LV.—*Note on The Liquefaction of Hydrogen and Helium.*

By Prof. JAMES DEWAR.

IN a paper entitled "The Liquefaction of Air and Research at Low Temperatures," read before the Chemical Society and published in the Proceedings, No. 158, an account is given of the history of the liquid hydrogen problem and the result of my own experiments up to the end of the year 1895. The facts are substantially as follows.

Wroblewski made the first conclusive experiments on the liquefaction of hydrogen in January, 1884. He found that the gas cooled in a capillary glass tube to the boiling point of oxygen, and expanded quickly from 100 to 1 atmos., showed the same appearance of sudden ebullition, lasting for a fraction of a second, as Cailletet had seen in his early oxygen experiments. No sooner had the announcement been made, than Olszewski confirmed the result by expanding hydrogen from 190 atmos., previously cooled to the temperature given by liquid oxygen and nitrogen evaporating under diminished pressure. Olszewski, however, declared in 1884 that he saw colourless drops, and by partial expansion to 40 atmos. the liquid hydrogen was seen by him running down the tube. Wroblewski could not confirm Olszewski's results, his hydrogen being always obtained in the form of what he called a "liquide dynamique," or the appearance of an instantaneous froth. The following extract from Wroblewski's paper (*Compt. rend.*, 1885, 100, 981) states very clearly the results of his work on hydrogen:—
"L'hydrogène soumis à la pression de 180 atm. jusqu'à 190 atm. refroidi par l'azote bouillant dans la vide (à la température de sa solidification) et détendu brusquement sous la pression atmospherique présente une mousse bien visible. De la couleur grise de cette mousse, où l'œil ne peut distinguer des gouttelettes incolores, on ne peut pas encore deviner quelle apparence aurait l'hydrogène a l'état de liquide 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'obtenu suivant les pressions employées des températures de −208° jusqu'à −211° C. Je ne peux pas encore dire dans quelle relation se trouvent ces nombres avec la température réele de la mousse et la température d'ébullition de l'hydrogène sous la pression atmosphérique, puisque je n'ai pas encore la certitude que la faible durée de ce phénomène ait permis à la pile de se refroidir complètement. Néanmoins, je crois aujourd'hui de mon devoir de publier ces résultats, afin de préciser l'état actuel de la question de la liquefaction de l'hydrogène." It is well to note that the lowest thermo-electric temperature recorded by Wroblewski during the adiabatic expansion of the hydrogen, namely, – 211° is really equivalent to a much lower temperature on the gas thermometer scale. The most probable value is – 230°, and this must be regarded as the highest temperature of the liquid state, or the critical point of hydrogen according to his observations. The above methods having failed to produce "static" hydrogen, Wroblewski suggested that the result might be attained by the use of hydrogen gas as a cooling agent. From this time until his death in the year 1888, Wroblewski devoted his time to a laborious research on the isothermals of hydrogen at low temperatures. The data thus arrived at enabled him, by the use of Van der Waal's formulæ, to calculate the critical constants and boliing point of liquid hydrogen.

Olszewski returned to the subject in 1891, repeating and correcting his old experiments of 1884, which Wrobleski had failed to confirm, in a glass tube 7 mm. in diameter instead of one of 2 mm., as in the early trials. He says, "On repeating my former experiments, I had no hope of obtaining a lower temperature by means of any cooling agent, but I hoped that the expansion of hydrogen would be more efficacious, on account of the larger scale on which the experiment was made." The result of these experiments Olszewski describes as follows, "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.*" Further, "The reason for which it has not been hitherto possible to liquefy hydrogen in a static state, is that there exists no gas having a density between those of hydrogen and of nitrogen, and which might be for instance 7—10 (H 1). Such a gas could be liquefied by means of liquid oxygen or air as cooling agent, and be afterwards used as a frigorific menstruum in the liquefaction of hydrogen."

Professor Olszewski, in 1895, determined the temperature reached in the momentary adiabatic expansion of hydrogen at low temperatures; just as Wroblewski had done in 1885, only he employed a platinum resistance thermometer instead of a thermo-junction.

For this purpose, he used a small steel bottle of 20 or 30 c.c. capacity, containing a platinum resistance thermometer; in this way, temperatures were registered which were regarded as those of the critical and boiling points of liquid hydrogen, a substance which *could not be seen* under the circumstances, and was only assumed at the most to exist for a second or two during the expansion of the gaseous hydrogen in the small steel bottle.

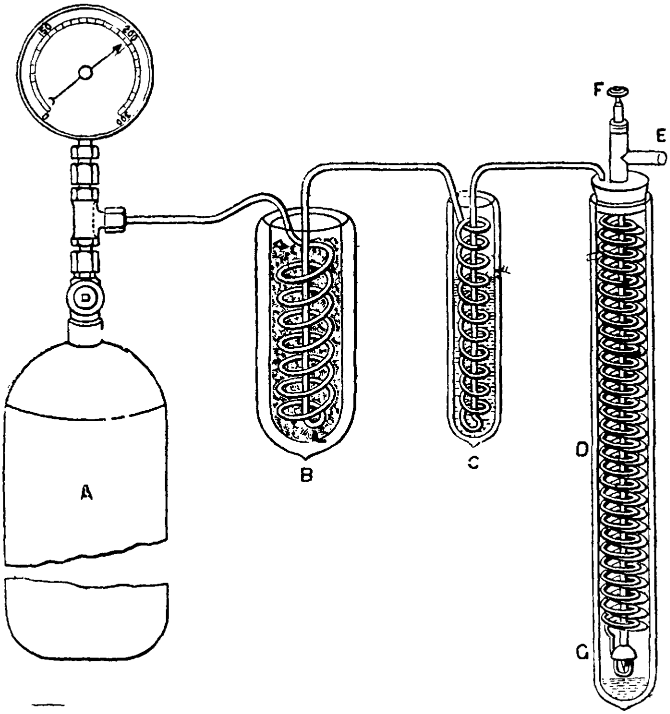
The results arrived at by Wroblewski and Olszewski are given in the following table.

	Wroblewski, 1885.	Olszewski, 1895.
Critical temperature...	– 240°	– 234°
Boiling point...........	– 250°	– 243°
Critical pressure	13At.	20At.

The moment the critical point is approximately defined, the boiling point is roughly known, and the critical pressure can be inferred from analogy with the behaviour of other substances.

In a paper published in the *Phil. Mag.*, September, 1884, "On the Liquefaction of Oxygen and the Critical Volumes of Fluids," the suggestion was made that the critical pressure of hydrogen was wrong, and that instead of being 99 atmos. (as deduced by Sarrau from Amagat's isothermals), the gas had probably an abnormally low value for this constant. This view was substantially confirmed by Wroblewski finding a critical pressure of 13·3 atoms., or about one-fourth of that of oxygen. The *Chemical News* (September 7, 1894) contains an account of the stage the author's hydrogen experiments had reached at that date. The object was to collect liquid hydrogen at its boiling point, in an open vacuum vessel, which is a much more difficult problem than seeing the liquid in a glass tube under pressure and at a higher temperature. In order to raise the critical point of hydrogen to about – 200°, from 2 to 5 per cent. of nitrogen or air was mixed with it. This is simply making an artificial gas containing a large proportion of hydrogen which is capable of liquefaction by the use of liquid air. The results are summed up in the following extract from the paper. "One thing can, however, be proved by the use of the gaseous mixture of hydrogen and nitrogen, namely, that by subjecting it to a high compression at a temperature of – 200° and expanding the resulting liquid into air, a much lower temperature than anything that has been recorded up to the present time can be reached. This is proved by the fact that such a mixed gas gives, under the conditions, a paste or jelly of solid nitrogen, evidently giving off hydrogen, because the gas coming off burns fiercely. Even when hydrogen containing only some 2 to 5 per cent. of air is similarly treated, the result is a white, solid matter (solid air) along with a clear liquid of low density, which is so exceedingly volatile that no known device for collecting has been successful."

The report of a Friday Evening Lecture on "New Researches on Liquid Air" (*Proc. Roy. Inst.*, 1896) contains a drawing of the apparatus employed for the production of a jet of hydrogen containing visible liquid. This is reproduced in the figure. A represents one of the hydrogen cylinders; B and C, vacuum vessels containing carbonic acid under exhaustion and liquid air respectively; D is the coil, G the pin-hole nozzle, and F the valve. By means of this jet, liquid air can be quickly transformed into a hard solid. It was shown that such a jet could be used to cool bodies below the temperature that it is possible to reach by the use of liquid air, but all attempts to collect the liquid hydrogen from the jet in vacuum vessels failed. No other investigator has, so far, improved on the results the author described in the Proceedings of the Chemical Society (No. 158), 1895, or, indeed, touched the subject since that date. The type of apparatus used in these experiments worked well, so it was resolved to construct a much larger liquid air plant, and to combine with it circuits and arrangements for the liquefaction of hydrogen, which will be described in a subsequent paper. This apparatus took a year to build up, and many months have been occupied in testing and making preliminary trials. The many failures and defeats need not be detailed.



Apparatus used in the production of the Liquid Hydrogen Jet.

On May 10th of this year, starting with hydrogen cooled to – 205°, and under a pressure of 180 atmospheres, escaping continuously from the nozzle of a coil of pipe at the rate of about 10 to 15 cub. ft. per minute, in a vacuum vessel doubly silvered and of special construction, all surrounded with a space kept below −200°, liquid hydrogen commenced to drop from this vacuum vessel into another doubly isolated by being surrounded with a third vacuum vessel. In about 5 minutes, 20 cubic centimetres of liquid hydrogen were collected, when the hydrogen jet froze up, from the accumulation of air in the pipes frozen out from the impure hydrogen. The yield of liquid was about 1 per cent. of the gas. The hydrogen in the liquid condition is clear and colourless, showing no absorption spectrum, and the meniscus is as well defined as in the case of liquid air. The liquid must have a relatively high refractive index and dispersion, and the density appears also to be in excess of the theoretical density, namely, 0·18 to 0·12, which we deduce respectively from the atomic volume of organic compounds, and the limiting density found by Amagat for hydrogen gas under infinite compression. Yet this may be a delusion due to its high dispersion. A preliminary attempt to weigh a small glass bulb in the liquid made the density about 0·08. My old experiments on the density of hydrogen in palladium gave a value for the combined element of 0·62, and it will be interesting to find the accurate density of the liquid substance at its boiling point. Not having arrangements at hand to determine the boiling point, other than a thermo-junction which gave entirely fallacious results, experiments were made to prove the excessively low temperature of the boiling fluid. In the first place, if a long piece of glass tubing, sealed at one end and open to the air at the other, is cooled by immersing the closed end in the liquid hydrogen, the tube immediately fills, where it is cooled, with solid air; a small tube containing liquid oxygen became a bluish solid. A first trial of putting the liquid hydrogen under exhaustion gave no appearance of transition into the solid state. The liquid hydrogen in its vacuum tube, which is immersed in liquid air so that the external wall of the vacuum vessel is maintained at about −190°, is found to evaporate at a rate not far removed from that of liquid air from a similar vacuum vessel under the ordinary conditions of storage. This leads me to the conclusion that, with proper isolation, it will be possible to manipulate with liquid hydrogen as easily as with liquid air. The second experiment was made with a tube containing helium.

The Cracow Academy *Bulletin* for 1896 contains a paper by Professor Olszewski, entitled, "A Research on the Liquefaction of Helium," in which he states, "As far as my experiments go, helium remains a permanent gas and apparently is much more difficult to liquefy than hydrogen." In a paper of my own in the Proceedings of the Chemical

Society, No. 183 (1896—7), in which the separation of helium from Bath gas was effected by a liquefaction method, the suggestion was made that the volatility of hydrogen and helium would probably be found close together, just like those of fluorine and oxygen. Having a specimen of purified helium, which had been extracted from Bath gas, sealed up in a bulb with a narrow tube attached, the latter was placed in liquid hydrogen, when a distinct liquid was seen to condense. The same experiment repeated, only using liquid air evaporating in a vacuum gave no trace of condensation. From this result, it would appear that there cannot be any great difference between the boiling points of helium and hydrogen.

All known gases have now been condensed into liquids which can be manipulated at their boiling points under atmospheric pressure in suitably arranged vacuum vessels. With hydrogen as a cooling agent, we shall get within 20 or 30 of the zero of absolute temperature and its use will open up an entirely new field of scientific inquiry. Even as great a man as James Clerk Maxwell had doubts as to the possibility of ever liquefying hydrogen, see *Scientific Papers*, 2, 412. In concluding his lectures on the non-metallic elements, delivered at the Royal Institution in 1852 and published the following year, Faraday said (See Faraday's "Lectures on the Non-metallic Elements" p. 292—3), "There is reason to believe we should derive much information as to the intimate nature of these non-metallic elements, if we could succeed in obtaining hydrogen and nitrogen in the liquid or solid form. Many gases have been liquefied; the carbonic acid gas has been solidified, but hydrogen and nitrogen have resisted all our efforts of the kind. Hydrogen in many of its relations acts as though it were a metal; could it be obtained in a liquid or solid condition, the doubt might be settled. This great problem, however, has yet to be solved; nor should we look with hopelessness on this solution when we reflect with wonder —and as I do almost with fear and trembling—on the powers of investigating the hidden qualities of these elements—of questioning them, making them disclose their secrets and tell their tales—given by the Almighty to man."

Faraday's expressed faith in the potentialities of experimental inquiry in 1852 has been justified forty-six years afterwards by the production of liquid hydrogen in the very laboratory in which all his epoch-making researches were executed. The "doubt" has now been settled, hydrogen does not possess in the liquid state the characteristics of a metal. No one can predict the properties of matter near the zero of temperature. Faraday liquefied chlorine in the year 1823. Sixty years afterwards, Wroblewski and Olszewski produced liquid air, and now, after a fifteen years' interval, the remaining gases, hydrogen and helium, appear as static liquids. Considering the step from the liquefaction of air to that of hydrogen is relatively as great in the thermodynamic sense as that from liquid chlorine to liquid air, the fact that the former result has been achieved in one-fourth the time needed to accomplish the latter proves the greatly accelerated race of scientific progress in our time.

The efficient cultivation of this field of research depends upon combination and assistance of an exceptional kind, but in the first instance money must be available, and the members of the Royal Institution deserve my especial gratitude for their handsome donations to the conduct of this research. Unfortunately, its prosecution will demand a further large expenditure. It is my duty also to acknowledge that at an early stage of the enquiry the Hon. Company of Goldsmiths helped low temperatures investigation by a generous donation to the Research Fund.

During the whole course of the low temperature work, carried out at the Royal Institution, the invaluable aid of Mr. Robert Lennox has been at my disposal, and it is not too much to say that, but for his engineering skill, manipulative ability, and loyal perseverance, the present successful issue might have been indefinitely delayed. My thanks are also due to Mr. J. W. Heath for valuable assistance in the conduct of these experiments.

Addendum.

Since the above paper was written, both the boiling point and specific gravity of hydrogen have been determined. The boiling point in the meantime given by the use of a platinum resistance thermometer involves, however, extrapolation of the curve correlating temperature and resistance; the result is that the boiling point of hydrogen is $-238°$ C. or 35° absolute. At this temperature, the tension of liquid air (which, of course, becomes solid) is less than 0·002 mm. The resistance of the thermometer used was 5·338 ohm at the melting point of ice, and this was reduced to 0·129 ohms when placed in boiling hydrogen. The absolute zero in platinum degrees of this thermometer was $-263{\cdot}27$, and the temperature measured on this scale is $-256{\cdot}29°$ or 6·38° from the point where the conductivity of the platinum would become infinite. The resistance of the platinum in the liquid hydrogen is reduced to nearly $\frac{1}{11}$th of what it is in liquid oxygen. It will be necessary to find out the electric conductivity of the fluid itself, and to repeat the observations with other thermometers, before we can arrive at more definite conclusions. The vapour of hydrogen at its boiling point is about eight times denser than the gas at ordinary temperatures, or it has about half the density of air, whilst the vapour coming off from liquid air at its boiling point is somewhat less than four times the density of air at the ordinary temperature. By evaporation in a vacuum, the temperature of liquid hydrogen will be lowered from 10° to 15°, but it will be practically impossible (so far as we can anticipate the results of experiment) to reach a lower temperature than – 250° C or 20° absolute by this means. At present, we can see no way of bridging over the last 20 to 25 degrees, and therefore the approach to the zero of absolute temperature and the study of matter and energy under such conditions must be confined to temperatures above 25° absolute.

The density of liquid hydrogen has been approximately determined by evaporating some 10 c.c. of the liquid, and collecting and measuring the gas produced, thereby ascertaining its weight. In this way, 8·15 litres at 14° C. and 753 mm. were collected over water from between 9 and 10 c.c. of liquid hydrogen. It appears, therefore, that the density of the liquid is about 0·07, using whole numbers as the calculation works out to 0·068 nearly. Liquid hydrogen is, therefore, a very deceptive fluid so far as appearance goes. The fact of its collecting so easily, dropping so well, and having such a well defined meniscus induced me to believe that the density might be about half that of liquid air. It was a great surprise to find the density only $\frac{1}{14}$th of water. Liquid marsh gas was the lightest known liquid, the density at its boiling point being 0·417, but liquid hydrogen has only $\frac{1}{6}$th the density of this substance. The density of occluded hydrogen in palladium being 0·62, it is eight times denser than the liquid.

Hydrogen in the liquid state is 100 times denser than the vapour it is giving off at its boiling point, whereas liquid oxygen is 255 times denser than its vapour. It appears, therefore, that the atomic volume of liquid hydrogen at its boiling point is 14·3, as compared with 13·7 for oxygen under similar circumstances. In other words, they are nearly identical. From this we can infer that the critical pressure need not exceed 15 atmospheres. The extraordinary properties theory requires hydrogen should possess, especially as regards specific and latent heat, become more intelligible from the moment we know that the density is so small. In other words, when we compare the properties of equal volumes of liquid hydrogen and air under similar corresponding temperatures, they do not differ more than might be anticipated.

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