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## RESEARCHES

ON THE ATTAINMENT OF

# VERY LOW TEMPERATURES

BY

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PART I



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# RESEARCHES ON THE ATTAINMENT OF VERY LOW TEMPERATURES.\*

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## PART I.

### I. INTRODUCTION.

The following is an account of a series of experiments which originated in the year 1900 in an attempt to obtain a small quantity of liquid hydrogen, to be used in separating the gas neon from helium and argon, with which neon is associated in atmospheric air. Sir William Ramsay and I had, at that time, succeeded in separating the gases argon, krypton and xenon from one another, by condensing mixtures containing them in bulbs cooled in liquid air, and submitting the solid or liquid to fractional distillation. This method could not, however, be applied to the separation of neon; for, as subsequent experiment has proved, the critical point of this gas lies below  $65^{\circ}$  abs., and consequently it could not be condensed at the temperature of liquid air. It was obvious that unless liquid hydrogen could be obtained, and applied to the separation of the neon from its companions, it would be impossible to obtain the gas in a pure state, and the work on the inactive gases would remain incomplete.

Experiments on the liquefaction of hydrogen were commenced in March, 1900. After some six or eight failures, mainly the results of attempts to adapt an old air liquefier to the new purpose, I devised and constructed an apparatus with which I was able to obtain the necessary quantity of liquid. The work was brought to a successful conclusion on July 6 of that year, and the separation of the pure neon was effected.

During the years 1901 and 1902 I was engaged, with the assistance of Mr. George Senter and Dr. Adrien Jaquerod, in making accurate measurements of the pressure-coefficients of hydrogen and helium, and in comparing the constant-volume hydrogen and helium thermometers over wide ranges of temperature. This investigation involved the measurement of the vapor-pressures of liquid oxygen and of liquid

\*The researches described by Doctor Travers were carried on with the aid of a grant from the Hodgkins Fund of the Smithsonian Institution. It is expected that further researches by Doctor Travers will be published as Part II.

hydrogen at temperatures on the scales of the two thermometers, corresponding to pressures below 800 millimeters of mercury. The liquid hydrogen employed in the researches was obtained by means of the apparatus already referred to. For this purpose, however, it was modified in some details so as to render the production of liquid hydrogen a matter of certainty. Indeed, eight out of nine experiments carried out during the summer of 1902 were successful; the one failure being due to the breaking down of the compressor. The results of these investigations have been published in the Philosophical Transactions of the Royal Society.

On concluding this work I turned my attention to the improvement of the apparatus for liquefying hydrogen, and to the theoretical investigation of the processes involved. An account of this work is contained in the following pages.

## II. HISTORICAL.

The researches of numerous investigators, notably those of Faraday and Thilorier, carried out during the early part of the last century, had resulted in the liquefaction of all the gases then known, with the exception of hydrogen, nitrogen, oxygen, carbon monoxide, nitric oxide, and methane, which hence received the name of permanent gases. Though Faraday had probably some conception of the explanation of their behavior, it was undoubtedly a matter of general opinion that the gases possessed in themselves a permanent character, or that they would ultimately liquefy were the pressure on them sufficient. It was not until 1869, when Andrews proved there is for each substance a critical temperature above which the liquid and vapor cannot be differentiated, that existence of permanent gases was explained.

No further advance towards the liquefaction of the permanent gases was made till 1877 when, on December 24, communications were received by the French Academy independently from M. Raoul Pictet of Geneva and from M. Louis Cailletet of Chatillon-sur-Seine, announcing the liquefaction of oxygen. A week later M. Cailletet described to the academy some experiments in which, by the process of compression and subsequent expansion of hydrogen, he had succeeded in producing in it a mist, presumably of liquid.

The following is transcribed from the paper which appeared in the *Comptes Rendus* (1877, 85, 1270):

“ Dans mes premiers essais, je n'avais rien reconnu de particulier; mais, comme il arrive souvent dans les sciences expérimentales, l'habitude d'observer les phénomènes finit par en faire reconnaître les signes dans les conditions où ils avaient d'abord passé inaperçus.

“ C'est ce qui arrive pour l'hydrogène. En répétant aujourd'hui même, en présence de MM. Berthelot, H. Sainte-Claire Deville et

Mascart, qui veulent bien m'autoriser à invoquer leur témoignage j'ai réussi à observer des indices de liquéfaction de l'hydrogène, dans les conditions d'évidence qui n'ont paru douteuses à aucun des savants témoins de l'expérience. Celle-ci a été répétée un grand nombre de fois. En opérant avec de l'hydrogène pur comprimé vers 280 atmosphères, puis brusquement détendu, nous avons vu se former un brouillard excessivement fin et subtil, suspendu dans toute la longueur du gaz et qui disparaissait subitement. La production même de ce brouillard, malgré son extrême subtilité, a paru incontestable à tous les savants. . . ."

In the light of our present knowledge of the properties of liquid hydrogen some other explanation must be given to the phenomenon observed by M. Cailletet and his colleagues. Possibly the mist was caused by the condensation of some impurity in the hydrogen.

Next year M. Pictet published a similar statement.\* Hydrogen was generated by heating potassium formate with caustic potash in a closed apparatus connected with a steel tube terminating in a stopcock. When the pressure had risen to 650 atmospheres, and the tube was cooled to about  $-140^{\circ}\text{C}$ ., the cock was opened. The jet of hydrogen issuing from the cock appeared steel-blue in color, and opaque for a length of twelve centimeters. The substance forming the jet struck the ground with a sound like that of hail falling on the earth. It is probable that the explanation of the phenomenon lies in the formation of carbon monoxide and carbon dioxide by the decomposition of the sodium formate.

The earliest experiments leading to results which can in any way be considered as reliable are those of the Polish chemists Wroblewski and Olszewski, which were commenced in 1882, and were carried out partly in conjunction, partly independently, during the succeeding years. That the work presented great difficulties may be imagined when we read of six cubic centimeters of liquid air referred to as "a large quantity."

The earlier experiments, described in letters to the Cracow Academy and in communications to the French Academy, are probably of little direct value, except in so far as they show the efforts which were being made. The following is an extract from one of Wroblewski's papers:†

"L'hydrogène soumis à la pression de 180 atm. jusqu'à 190 atm. refroidi par l'azote bouillant dans le vide (à la température de sa solidification) et détendu brusquement sous la pression atmosphérique présente une mousse bien visible. De la couleur grise de cette mousse, où l'oeil ne peut distinguer des grouttelettes incolores, on ne peut pas encore deviner quelle apparence aurait l'hydrogène à l'état de liquide

\* Comptes Rendus, 86, 106.

† Comptes Rendus, 1885, 100, 981.

statique et l'on est encore moins autorisé à préciser s'il a ou non une apparence métallique.

“J'ai pu placer dans cette mousse ma pile thermo-électrique et j'ai obtenu suivant les pressions employées des températures de  $-208^{\circ}$  jusqu'à  $-211^{\circ}\text{C.}$ ”

The last statement shows clearly that little weight can be attached to these experiments.

Professor Wroblewski's more important work consisted in an investigation of the isothermals of hydrogen at low temperatures, undertaken with a view to the calculation of the critical constants. In this work he was engaged at the time of his death, which occurred in 1888 through an accident with a paraffin lamp. The results were fortunately ready for publication, and appeared shortly afterwards in the *Sitzungsberichte* of the Vienna Academy (October 25, 1888). The following values for the critical constant were calculated by means of an equation of the “Clausius” form:

Critical temperature.....	$-240.4^{\circ}\text{C.}$
Critical pressure.....	$13.3\text{ atm.}$
Critical volume.....	$0.00335\text{ c.c.}$

An exhaustive account of Professor Olszewski's later experiments on the liquefaction of hydrogen has been published by him in the *Philosophical Magazine* for 1895.\* The paper also contains a general account of his researches on liquefied gases. The following is an account of his attempt to liquefy hydrogen.

Pure hydrogen was compressed into a glass tube 11 mm. in external diameter and 7 mm. in internal diameter, containing a very thin-walled glass tube, 6 mm. in diameter, to isolate the hydrogen from the warmer walls of the larger tube. The apparatus was cooled with liquid air boiling under less than 10 millimeters pressure. The remaining operations are described by the author in the following words:

“I introduced hydrogen into the tube by slowly opening the cock on the cylinder (which contained pure hydrogen under pressure) till the pressure rose to 140 atmospheres. When the hydrogen in the tube had come down to the temperature of the cooling agent, I little by little produced expansion by opening the screw-cock. The phenomenon of hydrogen ebullition, which was then observed, was much more marked and much longer than during my former investigations in the same direction. But even then I could not perceive any meniscus of liquid hydrogen.

“I have remarked in these experiments that with a slow expansion the phenomenon of sudden ebullition always appears under the same pressure, no matter how great the initial pressure may be, provided

\* Vol. 39, p. 188.



that value be not too low. So that by expansions made, beginning with the pressures of 80, 90, 100, 110, 120, 130, 140 atm., the phenomenon described constantly appeared at 20 atm.; but if the initial pressure was 70, 60 and 50 atm., the ebullition appeared at a lower and lower pressure. . . .

“To ascertain the truth of this statement I performed two series of analogous experiments with gases, the critical pressures and temperatures of which are accurately known, viz., with oxygen and ethylene. The critical temperature of oxygen is, according to my former researches,  $-118.8^{\circ}$  and its critical pressure is 50.8 atm. In the same apparatus which I used for the experiments with hydrogen I cooled oxygen by means of ethylene boiling under atmospheric pressure . . . and subjected it to slow expansion beginning with initial pressures, from 40 atm., up to 100 atm. The ebullition of oxygen always appeared at a pressure of about 51 atm., provided the initial pressure was not lower than 80 atm. . . .

“I made similar experiments with ethylene, using the apparatus of Cailletet. . . .”

These experiments confirmed those made with oxygen, indicating that this “dynamical method” is applicable to the determination of critical pressures, though it would only be employed in cases, like that of hydrogen, when no other course was possible.

The next paper published in the same year\* describes the application of these results to the determination of the critical and boiling temperatures of hydrogen. In place of the glass compression tube a steel vessel containing a very thin-walled glass tube was employed, the whole enclosing a resistance thermometer consisting of a very fine wire of pure platinum wound on a frame of thin mica. The wire had a diameter of 0.06 mm.; its resistance was determined at the following temperatures:

Temperature.	Resistance.
$0^{\circ}$	1,000 ohms.
$-78.2^{\circ}$	800 “
$-182.5^{\circ}$	523 “
$-208.3^{\circ}$	453 “

The hydrogen was compressed into the steel apparatus, which was cooled as in the previous experiment in liquid oxygen boiling under a pressure of 15 mm., and the expansion was carried out in the usual manner. The resistance of the coil was measured by means of a Wheatstone bridge and reflecting galvanometer, and resistance in the opposite arms of the balance was repeatedly adjusted, till on making the expansion no deflection of the galvanometer was observed. The following results were obtained:

\* Philosophical Magazine, 40, 202.

Hydrogen Expanded to	Resistance of Coils.	Temperatures.
20 atmospheres.	383 ohms.	— 234.5° Centigrade.
10        “	369       “	— 239.7       “
1 atmosphere.	359       “	— 243.5       “

The temperature in the last column was calculated by linear extrapolation from the resistance of the coil at temperatures corresponding to  $-182.5^{\circ}\text{C}$ . and  $-208.5^{\circ}\text{C}$ .

According to Dewar, though the method by which the measurements were made has not been published, the critical temperature of hydrogen is about  $-244^{\circ}\text{C}$ ., and the critical pressure less than 15 atmospheres. The boiling point of hydrogen according to Travers and Jaquerod\* is  $20.55^{\circ}$  on the helium scale and  $20.36^{\circ}$  on the hydrogen scale. Callendar† has pointed out the recalculation of Olszewski's results by means of his difference formula leads to the conclusion that the temperatures are about one degree higher than those given above; at the same time it is possible that the platinum thermometer may behave erratically at low temperatures. This latter view is confirmed by Dewar‡ who obtained  $-243.6^{\circ}$  and  $-237.9^{\circ}$  for the boiling point of hydrogen on two platinum thermometers; one of these values is almost identical with that obtained by Olszewski.

These facts may be taken as sufficient evidence that Olszewski obtained liquid hydrogen, first in the form of a mist or spray in a glass tube, and afterwards in a steel vessel. In the latter experiment it is probable that the liquid at its boiling point persisted for a sufficient time to cool a platinum resistance thermometer to that temperature.

### III. THEORETICAL DISCUSSION OF THE FOREGOING.

In discussing the principles on which the experiments of Cailletet, Pictet, Wroblewski and Olszewski on the one hand, and of Dewar and myself on the other hand, considerable confusion has arisen. Indeed several well-known text-books of physics, and even certain works devoted to the study of liquefied gases, attribute the cooling which takes place in every case to adiabatic expansion. Dewar's early papers make no mention of the fact that in his, as in my own experiments, the cooling is due to the fact that when hydrogen is cooled to the temperature of liquid air it, like air or carbonic acid, becomes cooled when allowed to expand without performing external work. The cooling may be the result of work done against internal forces. This matter is first discussed in my paper on the liquefaction of hydrogen published in 1901.

In the earlier experiments referred to above, the gas was compressed either into a tube over mercury, so that in opening a cock the mercury

\* Philosophical Transactions, 1902.

† Philosophical Magazine, 1899, 191.

‡ Bakerian Lecture, 1901.



escaped from the tube as the gas expanded; or the gas was compressed directly by means of a pump into a glass or steel vessel, and then part of it was allowed to escape directly through an orifice. In the first case the gas exerted a pressure on the mercury, and on expanding did work which was performed in giving the mercury a certain velocity through the escape cock, and partly in overcoming fluid friction. In the second case, part of the gas which remained in the vessel did work in driving the remainder through the orifice or cock, partly in overcoming friction at the orifice, partly in giving to the gas an increased velocity, which would quickly be dissipated in the formation of eddy currents outside the orifice.

If we were dealing with a perfect gas for which the simple law

$$pv = \text{const.}$$

were rigidly true, and if such a gas were allowed to expand, or were compressed, adiabatically, the relation between pressure and volume would be expressed by the equation

$$pv^k = \text{const.},$$

where  $k$  is the ratio of the specific heat at constant pressure to the specific heat at constant volume. If the gas were allowed to expand adiabatically under the conditions mentioned above, where  $p_1$  and  $p_2$  are the initial and final pressure, and  $T_1$  and  $T_2$  the initial and final absolute temperatures,

$$\frac{T_1}{T_2} = \left( \frac{p_1}{p_2} \right)^{\frac{k-1}{k}}.$$

Since the heat capacity of the gas is always considerably less than that of the vessel in which it is contained, the condition represented above is probably never approached, though, as Olszewski's later experiments show, a considerable degree of cooling can be effected. The practical application of the principle is probably only possible on a large scale.

Olszewski's observation that when the initial pressure in the apparatus exceeded a certain value the liquid always appears when the pressure falls to the critical pressure, is not further discussed by him; the phenomenon can, however, be simply explained by means of an Andrews diagram (fig. 1).

Suppose that the gas is compressed along the isothermal  $a' a'' a'''$ , and under the conditions determined by these points is, in successive experiments, allowed to expand adiabatically. In each case liquid should first appear at the point at which the adiabatic cuts the dotted line enclosing the area which represents the conditions under which the

liquid and gaseous phases can connect. The adiabatic  $a''' b'''$  passes through the critical point, so that in this case the liquid will first appear at the critical pressure. For higher initial compressions the adiabatics will lie on the left hand side of the critical point on the diagram, and

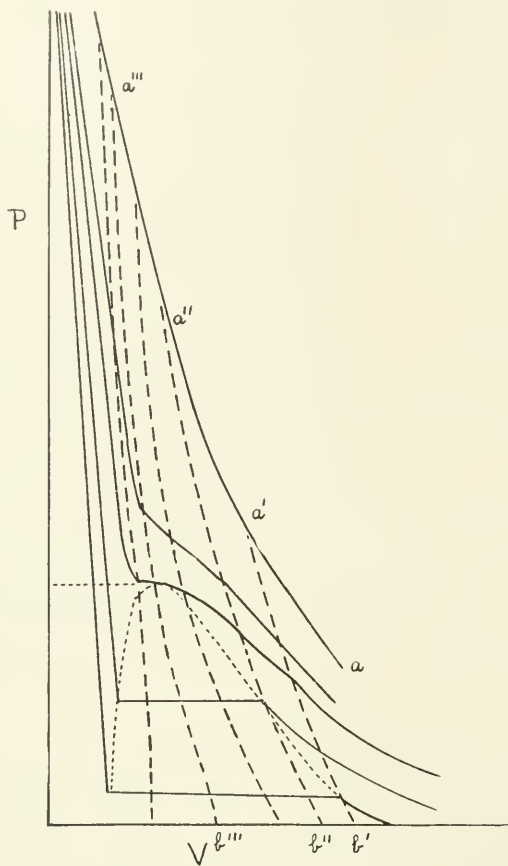


FIG. 1.—Andrews diagram.

liquid will first appear under conditions represented by the point at which they cut the horizontal line drawn through the critical point. For high pressures the adiabatics will, of course, lie very close together, and the horizontal line will differ but slightly from the curve joining the ends of the horizontal section of the isothermal.

#### IV. THE APPLICATION OF THE JOULE-THOMSON EFFECT TO THE LIQUEFACTION OF AIR.

The change in temperature which takes place when a gas is allowed to expand without performing effective external work was first studied by Joule and Lord Kelvin in 1848. The gas compressed to about two

atmospheres flowed in a steady stream through a plug of compressed fiber so that the increase in the kinetic energy of the gas, which would take place if the gas streamed through an orifice in a plate, was reduced to a minimum, and practically eliminated. In passing from the higher to the lower pressure work was done in overcoming internal friction, so that were the gas a perfect one its total energy content would remain constant, and there would be no change of temperature. In the case of air and carbon dioxide it was found, however, that a fall of temperature took place; hydrogen, on the other hand, became warmer.

The change of temperature must be attributed to the performance of work in overcoming internal stresses; though as to what the nature of these stresses may be we have at present no knowledge. In many text-books of physics it is stated that the direction of the change of temperature, the sign of the Joule-Thomson effect, is connected with the variation of the product " $PV$ " with pressure for the gas. Though for hydrogen (and helium) the value of the product increases with rise of pressure, while it decreases in the case of air and all other gases, this relationship does not really apply. For pressures above fifty atmospheres the value of the product  $PV$  for air increases with rise of pressure, yet, if we expand air from 100 atmospheres to 50 atmospheres, it still becomes cooled.

For small differences of pressure the change of temperature was found to be directly proportional to the difference between the pressure on the two sides of the plug. The results are stated by the original investigators in terms of degrees Centigrade per hundred inches of mercury differences of pressure; it is now more usual to express the value of the Joule-Thomson effect in terms of degrees per atmosphere difference of pressure.

The experiments which were carried out at temperatures between the boiling and melting points of water, showed that the magnitude of the effect varied with the temperature, and might be represented by the formula,

$$z = \frac{\alpha}{T} \pm \beta,$$

where  $z$  is the Joule-Thomson Effect,  $T$  is the absolute temperature and  $\alpha$  and  $\beta$  are constants. The values of the constants for air and hydrogen are as follows:

Air .....	$\frac{\alpha}{T}$ 64.1	$\beta$ -0.331
Hydrogen .....	441.5	0.697

These figures indicate that for either gas above a certain temperature, the inversion temperature of the Joule-Thomson effect, the effect

will be positive; below that temperature it will be negative. The inversion points calculated by Witkowski are  $633^{\circ}$  and  $193.7^{\circ}$  absolute for air and hydrogen respectively. Olszewski (*Nature*, 1902) confirms the second figure, finding  $192.5^{\circ}$  absolute for the inversion point for hydrogen. He points out that the inversion points are practically corresponding temperatures for the two gases.

The application of the principle of free expansion to the liquefaction of air was first made practicable by Hampson in England and Linde in Germany. Since Hampson and Linde's work paved the way to the production of liquid hydrogen, by a very similar process, and as my researches have been based upon their results, some mention must be made of their work. To Dr. Hampson I am particularly indebted for much advice and assistance in carrying out my investigations.

#### V. THE PERFORMANCE OF THE HAMPSON AIR LIQUEFIER.

The Hampson air liquefier is too well known to require a lengthy description. It consists of a coil formed by winding two, or in some cases four, copper tubes coaxially so as to build up a cylinder 100 cm. long and 30 cm. in diameter. The coil is enclosed in a metal case. Air enters the copper tube at the top under a pressure of 180 atmospheres, and expands at a valve, in which the tubes unite at the bottom of the coil. The air, cooled by expansion, presses upwards through the interstices of the coil, cooling the compressed air it contains. The cooling of the valve is therefore progressive, and results, after a few minutes, in the partial liquefaction of the escaping air. The liquid collects in a space at the bottom of the metal case containing the coil, and is drawn off from time to time through a cock.

The apparatus as installed in the Chemical Department of University College, London, is worked in connection with a Whitehead "torpedo compressor" driven by an electro-motor. To deliver about ten cubic meters of air per hour (measured under atmospheric conditions), and to maintain a pressure in the liquefier of 180 atmospheres, requires the expenditure of about 6.5 horse-power; the compressor runs at 360 revolutions per minute. An attempt has been made by Mr. Arnold Ogden and myself to determine the efficiency of the plant. I have also carried out a fairly complete investigation of the air liquefier.

The work done in compressing the air was determined by measuring the electrical energy absorbed by the motor under the following conditions:

Power required to run motor free .....	0.6	E. H. P.
Power absorbed by motor, belt and bearings (cylinders removed) ..	1.8	"
Power required to run motor with cylinder in place (no compression) .....	3.7	"

Power absorbed during trial.....	(a) 6.4 E. H. P.	(b) 6.2 "
Power absorbed in compressing the air.....	2.7 "	2.5 "
Weight of air compressed per hour.....	14.4 kilos	14.1 kilos
Weight of air compressed per E. H. P.....	5.3 "	5.6 "
Pressure .....	165 atm.	163 atm.
E. H. P. required to compress the same quantity of air isothermally.....	2.23	2.18

The energy put into the air is thus between 20 and 25 percent more than would be required for isothermal compression. The compression is carried out in two stages, the ratio of the initial to the final pressure being the same in each stage, so that thrusts on the two pistons were balanced. The pressure in the coil and pipe connecting the two cylinders was measured during one of the trials, and was found to vary between thirteen and fourteen atmospheres. In a larger compressor, working at a slower speed, the compression would approach much more closely to the isothermal. The efficiency, which is only about 0.13 in the Whitehead compressor, would also be much higher.

The investigation of the Hampson air liquefier proved somewhat troublesome as many factors had to be taken into consideration. It was necessary to measure :

The total quantity of air passing through the apparatus.

The quantity of liquid air produced.

The rate of absorption of heat by the coil through conduction, in terms of the liquid air evaporated.

The loss, through evaporation, of liquid air on drawing off the liquid from the cock at the bottom of the apparatus.

The pressure and temperature of the air entering and leaving the apparatus.

The temperature of the liquid air.

The total quantity of air passing through the apparatus was measured by connecting the exhaust pipe of the liquefier with a gas meter. This "sixty-light" meter was placed at my disposal by the Gas Light and Coke Company of London; to the manager of the Company I wish to tender my thanks.

The liquid air was drawn off at definite intervals into a weighed globular vacuum vessel, silvered between the walls. The vessel was half full of liquid air at the commencement of each experiment, and the rate at which liquid air evaporated from it was determined.

To measure the quantity of air lost by evaporation of the liquid, as it issued from the cock on the Hampson apparatus, the arrangement shown in fig. 2, A, B, was adopted. The mouth of the vacuum vessel *a* was fitted with a rubber stopper *b*, through which passed a tube *c* of the same diameter as the thumb-screw *f* on the liquid air valve *e* of the Hampson liquefier, with which it was connected by means of a piece

of wide rubber tube. The side tube *d* communicated by means of a flexible rubber tube with a small gasometer.

The vacuum vessel rested on the point at which it was finally sealed (fig. 2, B), so that when the liquid air cock was opened by rotating the

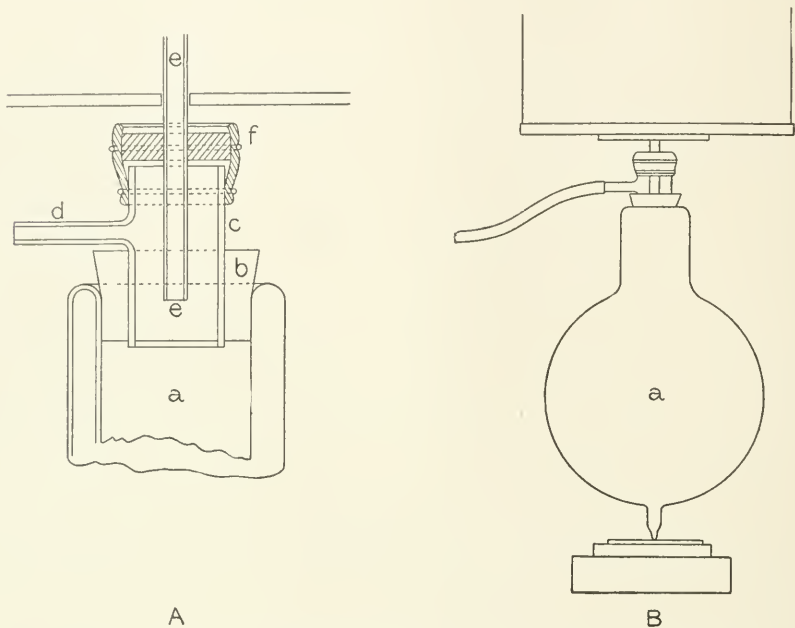


FIG. 2.—Apparatus for measuring air lost by evaporation of liquid.

thumb screw *f*, it merely turned on its axis. The quantity of gaseous air produced by the evaporation of the liquid air could be measured by measuring the rise of the gasometer attached to *d*. The quantity of liquid air collected in the vacuum vessel amounted to about one kilogram per hour; the loss by evaporation corresponding to the same period was usually seventy to eighty grams per hour.

The quantity of heat entering the Hampson apparatus through its insulating packing of animal wool was determined by stopping the compressor when the liquid air in the collecting chamber had been allowed to accumulate for five minutes, closing the expansion valve, allowing the air to escape from the regenerator coil by means of a side-cock outside the apparatus, and measuring the rate of evaporation of the liquid air from the inside of the apparatus, and the rate of change of temperature of the regenerator coil. The latter measurement was made by means of an air thermometer with a narrow cylindrical bulb which was inserted through the center of the coil in place of the valve spindle. The following is a record of the results of an experiment.



Time after Stopping Compressor.	Quantity of Air Collected per Minute.	Mean Temperature of Coil (Absolute).
0		
5	5.2 liters.	257
7	5.2	255
9	4.5	250
11	4.0	244
13	3.7	241
15	3.2	239.5
17	3.2	239
19	2.9	238.5
21	2.9	238.5
22	2.8	239

It will be seen that as soon as the circulation of the air through the apparatus was suspended the liquid air in it began to evaporate rapidly, heat being conveyed to it by conduction from the outside. However, long before the whole of the liquid air in the apparatus had evaporated the temperature of the coils had become steady and the quantity of liquid air thus evaporating per minute could be taken as a measure of the quantity of heat entering the apparatus during the process of liquefying air. This quantity corresponds to about 2.6 liters of gaseous air per minute, or to a loss of 200 grams of liquid air per hour.

During an actual experiment it was the duty of one assistant to maintain a steady current of air, escaping at an almost constant pressure, through the apparatus. The pressure gauges were read every minute; the gas meter readings were taken at the end of every half hour, the liquid air was drawn off every five minutes, and the vacuum vessels removed and weighed every half hour; the temperature at which the air entered and left the apparatus and the barometer readings were taken at intervals during an experiment. The following are the results of some observations:

December 14, 1902. Machine started at 10:20 A. M.

Duration of experiment.....	10:55 to 11:25	11:25 to 11:55
Weight of liquid air collected.....	460 gms.	490 gms.
Loss by evaporation.....	40 gms.	35 gms.
Loss due to heat absorption by liquefier.....	100 gms.	100 gms.
Weight of air passing through gas meter.....	6,620 gms.	6,525 gms.
Total weight of air passing through apparatus.....	7,120 gms.	7,050 gms.
Theoretical quantity of liquid air per hundred of gaseous air.....	8.4	8.9
Quantity collected per hundred of gaseous air.....	6.4	6.9
Efficiency of liquefier.....	76.2	77.5
Mean pressure.....	167 atm.	165 atm.
Temperature interchange.....	0.4° C.	0.4° C.

The results of other sets of observations led to practically the same result. The errors of the various observations probably reduce the

accuracy of the results to within about two percent of the truth. The final result leads to the conclusion that the theoretical quantity of liquid air which it should be possible to obtain by the Hampson-Linde principles, where the air is expanded from 180 atmospheres, is between eight and nine percent of the air passing into the apparatus.

The complete theoretical study of the Hampson-Linde process is impossible, both on account of its highly complicated nature, and of our ignorance of the thermodynamic properties of air over wide ranges of temperature and pressure. The results stated above lead however to conclusions which are interesting and are hardly likely to be merely a matter of chance.

If air were compressed to  $P$  atmospheres and allowed to expand, as in the Hampson machine, but so that the current of air did not flow back over the coil, the fall of temperature of the escaping gas at a short distance from the jet could be calculated from the formula

$$JT = \alpha(P - p),$$

and the heat absorbed by

$$JQ = \alpha(P - p)Cp.$$

where  $JT$  is the Joule-Thomson Effect and  $Cp$  is the specific heat at a constant pressure of one atmosphere.

Since the work done on the gas in bringing it toward the jet is practically equal to the work done by the gas in its passage away from the jet  $p\nu$  being very nearly constant, the quantity  $JQ$  is a measure of the change in the internal energy of the gas in passing from pressure  $P$  to pressure  $p$ . This being the case it should be possible to pass over intermediate stages to calculate the quantity of liquid air produced in the Hampson apparatus from known data.

The specific heat at a constant pressure of one atmosphere ( $Cp$ ) has been found by Witkowski\* to have the value of 0.237 between 100°C. and the temperature of liquid air; the same value was obtained by Regnault for the higher range of temperature. The Joule-Thomson effect at 10°, the mean temperature of the air entering the liquefier, was found by Joule and Lord Kelvin to be 0.25°C. per atmosphere. The latent heat of vaporization of air is about 50 cal.

Suppose the air enters the liquefier at 165 atmospheres pressure and at 9.5°C. If  $1/x$  of the air liquefies at 87° abs.,

Heat absorption on expansion =  $0.25 \times 0.237 \times 164$ ;

Heat absorption due to cooling and liquefaction of  $x$  parts of air =  $x \{50 + (0.237 \times 206)\}$ ;

Heat absorption due to cooling of unliquefied air =  $(1 - x)(0.5 \times 0.237)$ .

\* Philosophical Magazine, July, 1896.

Quantity of air liquefied = 9.5 to 10 percent.

This result is of considerable value in considering the phenomena connected with the liquefaction of hydrogen.

## VI. THE LIQUEFACTION OF HYDROGEN. PRELIMINARY EXPERIMENTS.

It has already been pointed out that the original experiments of Joule and Lord Kelvin showed that hydrogen, when allowed to expand freely, behaved differently from other gases, becoming heated instead of cooled. The magnitude of the effect depended upon the absolute temperature at which the experiment was performed, decreasing with fall of temperature. From their experiments it might be predicted that the effect would change sign at very low temperatures. Employing the formula,

$$x = \frac{a}{T} - \beta$$

to represent the experimental results, Witkowski found 64.1 and 0.331 for the values of the constants  $a$  and  $\beta$  respectively, and  $-79^{\circ}\text{C}$ . for the inversion point of the effect. Witkowski's prediction has recently been verified experimentally by Olszewski (p. 10).

In 1898 Dewar\* succeeded in obtaining a jet of hydrogen sufficiently cold to solidify air, and later constructed an apparatus with which he obtained liquid hydrogen in quantity. In his first experiments he compressed the gas into steel cylinders under 180 atmospheres, and then allowed it to pass through coils cooled in solid carbonic acid, and in liquid air boiling under reduced pressure, to a regenerator coil contained within a vacuum vessel. The gas escaped through a pin valve at the bottom of the regenerative coil, and became cooled, but before any liquid could be collected the opening had become blocked with some solid impurity, and the experiment was at an end. Later, Dewar constructed a larger apparatus, and succeeded in obtaining liquid hydrogen in quantity. He has not, however, published any description of it.

Dewar's first experiment had confirmed the prediction that hydrogen, when cooled to the temperature of liquid air, became further cooled on free expansion, but it did not throw any further light on the behavior of this gas. Indeed it still remained possible, though perhaps improbable, that it would only be necessary to cool the gas to the temperature of solid carbonic acid before allowing it to enter the regenerator coil of the liquefaction apparatus. Accordingly some preliminary experiments were set on foot in which a Hampson air liquefier, modified as occasion required, was employed.

\* Proceedings Chemical Society.

In my first experiments the hydrogen before entering the regenerator coil of the Hampson apparatus, which was cooled by making liquid air in it, was passed through a coil immersed in solid carbonic acid and alcohol ( $-78^{\circ}\text{C}.$ ). The result was negative; indeed, it appeared that the temperature of the inside of the apparatus began to rise as soon as the hydrogen was allowed to expand in it, for on opening the liquid air cock at the base of the apparatus the temperature of the gas which escaped ceased after the first few minutes from being extremely cold.

More than two months were spent in similar experiments with like results. If, however, these experiments led to no immediate results, they showed clearly that even though it might be theoretically possible to liquefy hydrogen by the method of free expansion without employing liquid air as a cooling agent, it was practically essential to cool the gas to the lowest attainable temperature before allowing it to expand. This knowledge, and the experience in dealing with compressed hydrogen, gained in the course of these experiments led me to design an apparatus with which I was at once successful in obtaining liquid hydrogen. The apparatus I constructed, with the assistance of Mr. J. Holding, without whom I could not have carried on these researches; it cost but a few shillings, and after being slightly modified it served me again in 1902 in my researches on the properties of liquid hydrogen.

## VII. THE FIRST HYDROGEN LIQUEFIER.

This apparatus has been fully described in a paper read before the Physical Society of London in November, 1900.\* Fig. 3, A and B, shows the general structure of the apparatus as first used, and the modifications which were introduced into it for my later experiments.

In the original form (A), the hydrogen, under a pressure of from 150 to 180 atmospheres, was first cooled to  $-75^{\circ}$  by passing through a coil *A* immersed in a mixture of solid carbonic acid and alcohol. It then passed through a coil contained within the central chamber *B*, which, during an experiment, was continually replenished with liquid air. The coil passed through the floor of the chamber *B* into a lower chamber *C*, which communicated with an exhaust pump through the pipe *f*. Liquid air was allowed to flow from *B* into *C* through a valve, which was controlled from above by the lever *b*, and evaporating under a pressure of 100 mm. reduced the temperature of the compressed gas to below  $-200^{\circ}\text{C}.$

The gas then entered the regenerator coil *D*, which was much shorter than in the Hampson air liquefier, being 180 mm. long and 50 mm. in diameter. The reason for taking these dimensions will be dealt

\* Philosophical Magazine, 1901, p. 411.

with later (Part II). The regenerator coil and the lower part of the chamber *C* were enclosed within the vacuum vessel *H*, which was secured to the metallic part of the apparatus by means of a gland *p* (fig. 4) which compressed a rubber ring into the space between the outer wall

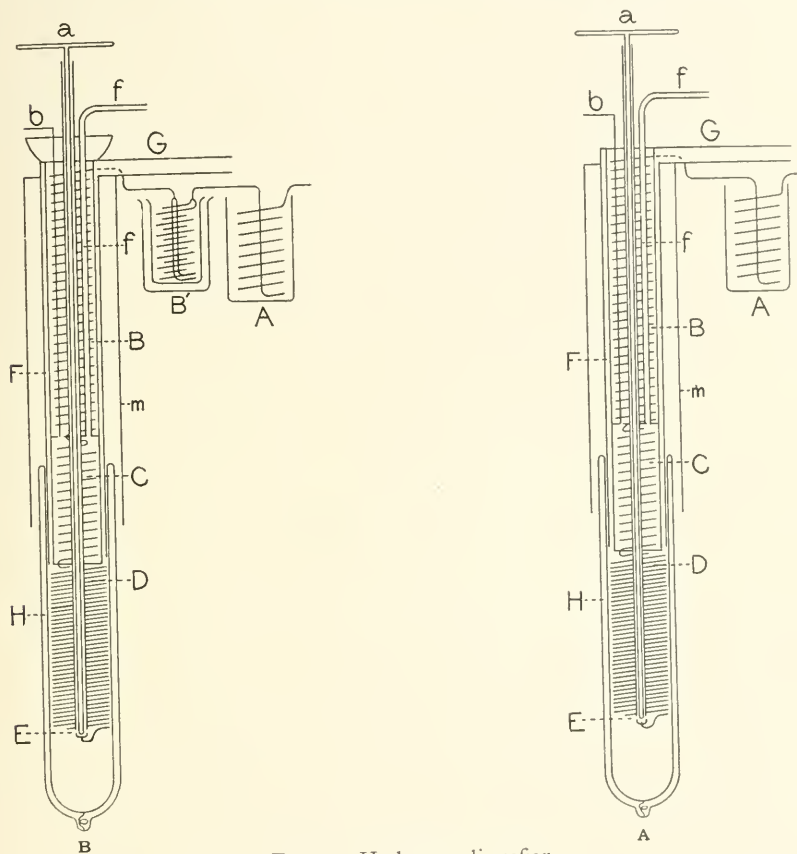


FIG. 3.—Hydrogen liquefier.

of the vacuum vessel and the inner wall of the tube *m*, making a gas-tight junction. The apparatus rested on a brass flange, soldered to the tube *m*, in a round hole in a wooden shelf fixed to the wall of the compressor room. The upper part was surrounded with a thick layer of natural wool.

The hydrogen expanding at the valve *E*, which was controlled by the lever *a*, became further cooled, and passing upward through the interstices of the coil, cooling it and the gas passing through it, so that after a short time liquid began to separate in the vacuum vessel. From the top of the regenerator coil the gas passed through the annular space *F*, surrounding the chambers *B* and *C*, and returned through the tube *G* to the compressor.



The hydrogen which liquefied in *H* was drawn off and collected by the method described on page 20. The arrangements for the compression and circulation of the hydrogen gas will also be dealt with later.

The modifications which were introduced into the apparatus, when I recommenced my experiments in 1902, were simple though important. As originally constructed the coil in the liquid air chamber *B* was so short that it did not present sufficient surface for the effective cooling of the compressed gas passing through it. Further, the chamber *B* was so narrow that not only was it difficult to fill it with liquid air, but if, through irregular adjustment of the valve, there was a sudden rush of gas through the coil, the liquid air boiled violently, and overflowed the chamber.

This difficulty was easily overcome by introducing between *A* and *B* (fig. 3, B) a coil *B'* consisting of two five-meter lengths of copper pipe wound into an open spiral. The pipes were carefully spaced by means of pieces of copper wire soldered to them at intervals. The coil was immersed in liquid air contained in the inner of two glass beakers, which were separated by pieces of cork, so as to leave an air space between them, and surrounded with a thick layer of natural wool.

A copper funnel was also soldered to the top of the tube which formed the chamber *B*, to facilitate the operation of filling it with liquid air. The apparatus as thus modified was used about ten times. Of these experiments only one failed through a break-down in the compressor.

### VIII. THE SECOND HYDROGEN LIQUEFIER.

Shortly after I had completed the researches I have just referred to, I was asked by Professor d'Arsonval of Paris, and by Professor Anschütz of Bonn, to design hydrogen liquefiers for their laboratories. As I had not then carried out any further experiments with a view to improving my method of liquefying hydrogen, and as the apparatus I had already constructed had given me perfect satisfaction, except that it was not very economic so far as the refrigerants, liquid air and carbon dioxide, were concerned, I designed another machine of the same principle but of a more compact form. The apparatus was constructed by Brin's Oxygen Company.

A section of the apparatus is shown in fig. 4. The hydrogen from the compressor enters the apparatus at the cross-piece below the pressure gauge and passes first through the coil in the chamber *A*, which is intended to contain a mixture of carbonic acid and alcohol. The whole system of coils is double, each component being of the same length. The total length of copper coil in each of the chambers *A* and *B* is about twenty meters. The cock *x* is intended to allow the hydrogen



to escape and return to the gasometer in case the expansion valve *E* becomes blocked. After passing through *A*, the compressed gas passes through the coils in the chambers *B* and *C*. The chamber *B* contains liquid air, some of which is allowed to flow into *C* through a pin valve which is regulated by the rod *b*. The liquid air in *C* evaporates under a pressure of about 100 millimeters of mercury, an exhaust being maintained by means of a pump communicating with *B* through the tube *f*, and reduces the temperature of the compressed gas to below  $-200^{\circ}\text{C}$ . The total length of coil in the chamber *C* is about five meters. The gas then enters the regenerator coil *D*, 180 mm. long and 50 mm. diameter, and passing through it expands at the valve *E*, which is controlled by means of the valve-rod and lever *a*. The expanded gas passes upwards through the interstices of the regenerator coil, and returns by way of the annular space *F* and the tube *G* to the compressor.

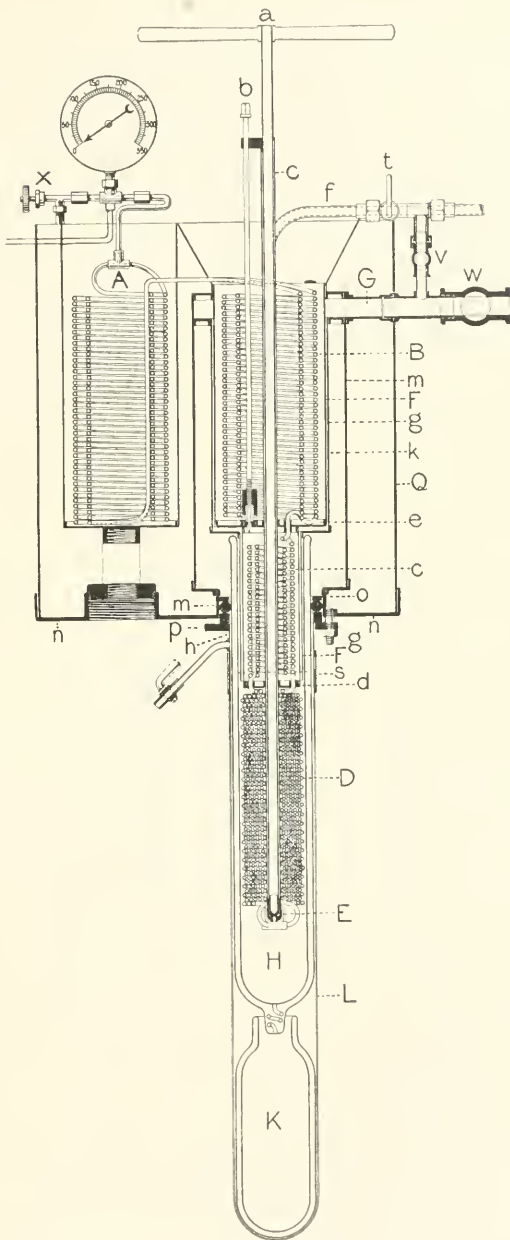


FIG. 4.—Section of hydrogen liquefier.

The accompanying diagram of this apparatus shows clearly how the gas-tight connection between the outer wall

of the vacuum-vessel  $H$  and the inner wall of the lower part of the supporting tube  $mm$  is made. The brass ring  $o$  is supported above by a slight flange on the inside of the lower portion of the tube  $m$ , and a rubber ring is compressed between this ring and a gland  $p$ , which is forced home by means of three screws, of which one is seen in the diagram. As the lower part of the tube  $m$  is continuous with the brass plate  $nn$ , it never becomes very cold, and the junction is always gas-tight.

The liquid hydrogen which is formed in the vacuum vessel  $H$  is collected in the vessel  $K$ . This vessel is placed inside a tube  $L$ , which is long enough to enclose  $H$  as far as the lower edge of the brass tube  $h$ , which forms part of the gland  $p$ . A rubber sleeve is secured by wire to  $h$  and  $L$  making a gas-tight junction. By opening the tap  $r$  gas can be allowed to escape from the space within  $L$ , and consequently liquid can flow from  $H$  into  $K$ . This enables one to dispense with a cock at the bottom of the vacuum vessel  $H$ . By connecting the cock  $r$  to the supply pipe from the gasometer (fig. 8,  $S$ ), loss of hydrogen can be avoided.

During an experiment, the tube  $L$  and its contents are enclosed within an arrangement of three concentric glass shades in order to shield off heat, and to prevent the condensation of moisture taking place.

The apparatus is supported on a cast iron stand with a vertical column 130 cm. high, which screws into the bottom of the brass plate  $nn$ . This latter is of oval shape and supports a brass case  $Q$  which surrounds the upper part of the apparatus, the intermediate space being packed with wool.

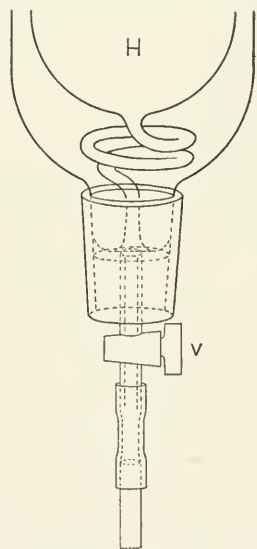


FIG. 5.—Brass tap to vacuum vessel.

The use of the cocks  $t$ ,  $v$  and  $w$  must now be pointed out. With this type of liquefier, the first step toward liquefaction of hydrogen is to cool the whole apparatus to the temperature of liquid air. With this object a small brass tap  $V$  (fig. 5) is fitted by means of a rubber cap to the nozzle of the vacuum vessel  $H$  and this is in turn connected by a short piece of rubber tube to a glass tube 300 mm. long. By closing the cocks  $t$  and  $w$ , opening the cock  $V$ , and starting the exhaust pump, liquid air can be drawn through the glass tube and the cock  $V$  into the vacuum vessel  $H$  from a vacuum vessel, usually containing two liters of the liquid. Liquid air is drawn into the vessel  $H$  till it rises above the top of the coil  $D$ ; then, by closing the cock  $V$  and maintaining the exhaust, the temperature of

the coil can be reduced to below  $-200^{\circ}\text{C}$ . Meanwhile liquid air is poured into the chamber *B*, and by opening the cock *t* some of it is drawn into the chamber *C*.

#### IX. HYDROGEN LIQUEFIER WITH SECOND REGENERATOR COIL.

In each of the different forms of the hydrogen liquefier which have hitherto been described there exists one very obvious defect: the hydrogen, after expanding at the valve *E* and passing through the interstices of the regenerator coil *D*, is at a temperature not far from  $-210^{\circ}\text{C}$ ., and in this condition it leaves the apparatus, absorbing heat from the walls of the tube through which it passes on its return to the compressor.

Now if we assume that the specific heat of hydrogen at a constant pressure of one atmosphere is equal to 3.41 units over the range of temperature we are considering (see page 14), the heat which each gram of hydrogen would absorb in returning to the normal temperature would be

$$3.41 \times 220 = 750 \text{ units.}$$

As approximately 1,000 grams of hydrogen pass through the apparatus per hour, this involves a loss of 750,000 heat units, the equivalent of fifteen liters of liquid air.

In order to estimate the relative advantage of employing the cold hydrogen in place of solid carbonic acid as a means of cooling the incoming gas, it would be necessary to determine the specific heat of the compressed hydrogen over the range of temperature. The measurements could not, however, be carried out with sufficient accuracy to be of any real value without great difficulty, and, indeed, it would make no appreciable difference were the specific heat of the hydrogen half again as great.

If one assumes that the relationship between the internal energy of the compressed and expanded hydrogen can be calculated, as in the case of air, from the formula (page —),

$$\mathcal{J}Q = K(\mathcal{J}p)Cp,$$

where  $\mathcal{J}Q$  is the heat generated or absorbed by the gas during its passage through the regenerator coils of the apparatus, *K* the Joule-Thomson Effect at which it enters the apparatus,  $\mathcal{J}p$  the fall of pressure in the apparatus, and *Cp* the specific heat of the gas under a constant pressure of one atmosphere,—to cool the gas compressed to 150 atmosphere from  $15^{\circ}\text{C}$ . to  $-75^{\circ}\text{C}$ . it is necessary to absorb

$$90 \times 3.41 + 0.09 \times 150 \times 3.41,$$

a quantity ten percent greater than that calculated on the assumption

that the thermal capacities of the compressed and expanded hydrogen are the same. This difference is insignificant and has no effect on the general problem.

It might be expected, then, as the result of employing a second regenerator coil of sufficient length to produce a heat interchange so complete that the temperature would not differ by more than one or two degrees, that the gas would enter the coil in the liquid air chamber at a temperature not far from  $-170^{\circ}$  C. instead of at  $-75^{\circ}$ , as in the earlier forms of the apparatus. The liquid air would then serve to cool the gas only through  $15^{\circ}$  instead of through  $110^{\circ}$ , and, when the apparatus was once cooled down, it should consume only about one fifth of the liquid air required to maintain the older machine in action.

Though it is practically impossible to obtain accurate figures for the quantity of liquid air used in an experiment, I am satisfied that the results which I had predicted were fully realized in the apparatus which I next constructed.

The form of the liquefier is shown in fig. 6. It is practically identical with that last described, only the carbonic acid cooling chamber is replaced by the regenerator coil *Z*, and consequently the position of the escape pipe *G* is changed.

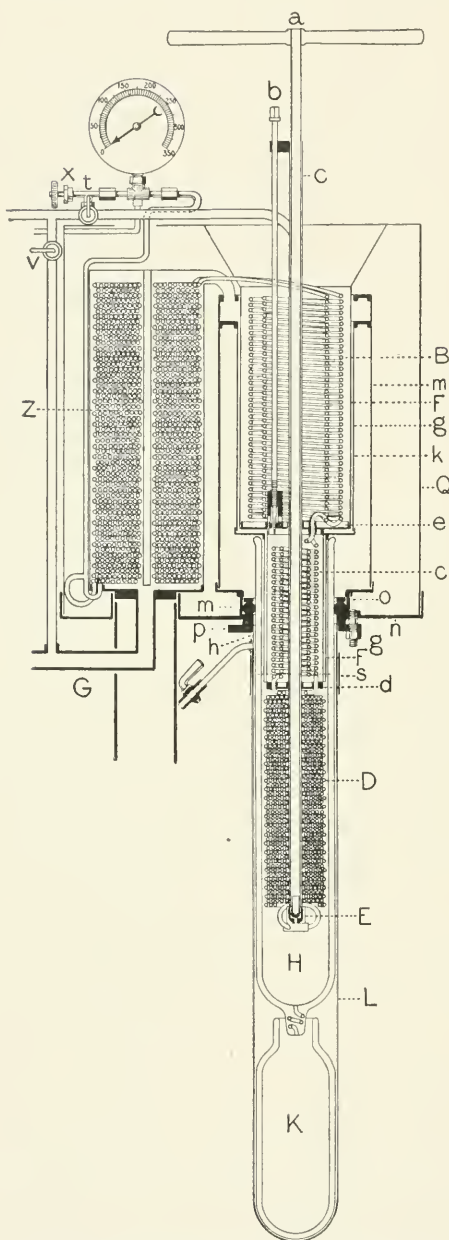


FIG. 6.—Hydrogen liquefier with second regenerator coil.

acid cooling chamber is replaced by the regenerator coil *Z*, and consequently the position of the escape pipe *G* is changed.

The hydrogen enters the apparatus from the compressor at a distributing cross piece below the gauge, as in the last model, and passes first to the bottom of the regenerator coil  $Z$ . This consists of two pipes of 3.2 mm. external and 2 mm. internal diameter, wound coaxially to form a coil 300 mm. long and 100 mm. in diameter. The coil is covered with a layer of flannel and fits tightly into a brass case communicating above with the top of the annular space  $F$  and at the bottom with the escape pipe  $G$ . The upper end of the coil communicates with the coil in the liquid air chamber  $B$ .

The structure of the remaining parts of the apparatus is identical with that of the last model and needs no further description; though there is a slight difference in the arrangement of the pipes  $f$  and  $G$  and of the cocks  $t$ ,  $V$  (and  $w$ ), their uses are identical and a description of the method of manipulation of either apparatus will serve for both.

Olszewski\* has described a liquefier somewhat similar to mine, though at the time at which his paper was published the apparatus had not been tested. He states that it is possible to liquefy hydrogen by cooling it to the temperature of liquid air boiling under normal pressure before allowing it to enter the regenerator coil ( $D$ , figs. 4, 6). It appears to me, however, that as the regenerator coil is of the same dimension as in my machine, Olszewski's apparatus will be found to be considerably less efficient.

Before describing my latest researches on the liquefaction of hydrogen it will be convenient to consider the method of compressing the hydrogen, and of manipulating the liquefier.

#### X. COMPRESSION OF THE HYDROGEN.

The Whitehead torpedo compressor, as employed in connection with the Hampson air liquefier, cannot be used for the compression of hydrogen without modification. In the usual form of this machine the packings of the pistons in both cylinders consist of cup-fibers carried on the ends of the pistons and moving with them. In fig. 7, A, the low pressure cylinder is shown in section. Air is drawn into the cylinder through the valve  $a$  and expelled through the valve  $b$ ;  $c$  is the piston, which carries the cup fiber  $d$ , and is actuated by means of the connecting rod  $e$ . The piston and cross head  $f$  are one solid piece of metal.

It will easily be seen that when gas is being compressed the contact between the edge of the cup-fiber and the walls of the cylinder is perfect, but that when gas is being drawn into the cylinder, the pressure in it falls below that of the atmosphere, and there is a tendency for air to enter it between the metal and the fiber. The extent to which this would take place would be considerably increased if the cross head became slightly worn and acquired a little side play.

\* Acad. des Sci. de Cracow, December, 1902.



In some of my earlier experiments I was considerably troubled by the presence of impurities in the hydrogen, and at last traced the trouble to this source. For some time I managed to get over my difficulties by replacing the low pressure cup-fiber each time I compressed hydrogen, but as this proved troublesome and unsatisfactory I resolved to modify the low pressure cylinder so as to completely eliminate all chance of further trouble.

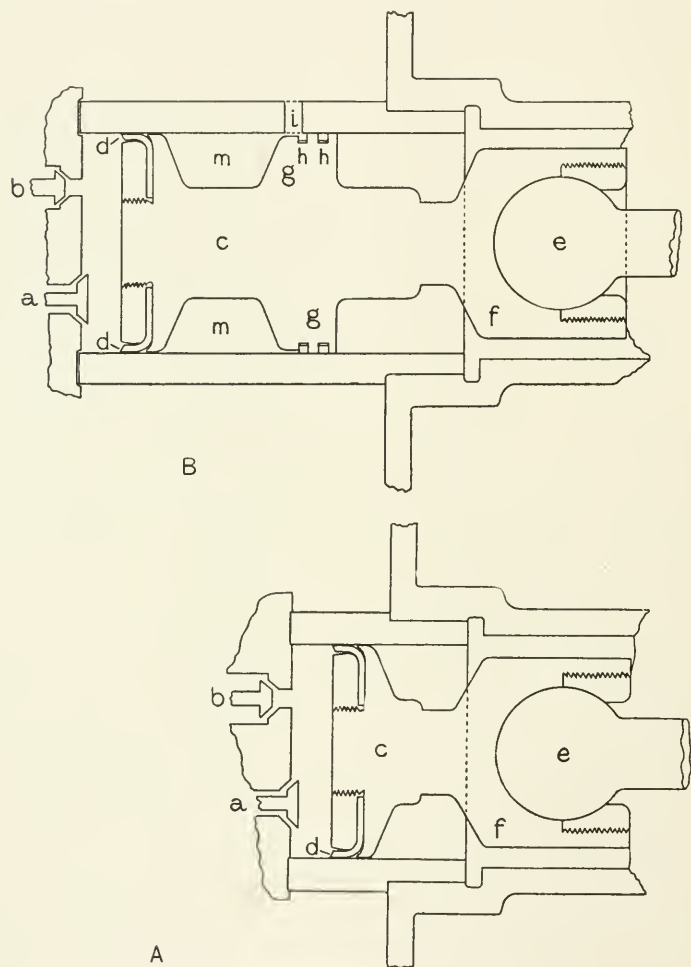


FIG. 7.—Hydrogen compressor.

The alterations were carried out by Brin's Oxygen Company. The new arrangement of the cylinder is shown in fig. 7, B. The length of the cylinder and of the studs which keep the cylinder cover in place was increased by 87 mm., the length of the stroke, and a second piston *gg*, with bronze rings of the usual pattern was introduced between the



original piston *c* and crosshead *f*. A hole *i* was bored in the top of the cylinder so that the space *mm* filled with water automatically from the tank in which the cylinder was immersed. If now the cup-fiber *dd* fitted the cylinder badly, only water could be drawn into the latter during the compression of the gas.

The whole arrangement for the compression and circulation of the hydrogen is shown in fig. 8. The hydrogen is conveyed from the gasometer, which is not shown in the figure, by a pipe *CC*, which communicates through a stopcock and connecting pipe with the low-pressure intake of the compressor *A*. The liquefying apparatus *I* have described was designed to work with about ten cubic meters of gas per hour. To deliver this quantity of gas the compressor must run at 360 revolutions per minute, and requires about seven horse-power to drive it.

Water mixed with about twenty percent of glycerol and one percent of caustic soda is drawn into the compressor from the reservoir *R*. The jet of the glass stopcock on *R* passes through a rubber cock in the neck of a small funnel which is connected below with the small cock on the intake pipe by means of a piece of rubber tube.

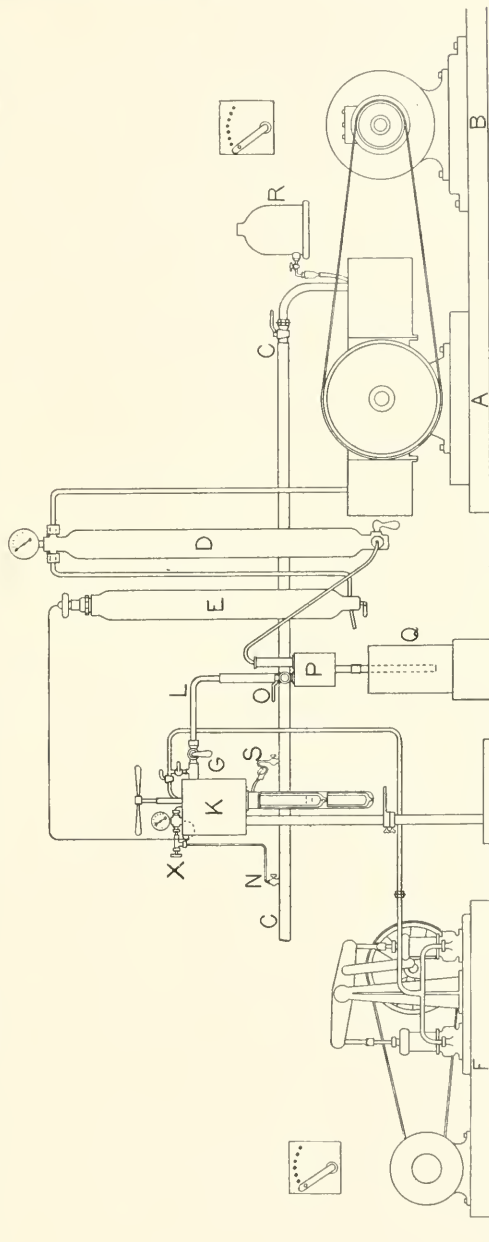


FIG. 8.—Arrangement of the liquefier, compressor, pump, etc.

The hydrogen is compressed in two stages, as described on page 23, and first enters the water separator *D* where the lubrication water is separated and discharged. The pipe from the cylinder *D* enters the collecting chamber *P*; the water runs into the tank *Q*, while the gas returns to the supply pipe *C*. The collecting chamber is shown in detail in fig. 9.

The compressed gas, which now contains only a trace of moisture, passes next through the cylinder *E* containing solid caustic potash, on its way to the liquefier *K*, which in the diagram is of the type described on pages 18-20. After undergoing compression, and partial liquefaction, the remaining gas returns by way of the pipe *L* to the distributing chamber *P*, and thence into the pipe *C*. Should the pressure rise suddenly through the blocking of the expansion valve, the cock *x* can be opened and some of the gas allowed to escape through a pipe which enters the supply pipe *C* through a small cock *N*. The connecting pipe *S*, which is of rubber, serves to prevent any waste through the escape of the hydrogen which passes out of the spiral opening at the bottom of the vacuum vessel *H* (figs. 5 or 6), when the liquid hydrogen runs into the receiving vessel (p. 20).

The operation of cooling down the liquefier has been described on page 19, and need not be dealt with again here. The next step in the operation was to remove the air from the compressor and purifying cylinders, and this was usually accomplished by starting the compressor two or three times, so as to take three or four cubic feet of gas into it on each occasion, and then allowing the compressed hydrogen to escape by opening a cock at the bottom of the potash purifier *D*. Later it was found to be much more effective to allow the hydrogen to pass completely through the apparatus and to escape at the expansion valve. In this case, the "washing out" of the apparatus had to be completed before the cooling down was commenced.

After washing out the apparatus the motor was again started and the pressure was allowed to rise.

Meanwhile the cap and the tap *V* (see page 20, fig. 5) had been removed from the bottom of the vacuum vessel *H*, and the liquid air was allowed to drain out of it. The collecting vessel *K* was now placed inside the tube *L* (figs. 4 or 6), and the latter was placed in position as shown in the figure. The connection between the tube *L* and the brass tube *h*, which formed part of the gland *p*, was made by means of a rubber sleeve *s*, secured to both by means of a tube of copper wire. When the sleeve was in position gas could only escape from the space within the tube *L* through the cock *r*, so that when the latter was closed the liquid which formed in *H* could not flow into *K*. When, however, the cock *r* was opened, liquid and gas could flow from *H* into *K*, the gas passing through the cock *r* and the tube *S*

(figs. 4, 6, 8) to the main hydrogen supply pipe. The cock *r* was not opened till the liquefaction of the hydrogen had commenced.

The tube *L* was usually surrounded either by a large vacuum vessel or by three concentric glass shades, spaced apart with asbestos mixed with a little pentoxide of phosphorus to absorb moisture from the surrounding air. This arrangement prevented the deposition of moisture on the walls of the tube *L* and enabled one to see what was taking place inside.

When the pressure in the apparatus had risen to 150 atmospheres the expansion valve was slowly opened and for a few moments the hydrogen was allowed to escape from the circulation system, either by bubbling through the water in the tank *Q*, fig. 8, or by opening the cock *O'* (fig. 9). When sufficient hydrogen had been allowed to escape, and the apparatus was considered to be free from air, the cock *O'* (fig. 9), was closed, the cock *O* was opened and the hydrogen was allowed to circulate through the system.

Shortly after commencing the expansion a small quantity of solid impurity always separated in the bottom of the vacuum-vessel *H* (figs. 4, 6). It is noteworthy that the solid impurity never blocked the coil, though it is probable that the latter was cooled to below the critical point of hydrogen, but seemed to encrust the valve at the point at which the expansion took place. Hannay\* pointed out some years ago that gases under high pressure, particularly in the neighborhood of their critical points, were able to hold solids in solution; considering the complete continuity of the liquid and gaseous states of matter this is hardly remarkable. To this phenomenon, which is allied to that of retrograde condensation in the case of mixed gases, is due the fact that the coils are never blocked by the presence of impurities, which at the temperatures to which the gas is cooled should behave as non-volatile solids, but which are dissolved by the compressed gas in the coil.

When the liquefier is working well it should require about half an hour from the time of commencing operations to fill a receiving vessel (*K*, figs. 4, 6) holding about half a liter. When once liquid hydrogen is formed, and the cock *r* is opened, the liquid falls in large drops from the nozzle of the vessel *H*. The liquid is usually slightly milky at first, but the solid impurity soon settles to the bottom of the receiving vessel, leaving the liquid clear.

When the receiving vessel is full the tube *L* can be lowered, and the receiving vessel drawn out of it by means of a wire attached to it. The receiving vessel is at once plugged with wool and placed inside a second vessel containing liquid air.

In machines which required solid carbonic acid about four kilos of that substance was required at each experiment, together with about

\* Proceedings of the Royal Society, 1879, Vol. 30, 484.

eight liters of liquid air. With these quantities the apparatus could be run for about thirty minutes. With the apparatus having the second regenerator coil, which did not require carbonic acid, five liters of liquid air fully sufficed to cool the apparatus in the first place and to cool the hydrogen during a run of more than twice the duration of the former experiments.

The collecting chamber referred to on page 20 is a cylindrical brass box about 80 mm. in diameter and 100 mm. high. The tube  $\gamma$  is con-

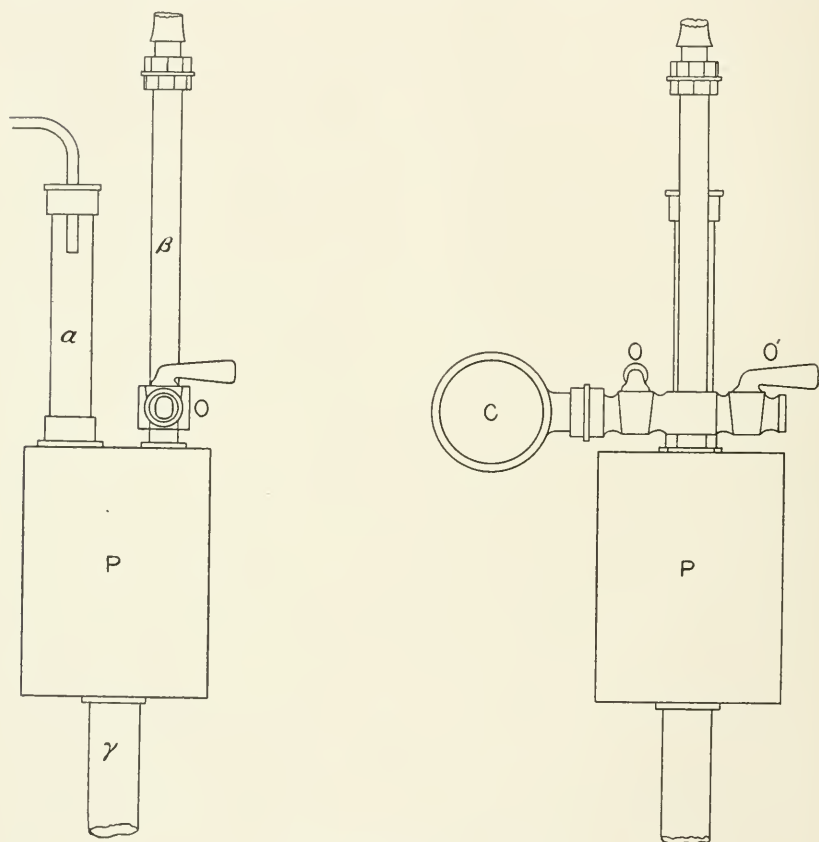


FIG. 9.—Collecting chamber.

nected by means of a piece of wide rubber tube with a brass tube of similar diameter which dips about 50 cm. below the surface of the water in a tank  $Q$ , fig. 8. The tube  $a$  is of glass, joined by means of a socket with the cylinder  $P$ , and by a cap with the pipe through which water is discharged from the water separator  $D$ , fig. 8. By means of this arrangement the gas discharged together with the water is saved. The pipe  $\beta$  is connected by means of a crosspiece with the body of the apparatus and with the two cocks  $O$  and  $O'$ . The cock  $O$

communicates directly with the pipe *C* leading from the gasometer to the compressor, and through it the hydrogen which returns from the liquefier through the tube *G*, figs. 3, 4, 6, *L* fig. 8 and *a* fig. 9, can be returned to the circulation system. The hydrogen which escapes from the liquefier when the expansion is first commenced, is allowed to escape through the cock *O'*, which is closed before the cock *O* is opened. The pipe *γ* serves not only to discharge the water delivered through *a*, but also as a safety valve.

## XII. THE PREPARATION OF THE HYDROGEN.

In my earlier experiments I prepared the hydrogen by the action of dilute (25 percent) sulphuric acid on commercial zinc, contained in a beer barrel, which had received several coats of enamel paint. Since, however, it appeared that the gas suffered both loss and contamination by diffusion through the walls of the barrel, I replaced it by a lead vessel. The apparatus for generating the hydrogen is shown in fig. 10.

The vessel *A*, which was 500 mm. high and 300 mm. in diameter, was made of sheet lead, "burnt" at the junctions in the oxy-hydrogen blow-pipe. At the commencement of each operation it usually contained about fifteen kilograms of pure granulated zinc. Dilute sulphuric acid containing little copper sulphate was run into *A* in a steady stream from the reservoir *B*, and as the zinc sulphate solution accumulated it was run off through the stop-cock *E*. The hydrogen could either be allowed to escape through the pipe *C*, which was plunged into a deep vessel filled with water, and acted as a safety valve, or to pass along the pipe *D* into the purifying towers *F*, *F'*.

The towers *F*, *F'*, *F''* were filled with broken pumice, which was kept wet by means of solutions of the reagents contained in the reservoirs *G*, *G'*. The first of these, which supplied the first two towers, contained an acid solution of chromic acid, the second contained silver nitrate solution, which served to remove arseniureted hydrogen from the gas. The excess of the reagents flowed through inverted syphons, which acted as gas traps, at the bottom of the towers, and was collected in the vessels *H*, *H'*.

The gas finally passed through a solution of caustic potash contained in the vessel *K* and entered the pipe leading to the gasometer through the cock *L*.

If the gasometer already contained some hydrogen this gas could be used to wash out the generating apparatus before introducing the fresh quantity of gas. This could easily be done by first lowering the reservoir *J*, so as to empty the vessel *K*, and thus raising the tube *C* till the gas bubbled through the water in which it was immersed, and escaped.

## XIII. THE GASOMETER.

The gasometer in use at University College, London, is of the simple type shown in fig. 11, A. It consists of two cylindrical tanks, one enclosing the other. The outer tank is 2,000 cm. high and 1,500 cm. in diameter, the inner one is 1,800 cm. high and 1,450 cm. in

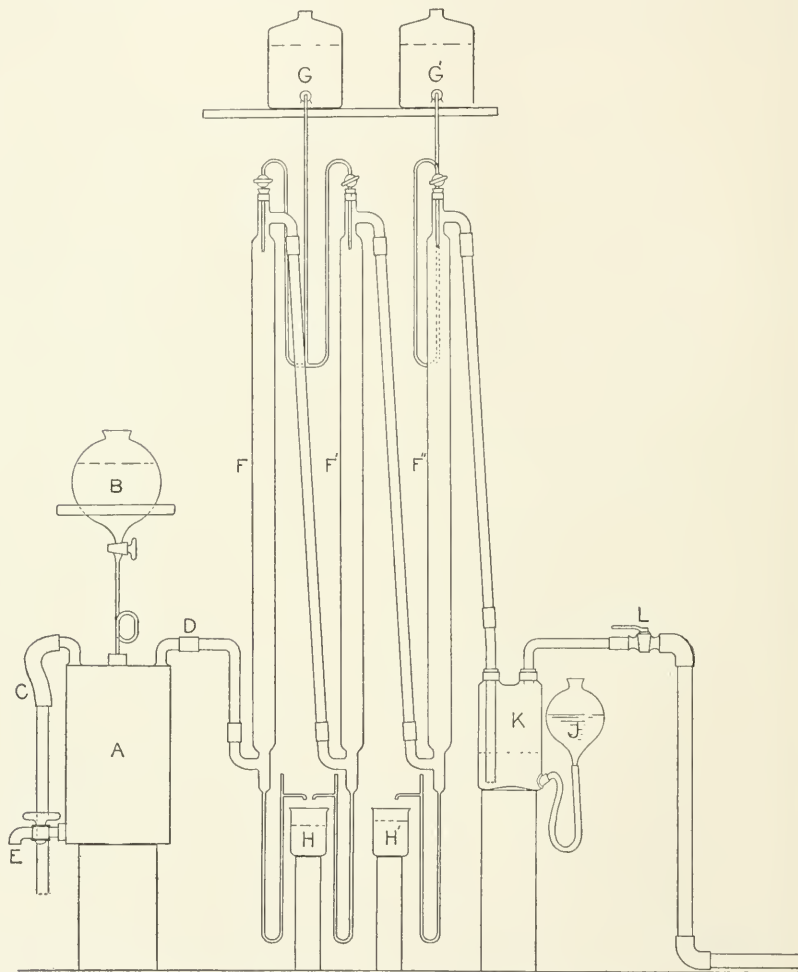


FIG. 10.—Apparatus for generating the hydrogen.

diameter. The outer tank is filled with water to just above the level of the top of the inner tank. The supply pipe passes through the center of the gasometer, and opens inside a small dome in the top of the inner tank. This enables practically the whole of the gas to be easily expelled from the gasometer.



When it was first placed in position the water in the gasometer was saturated with hydrogen by passing a stream of that gas through it from a small generator. The gas passed to the bottom of the tank by

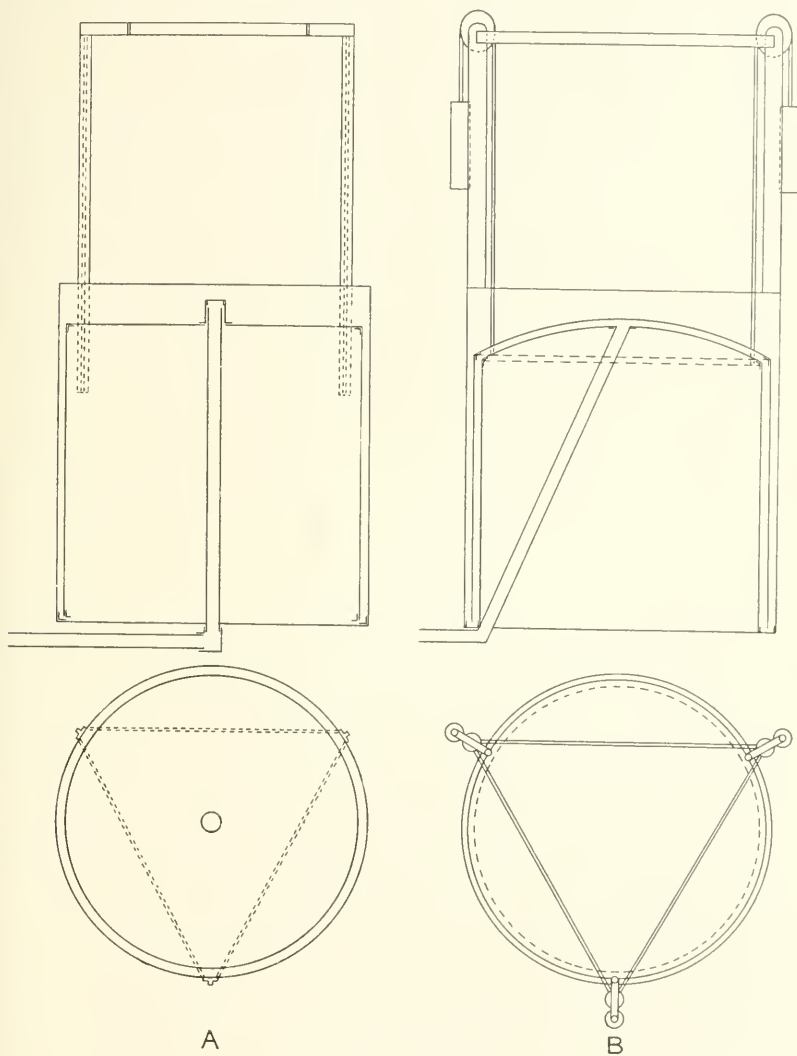


FIG. 11.—Gasometers.

means of a piece of composition gas pipe. The operation of saturating the water occupied nearly a week; it was not, however, necessary to repeat it as the gasometer always contained hydrogen.

The pressure inside the gasometer was equivalent to about 500 mm. of water.

Though for financial reasons I was obliged to content myself with

a gasometer of the type I have described, there is a considerable advantage in one of the kind shown in fig. 11, B. Such a gasometer is in use in connection with the liquefaction plant which I designed for Professor Auschütz of Bonn. Gasometers of this type are used for the storage of acetylene.

#### XIV. CONCLUSION OF PART I.

I have so far succeeded in designing an apparatus by means of which I can at a comparatively small cost produce quantities of liquid hydrogen sufficient for experimental purposes. I have usually obtained half a liter as a maximum quantity, as it has always been sufficient for the experiments I have had in hand.

I am at present engaged in designing an apparatus in which the liquid hydrogen will be produced inside a metal chamber, and will be drawn off through a cock. The elimination of the glass vacuum vessel presents obvious advantages. At the same time I am investigating the conditions most favorable to effective heat interchange in the regenerator coil *D*, figs. 4, 6, of the apparatus. The dimensions of the coils (p. 16) in the machines I have already experimented with has always been one quarter of the size of the coil of the Hampson air liquefier, the temperature gradient being in one case  $50^{\circ}$  and in the other  $200^{\circ}$ . The results of my experiments appear to indicate that these dimensions are too small, for the reason that the heat interchange is a function not only of the conductivity of the metal of which the coils are constructed, but also of certain properties of the gas. Further, it appears probable that the spacing of the coils will have a considerable influence on the efficiency of the apparatus, and that for hydrogen, which has a low viscosity, the coils should be closer together than in a machine which is designed to liquefy air.

In conclusion I wish to express my indebtedness to the Smithsonian Institution for the assistance it has given me in carrying out these investigations.