate  | Part-time   |
| Mr. J. O. Blomeke | Research Assistant  | Part-time   |
| Mr. R. A. Young   | Research Assistant  | Part-time   |
| Mr. W. A. Carter  | Research Assistant  | Part-time   |
| Mr. George Cook   | Technical Assistant | Part-time   |

Respectfully submitted:

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VIII. BIBLIOGRAPHY

- (1) Jantsch, G., Grubitsch, H., Hoffman, F., and Alber, H., Zeit. f. anorg. Chem. 185, 49 (1930).
- (2) Kleinheksel, J. H. and Kremers, H. C., J. Am. Chem. Soc. 50, 957 (1928).
- (3) Smith, P. L. and Taylor, N. W., J. Am. Cer. Soc. 23, 139 (1940).
- (4) Taylor, N. W. and Rast, W., J. Chem. Phys. 6, 612 (1938).
- (5) Ziegler, W. T., Investigation of Fundamental Properties of Elements and Their Compounds Including the Rare Earths at Very Low Temperatures with Particular Emphasis Upon Superconductivity, Project No. 116-18, Navy Department, Office of Naval Research Contract No. N6-ori-192, Task Order I. Progress Report No. 12, March 31, 1949.
- (6) Ibid., Status Report No. 13, June 30, 1949.