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The Production of Liquid Hydrogen without Expensive Equipment. Low Temperature Studies No. I

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Introduction

The standard procedure for the production of liquid hydrogen and helium requires costly compressors, hydrogen generators, and gas tanks, along with the diversion from research of time and money for operation and upkeep. It is because of the excessive cost of low temperature refrigeration that so few centers for research at the lowest temperatures exist. Certainly in the United States, with its abundance of helium, there is an unusual opportunity for the promotion of research at low temperatures provided inexpensive facilities can be developed.

The present paper sketches briefly the theory of liquefaction by the use of the Joule–Thomson effect and describes some improvements in the interchanger–liquefier together with a proposed procedure for lowering the fore-temperature of hydrogen entering the liquefier. It will be shown that it is possible to produce liquid hydrogen[1] wherever tanks of compressed hydrogen[2] are available by using equipment which can be fabricated inexpensively. A source of liquid air, preferably liquid nitrogen, is of course required.[3] Fortunately liquid nitrogen can be obtained from the many operating branches of the oxygen producing companies.

The technique of low temperature experimentation has hitherto often required formidable elaborations of glass construction. We have sought to explore the possibilities of increasing the scope of low temperature experimentation and in the course of our efforts the use of glass has been eliminated largely with important improvements in economy of refrigeration. The details of construction and methods employed to carry out low temperature measurements are best conveyed as the investigations are published but the general principle employed will be illustrated in the design of the hydrogen liquefier and desorber-precooler.

General Observations

The most convenient principle to employ for the production of liquid "permanent" gases is that exemplified in the temperature reduction experienced through the Joule–Thomson effect. Liquefaction may also be obtained by allowing a gas to expand while performing work, and the process is used in the Claude system for liquefying air. Kapitza's recent success in surmounting the difficulties of applying similar principles for the production of liquid helium is a notable achievement.[4]

At present the skill and effort required to produce small amounts of liquid hydrogen and helium (or nitrogen, of course) in the laboratory appear to be less by utilizing the Joule–Thomson cooling effect. The following are a few comments on the conditions which should be fulfilled to obtain a satisfactory yield of liquid.

The thermodynamic equation for the Joule–Thomson effect is

$$\mu = \left(\frac{\mathrm{d}T}{\mathrm{d}p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{C_p} = -\frac{\left(\frac{\partial v\tau}{\partial \tau}\right)_p}{C_p} \quad (1)$$

where T is the absolute temperature, p the pressure, H the enthalpy or chi function of Gibbs ($H = U + pv$), C_p the constant pressure heat capacity and τ a symbol for T^{-1}. Evidently μ may be positive, zero or negative.

It is seen readily that the H function may be represented as

$$H = \mathrm{f}(T) - \int_0^p \mu C_p \,\mathrm{d}p = \int C_p{}^0 \,\mathrm{d}T - \int_0^p \mu C_p \,\mathrm{d}p + h \ldots \quad (2)$$
$$= C p^0 \,\mathrm{d}T + \int_0^p \frac{\partial v\tau}{\partial \tau} \,\mathrm{d}p + h$$

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(1) A later paper will discuss the production of liquid helium by modifications of standard practice.

(2) Martin Ruhemann, *Z. Physik*, **65**, 67 (1930), has described an apparatus for the preparation of small amounts of liquid hydrogen and liquid helium (5 cc.) where the gases are available under pressure in tanks. Some five years earlier W. M. Latimer, R. M. Buffington and H. D. Hoenshel, THIS JOURNAL, **47**, 1571 (1925), suggested the possibility of dispensing with a compressor for the liquefaction of hydrogen provided hydrogen of high purity could be procured in tanks under pressure. Electrolytic hydrogen of high purity is now available in tubes under 136 atm. pressure.

(3) The use of nitrogen for precooling is not nearly as satisfactory as the use of an expansion engine. P. Kapitza has been successful in developing a low temperature unit.

(4) P. Kapitza, *Proc. Roy. Soc.* (London), **147A**, 189 (1934).

where h is a constant. It is quite clear from (2) that for the homogeneous gaseous phase the variations in H will under certain conditions be governed largely by the variations in the quantity μC_p and that variations in C_p^0, the heat capacity at zero pressure, will be small (H_2 below 70°).

The performance of the ideal liquefier will evidently be qualified by the requirement that the temperature of the unliquefied effluent gas attain the temperature of the entering high pressure gas and that the entire system be thermally isolated.[5] Granting these conditions ideally satisfied and taking ϵ to represent the fraction liquefied, H_1 the enthalpy of the entering high pressure gas, H_0 that of the effluent gas, and H_f that of the liquid, we obtain the relation

$$H_1 = H_f\epsilon + H_0(1 - \epsilon), \text{ or}$$
$$\epsilon = (H_0 - H_1)/(H_0 - H_f) \qquad (3)$$

The enthalpy of the liquid, H_f, corresponding to liquid boiling at atmospheric pressure (or any other saturation pressure, of course) may be assumed zero in the formulation of the H equation. We then have for the fraction liquefied the simple relation $\epsilon = 1 - H_1/H_0$. It is clear that for ϵ to be large H_1/H_0 must be small numerically. Meissner[6] has discussed the conditions for a maximum of ϵ and used the reduced equation of state of Kamerlingh Onnes for hydrogen as a basis for computations in the deduction of the temperature and pressure required for a true maximum of ϵ, namely, the temperatures and pressures satisfying the two equations $(\partial\epsilon/\partial T)_p = 0$ and $(\partial\epsilon/\partial p)_T = 0$. Meissner was not able to show that any unique pressure and temperature corresponding to a maximum of ϵ existed for hydrogen. The limitations in the range of the data available (60 atm.) placed a restriction on the computations.

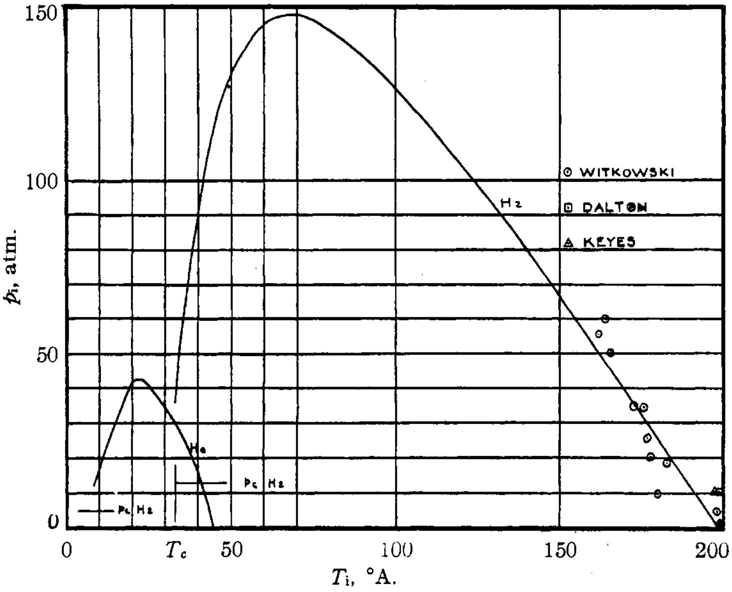

Fig. 1.—The hydrogen inversion curve based on Jakob's formulation of all available data. The helium curve is computed from an unpublished equation of state for helium.

At an earlier date, M. Jakob[7] had gathered together all available data on inversion temperatures for the Joule–Thomson effect; that is, the pressures and temperatures for which $(\partial v_T/\partial \tau)_p$ is zero for ether, carbon dioxide, ethylene, oxygen, air, nitrogen, and hydrogen. Jakob found that the data, when entered upon a coördinate diagram using the reduced pressures, $\pi = p/p_c$, and temperatures, $\Theta = T/T_c$, gave a single curve whose equation was as follows

$$\pi = 23.37 - 1.174\, R\,\Theta - (178.6/R^2\Theta^2) \qquad (4)$$

Taking for hydrogen p_c = 12.8 I. atm., T_c = 33.2°K. and R = 3.27, the inversion curve is given by the equation

$$p_{\text{inv.}}^{\text{I. atm.}} = 298.56 - 1.4772\, T - (235201.0/T^2) \qquad (5)$$

Figure 1 reproduces the curve corresponding to equation 5 which is quite similar in form but enclosed by Meissner's curve based wholly on the Kamerlingh Onnes series equations for hydrogen to 60 atm.

The significance of the inversion curve for the Joule–Thomson liquefaction process has been pointed out long ago.[8] As already stated the objective sought in liquefier operation is the point or points if they exist, of pressure and temperature corresponding to a maximum in ϵ. We find using the criteria for an extremal and equation (2)

$$\left(\frac{\partial\epsilon}{\partial p}\right)_T = \frac{\partial}{\partial p}\left[\frac{\int_{p_0}^{p_1}\left(\frac{\partial v_T}{\partial \tau}\right)_p \mathrm{d}p}{H_0}\right] = 0 \qquad (6)$$

and an analogous equation for $(\partial\epsilon/\partial T)_p$.

The pressure p_0 and p_1 in the integral of the

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(5) See page 68, E. B. Millard, "Physical Chemistry for Colleges," McGraw-Hill Book Co., Inc., New York, 1936, for a diagrammatic representation of the liquefier apparatus scheme.

(6) W. Meissner, *Z. Physik*, **18**, 12 (1923).

(7) M. Jakob, *Physik. Z.*, **22**, 65 (1921).

(8) No attempt at completeness of citations to the literature will be made in the material to follow. The standard hand-books may be relied upon for an abundant bibliography.

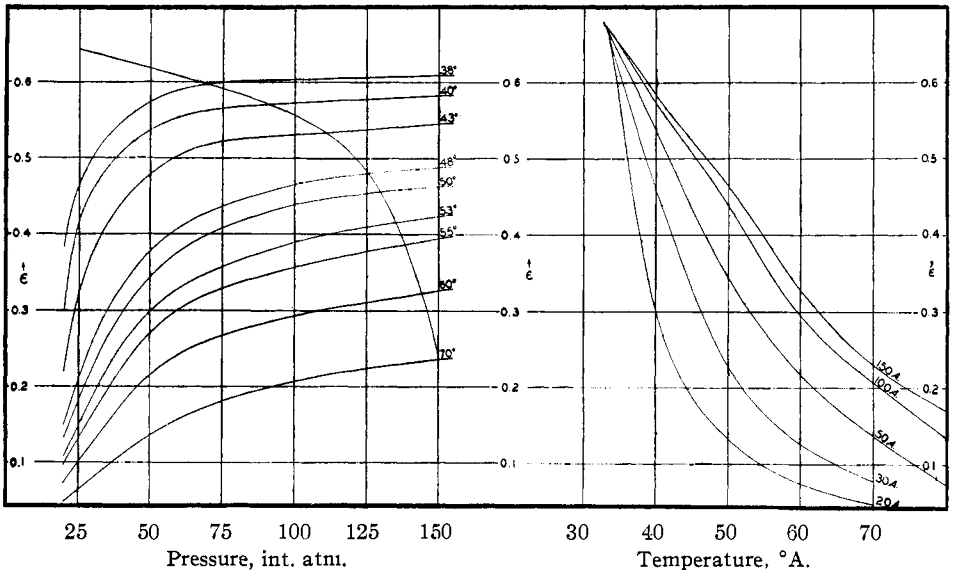

Fig. 2.—Fraction of hydrogen liquefied in relation to temperature and pressure deduced from the Keesom–Houthoff chart. The line starting from 70° in the ϵ *vs.* p plot and crossing the isothermals is drawn from the Jakob inversion curve and should intersect the isothermals at their maxima. The absence of the maxima is due to the limitations of the data which does not exceed 60 atm.

right hand member represent the pressures of the effluent and high pressure gas entering the liquefier.[9] In practice the effluent pressure is usually fixed at one atmosphere and the fore-pressure may be varied to produce the maximum yield. If the fore-temperature is fixed by employing liquid air boiling at reduced pressure or otherwise, the maximum yield will be obtained for the pressure corresponding to $(\partial v_\tau/\partial \tau)_p = 0$. Thus, using the Jakob inversion curve we find for fore-temperature 63°K., 146 atm., and from Meissner's inversion curve, about 158 atm.

When the fore-temperature and the fore-pressure may be adjusted at will, the favorable values of these variables leading to a true maximum are of interest. The remarks above indicate that there are scarcely sufficient data available for hydrogen to fully investigate the point. Apart from this, however, it is known that $(\partial v_\tau/\partial \tau)_p$ becomes infinite at the critical temperature and pressure. Thus the value of H changes with extreme rapidity in the neighborhood of the critical density, and in fact $(\partial H/\partial p)_T$ and $(\partial H/\partial T)_p$ become infinite for the fluid in the critical condition. It would appear therefore that if any unique fore-pressure and fore-temperature exist they should lie in the critical region. Of course if fore-temperatures are available below the critical temperature (for hydrogen 33.2°K.) the production of liquid merely requires a surface condenser and the means of forcing hydrogen to the condenser at the saturation pressure corresponding to the temperature available. The fore-temperatures and fore-pressures relevant to the discussion of liquefying apparatus based on the Joule–Thomson effect will be supposed not inferior to the critical temperature and pressure.

The simplest survey of the possibilities with respect to maximum yield of liquid at the present time may be obtained by plotting ϵ *versus* fore-temperature for various constant pressures. Fortunately a chart of the thermodynamic properties of hydrogen has been constructed by W. H. Keesom and D. J. Houthoff[10] providing data for the chart represented in Fig. 2. It will be remarked that the lines from 20 to 150 atm. all tend to converge in the region of the critical temperature where ϵ amounts to about 0.67. The figure also exhibits $(\epsilon)_T$ *vs.* pressure for several fore-temperatures. It is quite evident that 150 atm. is approximately the highest pressure that need be employed and with fore-temperature 63°K., $\epsilon = 0.295$. At 40°K., however, nearly 50% of

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[9] Fore-temperature and fore-pressure are convenient terms for use in designating the temperature and pressure of the high pressure gas entering the liquefier. The low pressure, or unliquefied, fraction of gas leaving the liquefier will be designated "effluent."

[10] W. H. Keesom and D. J. Houthoff, *Comm. Phys. Lab. Univ. Leiden*, Suppl. No. 65, 1928.

liquid may be obtained at fore-pressure 35 atm., while 5° lower 15 atm. suffices for a like yield.[11]

The Realization of Fore-Temperatures Lower than 63°K.—One procedure readily applicable for reducing the fore-temperature would be to design the "liquid air" fore-cooler interchanger for efficient functioning with solid nitrogen. In this way, using modern high capacity vacuum pumps, it is possible to reach temperatures approaching 53°, thereby raising ϵ to 0.42 for 135 atm. fore-pressure, a 40% increase over the case for 63° and 150 atm. fore-pressure. We have used a first approximation design for such an interchanger and there is no doubt that the scheme is practical.[12]

There are no readily available liquids other than air, oxygen, or nitrogen, which may be used to fix the fore-temperature. It was noticed some years ago,[13] however, that the heat of adsorption of hydrogen on charcoal was some eight-fold the normal heat of evaporation, while in the case of helium some seventeen-fold. The possibility presented itself, therefore, that refrigeration at a lower temperature than that customarily obtainable with liquid air might be practical by desorption. The requisite data for apparatus design on the amounts of hydrogen adsorbed per unit of charcoal as a function of pressure and temperature were finally accumulated by one of us (H. T. G.) and formulated analytically. An examination of the data indicated the practicability of refrigeration at temperatures approaching 40°K. by desorption of the hydrogen adsorbed at 63°K. or preferably somewhat lower, provided vacuum pumps of large capacity (1000 to 5000 l./min.) were available. Under favorable conditions a fore-temperature of 40°K. appears actually realizable.

Granting that refrigeration at 40 to 50°K. can be secured, an average yield of about 45% of liquid may be obtained for a fore-pressure range beginning at 135 atm. and dropping to 20 atm. The possibility therefore presents itself of dispensing with a compressor and utilizing compressed electrolytic hydrogen in tanks for liquefying hydrogen in the laboratory.

In localities where compressed electrolytic hydrogen at 2000 pounds or 136 atm. is available in cylinders it is demonstrable that even at current prices the amounts of liquid hydrogen used may amount to three thousand liters a year before the cost of installation, maintenance and operation of a compressor and gasometer system can be justified. When the cost of space, light, power and overhead, together with the hazards of compressing and storing hydrogen are given consideration, the use of liquid hydrogen could reach, at least for a university laboratory, large proportions before the standard equipment need be installed.[14] There are also attractive possibilities of reducing the quantities of refrigeration required by modifications of cryogenic technique. The initial steps taken in this direction indicate that often a fourth to a third of the usual volume of liquid hydrogen is required.

Precooling Interchangers.—Experience to date indicates economy in the use of solid carbon dioxide or "dry ice" as the first precooler, depending upon the cost of liquid nitrogen.[15] This may be followed by a liquid air or better, a liquid nitrogen precooling interchanger, and finally by a reduced pressure solid nitrogen precooling stage. The scheme of preceding the solid nitrogen vacuum precooler with an open liquid air or nitrogen precooler reduces the load on the former unit, thereby prolonging the intervals of replenishment of nitrogen.

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(11) The chart of thermodynamic properties was extended by Keesom and Houthoff to 150 atm. to satisfy the need for guidance at the higher pressures. The actual data, which do not exceed 60 atm. at the lower temperatures, were extrapolated on the assumption that the isometrics are linear with the temperature.

(12) Some thought has been given a design whereby the liquid nitrogen is sprayed onto the interchanger coils in vacuum thereby maintaining a coating or layer of solid nitrogen on the coils. When the coils are merely imbedded in the solid nitrogen a gas envelope or pocket forms about the coils, retarding heat transfer. Other designs may be attempted based on a heat distributing disk system. (See F. G. Keyes, U. S. Patent No. 1,622,523, March 29, 1927.)

(13) F. G. Keyes and M. J. Marshall, THIS JOURNAL, **49**, 1561 (1927).

(14) Improved yields of liquid helium through the use of a desorption precooler seem assured by the data already obtained by one of the authors (H. T. G.). A new investigation is in progress, however, which will provide more exact and comprehensive data for the design of a desorber unit to be used with a helium liquefier similar to the hydrogen liquefier described in the present paper.

F. Simon and J. E. Ahlberg [*Z. Physik*, **81**, 816 (1933)] have reported the production of liquid helium by releasing the compressed gas from an isolated container at temperatures 21, 15, and 12°K. Fifty per cent. of the initial mass of gas is stated to remain in the container as liquid on release from 100 atm. at 12°. Our computations indicate that small amounts of liquid hydrogen may be produced profitably by a pressure-release device provided fore-temperatures of about 40°K. may be realized. Details of a desorber precooled pressure-release device for use with either helium or hydrogen will be described later. The case for hydrogen has also been investigated [F. Simon, A. H. Cook and H. Pearson, *Proc. Phys. Soc.*, **47**, 678 (1935)].

(15) We have preferred to use liquid nitrogen for two reasons, the first being that it is safer than liquid air and the second that the pumping pressure is higher for the same temperature (ten-fold roughly compared to oxygen at −210°). The hazard in using liquid air is by no means an illusion. To illustrate, on one occasion we used liquid air to cool the desorber precooler. As the pumping progressed the vapor coming from the container within the desorber became progressively richer in oxygen until a point was reached where the oxygen and oil fog in the exhaust oil tank of the pump exploded, fortunately without causing damage. Quite disagreeable effects are possible under such conditions and the use of liquid nitrogen is at least prudent.

It was suggested above that temperatures lower than the triple point of nitrogen are possible provided a precooler is designed to operate in solid nitrogen. By reducing the total load on the precooler as suggested in the preceding paragraph, the capacity of the pump maintaining the bath temperature is less taxed and lower temperatures more readily realized. We have made a first approximation in this direction and much better success with an improved interchanger design is indicated. It is certain that fore-temperatures as low as −215° or even approaching −220° may be obtained when the design of the solid nitrogen precooler is perfected further.

The objective sought in the interchanger design is the rapid acquisition by the flowing gas of the temperature of the bath or environment in which the interchanger is used. Small mass and ease of construction are also desirable. The hydrogen employed is deprived of oxygen by passage over a palladium–asbestos catalyst and nitrogen is removed by passage through a charcoal container forming part of the liquid nitrogen interchanger. The order of precooling first used was to conduct the high pressure or tank hydrogen from the catalyst chamber through an interchanger immersed in liquid nitrogen to deprive the gas of water vapor. The gas left the unit at the same temperature that it entered, and was cooled to −78° in dry ice. Leaving the interchanger in a vacuum jacketed line, it entered a reduced pressure nitrogen bath with the charcoal container attached.

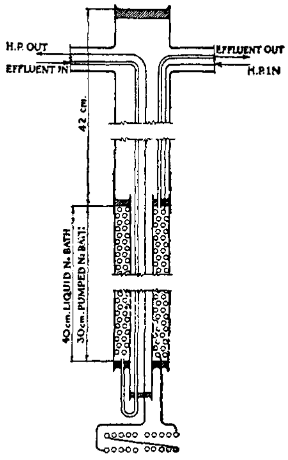

Fig. 3.—Interchanger design for use in liquid baths. The case is of thin-walled brass tubing 38 mm. in diameter.

The scheme is, however, not the most satisfactory, and in the future a solid nitrogen precooler will be used. The presence of the charcoal in the precooling unit gives rise to a shift in the para–ortho hydrogen ratio with attendant heat evolution of 87 cal. per mole of hydrogen at 78°K. and 155 cal. at 55°K. Because of this heat effect it is clearly preferable to place the charcoal container in an open nitrogen bath along with an interchanger and then cause the hydrogen to enter the solid nitrogen interchanger at about 78°K. The thermal load on the latter is accordingly greatly lightened and corresponds at most to cooling 50 mole per cent. para hydrogen through some 23°.

It will be perceived that when liquefying hydrogen under the conditions of a falling fore-pressure the magnitude of the resistance to flow of the high pressure hydrogen is important. In our practice of the liquefaction process the fore-pressure may be allowed to fall to 20 atm. and to ensure a small pressure fall in the interchangers we did not use the twister-tube design, employed for the liquefier-interchanger. The interchanger fully reduces the temperature of the effluent gas to the temperature of the high pressure gas entering the interchanger. The latter gas must at the same time leave the interchanger at the temperature of the nitrogen bath used. Our interchangers have proved quite satisfactory in practice.

Figure 3 indicates the elements of the design of the open nitrogen-bath interchanger. For the catalyst tube of stainless steel which served also as a first stage water separator, 12 meters of the standard copper interchanger tube (3.56 mm. o. d.; 2.54 mm. i. d.) was used made up into a solenoid-like coil 40 cm. in length wound to occupy the cross section of the stainless steel tube (38 mm. o. d., 3.28 wall). The dry-ice precooler is satisfactory when its interchanger design is identical with that used for the liquid nitrogen-bath. The last traces of water vapor may be removed conveniently by using an interchanger placed in the open nitrogen-bath. The dry hydrogen passes to the dry-ice precooler and then to the open nitrogen precooler and charcoal denitrogenizer, and finally to the solid nitrogen precooler. From the solid nitrogen precooler the gas may be further precooled by the desorber precooler or delivered to the liquefier unit.

If the desorber is omitted and with a fore-temperature of 55°, the average value of ϵ for the fore-pressure falling from 135 to 20 atm. will be $\bar{\epsilon} = 0.302$. With the desorber precooler and a fore-temperature of 43°K. for the same fore-pressure range we have $\bar{\epsilon} = 0.49$, an increase of liquid relative to 53° fore-temperature amounting to 62%.

The Desorber Precooler.—At the time the desorber design was under construction liquid nitrogen was not available for precooling. Liquid air, the usual refrigerant, is scarcely serviceable for precooling below 61 or 63° unless very large capacity pumps are available. Of course the triple point of oxygen (54.33°K., vapor pressure 1.2 mm.) is considerably lower than that for nitrogen (63.14° K., vapor pressure 94.6 mm.) and the advantage of a liquid bath for the interchanger is great, were it not offset by the danger of pumping practically pure oxygen. A satisfactory interchanger design for the use of solid nitrogen is however entirely practical and if temperatures approaching 55° may be realized as now seems likely, the importance of the charcoal desorber is lessened especially where only small quantities (5–10 liters) of liquid hydrogen are required at irregular intervals.

The data obtained for designing the precooler indicated that the heat of adsorption is a function of the temperature and the amount of hydrogen in the adsorbed state. At 63° and about 4 atm., for example, the amount adsorbed is 300 cc. per gram of coconut charcoal[16] and the mean heat evolved in the adsorption is 1326 cal. per mole of hydrogen (1 cal. = 4.1860 I. j.). At 43° with 175 cc. of hydrogen adsorbed, the equilibrium pressure of the hydrogen is 1.1 mm. The heat of desorption available for refrigeration would be 1105 cal. per mole of hydrogen desorbed. The refrigeration to be effected is (a) the cooling of the charged charcoal and its container with the adsorbed hydrogen, for example from 63 to 43° (heat capacity about 1.6 cal./mole); (b) compensation for the heat required in the change of the para–ortho ratio from that at 63° to that at 43°, assuming the ratio in the adsorbed, state is the same as for the equilibrium gaseous state

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[16] Steam activated coconut charcoal supplied by the National Carbon Co. of a size to pass a 14-mesh sieve and be retained on a 20-mesh sieve.

TABLE I

MEAN VALUES OF THE FRACTION OF HYDROGEN LIQUEFIED

Pressure range, atm.	Smoothed values										
	70	63	60	55	53	50	48	45	43	40	38
20–135	0.166	0.217	0.245	0.302	0.330	0.375	0.406	0.455	0.490	0.541	0.576
30–135	.178	.230	.263	.325	.353	.396	.429	.475	.508	.556	.590
Max. at p_i	.236		.323		.415		.480		.516		.598

(62.4% at 63°; 84.9% at 43°); and (c) the fore-cooling of hydrogen at fore-pressure p.

The question of interest is the amount of charcoal required per liter of liquid hydrogen produced at specified fore-temperature and fore-pressure for various temperatures of charging the charcoal in the precooler with hydrogen. The capacity of the pump used to desorb the hydrogen will also be important since the pressure of hydrogen falls rapidly as the amount of hydrogen in the adsorbed state diminishes, and a high rate of precooling will depend on the rapidity of desorption. It may be assumed also that for many purposes a production of two liters of liquid hydrogen per hour would be satisfactory. This rate could of course be increased several fold by changes in design.

Assume that it is desired to produce liquid hydrogen at fore-temperature 38°K. The efficiency, ϵ, for this condition is 0.6 (p_i = 70 atm.) and the amount of charcoal per liter of liquid hydrogen produced is required for various temperatures of charging the charcoal with hydrogen. Figure 4 indicates the amounts required for fore-temperatures 38, 43, and 48°K. as a function of the charcoal charging temperatures. In making the calculations it was assumed that charging was always carried out at 4 atm. pressure.

For fore-temperature 48° the fraction of circulating gas liquefied for a fore-pressure range 135 to 20 atm. is on the average 0.406. If the desorber precooler is charged at 63° the chart indicates that 1000 g. of charcoal will be required per liter of liquid produced, or 5200 g. charcoal for a five-liter unit. Our particular sample of charcoal would occupy a volume of 10.25 liters. The increased yield of liquid over that obtainable for fore-temperature 63° amounts to 87%. Charging at 58°, however, reduces the amount of charcoal required per liter of liquid to 550 g. The increased yield at 48° fore-temperature over that possible at fore-temperature 58° (0.265) is now 53%. Charging at 53°, possibly the lowest temperature obtainable using solid nitrogen, diminishes the amount of charcoal to about 200 g. but the increased yield of liquid due to the five degrees additional precooling becomes 23%.

The lowest practical fore-temperature, according to the present data, cannot be much less than 38°. All things considered it appears best to fix on 43° as the most suitable fore-temperature where $\bar{\epsilon}$ for pressure range 135 to 20 atm. is 0.490. Using a charging temperature of 53° the amount of charcoal required per liter of liquid hydrogen is 500 g. or 5.00 liters of charcoal for the five-liter unit. The increase in yield of liquid at 43° as compared with 53° is 48.5% or 5 liters compared with about 3.37°.

From Fig. 2 it will be observed that the constant temperature ϵ, p lines rise progressively more rapidly with pressure as lower temperatures are considered. In consequence of this fact the significance of the lower fore-temperatures is emphasized since the average value of ϵ will be greater for fixed pressure limits. Table I gives a few values of $\bar{\epsilon}$ and ϵ for various temperatures.

The heat capacity of charcoal is conveniently small for the precooler purpose here considered, while the heat conductivity and density are unfortunately very small. It is also necessary to provide for free circulation of the gas throughout the charcoal in order that no appreciable pressure drops may occur within the container. The design adopted was in general accord with the ideas described some years ago for a generator employing a poor heat conducting gas storage material.[17]

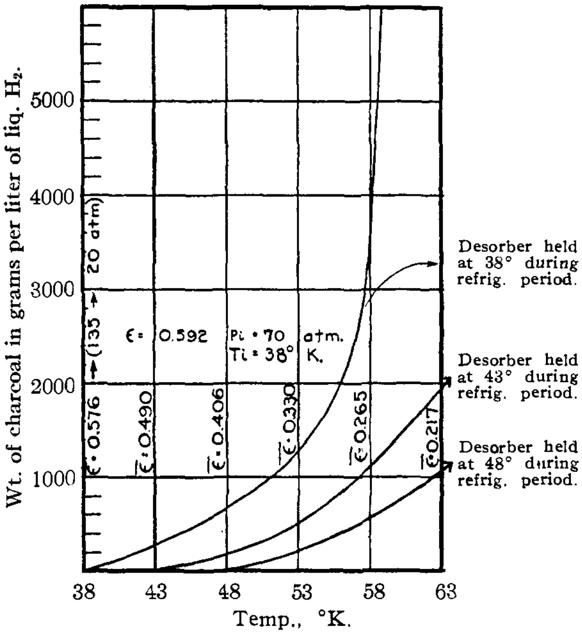

Fig. 4.—The curves show the amounts of charcoal required for precooling hydrogen to 48, 43, and 38°K. in the production of one liter of liquid hydrogen where the charcoal is charged with hydrogen at various temperatures.

The amount of charcoal used in the first desorber was 7000 g. or about 15 liters. A cylindrical copper container 15.75 cm. in diameter and 46 cm. long was constructed to serve for holding the liquid nitrogen used for cooling the charcoal and container. Spun copper (0.4 mm. thick) disks slightly less in diameter than the nitrogen cylinder were pressed onto the cylinder and soldered in place with ordinary soft solder. To the first disk a double turn of the copper interchange twister-tube type coil (Fig. 9) was soldered, then a second and the succeeding disks pressed onto the cylinder. The interchange coil was brought through cuts in the sides of the disks. In the preparation of the heat distribution disks 0.65-mm. holes were drilled along the path of the coil turns on each disk to serve for copper wire attachments used in holding the

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[17] F. G. Keyes, U. S. Patent No. 1,622,523, March 29, 1927.

turns of interchanger coil in contact with the disk while soldering.[18]

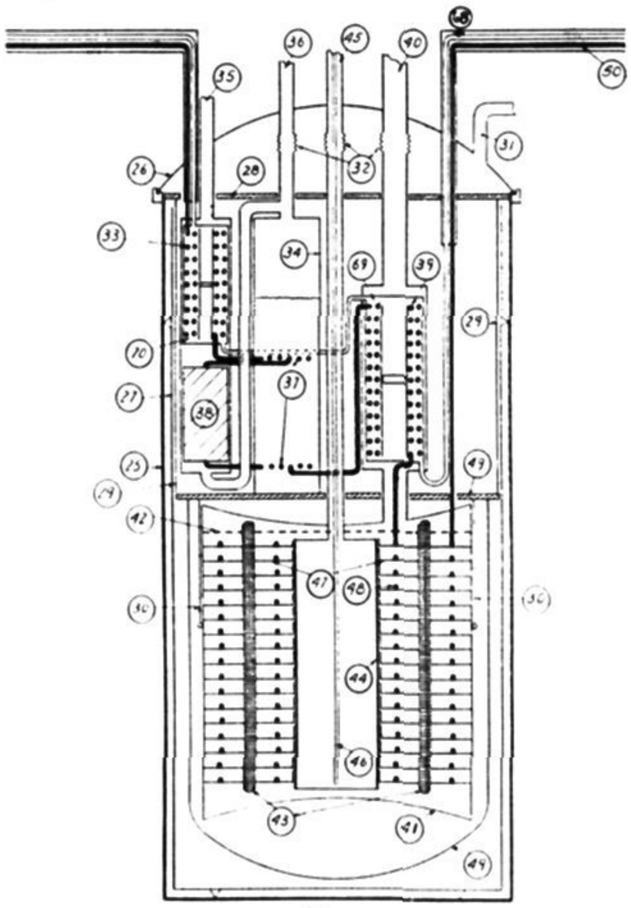

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Fig. 5.—25, steel case for desorber unit; 26, spun monel cover; 27, floating radiation shield; 28, support plate; 29, suspension-support plate to cooled radiation shield; 30, suspensions for charcoal container; 31, high vacuum connection; 32, expansion bellows; 33, interchange coils −195 to −210°; 34, container for pumped liquid nitrogen; 35, liquid nitrogen pump-off connection; 36, tube for adding liquid nitrogen to 34; 37, cooling coils −210° bath; 38, charcoal clean-up trap; 39, interchange coils −210° to desorber temperature; 40, hydrogen pump-off from desorber charcoal; 41, charcoal container; 42, screen for retaining charcoal; 43, screens for pumping through charcoal; 44, copper container for liquid nitrogen used for cooling while charging charcoal; 45, pump-off tube for liquid nitrogen container; 46, blow-out tube for liquid nitrogen container; 47, copper disks containing hydrogen coils; 48, copper tubing coiled on disks 47; 49, radiation shield cooled by 34; 50, vacuum jacket containing tubes from D to L; 69, low pressure through interchanger 39; 70, low pressure through interchanger 33.

Staggered holes about 1 cm. in diameter were made in each plate to allow the charcoal to pass freely throughout the volume when the container was loaded with charcoal. In addition, four holes 2.5 cm. in diameter to receive gauze monel metal tubes were made in each disk 9.15 cm. from the edge of the 15.75-cm. hole in the center of the copper disks. The ends of these tubes passed through a gauze charcoal-retaining diaphragm in the head of the container which carried the vacuum pump tube. By this device each layer of charcoal could receive and deliver gas with little drop in pressure and the gas flow resistance of each layer was uniform with every other.

The attempt was first made to use sheet metal for the container with a folded hard soldered seam along the cylinder. The heads of spun monel metal were set in place by means of monel screws and also hard soldered. In our hands the container was not a structural success in spite of the use of several varieties of design for the heads. Stainless steel was finally employed throughout and all the joints made by the use of atomic hydrogen. The material is stronger than monel metal and all welds tested proved as strong as or stronger than the original stock. The items of Fig. 5 convey an impression of the final design. Figure 6 is a reproduction of a photograph of the first disk system and monel container which makes clear the appearance of the disk assembly.

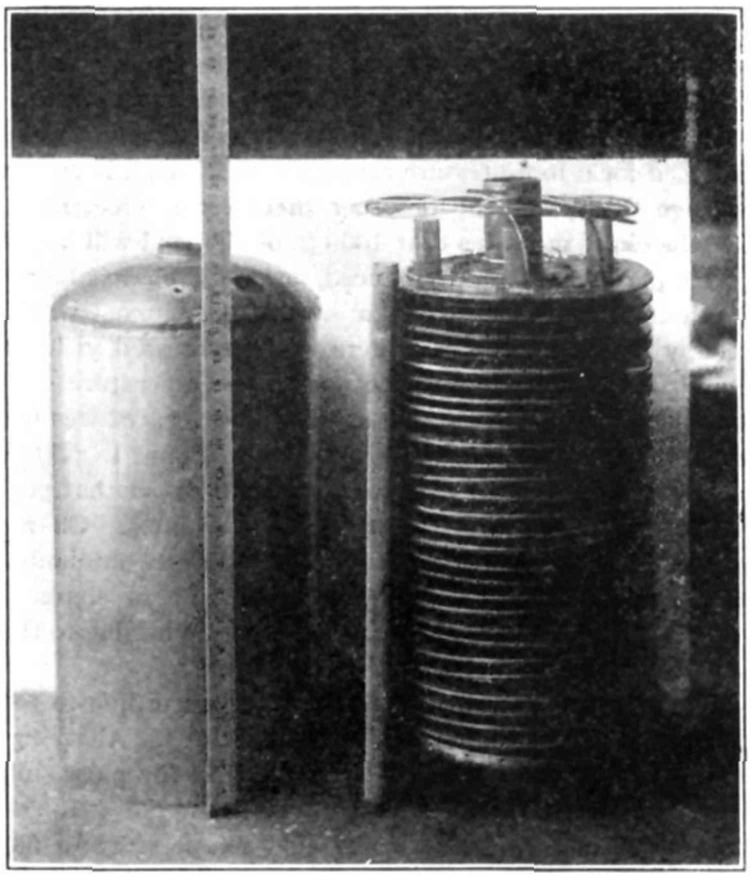

Fig. 6.

The complete desorber was suspended from a copper plate (49), the top of which also served as a support for a cooling cylinder soldered into contact therewith and the enclosing radiation shield soldered at the edges. This assembly was in turn suspended from a brass plate turned to fit the top of the 30.5-cm. iron vacuum case. All leads were of course constructed of German silver tubes, and "hydron" bellows were used where expansion or contrac-

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(18) The high pressure hydrogen interchanger coil should preferably pass at once to the first lower disk and be wound two turns to the disk. The gas is admitted to that end of the tube leaving the top disk of the container next to the vacuum pump lead. By using this order of circulation the top of the desorber will tend to be warmer relative to the lower end of the desorber and the vapor pressure of the charcoal nearest the pump tube will be correspondingly higher. The exit end of the interchanger tube should preferably pass out of the bottom of the container. This detail of design is important and was insufficiently considered in the present desorber.

tion would introduce strains. In Fig. 7 the larger of the two cylinders to the left is the desorber and next to it the liquefier. At the right of the liquefier is the pumped nitrogen-bath and dry-ice precooler. On the floor near the liquefier is the liquid hydrogen transfer dewar. The meters are used to follow the quantitative performance of the cycle.

The new desorber will follow the same general principles described but the interior of the central cooling cylinder of the desorber will be designed to take advantage of lower charging temperatures obtainable through the use of solid nitrogen at reduced pressures. With a large desorber the direct use of nitrogen in the cooling cylinder is inconvenient because of the desirability of relatively small size and uninterrupted pumping. The difficulty may possibly be surmounted by using oxygen as a heat transfer medium with its temperature controlled by a solid nitrogen condenser external to the desorber. There are also advantages in combining cooling by heat transfer with a final stage using solid nitrogen in a separate compartment of the cooling cylinder.

An item of importance is the total quantity of refrigeration required to cool the desorber precooler to the loading temperature. Once this temperature is attained, however, it may be preserved with the use of moderate quantities of liquid air for maintaining the radiation shield temperature. It is clear that if small amounts (5 to 10 liters) of liquid hydrogen are required at somewhat long intervals it will be more economical to accept a smaller efficiency or higher fore-temperature and omit the desorber precooler from the cycle. In the daily production of considerable liquid hydrogen over a long period, however, the cost of operating the desorber unit will be balanced by the more efficient use of tank hydrogen. A double unit would of course make continuous desorber refrigeration possible.[19]

The Liquefier Expansion-Interchanger.—The current designs of liquefier-interchanger have been represented fully and discussed in the handbooks. It is desirable in this device to reduce heat transfer as much as possible from the low temperature or expansion end of the coil (20.4°K.) to the high temperature or fore-temperature end (63°K. in standard practice). Heat, however, must be interchanged as rapidly as possible transversely or between the flowing high and low pressure gases. The mass of metal employed *should likewise be small, thereby reducing the induction* period or time required to reach a steady state of liquefaction. This feature is evidently important from the point of view of economy where tank hydrogen is employed in lieu of a compressor. The liquefier No. 1 now in use and cooled to 78°K. begins to produce liquid five minutes after hydrogen (temperature 63°K. or less) is admitted. The total quantity of hydrogen used to reach this stage amounts to 44 moles or about a fifth of the contents of a standard tank of hydrogen. Liquefier No. 2, now in construction, will be of larger capacity but the induction period will be less.

The interchanger high pressure tube[20] used consists of a copper tube drawn down upon a twisted ribbon of copper 0.25 mm. thick. The high pressure gas in such a tube is thus caused to follow a spiral path and tests indicate complete turbulence for the lowest rates of flow practicable. The twisted ribbon was prepared by first rolling a 0.65-mm. annealed copper wire to a ribbon of width 1.09 mm. After rolling it was re-annealed and twisted to the extent of 3 turns per cm. The twisted ribbon was next drawn into a clean annealed 1.305-mm. bore copper tube 1.99 mm. in outside diameter. The twisted ribbon having been drawn into the tube, the latter was drawn down to a diameter of 1.66 mm. The compound tube "twister-tube," about nine meters in length, was then annealed thoroughly and given finally a single draft through the draw plate before being wound 0.85 turn to the cm. on an aluminum mandrel.

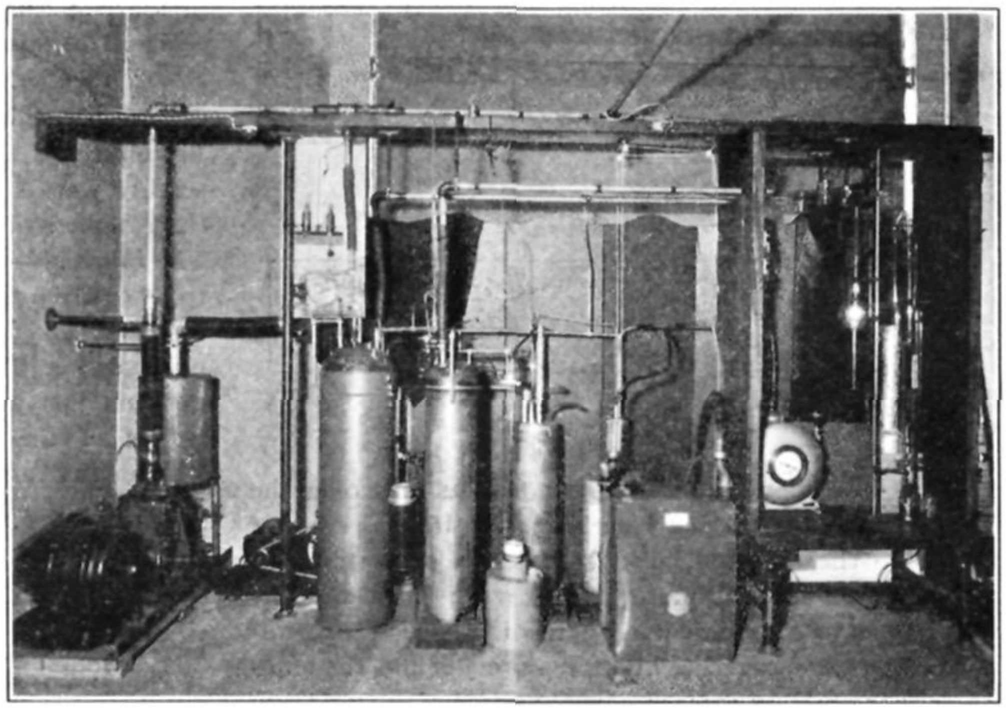

Fig. 7.

The winding was done on a lathe with moving slide rest using a special brass tool held in the tool-post. The resulting coiled twister-tube was next drawn into a 2.7-m. length of 0.2-mm. wall German silver effluent tube 4.76 mm. in outside diameter. The aluminum mandrel was next loosened by treating it with caustic soda and withdrawn. After filling the interchanger with diphenyl-

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(19) The desorber refrigeration principle is also of interest in the construction of constant temperature baths operable in the interval 63 to 38° through hydrogen desorption and between 20 and 6° through helium desorption. A double-walled charcoal filled metal dewar tube has been constructed to test this idea and the result indicates that a wide range of application is possible. It seems clear that the much discussed gaps in the temperature scale can be bridged by the use of desorber refrigeration. There is in use, however, another convenient method of maintaining constant temperatures at any selected point which will be described later. See M. Ruhemann, A. Lichter and P. Komarow, *Physik. Z. Sowjetunion*, **8**, 328 (1935).

(20) F. R. Bichowsky, *J. Ind. Eng. Chem.*, **14**, 62 (1922), gives data for the George Nelson twisted flat-tube interchanger.

amine it was wound into a coil of about 10 cm. diameter.[21]

The liquefier now in use for a little over a year was provided with four expansion-interchanger coils (of the kind described) in parallel. The capacity, indicated from tests made during construction, permits the expansion of sufficient hydrogen to produce 2 to 4 liters of liquid per hour (depending on fore-temperature and pressure). Figure 8 shows the twister-tube in sectioned portion. In Fig. 8A, a sectioned portion of the German silver effluent return tube containing the coiled high pressure twister-tube is shown.

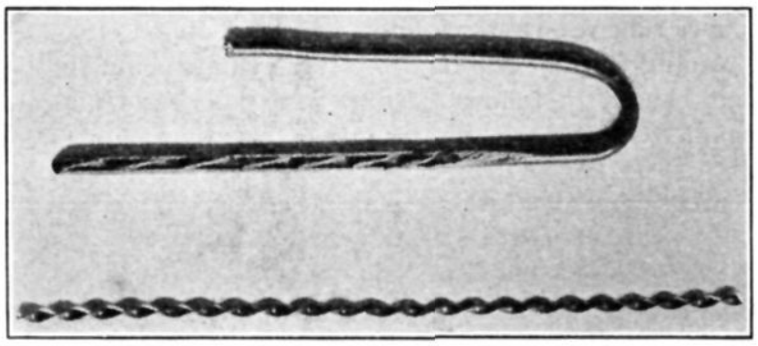

Fig. 8.

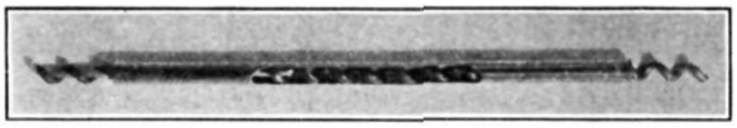

Fig. 8A.

It will be evident that the expanded gas flow over the coiled twister-tube in the German silver tube is counter current to the flow of the high pressure gas within the twister-tube. The ultimate efficiency of the liquefier-interchanger may be indicated by the difference in temperature between the entering high pressure gas and the effluent. At the highest rates of flow of hydrogen the temperature difference has amounted to little more than the sensitivity of the single copper–constantan couple used as the indicator; about 0.1°. At 63°K. and 100 atm. fore-temperature and fore-pressure a defect of one degree in the effluent temperature corresponds to about 4% less liquid formed. The defect in efficiency due to failure of the effluent to attain the fore-temperature increases rapidly, however, with diminishing fore-pressure.

The four liquefier-interchanger tubes really comprise eight tubes since the four German silver effluent tubes each contains a high pressure spiral tube. The German silver tubes were soldered into one-half of a double chamber box and the high pressure tubes brought through the partition and soldered in place. The high and low pressure compartments of the box were then suitably sealed and connected with the high pressure supply and the effluent to the interchanger used for cooling the high pressure supply.

The lower ends of the four German silver compound tubes passed through the brass cover of the liquid hydrogen receiver and were securely soldered. The high pressure tubes were next brought to the expansion valve on the under side of the brass cover and soldered into the expansion valve. The cover was finally soldered to the copper ring of a sheet monel metal receiver. Provision was made also, of course, for a receiver discharge tube for withdrawing liquid hydrogen. The expansion valve was of a simple threaded-stem cone type driven by means of a 500-mm. length of 3.18-mm. diameter stainless steel rod enclosed in a 4.76-mm. o. d. German silver tube. A stainless steel tube of the same outside diameter and 0.25-mm. wall will be used in future.

The use of four independent liquefier-interchanger tubes in parallel in the design here described is not desirable, for should plugging of one high pressure spiral tube occur, a quarter of the effluent fails to exert its refrigerant effect on the full amount of high pressure gas flowing in the remaining three spiral tubes. While stoppage of the high pressure spirals in No. 1 liquefier has never occurred, we will use a single liquefier expansion-interchanger in the No. 2 liquefier.

The Mounting and Heat Isolation of the Liquefier Assembly.—The receiver and liquefier-interchanger assembly were suspended from a brass plate by means of three monel metal wires attached to the receiver cover. The brass plate formed the main support and was turned to fit easily into a shoulder at the top of a 20.3-cm. brass case 86.3 cm. in length. Also suspended from the brass plate was a 6.35-mm. thick copper disk adjusted to a position just above the double box constituting the entrance of the liquefier-interchanger coils. A 1.59-mm. wall copper radiation shield, with bottom, could be raised about the liquefier and receiver completely enclosing the assembly. By means of screws the shield could be attached to the copper disk and good thermal contact obtained by soldering. The cooling of the shield was effected by soldering a copper cylinder of 1500-cc. capacity to the upper surface of the copper disk. All connections to vessels were made by means of thin-walled German silver tubes.

Polished silver is commonly supposed to constitute the best practical reflecting surface. An examination of the data, however, indicates that the fraction of incident radiant energy reflected tends to approach the same value for a number of metals as the wave length passes to large values. Silver, gold and copper, for example, appear to have reflectivities 0.987, 0.980 and 0.984, respectively, for wave length 9 μ. The resistance of the metal to oxidation would of course be an important factor from a practical point of view. The silver or gold plating of large objects proved in our experience to be a burdensome task. To obtain some practical indications for our guidance, tests of the amount of liquid air evaporated from a vacuum contained copper cylinder were made under controlled conditions. It was found that a freshly deposited electrolytically-produced copper surface (from an acid bath), which had been rinsed with distilled water and mounted in the vacuum case without drying, gave a very highly reflecting surface (0.983). Drying in the air and exposure, however, caused marked deterioration. Multiple surfaces of thin aluminum foil also proved to be as satisfactory in net reflecting power as the best copper or silver surface. It is important of course to prevent, as

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(21) The advantage of this substance as a filler for bending or drawing tubes to thin wall lies in its low melting point (54°C.), (and also in an unctuous quality suiting it better to the purpose than for example naphthalene). Its great solubility in alcohol of course simplifies cleaning after operations.

far as possible, thermal contact between the successive aluminum foil layers.

The cooled copper radiation shield was buffed to a high polish[22] and surrounded by a silver plated uncooled copper radiation screen which enclosed the entire apparatus suspended from the brass support disk. The liquid air cylinder soldered to the copper radiation screen supporting disk was also wrapped with several layers of aluminum foil and the liquid hydrogen receiver likewise. Figure 9 gives an impression of the apparatus before being soldered into the brass vacuum case. Figure 10 is a diagram of the assembly.

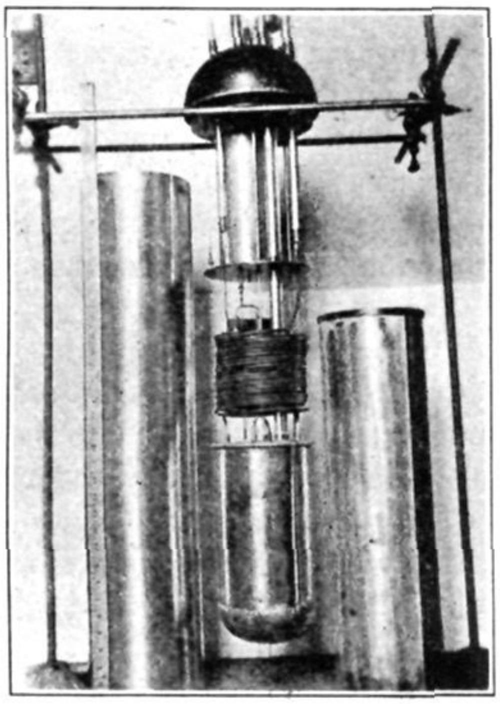

Fig. 9.

Thin-walled (0.1 to 0.15 mm.) German silver tubes served as the means of communication to the various vessels of the assembly. A "hydron" bellows was used on the lead from the liquid air cylinder to relieve strains due to contraction.[23] The assembly was lowered into the brass vacuum case which bore a copper ring hard soldered on the exterior wall of the upper end. The latter ring carried a groove or trough made to receive the edge of an hemispherical closure cap pierced at the proper points and provided with bushings, to permit the egress of the communication tubes of the contained apparatus. After the brass suspension plate is in place and the cap adjusted closure is effected by filling the copper groove with solder and of course the German silver tubes passing through the brass bushings are soldered. The vacuum maintained in the vacuum case should not be inferior to 10^{-6} mm. for the most satisfactory results.[24]

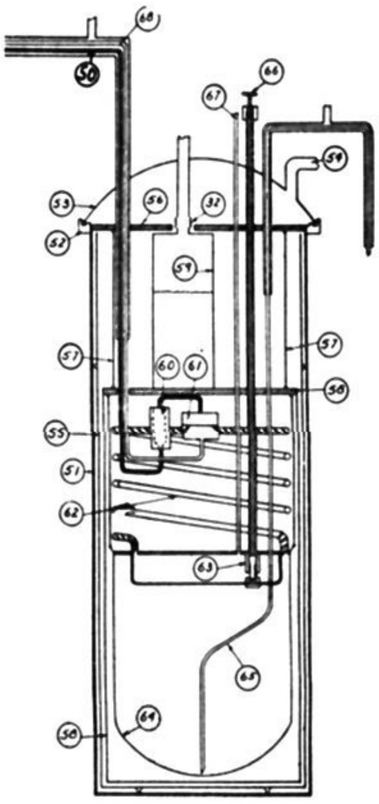

Fig. 10.—50, vacuum jacket containing tubes from D to L; 51, brass case; 52, copper ring hard soldered to case; 53, spun monel cover; 54, high vacuum pump-off; 55, floating radiation shield; 56, support plate; 57, supports from 56 to cooled radiation shield 58; 58, cooled radiation shield; 59, liquid nitrogen container to cool 58; 60, high pressure filter thimble; 61, high and low pressure header box; 62, interchange coils D temp. to hydrogen temp.; 63, expansion valve; 64, liquid hydrogen container; 65, liquid hydrogen transfer tube; 66, expansion valve control; 67, safety tube to relief diaphragm; 68, low pressure return to D.

During the first test operations of the liquefier an abnormally large quantity of hydrogen was used before the temperature of the receiver fell to the temperature of boiling hydrogen. This effect is due, in the opinion of the writers, to the small value of the accommodation coefficient of hydrogen for collisions with the monel wall of the receiver at higher temperatures. Without attempting to sustain this view by arguments which now seem plausible, the following simple device[25] sufficed to bring the quantity of hydrogen required for the induction period into agreement with the amount calculated from the known heat capacities of the liquefier-interchanger, receiver and parts. A small cylindrical brass box of 5-cc. capacity was soldered to the brass cover of the receiver and provided with a German silver tube which passed along the side of the liquid air cylinder and was soldered thereto. The tube passed out of the vacuum case and connected with a flask containing about two liters of oxygen gas. The shield cooling cylinder contained liquid nitrogen and it will be perceived that the oxygen would condense in the tube soldered to its side and maintain itself in a constant state of reflux, thereby transferring heat from the receiver. The cooling of

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(22) It seems doubtful that a polished surface offers any advantage *per se* from the point of view of superior reflecting power. Buffing does reduce the extent of surface and oxidation appears to be retarded. It seems advisable to remove the grease layer left from the use of the buffing rouge with clean benzene.

(23) At low temperatures soft solder must be used only for sealing and should not be subjected to stress. It is worth emphasizing that every vessel and tube must be tested meticulously and proved tight for the highest vacua before being incorporated in the assembly. The initial testing may be performed with nitrogen at a few atmospheres pressure but the ultimate test of holding a high vacuum (10^{-5}–10^{-6} mm.) unaltered for long periods must be met by every piece. It is advisable, even necessary, to carry out the final tests at liquid air temperature.

(24) It often will be observed that objects, contained within a vacuum case, which have not been cooled previously, give up, or appear to give up, considerable gas when suddenly cooled with liquid air. One of the writers noted many years ago that a large fraction of the "adsorbed" gas on surfaces appeared to be dissolved, in part at least, in the strongly adhering water layer invariably acquired by surfaces exposed to atmospheric air and this layer is not completely removable in vacuum at room temperature (see footnote, p. 21, Keyes and Brownlee, "Thermodynamic Properties of Ammonia," John Wiley and Sons, Inc., New York, 1916). It seems possible that the sudden appearance of non-condensable gas appearing in the McLeod gage on cooling is due to the de-solution of the gases, air, carbon dioxide, from the water layer at the lower temperatures. Tests arranged (H. T. G. and J. F. G. H.) to explore this possibility appear to confirm the notion.

(25) Suggested by Dr. Richard W. Blue.

the receiver to 78° was found to proceed promptly through the action of the device described and the lag in the induction period was eliminated. The computed induction period is about five minutes and the computed amount of hydrogen required, 40 moles, is in very good agreement with experience.

Vacuum Jacketed Lines.—The high pressure hydrogen line of German silver outside the vacuum case of the liquefier was continued with copper tubing (3.56 mm., 0.5 mm. wall) along with the effluent line, must of course be within a vacuum jacket. It is convenient to use for the purpose 15.2 mm. hard drawn German silver tubing of 0.15 mm. wall which is large enough to contain both lines. Elbows are best turned from single pieces of brass and made to receive the jacket tubes. Joints in the gas lines can be made by soft soldering well fitting telescoping pieces of copper or brass slipped over the tubes. Two sizes of jacket tube are necessary, one of which is large enough to telescope the 15.2-mm. size with a play of about 0.05 mm. A section of the larger size can be used for sliding over the smaller diameter vacuum jacketed tube to expose a gas joint where necessary. The German silver "takes" soft solder easily and the metal vacuum lines may be extended to almost any length. With long lines and at elbows, disks or pieces of thin mica may be serviceable to prevent contact of the lines with the vacuum jacket.

Purification of the Hydrogen.—We have been using electrolytic hydrogen, each tank of which is submitted to test[26] for oxygen content.[27] The oxygen content is frequently as low as 0.01 mole per cent. and seldom greater than 0.05. Purification means as indicated earlier have been adopted for oxygen and gases adsorbable on charcoal at 80° and the fore-pressure in use.

The gas first enters a charcoal trap at ordinary temperature for the purpose of removing any traces of oil vapor or fog. It next enters a chamber at one end of a 3.82-cm. o. d. stainless steel tube of 0.328-cm. wall, 0.80 cm. long, containing palladinized asbestos. On the way to the chamber the gas is warmed by interchange with the gas issuing from the catalyst maintained at about 130°. In this way the gas enters and leaves the catalyst at room temperature. At the bottom of the tube a drain is provided to withdraw condensed water formed by the reaction of the oxygen present in the gas with hydrogen. The gas next passes to a dehumidifying interchanger trap at about 80° from which it leaves at the room temperature of entrance. The hydrogen next enters the precooler, which in the present system also contains a chamber with 200 cc. of charcoal[28] and thence by vacuum jacketed tube to the pumped nitrogen precooler-interchanger and the desorber if the latter is in the circuit. No difficulties have as yet appeared due to impurities in the purifying precooling train.

Description of the Liquefaction Process

The present demands upon the laboratory supply of liquid hydrogen have not been sufficiently great to warrant the extra cost of the desorber unit in routine liquefaction. Consequently this unit is omitted in the following description.

Prior to the admission of any hydrogen to the system, air is removed by flushing with nitrogen at room temperature. Both the high and low pressure systems are next evacuated to 0.1 mm. pressure. Commercial electrolytic hydrogen obtained in cylinders at 135 atm. pressure is analyzed for oxygen.[26,29] No hydrogen containing more than 0.05 mole per cent. of oxygen as indicated by the analysis has ever been passed into the system.

After the battery of supply tanks has been connected to the line, a metal stopcock assembly allows thorough flushing of the tank to the stopcock connections. The high and low pressure systems are flushed with the commercial hydrogen and a pressure slightly above atmospheric is maintained during the cooling of the liquefier. After container 59, Fig. 10, is filled with liquid nitrogen, about six hours elapse before the liquid hydrogen receiver is cooled to 78°K. The precoolers are then cooled to operating temperature. The initial flow of hydrogen is at the rate of 95 liters per minute, and the flow is controlled by means of the expansion valve. About five minutes later liquid hydrogen collects in (64) and is produced at the rate of 4 liters per hour at 135 atm. to 1 liter per hour at 20 atm. The course of the liquefaction is followed by means of thermocouples attached to (61), (63), and (64), and the process halted to replenish the pumped precooler dewar when the hydrogen fore-temperature rises to 60°K. Either during or after liquefaction, liquid hydrogen may be siphoned through the transfer valve into the transfer dewar and transported to the cryostat. The dewar of liquid hydrogen is carried on a copper truck which is in good electrical contact with its copper tired wheels. Likewise the liquefier and cryostats are all electrically grounded.

With the entire liquefying system at room temperature, a supply of 25 liters of liquid nitrogen will suffice to produce 5 liters of liquid hydro-

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(26) Binder and Weinland, *Ber.*, **46**, 255 (1913), as recommended by Latimer, THIS JOURNAL, **47**, 1592 (1925).

(27) Should solid oxygen collect on the expansion valve or possibly elsewhere in the liquefier system, disagreeable explosions become a possibility.

(28) One gram of charcoal of the variety in use with 2 cc. of nitrogen adsorbed possesses an equilibrium pressure of about 0.01 mm. at 90°. We do not know the amount of nitrogen present in the tank hydrogen. In runs where 12 liters of liquid have been produced no plugging has occurred. The inference is that probably the nitrogen present can scarcely exceed 1×10^{-3} mole per cent. The charcoal chamber must be pumped at room temperature at the conclusion of each run.

(29) Although it is extremely unlikely that an explosive mixture would be pumped into the commercial cylinders, the reactive nature of the catalyst requires this routine precaution of analysis.

gen; 1.3 liters of liquid hydrogen are obtained from each cylinder containing 200 cu. ft. of hydrogen gas. Liquid hydrogen may be stored in container (64) with the consumption of 800 cc.[30] of liquid hydrogen and 2000 cc. of liquid nitrogen per day. When the system is not in use, hydrogen slightly above atmospheric pressure is maintained in the lines. The liquefier has been installed for a period of eighteen months, during which time it has produced some 50 liters of liquid as required. It has always performed satisfactorily.

The design of this system was executed by the laboratory mechanicians, Mr. Charles Gallagher and Mr. Knut Wilhelmson.

Summary

A hydrogen liquefying system which depends upon commercial electrolytic hydrogen as the source of high pressure gas has been described. This involves the use of metal dewars, improved means of thermal isolation and heat exchange, and a means for producing lower fore-temperatures in the form of a charcoal desorption unit. The theory and economy of hydrogen liquefaction have been discussed.

CAMBRIDGE, MASS. RECEIVED MAY 3, 1937

[30] By use of a copper plated container this figure can be reduced to 400 cc. per day. The monel surface catalyzes ortho-para conversion.

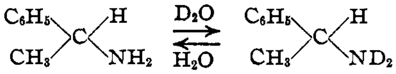
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND MILLS COLLEGE]

Stereochemistry of Deuterium Compounds. II. α-Methylbenzylamine

BY LEONA E. YOUNG AND C. W. PORTER

The change in the optical properties of 2-octanol, produced by the substitution of deuterium for hydrogen in the hydroxyl group, has been reported by us[1] and similar results have been obtained by Erlenmeyer and Schenkel with mandelic acid and with atrolactic acid.[2]

We have now measured the optical rotation of an asymmetric primary amine in which deuterium was substituted for hydrogen in the amino group. The compound used was α-methylbenzylamine (α-phenylethylamine). Equilibrium between light and heavy hydrogen atoms in the amino group is established rapidly when the amine is treated with deuterium oxide. If, then, the equilibrium mixture of light and heavy water is removed by distillation and the amine is again treated with pure deuterium oxide the substitution becomes more nearly complete. The number of times the process must be repeated to accomplish complete substitution depends upon the amount of deuterium oxide used in each treatment. The deutero-amine may then be reconverted into the ordinary form by a similar series of treatments with ordinary water.



There is perhaps a slow exchange in other positions in the molecule but the difference in rates between the exchange on the nitrogen atom and an exchange elsewhere in the molecule is enormous. We experienced no difficulty in obtaining constant values for the rotations after five or six treatments, using each time approximately two equivalents of deuterium oxide or of water.

The amine was made from acetophenone by treatment with formamide.[3] It was resolved through the fractional crystallization of the salt formed with *l*-malic acid.[4] The dextro form of the amine was obtained from the first crop of crystals in a nearly pure state. The levo form of the amine was obtained optically pure through the procedure described in the experimental part. The rotations, boiling points and densities of the amines are shown in the table. The formula RNH_2 stands for α-methylbenzylamine.

Compound	α^{20}_{5461}	Density at 24°	B. p. (corr.), °C.
RNH_2	−45.39° +44.66°	0.9458	187.4
↓			
RND_2	−43.77° +42.88°	.9615	188.4
↓			
RNH_2	−45.34° +44.54°	.9458	187.4

In each case the deuterium compound has the lower rotation, the average difference between the corresponding forms being 1.65°. The read-

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[1] Young and Porter, THIS JOURNAL, **59**, 328 (1937).

[2] Erlenmeyer and Schenkel, *Helv. Chim. Acta*, **19**, 1199 (1936).

[3] Ingersoll, Brown, Kim, Beauchamp and Jennings, THIS JOURNAL, **58**, 1808 (1936).

[4] (a) Ingersoll, *ibid.*, **47**, 1168 (1925); (b) Lovén, *J. prakt. Chem.*, [ii], **72**, 307 (1905); (c) Ingersoll, *Org. Syntheses*, **17**, 80 (1937).