# FIVE YEARS OF APPLIED SCIENCE IN THE LOW-TEMPERATURE FIELD[1]

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For a five-year period ending in 1945 a large fraction of the M.I.T. group interested in low-temperature research turned to the development of compact light-weight oxygen-producing units based on distillation of liquefied air. The units were designed for the special purposes of the armed services: gaseous oxygen for respiratory use, for welding and cutting, and liquid oxygen for other requirements. The last units designed produced liquid oxygen and high-pressure gaseous oxygen as desired, but the development was interrupted upon cessation of hostilities. The model units built in the Institute shops are described, and also the units manufactured on the basis of the models. Attention is called to important gaps in published scientific information needed for the rational design of gas-liquefying apparatus and devices for the separation of constituents by distillation.

## I. INTRODUCTION

The first project discussed in the summer of 1940 was that of the large-scale production of liquid oxygen on board submarines, amounting to from 1000 lb. to 5000 lb. per hour. The equipment was to be placed in a submarine space measuring 382.5 cu. ft., and the total weight was not to exceed 275,000 lb. The means suggested by the group at the Massachusetts Institute of Technology involved the use of turbo compressors and expanders, but no facilities existed therefor beginning such a development. Indeed, we had no knowledge of a turbine expander having been designed in the United States, but large-capacity turbo-compressors had been developed in Europe. According to estimates, even if the turbo equipment were available, the submarine space allotted for the equipment (382.5 cu. ft.) was too small for the production of 1000 lb. per hour of liquid oxygen.

The basis of experience available to the M. I. T. Oxygen Group lay in the design and operation over many years of laboratory liquefaction systems principally for air and hydrogen. During the two years preceding 1940, however, considerable time had been given by Dr. Samuel C. Collins to the design and

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[2] The work of the project was carried out by the following associates: Samuel C. Collins—October 1940 to July 1942; Howard O. McMahon—October 1940 to September 1942; Robert P. Cavileer—October 1940 to May 1945; Kendall C. Valentine—October 1940 to August 1942; James A. Beattie—June and July 1941; James L. Hildebrand—January 1941 to October 1942; Charles L. Gallagher—July 1941 to March 1945; Knut W. Wilhelmson—July 1941 to June 30, 1945; Clark C. Stephenson—February 1942 to June 1942; Dudley A. Williams—April 1942 to June 30, 1945; Thomas E. White—July 1942 to May 1945; Charles E. Teeter, Jr.—August 1942 to February 1945; Norman B. Carter—April 1943 to June 30, 1945.

operation of expansion engines. Out of this effort there came, among other developments, a diaphragm expander tested considerably in a helium circuit producing temperatures of 10°K. and directed at the time to the production of liquid helium without the use of liquid hydrogen or liquid air. The experience led to the development and construction by Dr. Collins—under the oxygen program—of the reciprocating gas-lubricated expansion engine, later manufactured by Clark Brothers at Olean, New York.

Prior to embarking on the oxygen program for the National Defense Research Committee, the members of the laboratory interested in low-temperature research had devoted considerable discussion to the advantage of a novel compressor employing no liquid lubrication, suggested by Dr. Collins. There had also been emphasized the need of efficient heat interchangers in low-temperature maintenance, an emphasis which led to a considerable testing program for different types of construction several years prior to 1940. The developments were continued under the N. D. R. C. contract but on an extended scale.

During the autumn of 1940 and throughout the following winter the problem of a liquid-air rectifier for the production of oxygen aboard vessels or airplanes was considered, and a number of designs were tested. A satisfactory solution of the problem meeting the restricting conditions proved difficult of attainment, and work was still in progress in the fall and winter of 1941–42. A successful application of Dr. McMahon's work on rotating columns was embodied, however, in the final oxygen producer completed by Dr. Collins and Dr. McMahon. A further application of the rotating column for shipboard use with modifications is represented by the high-pressure oxygen gas–liquid oxygen unit completed in the spring of 1944.

The first model of the airplane unit of Collins and McMahon was shipped to Dayton, Ohio, for test in the interest of the Wright Field Air Force group in September 1942. The further development and perfection of the unit by Drs. Collins and McMahon took place at the plant of the Frigidaire Company at Dayton. Numerous examples of the Collins–McMahon unit embodying Dr. Collins' special interchanger clean-up system for water and carbon dioxide were manufactured commercially for the Armed Services.

Request for a unit for replenishing the respiratory oxygen on submarines was made in the late summer of 1942 and led to the design of a compact high-pressure unit to operate with or without precooling. The unit was to be supplied with air feed from either of the two submarine compressors normally used to charge air into the air flasks of torpedoes. The normal capacity of the submarine compressors is 300 lb. of air per hour at 3000 p.s.i. The yield of oxygen obtainable without precooling is 20 lb. per hour of liquid oxygen, and 35 lb. per hour with precooling to $-40$°C. Purity ranges were from 0.985 to 0.99 mole fraction (m.f.) or better. The model unit was tested and inspected at the Engineering Laboratory of the U. S. Naval Academy at Annapolis, Maryland. Four examples of the unit were later made by Servel Inc., two of which were sent to England.

In February 1943 the request was made on the part of the Bureau of Ships of the U. S. Navy for the development of a dual-purpose oxygen-producing unit to produce liquid oxygen without and with precooling, and also to produce high-pressure oxygen gas directly. Since the unit was to be used on supply ships it was necessary to provide a rotating column. The unit was to be adapted for air feed in amounts of 120 cu. ft. per minute (c.f.m.) at 3000 p.s.i., or 540 lb. per hour. The purity of the oxygen was to be 99.5 per cent; the quantity of oxygen obtainable was to be not less than 70 lb. per hour.

A unit of the above description will produce the maximum amount of liquid oxygen when fed with precooled air (−45° to −50°C.) at the full 3000 p.s.i. For the production of gaseous oxygen at 2000 p.s.i. pressure, however, a much lower pressure of the air feed is required (1500 p.s.i. roughly) with no precooling, since the conversion of the liquid oxygen into gas in the interchanger provides ample refrigeration for the production of the maximum amount of oxygen consistent with the use of a simple stripping rectifier.[3]

In order to realize the type of unit suggested it was necessary to produce a liquid-oxygen injection pump which would take liquid from the boiler of the rectifier, raise it to 2000 p.s.i. or more, and inject it into the main heat interchanger. The pump evolved operates or is driven by air pressure supplied by a branch line from the air feed, the cool exhaust therefrom being introduced into the low-pressure channel of the interchanger at the appropriate temperature.

Photographs of the model units constructed at M. I. T. are reproduced and also of units manufactured on the basis of the models by Servel Inc. at Evansville, Indiana, and the Independent Engineering Company at O'Fallon, Illinois. Several of the earlier types of interchangers (3, 5) were also retested. Several new types were, however, brought to a perfected state of development, notably the edge-wound copper-ribbon-packed interchanger devised by Dr. Collins, which contributed so largely to the satisfactory clean-up performance of his alternating channel feed–effluent heat interchanger, whereby in low-pressure units cargon dioxide, oil vapors, and water vapor are completely removed.

## II. THE COLLINS–McMAHON AIRPLANE UNIT

Early in the program (spring 1940) the National Defense Research Committee brought to the attention of the group information pertaining to the development of a high-pressure oxygen unit at the Mond Laboratory of the University of Cambridge, England. The work had been undertaken on the request of the British Air Services for an air-borne oxygen-producing unit to supply respiratory oxygen. The Mond model unit was received at M. I. T. and tests were conducted after some minor substitutions of parts and adjustments, together with the construction of a solid potassium hydroxide remover for carbon dioxide and an alumina dehydrator. The unit produced 8.5 lb. per hour of gaseous oxygen of 0.95 m.f. purity. Meanwhile, and prior to the receipt of the Mond model unit, the airplane unit referred to above had been designed and executed by Dr. Collins and Dr. McMahon, tests upon which were reported in September 1942.

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[3] It is established commercial practice with certain systems to use precooling in the production of gaseous oxygen at low pressure. Similarly, precooling could be used with the unit described above in producing high-pressure gas, thereby bringing about a substantial further reduction of the pressure of the air feed.

This unit weighed a total of 320 lb. complete, exclusive of the compressor.[4] Among other novel features, the unit was provided with the edge-wound copper-ribbon-packed interchanger channels and the gas-lubricated piston expander (weight complete, 46.5 lb.). The rotating column was designed and built by Dr. McMahon for the unit on the basis of his work on rotating columns begun early in the program. The complete column weighed but 19.5 lb. The unit operated with air feed at 150 p.s.i.a. in the amount of 1500 cu. ft. per hour (c.f.h.) or 25 cu. ft. per minute (c.f.m.). Production of gaseous oxygen proved to be: 200 c.f.h. of purity 0.97 m.f.; 150 c.f.h. of purity 0.99 m.f.; 110 c.f.h. of purity 0.995 m.f. The starting time from the warm condition was 2 hr.; if the unit had been operated the previous day, 1 hr.[5]

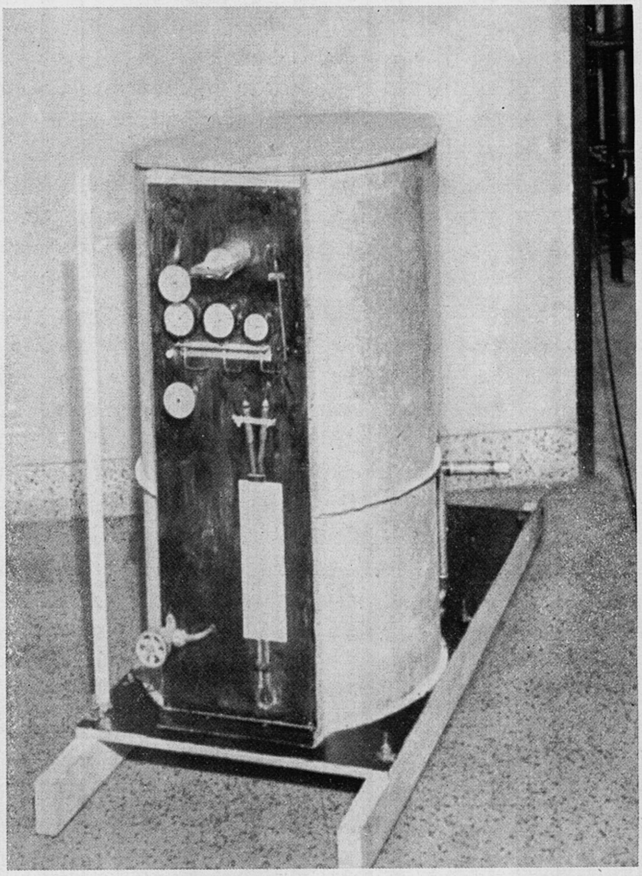

FIG. 1. Front view of Collins–McMahon airplane unit (M. I. T. model)

Figure 1 shows the front view of the instrument and control panel view of

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[4] The insulation used in the model unit was of greater density than desirable and added considerable weight over that realized later when glass wool was employed. The insulation, of course, had to be incombustible.

[5] Later, when insulating material of less density was used, the starting time was reduced.

the Collins–McMahon model airplane unit as it was being prepared for shipment. Figure 2 is the rear view, showing the expander valve timing gears and exchanger alternating channel shift timing. Figure 3 gives an impression of the unit with case and insulation removed, viewed from the timing-gear side. The gas-lubricated expansion-engine cylinder in the foreground is mounted directly on the cross-head unit, while the column is surrounded by the heat interchanger.

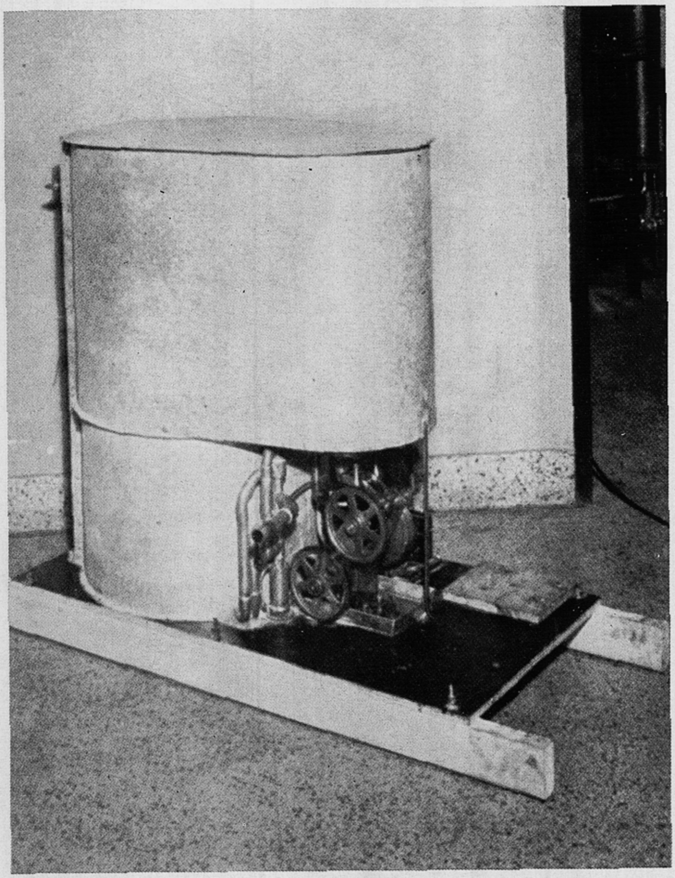

FIG. 2. Rear view of Collins–McMahon airplane unit (M. I. T. model), showing engine

Figure 4 gives a view of the gear side, the opposite side from that represented in figure 3.

### III. THE SUBMARINE LIQUID-OXYGEN PRODUCER

The replenishment of respiratory oxygen in submerged submarines was discussed in the spring of 1942. The plan was to use the torpedo compressors to supply the air for the oxygen producer. The space available for the unit was a floor area not to exceed 4 sq. ft. and a height of 6 ft. Another requirement was that the unit should start producing liquid oxygen in the shortest possible time, since production would be limited to relatively short intervals when the vessel which would not be deranged when the unit was inverted or laid upon its side, as would be likely to occur in introducing the unit through the submarine hatch or in the course of installation. Accordingly, a sensitive-diaphragm gauge

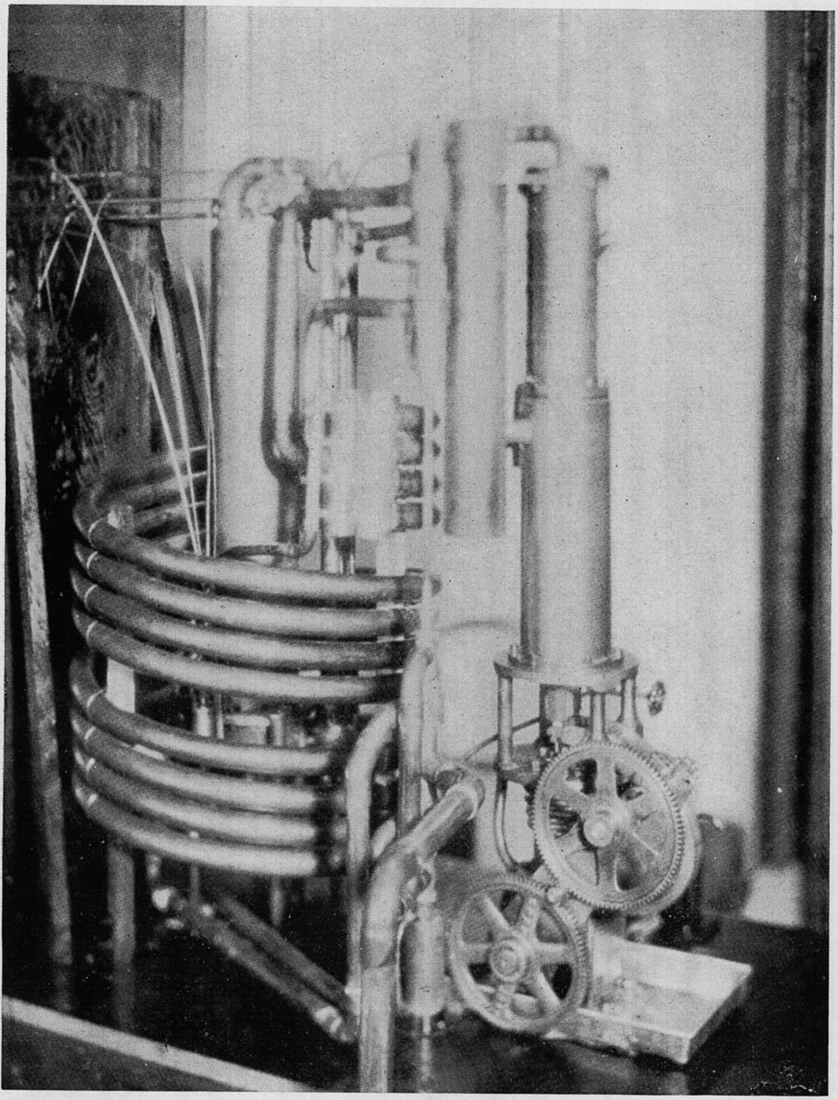

FIG. 4. Collins–McMahon airplane unit (M. I. T. model) with case and insulation removed; interchanger channel switch side.

mechanism was made use of in a hermetically sealed case. The liquid level of the boiler case was used for the connection to the gauge case, and the floor of the liquid-oxygen chamber for the connection to the gauge diaphragm to which the translating mechanism and indicating needle of the gauge were attached. The which would not be deranged when the unit was inverted or laid upon its side, as would be likely to occur in introducing the unit through the submarine hatch or in the course of installation. Accordingly, a sensitive-diaphragm gauge mechanism was made use of in a hermetically sealed case. The liquid level of the boiler case was used for the connection to the gauge case, and the floor of the liquid-oxygen chamber for the connection to the gauge diaphragm to which the translating mechanism and indicating needle of the gauge were attached. The

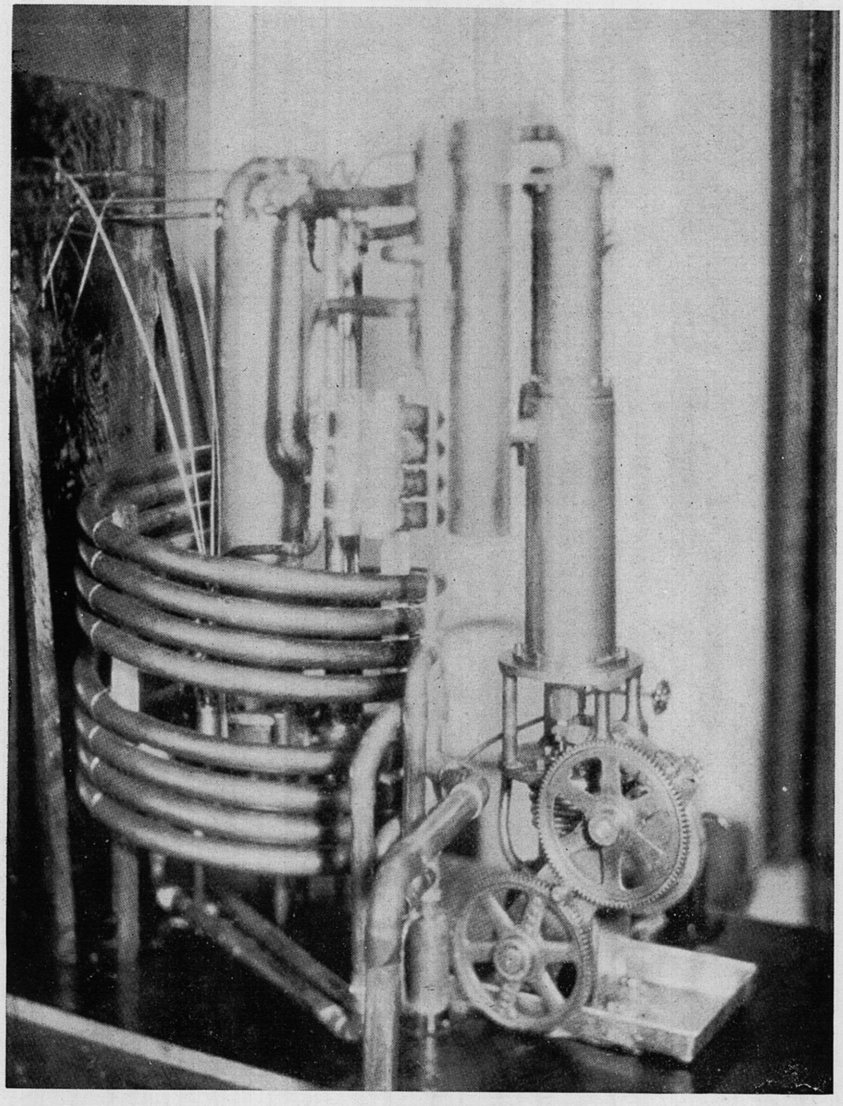

Fig. 4. Collins–McMahon airplane unit (M. I. T. model) with case and insulation removed; interchanger channel switch side.

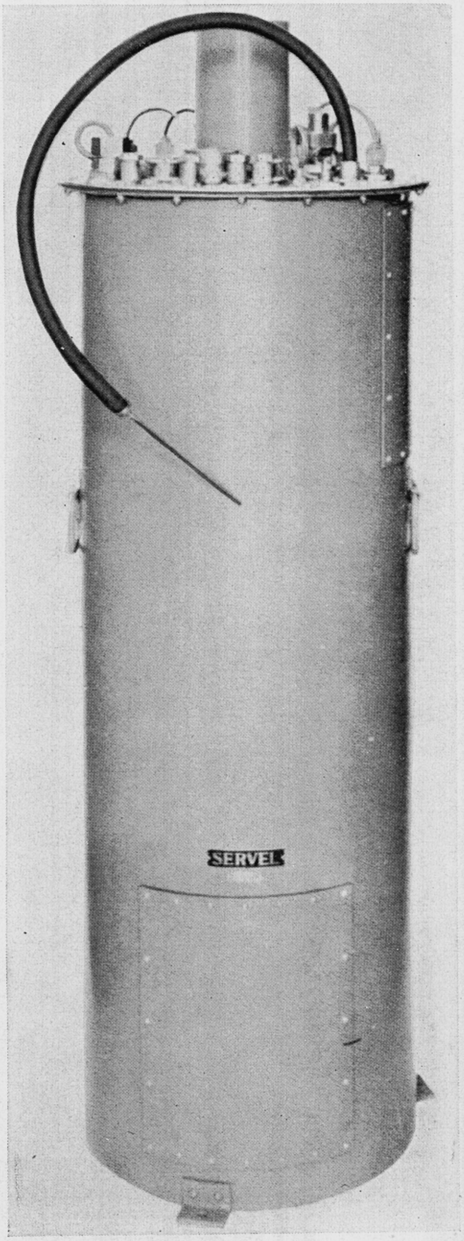

FIG. 5. Submarine liquid-oxygen unit (respiratory oxygen). Capacity 20 lb. per hour of liquid oxygen of 0.995 m.f. purity, 300 lb. per hour air feed unrefrigerated, pressure 3000 p.s.i.g. Capacity 35–40 lb. per hour of liquid oxygen of 0.98–0.985 m.f. purity with feed refrigerated at $-40°C$.

details of installation of the tubular leads are important, but chief of these is the soldering of one end of a copper wire (16 to 18 gauge) to the liquid tubular lead of cupronickel alloy near its connection to the liquid-oxygen holder, while the other is soldered to a rod of the chassis of the unit to provide a gentle flow of heat to the tube. In this way it is possible to prevent the liquid phase from entering the tube beyond the level corresponding to the bottom of the liquid-oxygen holder.

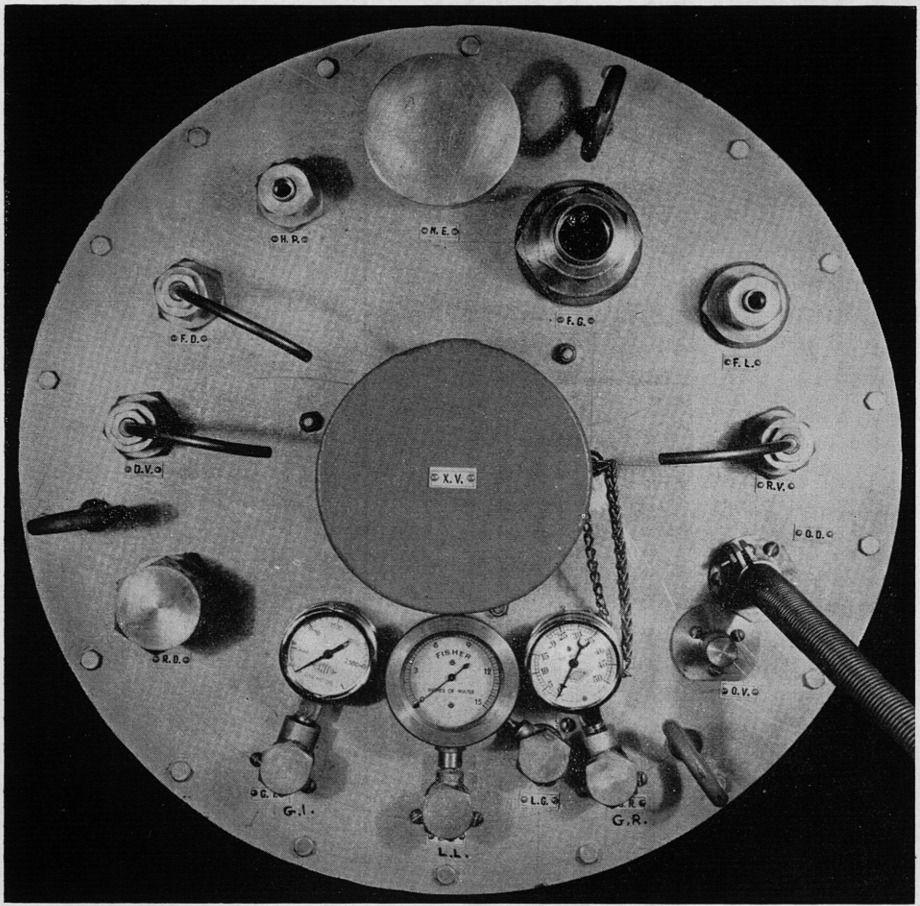

Fig. 6. Top deck of S-unit
H.P. = high-pressure air connection
N.E. = "nitrogen" effluent outlet
O.D. = oxygen product (liquefied) delivery
L.L. and L.G. = liquid-level attachment joints
O.V. = hand-operated liquefied-oxygen delivery valve
R.V. = relief valve on high-pressure line
R.D. = rectifier relief diaphragm
G.X. = pressure gauge ahead of expansion valve
G.R. = pressure gauge to rectifier
X.V. = expansion-valve cover
F.L. = liquid freon-12 line
F.G. = gaseous freon-12 line
F.D. = oil drain on freon interchanger
D.V. = oxygen drain valve

Another important feature of the unit was the means of withdrawing liquid oxygen. The simplest and most desirable plan would be to have the liquid oxygen flow continuously and without attention from the bottom or boiler portion of the rectifier. Use was made of a float enclosed in a cage to which liquid oxygen had access at about the required level above the boiler coils. Access was through holes in the cage covered with monel gauze of 300 mesh to prevent dust particles (solid carbon dioxide) from reaching the valve.

A principal difficulty with a float is the choking of the flow owing to accumulated carbon dioxide dust or other sediment. The seat and needle design was arranged to be self clearing as the float operated, and the seat could be easily removed either for renewal or for inspection through an access cover without dismantling the unit. The delivery of liquid began without attention as soon as the level in the boiler exceeded the predetermined level, and delivery was through a flexible metal vacuum-jacketed hose, visible in figure 5.

The regime of the column proceeds best when the pressure in the column is maintained constant. For this purpose an automatic expansion valve[6] was devised, which obviated the necessity of adjustments once the unit was brought into operation. Ultimately, two principal types of self-adjusting expansion valves were constructed, the second of which can also be used in cases where variations in atmospheric pressure occur (airplanes).

Finally, the unit was provided with a heat interchanger for feed precooling; for by precooling the air feed to −40° to −50°C. the yield of liquid oxygen can be approximately doubled. The Servel Inc. unit (2T-200F), using freon-12, was used with a liquid-freon subcooler.

The clean-up system for the air feed (300 lb. per hour) consisted of two steel tubes containing solid potassium hydroxide used in series, together with a tube of activated alumina. The latter tube contained an electric heater for reactivating the alumina after 50 hr. of use, which was placed in a central tube reëntrant to the alumina container tube. Heat-conducting disks were pressed upon the reentrant tube before assembly for the purpose of diffusing the heat throughout the alumina without creating too great temperature differences. The entire clean-up system fully charged (70 lb. potassium hydroxide, 70 hr. operation) and with its supporting stand, designed by Servel Inc., weighed about 700 lb. The model unit weighed 180 lb. Units complete with clean-up system were manufactured by Servel Inc. from drawings based on the model unit.

A complete set of operating and maintenance instructions for the submarine units was produced by Mr. Dudley A. Williams with the assistance of Mr. Robert P. Cavileer after many weeks of tests with both the model unit and the units manufactured by Servel Inc.

The purity of the liquid oxygen from the S-unit depends upon the quality of the column or rectifier packing.[7] Originally the requirement was for oxygen of

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[6] A protective cover conceals the valve in figure 5.

[7] The packing in the original S-units was No. 2 Madison shoe eyelets. The h.e.t.u. (height of the equivalent transfer unit) was 3.8 in., as shown by tests conducted by Prof. B. F. Dodge.

purity 0.95 to 0.96 m.f. The original tests of the model units were conducted at the laboratories of the Air Reduction Company in Stamford, Connecticut, and with the normal supply of 300 lb. per hour of air at 70°F., 17.5 lb. per hour of liquid oxygen in the receiver was obtained of purity 0.975 m.f.[8] The precooling refrigerating unit was not received until the tests at the U. S. Navy testing laboratories at Annapolis were undertaken a month later. With precooling at the $-24$°F. level, the yield of oxygen of purity 0.95 to 0.96 m.f. was 33 lb. per hour.

Meanwhile request was received to increase the purity of oxygen in order that the S-unit might be used in applications other than the re-oxygenation of submarine air. It was found possible to raise the purity to 0.995 m.f. by employing the gauze saddle column packing devised by Dr. McMahon, along with improvements in the liquid distributor and an improved anti-entrainment device worked out by Mr. D. A. Williams. Two of the modified Servel units were also forwarded to England, where they were reported to have performed according to the indications given in the D. A. Williams *Instruction Book*.

## IV. THE SUPPLY SHIP UNIT

In February 1944 a request was made for an oxygen unit which would produce liquid oxygen or deliver high-pressure gaseous oxygen directly to a manifold to which standard oxygen cylinders could be attached for charging to 2000 p.s.i.g. After the model had been built it was further desired that precooling means be included to increase the yield of liquid oxygen. The purity desired was 0.995 m.f.

A unit of the kind described would have the advantage that no separate oxygen compressor would be required to charge cylinders,—a saving in expense, weight, and maintenance of the compressor. Moreover, the oxygen would be delivered absolutely dry and as pure as it was produced directly from the rectifier, i.e., uncontaminated by the operation of compressing in a multistage compressor in contact with warm oil vapor.

The question of the design of the liquid-oxygen pump presented some difficulty, since the unit was to be self contained, which meant that the pump must be driven by the compressed-air feed. There was also the problem of the liquid-oxygen piston leak, for the viscosity of liquid oxygen at 90°K.(0.002 C.G.S. units) is not far from one-fifth that of water at room temperature. Also, the use of piston-rod packing seemed desirable to avoid if possible; and problems of heat leak, gas "lock", valves, and choice of materials entered along with the difficulties posed by lubrication.

For the power or drive portion of the pump there arose the questions of meter-

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[8] The model S-unit was provided with a direct connection or conductor for liquid oxygen from the boiler to the hose. Now the rectifier pressure is about 1 atm. above atmospheric pressure; accordingly, when liquid oxygen is released from this higher pressure there is compensation for the change in state in the form of evaporation of some of the liquid. The loss amounts to about half a pound of liquid per hour. In later units the liquid oxygen was precooled by the effluent, whereby the liquid issued into the receiver slightly lower than the normal boiling temperature.

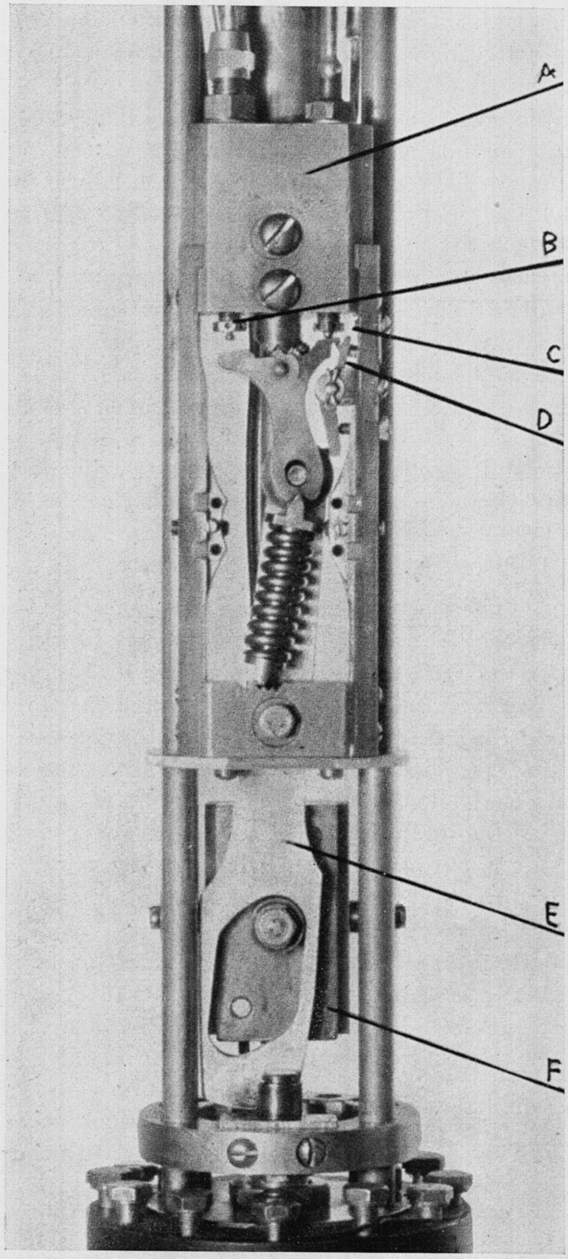

FIG. 7. Liquid-oxygen injection pump. Valve mechanism at beginning of power stroke. A, valve block; B, exhaust-valve push rod; C, inlet-valve push rod; D, latch to hold inlet valve open until loaded spring mechanism is just past the equilibrium position in the direction of opening the exhaust valve; E, cam arm at beginning of power stroke; F, roller block rigidly fastened to piston rods.

ing the air charge, the durability of materials, heat insulation, lubrication, and speed control,—to refer to the principal items. As far as is known, no air drive for compressing a cold liquefied gas has been described.

One obvious recourse in the case of the oxygen piston would be to use a hardened nitralloy piston and cylinder for the liquid-oxygen compression, employing as close a fit as permissible. A piston-rod packing would be required if this expedient were adopted, but the packing need not have to resist the full pressure of the desired oxygen pressure (2000 p.s.i.). The amount of leak for such a piston cylinder is easily computed, using Poiseville's Law for an annular clearance. Thus the weight, $W$, of liquid oxygen escaping under a pressure difference $\Delta p$ is given with sufficient exactness by the expression

$$W = g\,\frac{\Delta p}{L} \times \frac{\pi D \bar{\rho} t^3}{12\mu}$$

where $D$ is the piston diameter, $L$ the length of the leak path, $\bar{\rho}$ the mean density, and $t$ the annular clearance (difference between the radii of the cylinder and the piston). For a clearance of 0.0002 in. the leak is $4.53 \times 10^{-3}$ lb. (2.06 g.) per second of exposure to a pressure difference of 2000 p.s.i., assuming $D = 0.75$ in., $L = 1$ in., and $\mu = 1.34 \times 10^{-4}$ lb./ft. sec. If the travel or stroke of the piston could be accomplished in 1/20 sec., the leak would be but 0.1 g. or about 1.2 per cent of the leak of the full charge for a 1-in. stroke. The attempt was made, however, to devise a piston self sealing against leak, which would also obviate the possibility of metal–metal contact.

The pump completed for the model unit was contained in a case in two sections separated by a 2-in. thick heat barrier. The case was 3 in. in diameter, the upper section was $20\frac{3}{8}$ in., the lower section 14 in. in length. Both the power piston (in the upper case) and the oxygen piston were designed to be self sealing through the use of piston rings made of cordovan leather. The leather, however, was compressed to about 5000 p.s.i. prior to cutting and finishing the rings, and the annular area normal to the piston axis was adjusted to approximately double the unit pressure imposed upon the piston. The amount of the expansion of the leather rings in the case of the power piston was limited by the brass-piston design to about 0.002 in. on the diameter. The leather was soaked in a high-pressure lubricant mixed with very finely powdered natural graphite prior to mounting the assembly of leather and brass spacing rings. The cylinder liner was of high polished nitralloy. No appreciable leak of air past the piston was observable with 2000 p.s.i. air pressure after considerable operation.

The oxygen piston was constructed similarly to the power piston, but of course had to be used without liquid lubricant. The metal employed was beryllium-copper. The cylinder, 0.75 in. in bore diameter, was of the same material, but after heat treating to obtain maximum hardness the inner surface was lapped and highly polished. The diameter of the metal base of the oxygen piston was made 0.004 in. smaller than the cylinder base and slightly tapered toward the ends. At one end flexible connection was made with the piston by means

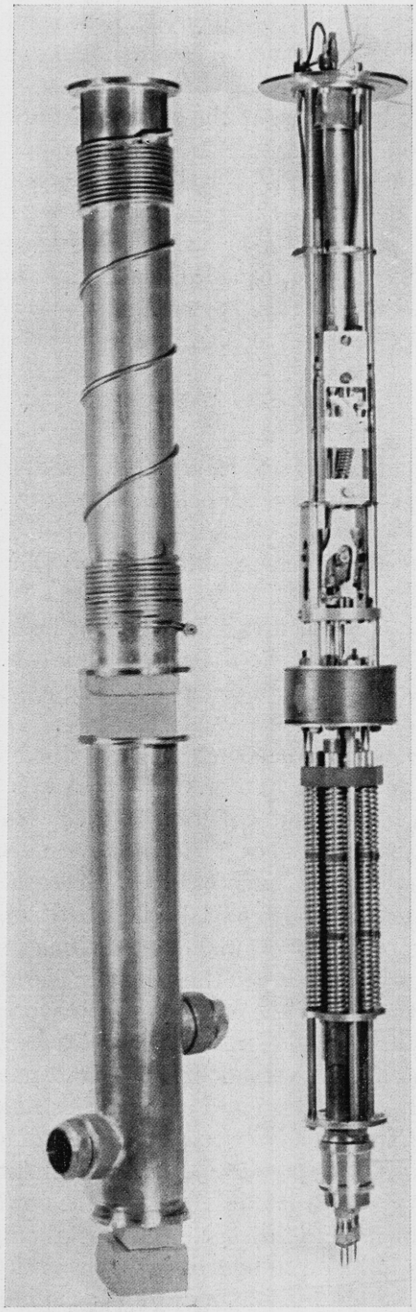

FIG. 8. Pump No. 2 and pump cases

of a split threaded locking piece, as a means of obviating any slight misalignment of rod and piston.

The rings were assembled as follows: First a single leather ring (0.040 to 0.050 in. thick), next a 0.09375-in. thick fine-texture graphite ring followed by two leather rings, a beryllium-copper ring (0.004 in. less than the cylinder in diameter), two leather rings, a brass ring, and a single leather ring. The middle ring was again graphite, and the arrangement was repeated in inverse order to that above described. There was therefore a total of twelve leather, four beryllium-copper, and three graphite rings.

The cutting of the leather rings and their adjustment to final size proved to be an exacting problem. Also, before use the fat or oil with which the leather is impregnated must be extracted (with xylol); upon doing so it will be found that the leather is entirely flexible at liquid-hydrogen temperatures.[9]

It will be perceived that the contraction of the various substances must be known and allowed for; otherwise, too great friction or too loose a fit will result. The function of the graphite rings is particularly important. They were used principally as a means of preventing contact of the metal portions of the piston with the cylinder wall under sudden thrust, because at low temperatures metal surfaces on contact appear to abrade much more readily than at room temperature. The quantitative aspect of the temperature contraction is as follows: The mean coefficient of contraction from 20° to $-190$°C. observed for the graphite used was $3.5 \times 10^{-6}$ cm. per 1°C. per centimeter length. The same coefficient for the beryllium-copper proved to be $12.5 \times 10^{-6}$ in the same units, while the leather (dry) gave a coefficient of $32 \times 10^{-6}$. The metal cylindrical base upon which the rings were fitted was 0.5 in.; the outside diameter of the rings was 0.75 in.

There will be an axial contraction on cooling as well as a contraction along the diameter. The importance of the axial contraction lies in the fact that it is necessary to limit the amount of the dilation of the compressible leather rings to avoid excessive friction. The setting of the stop, which is obtained partly by the use of leather rings of slightly varying thickness and finally by machining a metal part of the piston, is of course done at room temperature, and a value is determined which will result in an effective cylinder wall seal at liquid-oxygen temperatures.[10]

Because the graphite has a smaller contraction it is possible to adjust the diameter of the ring at room temperature to a value which will leave it with a fit to the cylinder of 0.0001 in. at the operating temperature. The leather is not perfectly uniform in thickness, and when the sudden thrust takes place at the power stroke the presence of the graphite rings insures that no metal–metal

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[9] Space is not available here for all the details of the various operations. However, the more important steps in the solution of the several problems are presented. The author will be glad to supply details, through private correspondence, to those interested.

[10] Some concern regarding explosive hazard is justified in the absence of positive knowledge when leather is brought into contact with liquid oxygen. The author had not been able to ignite pieces of leather on transferring them rapidly from a jar of liquid oxygen to an adjacent flame. The amount of leather in actual contact with liquid oxygen in the case of the piston is very small (0.05 cc.).

contact occurs and the piston alignment is accordingly preserved. The graphite is also anti-frictional and no wear has been observed against polished beryllium-copper.

The adjustment of the movement of the metal piston parts controls the degree of expansion of the leather rings and may be considered in the light of the temperature contraction data given. The axial contraction for an actual piston is given in table 1.

This amount of contraction enlarges the gap or distance through which on application of pressure the leather will be compressed, or the leather would be compressed too much. Now the diameter contraction is 0.0030 in. and allowance can be approximated for the axial contraction by computing the relation between the change of thickness of the leather and the unrestricted increase in diameter resulting from compression normal to the plane of the ring. The formula is found to be, on the basis of no net volume change:

$$\delta D = \frac{\delta t}{t_0} \times \frac{D_0}{2}\left(1 - \left(\frac{D_1}{D_0}\right)^2\right)$$

TABLE 1

*Temperature contraction for a temperature drop of 210°C.*

| | | |
|---|---|---|
| Leather | 0.528 in. × 210°C. × (32.0 − 12.5) × 10⁻⁶ = | 0.00216 in. |
| Beryllium-copper | 0.240 in. × 210°C. × (12.5 − 12.5) × 10⁻⁶ = | 0.00000 in. |
| Graphite | 0.281 in. × 210°C. × ( 3.5 − 12.5) × 10⁻⁶ = | −0.00053 in. |
| Net contraction | | 0.00163 in. |

Taking the total thickness of the leather rings given in table 1, $t_0 = 0.528$ in., and the value of $\delta t$ to be compensated as 0.00163 in., it is found that a diameter increase of 0.000643 in. would ensue under no lateral force if the leather were reduced in thickness by pressure by 0.00163 in. Therefore the gap must be adjusted not to allow 0.003 in. lateral expansion at room temperature but 0.0030 − 0.000643 in. or 0.00236 in. In practice the pistons were run in at room temperature for several hours before adjustment to a gap giving a diameter increase of 0.0025 in. under full compression at room temperature.

The air-driven oxygen piston pump operated very well in the model unit after experience had guided the development. However, the model pump unit (figure 10) could not be operated continuously for long periods, owing to lack of facilities and personnel. Indeed, testing of all kinds was carried out by Mr. D. A. Williams, Mr. R. P. Cavileer, and Mr. T. E. White using air compressors whose upkeep consumed a large portion of their time and energies. As a consequence a second pump was constructed and sent to the Independent Engineering Company at O'Fallon, Illinois, for continuous accelerated test at room temperature. Through these tests many deficiencies of design detail and of durability were revealed and corrected. The more important of these items were the wearing qualities of the bearings of the valve-actuating mechanism, air-valve durability, valve push-rod packing characteristics, valve-spring life, permanency of adjustments, properties of the self-sealing air piston, the durability of the 2-in. thick bakelite gear-stock heat barrier separating the oxygen portion from the power portion of the pump, the durability of the brass springs used to accomplish the return stroke, the wear qualities of the dry leather piston-rod packing in the heat barrier, to cite principal items.

FIG. 9. Pump unit with rotating column for producing either liquefied oxygen or high-pressure gaseous oxygen.

During the first stage 537,600 strokes (nominally equivalent to 450 standard tanks filled) were completed before a breakdown due to failure to lock securely the compression-limiting locking nut on the oxygen piston. The second stage saw 467,700 strokes completed. The cause of failure was fatigue of a hardened

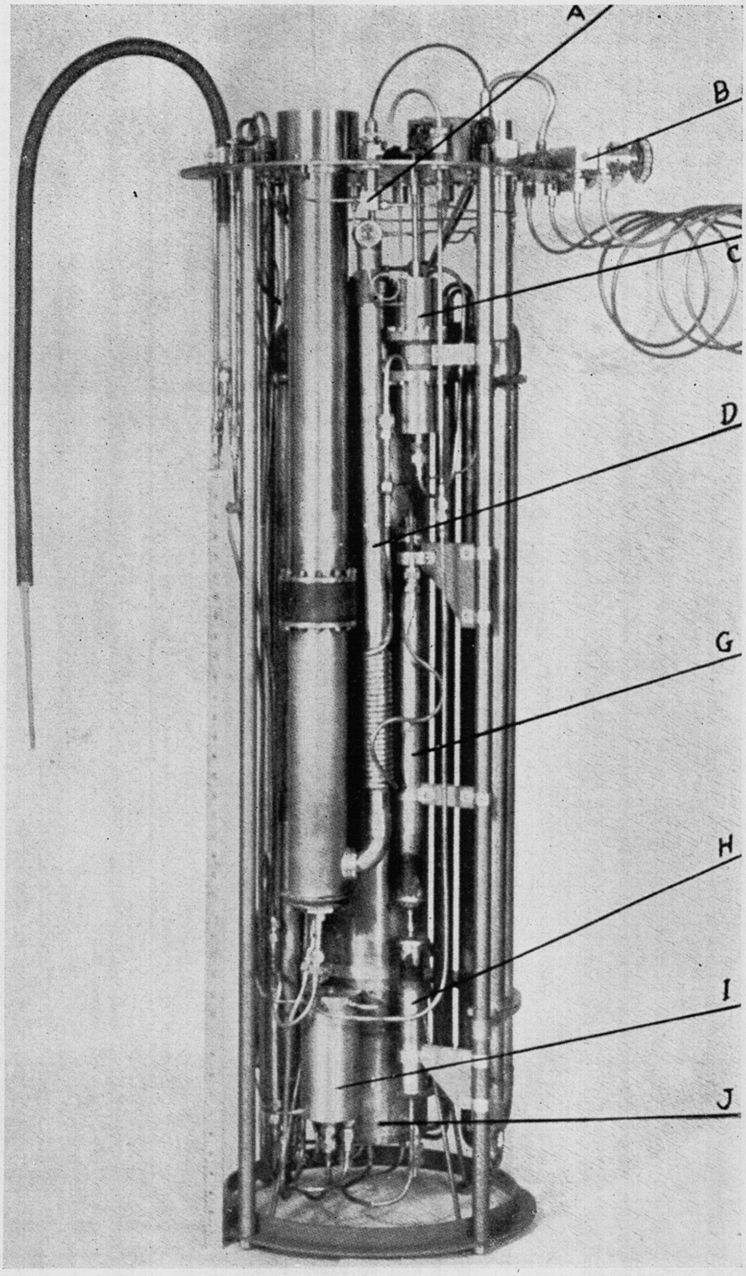

FIG. 10. View of pump unit No. 3. A, air admission valve to power section of pump; B, high-pressure oxygen-gas delivery manifold; C, automatic expansion valve; D, effluent delivery from rectifier; G, filter; H, charcoal adsorber for hydrocarbons following boiler coil; I, float case; J, rectifier boiler.

part of the valve-actuating mechanism but the valves, having run for over a million strokes, were badly worn and a change in design was begun which probably has not yet been sufficiently extended. No appreciable bearing wear was observable, although intentionally no lubrication had been employed on the valve-operating gear. The third period comprised 330,000 strokes. During this test, however, several innovations were under examination, particularly directed toward developing valves of long life. The fourth period ran to 466,356 strokes, when the brass return-stroke springs collapsed completely at a total of 1,801,656 strokes. The entire return spring system was changed as a result of the test.

Moving pictures of the operating pump taken by the Independent Engineering Company's personnel indicated that the free-running pump at room temperature completed its power stroke in less than 0.02 sec., roughly the limit of the speed of the camera. The maximum speed of the three pumps which have been constructed is 240 strokes per minute. However under load, pumping liquid oxygen at 2000 p.s.i., the power stroke requires a much longer time, depending only partly upon friction of the oxygen piston, as was indicated by using a nitralloy piston where no appreciable piston friction could develop, and partly on the added time required to load the power piston with the compressed air. In its present stage of development the working speed has not been brought to exceed fifty to sixty strokes per minute, equivalent to the same number of pounds of oxygen per hour. There developed however an unexpected difficulty, the description of which may be of interest.

The model pump unit (figures 7 and 8) was completed and installed in the winter of 1944 when atmospheric moisture was negligible. The model pump unit on test at the Independent Engineering Company performed satisfactorily on test periods extending to over 60 hr. when the tanks were filled to pressures exceeding 2000 p.s.i.[11] The course of the tests was finally terminated, owing to the fact that acetylene gained access to the compressor air intake and, finding its way to the oxygen cylinder of the pump, exploded and demolished the pump.

The second example of the pump was forwarded for installation in one of the larger pump units described below but was held in the humid midwest summer climate some time before installation. The leather rings of the oxygen piston absorbed enough moisture during the delay to bring about a volume change in them sufficient to cause great friction on the pumping stroke and consequent malperformance.

It was later found that the defatted leather does change volume greatly on exposure to moist air. Of course, special packing cases could be devised which would prevent access of moisture to the leather, but time and opportunity to do this were lacking. It is not altogether unlikely that certain substances might be adsorbed on the defatted leather which would destroy the extraordinary affinity

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[11] A request was made to pump oxygen to pressures of 3500 p.s.i.; this the pump accomplished without any detectable leak at the oxygen piston.

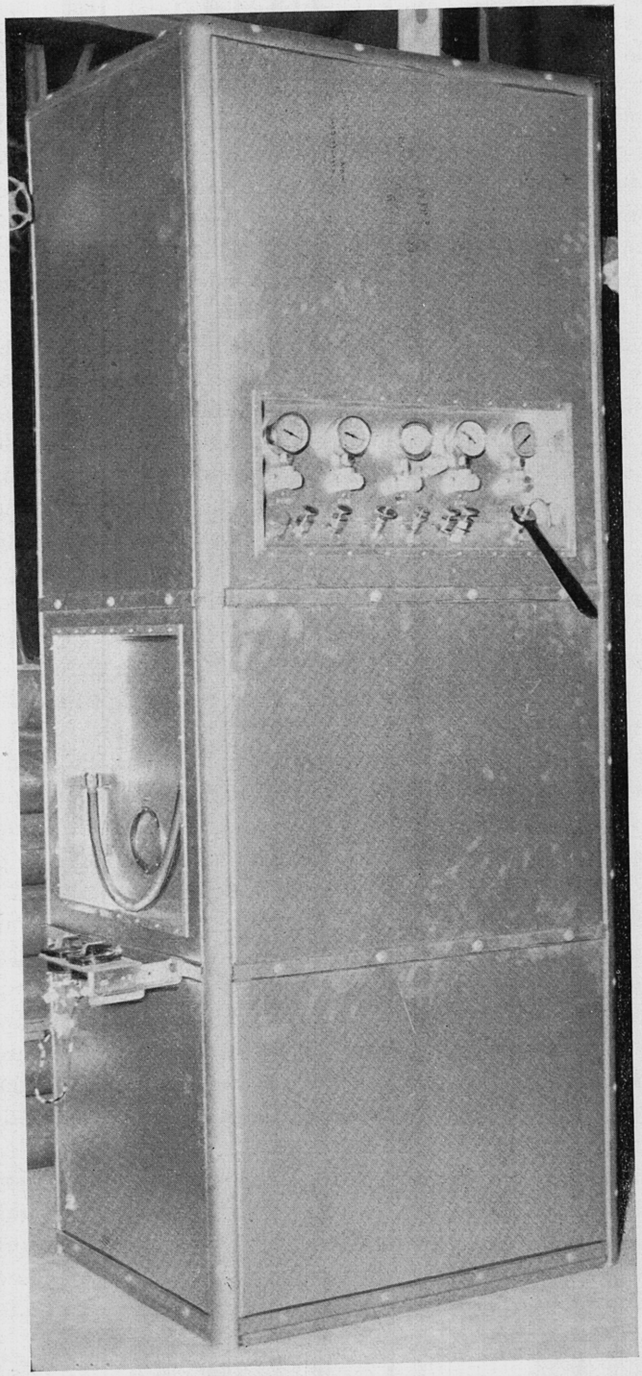

FIG. 11. K30MS unit. Precooled-feed dual-purpose unit to produce 70 lb. per hour of liquid oxygen or high-pressure (2000 p.s.i.) oxygen gas.

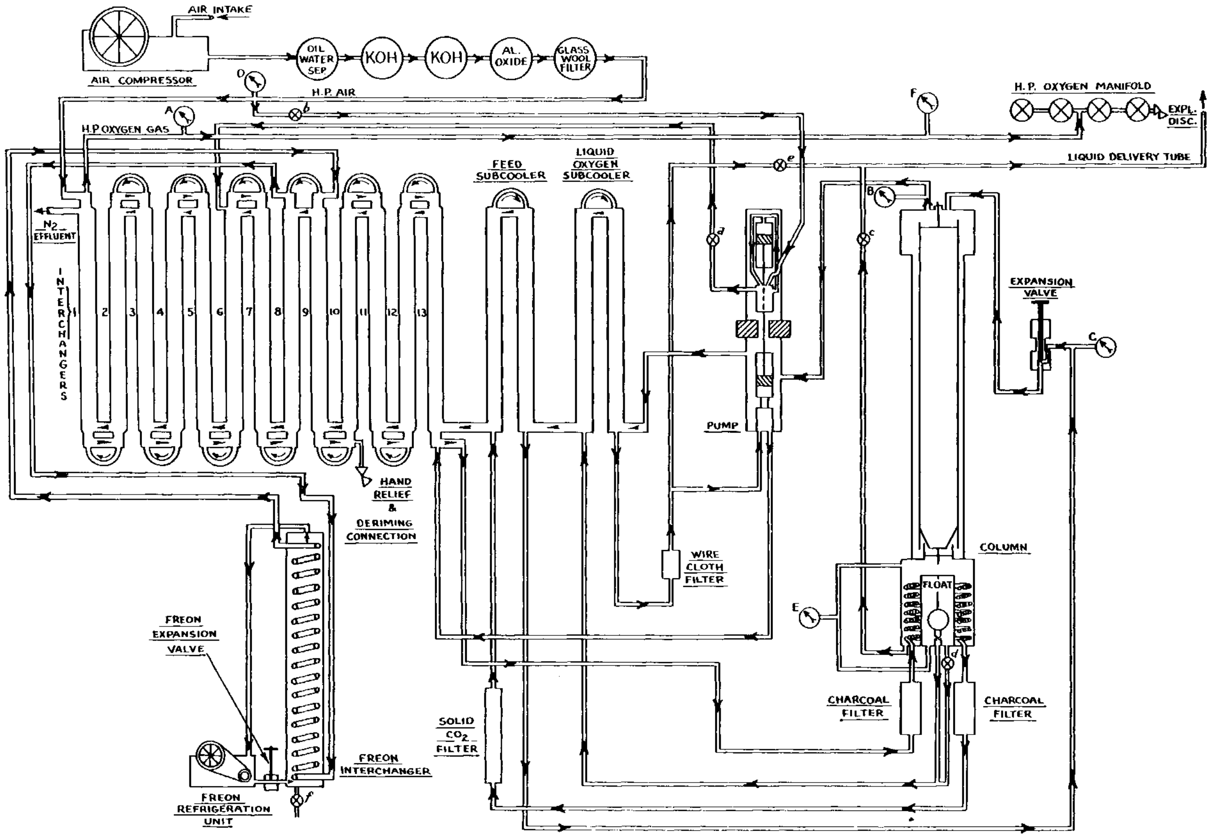

Fig. 12. Flow diagram of large pump unit for use with high-pressure air feed.

A = high-pressure oxygen 0–3000 lb. pressure gauge
B = rectifier 0–50 lb. pressure gauge
C = high-pressure expansion valve 0–4000 pressure gauge
D = air inlet 0–4000 lb. pressure gauge
E = liquid-level gauge 0–15 in. of water
F = oxygen manifold 0–3000 lb. pressure gauge
a = air-exhaust pump valve

b = air-inlet pump valve
c = boiler drain valve
d = gas valve
e = liquid valve
f = oil drain
g, h, i = air switchover valves for freon interchanger

of the defatted material for water, but experiments in this direction are uncompleted.[12]

### V. THE LARGE PUMP UNITS FOR USE WITH HIGH-PRESSURE AIR FEED

The decision was taken by the division of the N. D. R. C. in control of oxygen development to construct two units along the lines of the model pump unit but with the addition of precooling means to satisfy the interest in larger quantities of liquid oxygen. The units were also to be twice the capacity of the model unit and to have rotating columns. The units were to be constructed by the Independent Engineering Company but the design was the problem of the M. I. T. group.

The experience available for the design of the two units was limited to the small model unit and such intimations regarding deficiencies or inadequacies of design as had come to light through tests of the model unit, which through lack of facilities could not be pushed as far as was desired. The general features of the design were as follows:

Instead of the cylindrical shape with instruments and connections on the top surface used for the S-unit (figure 6), dictated by the small space available for installation, another design was envisaged. The unit proper was built into or the parts mounted in a strong rectangular-section steel chassis consisting of rigid steel plates at top and bottom connected by heavy-walled steel tubing. Outside of the chassis a covering of the Lindsay type was adopted. The resulting aspect of the unit was a rectangular shape some 80 in. in height and 22 x 32 in. in section with connections and instrument panel, vacuum-jacketed delivery tube panel, and drains all recessed to present plane surfaces (figure 11). The flow diagram is given in figure 12.

The elements of the unit will be described in their principal features, beginning with the air feed. It scarcely needs comment that the units represent a stage in the development of the type rather than a culmination. Extensive tests on the units were not completed at the time the contract terminated, but sufficient information was obtained to indicate some of the design modifications and improvements which would be desirable.

#### *A. The Joule–Thomson–Siemens interchanger*[13]

The model unit was equipped with an interchanger of the encased seven-tube

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[12] The present design of pump could be easily adapted for motor drive, but a speed control would have to be devised which would duplicate the nicety of control attained by regulating the time of exhaust in the case of the air drive. The motor drive would also make variations in the friction characteristics of the expansible leather rings of the piston of little or no practical importance. A disability of the ordinary motor drive, however, is the difficulty of devising a rapid power stroke (1/10 sec. or less) with controllable slow return stroke, a feature of the air drive which is very attractive.

[13] The author is aware that "Joule–Thomson interchanger" is the designation usually employed for this heat interchanger. The record shows, however, that neither Joule nor Thomson had anything to do with this type of interchanger, whereas William Siemens filed a patent on the device in 1857, or at least a device whose principles are embodied in the heat interchanger used by Hanson and Linde in the 1890's for the production of liquid air. In what follows the interchanger will be referred to as the J–T–S interchanger.

variety, which in some respects is very well adapted to serve the purpose of the type interchanger. In the first place the mass distribution may be dealt with advantageously, since the central tube may be used for the feed, one of the six surrounding tubes for gaseous oxygen, and the remaining five tubes for the nitrogen. Relative to a weight unit of air there is 1/4.3 of pure oxygen and 1/1.3 of "nitrogen", so that the heat-transfer surface available to each fluid bears a rough approximation to the weight fractions nature has established for the principal components of air. In the second place the situation may be dealt with more easily than some other types in applying the algebra of design for computing the heat transfer and dimensions of the constituent metal parts. In the third place the interchanger is easily assembled and bonded as by soldering.

The interchanger was to be used for high-pressure oxygen production and if desired also for liquid-oxygen production. Since the simple type still or rectifier was to be employed, at most some 0.65 weight fraction (w.f.) of the total oxygen was to be extracted from the feed (0.75 w.f. approximately is the limit), or 15.1 lb. of oxygen per 100 lb. of air feed. When gaseous oxygen (2000 p.s.i. pressure) was being produced the interchanger would operate in mass balance and heat-capacity unbalance. In the production of liquid oxygen both mass and heat-capacity unbalance results.

The high-pressure oxygen channel of nickel–copper alloy (0.70 copper and 0.30 nickel, 0.155 in. O.D., 0.015 in. wall) was placed coaxially in the central feed tube of nickel–copper alloy; the six surrounding tubes (0.523 in. O.D., 0.025 in. wall) and the twelve channels comprising the spaces exterior to the outside diameter of the seven tubes and the case were available for the effluent.[14] It was desired that the pressure drop for the effluent channel should not exceed 5 p.s.i.g., and considerations of design indicated that a tube having an outside diameter of 1.625 in. should be used for the case. Standard fittings are available for ends, and the oxygen channels were connected from one section to the following by means of special castings into which the channels and interconnecting tubes were silver soldered. The total length of each of the thirteen sections was 54 in., making a total of 58.5 ft.

The effluent before reaching the J–T–S interchanger passed from the top of the rectifier through the case surrounding the oxygen end of the pump, thence through a liquid subcooler, and a subcooler for the air feed on its way to the expansion valve. The first of the foregoing three cooling stages was to maintain the pump oxygen cylinder below the temperature of the incoming oxygen as a measure preventing vapor lock;[15] the second to enter the liquid oxygen to the pump well below the boiler temperature to create loading pressure and also when producing liquid oxygen to eliminate "flash gas" loss on delivery to the containers. The liquid-feed precooler, by diminishing "flash gas" when the liquid air leaves the expansion valve, diminished certain difficulties of head design.

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[14] The design of a three-channel interchanger presents some features which appear not to have been dealt with, as far as can be determined from a far from exhaustive search of the literature.

[15] Calculation shows that liquid oxygen on adiabatic compression to 2000 p.s.i. heats about 3°C.; thus cooling of the oxygen injection cylinder also removes this heat.

The feed channel is interrupted at a point of its course for the connection of the freon-12 interchanger for precooling the gaseous air feed. The freon refrigerating units are designed to allow the freon vapor to leave the refrigerator coils at nearly the temperature of the coil. Also at the temperatures employed, −45° to −50°C., a liquid-freon precooler was employed cooled by the cold return vapor. For 540 lb. per hour feed an 8-horsepower (0.8 ton) refrigerating unit was employed, a size which proved satisfactory in service.

Under conditions out of complete control it may happen that water will be incompletely removed from the feed, in which case it is convenient to be able to interrupt operation for the purpose of warming the J–T–S interchanger to remove the water. For this purpose a relief-valve connection is incorporated at a point in the feed channel beyond which ice will not collect. By means of a warm air current the light-weight heat interchanger is quickly warmed, the ice plug melted, and the water blown out. By this device a prolonged shut-down is avoided and normal operation quickly restored.

It will be noted on the flow sheet (figure 12) that high-pressure air near the entrance to the unit is taken by a branch line connecting to a coil soldered to the upper or power side case of the pump. The coil is connected on its cool side to the feed at a point further down stream. The purpose served is to remove refrigeration reaching the upper pump case and prevent the valve mechanism from cooling. It will be observed that the refrigeration lost by cold leak is partly recovered.

### *B. The rotating column*

The column is considered to include the head and boiler with its feed coil, float, and other parts relating to the operation of distillation.

The bearings of the rotating part (10 to 12 R.P.M.) which contained the column packing were made of beryllium-copper for the races and stainless-steel balls. The thrust bearing was mounted on the top of a pedestal supported on the float cage and braced by a cast-alloy spider supported from the walls. The upper bearing and shaft were contained in the head, and when the cover was removed the column could be easily lifted out of the column case. The use of a skirt at the lower end of the column permitted the use of a liquid-oxygen seal for the bottom of the column.

The column head is a matter of considerable importance, for the design must allow the liquid to be evenly distributed over the packing and at the same time liquid feed must not be entrained by the current of vapor passing up the column. The difficulties of the situation will be perceived to be enhanced by a species of discontinuity peculiar to the type of rectifier used. Thus liquid air passes to the rectifier from an expansion valve where liquid is accompanied by 10 or more per cent of its weight of gas at substantially the rectifier pressure. The liquid and gas mixture is discharged into the rectifier head, the gas creating with the upcoming vapor a junction involving a sudden velocity increase. This is the discontinuity referred to and it can be the seat of considerable entrainment of liquid feed if the velocity of the vapor in the column is near the critical velocity and the discontinuity occurs in the packing.

To avoid the vapor velocity discontinuity in the packing Mr. D. A. Williams designed a head comprising the following features: The liquid air and flash gas were received from the expansion valve into a space from which the mixture passed to an annular box soldered to the top of the rectifier cover. From the under side of the box twelve tubes projected the mixture tangentially into a bowl which was mounted on the top of the rotating column. In the bowl the vapor separated and passed out at the top to join the vapor leaving the packing from its last contact with the liquid which by gravity flow was discharged through multiple tubes over the top of the packing. By this means a vapor velocity discontinuity *in the packing* was avoided, and no entrainment takes place unless the vapor velocity through the packing exceeds a value characteristic of the particular packing used.

There is, however, another discontinuity at the bottom of the column which caused considerable difficulty during tests of column packing in the model pump unit. The bottom support for the packing was originally designed to be a cone formed of perforated brass. The angle of the cone was finally chosen of a value which would present a total area of perforation openings equal to the cross-sectional area of the column.[16] This provision, however, did not allow the liquid to drain regularly from the bottom of the column. After attempting various devices Mr. Williams, acting on a suggestion of Dr. Teeter, placed a number (twenty-four in one test) of $\frac{1}{10}$-in. thin-walled drain tubes suspended from the packing support plate. The device proved to be very satisfactory. The liquid hold-up or instability effect is most evident when the column regime is changed abruptly, as by increasing the throughput rapidly, and was exhibited by various eyelet-type packings and also the metal-cloth saddles devised by Dr. McMahon. The latter, however, exhibit superior throughput characteristics without flooding relative to the eyelets, except possibly the Madison No. 2 eyelets.

### *C. The boiler coil*

The design of boiler coils was based on the heat-transfer data for liquid oxygen supplied by Professor W. F. Giauque (1). The temperature difference between the incoming gaseous feed and the liquid oxygen amounts to about 65°C., which makes for very poor heat transfer in the first section of the coil. The final design and mode of fabrication were worked out by Mr. Williams. Figure 13 exhibits the winding frame and the finished coil. The spacing is very important because of the Leidenfrost phenomenon and extremely violent boiling along the first section.[17] The incoming warm feed enters the outer turns of the coil. It is also proved good practice to provide for a low vapor velocity in the space immediately above the coil.

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[16] If $\theta$ is the half-angle of the cone ($\theta < \pi/4$), and $n$ the number of screen openings per unit area each of area $a$, then $\tau\theta = na$. For a perforated plate of total hole area ratio 0.5, $\theta$ is about 27°.

[17] Observations were made of the boiling induced in a typical boiler coil set up in an unsilvered Dewar tube. The turbulence in the liquid surpassed expectations and made evident qualitatively the need of working out the coil design to allow the gas bubbles to escape freely from between the multiple turns of the coil.

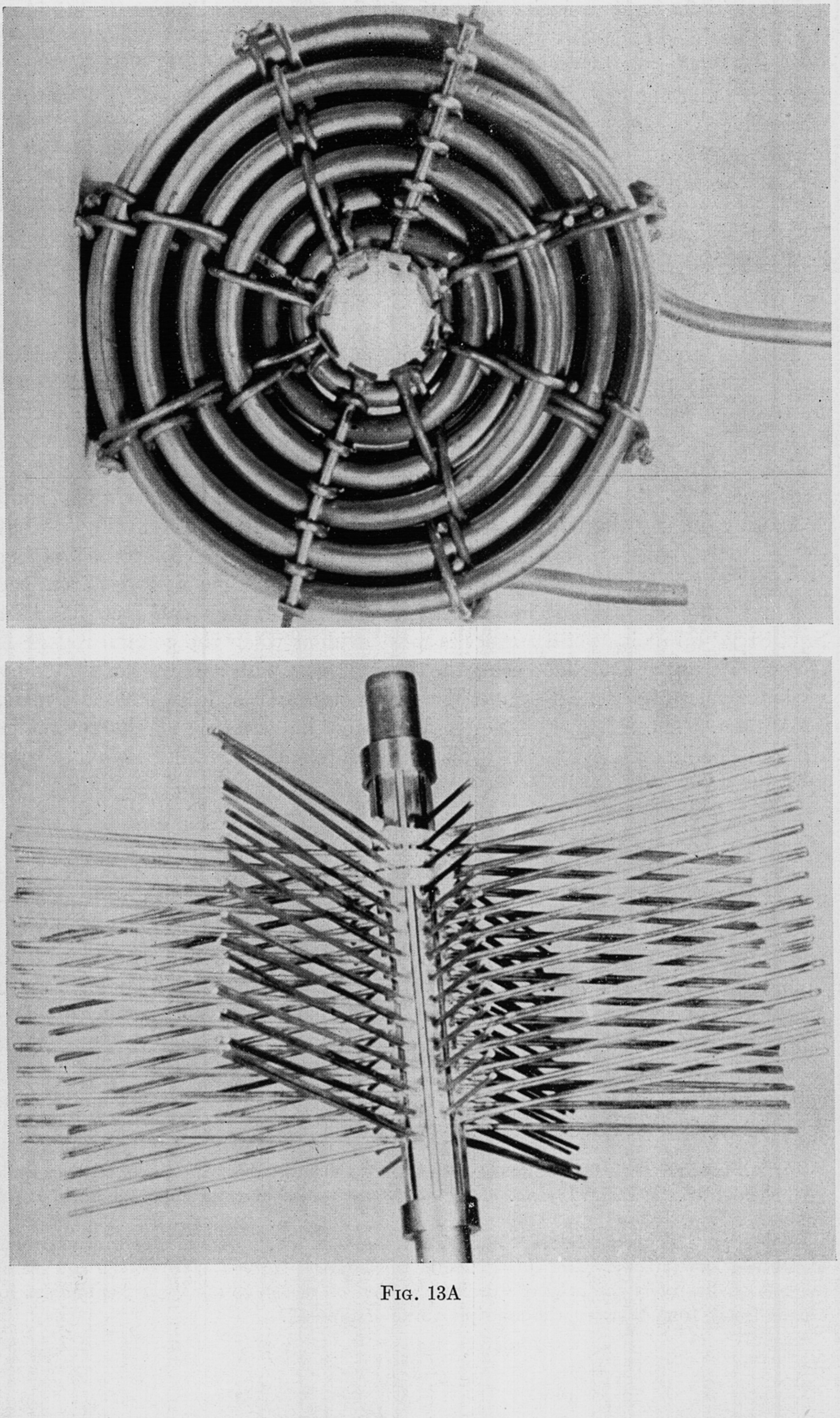

Fig. 13A

The flow diagram (figure 12) shows the presence of charcoal-filled tubes through which the feed passes in the dense gaseous state into the boiler coil. This provision was for the purpose of intercepting by adsorption any acetylene or traces of hydrocarbon vapors. The amount of steam-activated charcoal used in each tube was about 100 g., and it is important that the adsorbed water be driven from the charcoal by heating to 150°C. prior to installation; otherwise the activity and retentivity of the charcoal for the hydrocarbons are markedly reduced. An additional object was to catch any solid carbon dioxide which experience seemed to indicate deposits on the interior of the boiler coil with attendant reduction in heat transmission. The major purpose, however, was the interception of hydrocarbons.

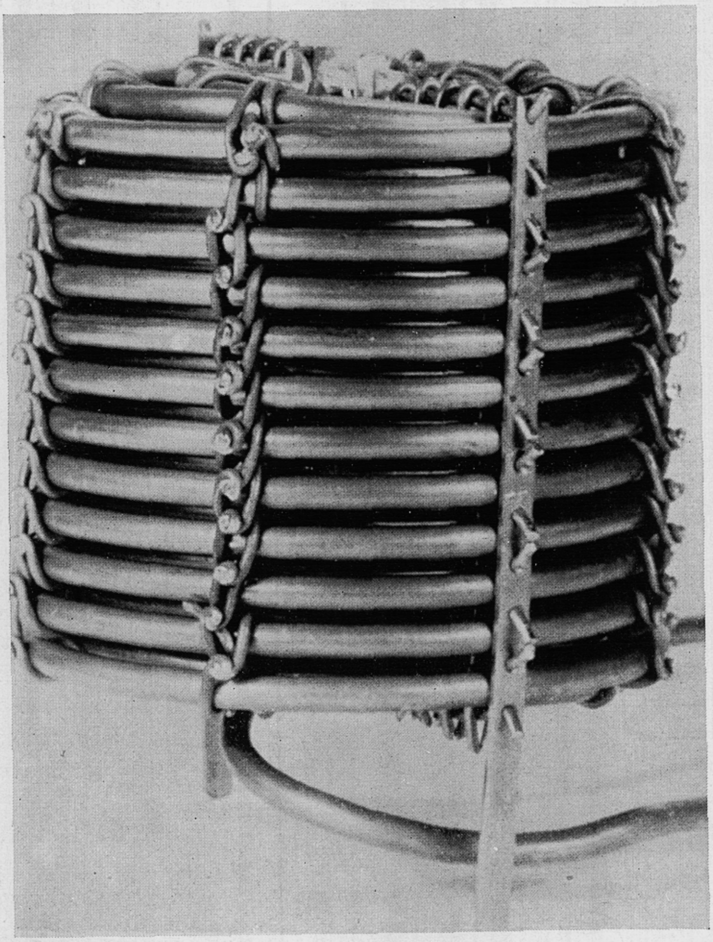

FIG. 13B

FIG. 13A and B. Boiler coil spacer and finished coil (devised by D. A. Williams)

The second charcoal and filter tube through which the compressed liquefied air passed was intended to catch any particles of solid hydrocarbons or hydrocarbons in solution in the liquid air[13] and on the felt filter, a final guard against particles to insure freedom from clogging at the expansion valve. No trace of sediment was ever observed in the liquid oxygen delivered by the test units except when quantities of gasoline vapors or acetylene detectable by odor from nearby trucks and an acetylene generator gained access to the compressor intake for a considerable period of time.

### *D. Column packing*

The question of the design and control of packing for columns turns on many factors, and the quantitative state of knowledge is insufficient for consolidation of known factors into a satisfying and coherent theoretical structure. However, the convenience of the packed columns where lightness and rapid attainment of a steady regime is desired needs little urging. In the case of the S-units, recourse was had to Madison No. 2 brass shoe eyelets,[19] a 3.8-in. height of which was equivalent to a plate of the conventional[20] column as obtained from distillation tests on liquid air. The weight per liter is 1.77 lb.

Another eyelet type, No. 3 short eyelets, exhibits a considerably shorter height equivalent—namely, 3.3 in.—based on the use of the test mixture benzene–carbon tetrachloride. The throughput characteristics are, however, somewhat inferior to those of the Madison No. 2 eyelets and also the weight per liter is 2.2 lb.

The metal-cloth $\frac{1}{4}$-in. saddles devised by Dr. McMahon gave on test with the benzene–carbon tetrachloride mixture a 2.8-in. height equivalent, and the weight per liter is most favorable, 0.94 lb.[21] Many actual column tests with the pump unit in the course of air distillation seemed to indicate little choice between the No. 3 short eyelets and the McMahon saddles, but the throughput characteristics were definitely superior in the case of the saddles. For the shipboard units, special No. 3 short eyelets were made of 0.006-in. thick metal of weight about 1 lb per liter. The unit with case and packing removed is represented in figure 14.

In the distillation of liquid air it is necessary to consider the fact that where oxygen of 0.995 m.f. or higher purity is desired, the impurity is substantially all argon; consequently the bulk of the argon must escape with the nitrogen or accumulate in the column to the detriment of the oxygen purity. It will be observed that where 0.96 to 0.98 m.f. purity is desired, the amount of argon retained by the oxygen will be large and the problem of argon disposal through the effluent is not a problem.[22]

[18] Certain oils have been observed to dissolve in liquid oxygen in small amounts.

[19] Obtainable from the United Shoe Machinery Company of Boston, Massachusetts.

[20] More correctly, the figure is a measure of the height of a transfer unit.

[21] Thanks are due Professor Avery A. Morton for the distillation tests which led to the numbers given.

[22] No data have been found bearing on the solubility of solid argon in liquid oxygen, liquid nitrogen, or mixtures at temperatures below the freezing point of argon. At a rectifier pressure of 1 atm. the effluent temperature would be 78.2°K., which is lower by 5.71°

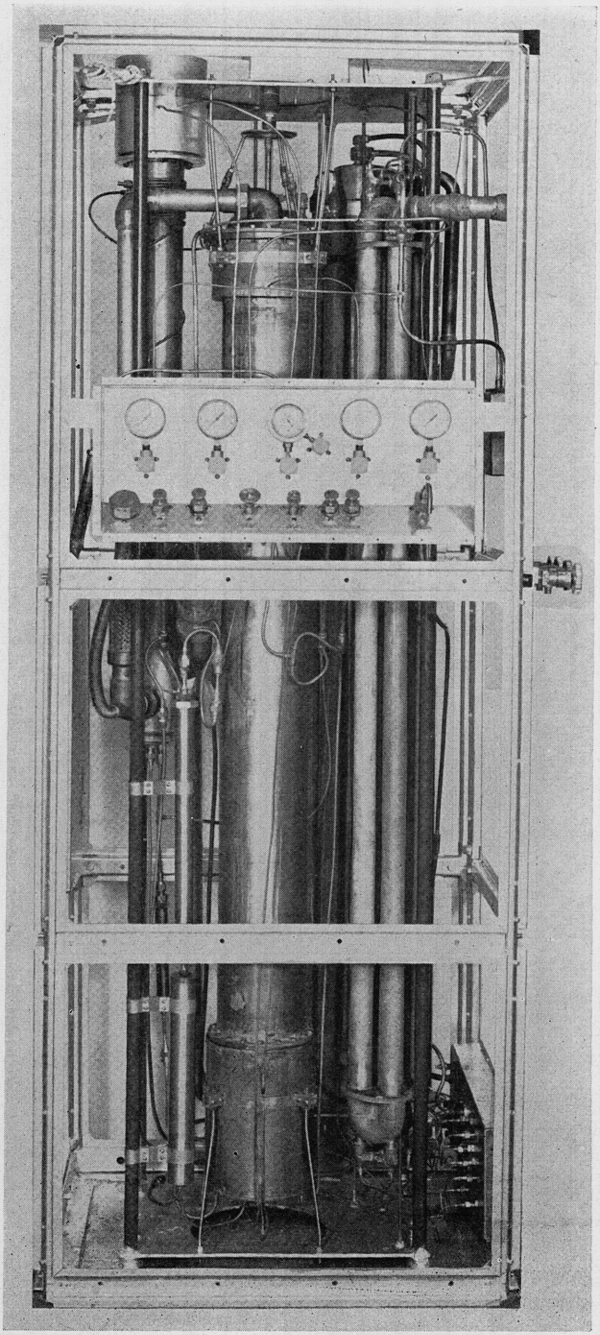

FIG. 14. K30MS unit. Oxygen gas manifold at the right; flexible metal delivery hose at left (not shown); in the center of the chassis is the rectifier with the pump at the left and interchanger on the right; the lower right side of the chassis contains the panel for all drains and purge lines.

## VI. PROBLEMS SUGGESTED

The brief sketch given above of the major tangible results of the effort of the M. I. T. group to assist in the development of small, short-period operation oxygen producers does not make explicit mention of various problems which the striving for practical results brought to light and emphasized as important for future research. In what follows reference will be made to a few of these instances in the hope that the younger students of science or engineering may find the subjects interesting and on this account worthy of being taken up with a view to providing invaluable new information.

The most recurrent difficulty was perhaps the almost entire lack of heat-transfer data at low temperatures for the compressed gases air, nitrogen, and oxygen. The data available for interchanger design are old and have been taken at room temperatures or higher for pressures in the case of air of about 16 atm. It was therefore necessary to attempt an extension of the equation recommended by Dr. McAdams (4). About 1943 the results of some measurements of transfer coefficients by Professor W. F. Giauque (1) became available, and these fortunately confirmed the essential reliability of the modified McAdams equation. The need is considerable, however to extend the measurement systematically for pressures ranging from 50 to 200 atm. and temperatures from room temperature to near the critical temperature of each gas. It is also important to obtain coefficients for the heat transfer of flowing liquid gases such as oxygen, nitrogen, and air at several higher pressure levels. Professor Giauque has measured the transmission coefficients for boiling liquid oxygen and air, and the values were most welcome for design. They will doubtless become a part of the scientific literature in due course.

A problem which has received much less attention than is desirable is the determination of the heat-transfer characteristics for other than circular-section channels. Thus, annular channels with and without bonded straight and spiralled spacers, the circular section with bonded twisted copper ribbon, the singly and multiply connected coiled high-pressure encased types and feed precoolers used in the S-units, and other types are amenable to design at present only through the use of McAdams' equation 4c, and the use of the hydraulic radius concept. Systematic tests at low temperatures and under pressure conditions common in the low-temperature field would after correlation place the design of these important interchanger types on a sound basis and give the designer confidence in introducing novel designs of heat-transfer equipment as occasion arose.

In the course of the design of the J–T–S interchanger and the subsequent checking of the design through temperature readings of the fluid streams along the

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than the triple point of argon. Accordingly, if the solubility is small enough a concentration of argon is conceivable in the column at a temperature corresponding to the triple point where crystals of argon would not only separate but accumulate. A column at a pressure of 1.68 atm. would have an effluent temperature of about 83.7°K., corresponding closely to the triple-point temperature of argon (83.91°K.), and argon crystals could scarcely form unless solid argon were quite insoluble in liquid nitrogen or the equilibrium liquid nitrogen–oxygen mixture at the top of the simple column.

interchanger, it became clear that the heat transferred at the cold end of the interchanger is far greater than would be predicted on the basis of the McAdams equation. It will be observed that both streams are in the gaseous state but the high-pressure air stream is of great density and great fluidity. It seems not unlikely that the cause of the increased heat interchange beginning at the cold end and dying out rapidly is due to a turbulence induced particularly in the high-pressure gas by the very large temperature difference which at the extreme cold end is 75°C. with a column pressure of 12 p.s.i.g. Empirically the behavior of one type of interchanger is as though the heat-transfer coefficient decreased from the cold end in accordance with the algebraic form

$$H = H_n \times 10^{c(l-z/l)^4}$$

where $z$ is the distance reckoned from the cold end for an interchanger of total length $l$, and $H_n$ is the normal over-all coefficient calculated, for example, by McAdams' equation. The experience suggests the need of investigating heat-transfer coefficients for large temperature differences where heat is being transferred between channels bearing dense gases. The measurements should also be extended to include liquids under pressure, a practical case in point being the boiler coil design.

There is also the incompleted general problem of the formulation of design procedure for the J–T–S interchanger. Two-channel interchangers often offer sufficient difficulty, and the three-channel case illustrated by the pump unit exhibits enhanced difficulty of attaining a satisfactory solution, for it is known that the transfer coefficients, the viscosity, and the heat conductivity vary with temperature as do also the heat capacities of the fluids, particularly high-pressure gases. A part of the general problem is also the calculation of the allowable thickness of the metal barriers along which heat must flow in order that heat flow over the interchanger section may take place without unduly large or irregular temperature differences. The application of the standard heat-flow theory to these cases could be made, but with a better knowledge of surface heat-transfer coefficients many cases could be solved completely. The heat conductivity of some metals such as copper, it is worth mentioning, changes rapidly as lower temperatures are reached and from 20° K. down very rapidly indeed.

Of course there is a great lack of knowledge of the viscosity as a function of pressure at low temperatures for gases and an even greater lack of heat-conductivity values, data which are essential for the correlation of heat-transfer coefficients.

A most interesting situation which is still in a far from satisfactory state is the extension of our knowledge of the equilibrium properties of the ternary mixture nitrogen–oxygen–argon. The amount of confirmed published knowledge is far from extensive and the results have a high practical value.

There is also the interesting question of the solubilities and mixture properties generally of the rare gases apart from argon. Such knowledge as exists forms the basis now for the extraction of these gases, supplied by the Linde Company and the Air Reduction Company, but extended knowledge of the properties of these mixtures will inevitably lead to improvements in processes and greater availability to satisfy the increasing practical uses of the rare gases.

The thermodynamic properties of air are fairly well known (2), at least relative to nitrogen and oxygen. A considerable amount of additional data is, however, needed to compile definitive thermodynamic charts covering the liquid and gaseous phases to 200 atm. for the gases comprising the atmosphere.

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