

occupy. The number 22.51 must be taken as a minimum density. If we may hazard a conjecture it is that krypton will turn out to have the density 40, with a corresponding atomic weight 80, and will be found to belong to the helium series, as is, indeed, rendered probable by its withstanding the action of red-hot magnesium and calcium on the one hand, and on the other of oxygen in presence of caustic soda, under the influence of electric sparks. We shall procure a larger supply of the gas and endeavor to separate it more completely from argon by fractional distillation.

It may be remarked in passing that Messrs. Kayser and Friedlander, who supposed that they had observed  $D_3$  in the argon of the atmosphere, have probably been misled by the close proximity of the brilliant yellow line of krypton to the helium line.

On the assumption of the truth of Dr. Johnstone Stoney's hypothesis that gases of a higher density than ammonia will be found in our atmosphere, it is by no means improbable that a gas lighter than nitrogen will also be found in air. We have already spent several months in preparation for a search for it, and will be able to state ere long whether the supposition is well founded.

#### LIQUID HYDROGEN.

##### PRELIMINARY NOTE ON THE LIQUEFACTION OF HYDROGEN AND HELIUM.\*

In a paper entitled 'The Liquefaction of Air and Research at Low temperatures,' read before the Chemical Society, and published in their 'Proceedings,' No. 158, an account is given of the history of the hydrogen problem and the result of my own experiments up to the end of the year 1895. The subject is again discussed in a Friday Evening Lecture on 'New Researches on

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Liquid Air,'\* which contains a drawing of the apparatus employed for the production of a jet of hydrogen containing liquid. It was shown that such a jet could be used to cool bodies below the temperature that could be reached by the use of liquid air, but all attempts to collect the liquid in vacuum vessels failed. No other investigator has so far improved on the results described in 1895. 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, admirably constructed by the engineers, Messrs. Lennox, Reynolds, and Fyfe, 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.

On May 10th, starting with hydrogen cooled to  $-205^{\circ}$  C., and under a pressure of 180 atmospheres, escaping continuously from the nozzle of a coil of pipe at the rate of about 10 cubic feet to 15 cubic feet per minute, in a vacuum vessel double-silvered and of special construction, all surrounded with a space kept below  $-200^{\circ}$  C., liquid hydrogen commenced to drop from this vacuum vessel into another doubly isolated by being surrounded with a third vacuum vessel. In about five minutes, 20 cc. of liquid hydrogen were collected, when the hydrogen jet froze up from the solidification of air in the pipes. The yield of liquid was about 1 per cent. of the gas. The hydrogen in the liquid condition is clear and colorless, showing no absorption spectrum, and the meniscus is as well defined as in the case of liquid air. The liquid has a relatively high refractive index and dispersion, and the density appears to be in excess of the theoretical density, viz., 0.18 to 0.12, which we

\*'Roy. Inst. Proc.' 1886.

deduce respectively from the atomic volume of organic compounds and the limiting density found by Amagat for hydrogen gas under infinite compression. My old experiments on the density of hydrogen in palladium gave a value for the combined body of 0.62, and it will be interesting to find the real density of the liquid substance at its boiling point. Not having arrangements at hand to determine the boiling point, two 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. 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 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. A similar experiment made with the use of liquid air under exhaustion in the same helium tube (instead of liquid hydrogen) gave no visible condensation. From this result it would appear that there cannot be any great difference in 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.\* 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 that the step from the liquefaction of air to that of hydrogen is relatively as great in the thermo-dynamic 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 rate 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. The handsome contribution made by the Goldsmiths' Company ought also to be mentioned as very materially helping the progress of the work.

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 engi-

\* See 'Scientific Papers,' Vol. 2, p. 412.

neering 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.

#### THE BOILING POINT AND DENSITY OF LIQUID HYDROGEN.\*

THE boiling point of liquid hydrogen at atmospheric pressure has been determined by a platinum resistance thermometer. This was constructed of pure metal and had a resistance of 5.3 ohms at 0° C., which fell to about 0.1 ohm when the thermometer was immersed in liquid hydrogen. On reduction of this resistance to normal air temperatures the boiling point is found to be —238.2° and —238.9° respectively by two methods, and to be —237° by a Dickson formula calculated for this thermometer (*cf. Phil. Mag.*, 1898, 45, 525). The boiling point of the liquid is, therefore, about —238° C., or 35° absolute, and is thus about 5° higher than that obtained by Olszewski by the adiabatic expansion of the compressed gas, and about 8° higher than that deduced by Wroblewski from van der Waals' equation. It may be inferred that the critical point of hydrogen is about 50° absolute, and that the critical pressure will probably not exceed 15 atmospheres. As molecular latent heats are proportional to absolute boiling points, the latent heat of liquid hydrogen will be about two-fifths that of liquid oxygen. From analogy it is probable that the practicable lowering of temperature to be obtained by evaporating liquid hydrogen under pressures of a few mm. cannot amount to more than 10–12° C., and it may be said with certainty that no means are at present known for approaching nearer than 20–25° to the absolute zero of temperature. The platinum resistance thermometer used had

a zero point of —263.2 platinum degrees, and when immersed in boiling liquid hydrogen indicated a temperature of —256.8° on the same scale, or 6.4 platinum degrees from the point at which the metal would become a perfect conductor. The effect of cooling platinum from the boiling point of liquid oxygen to that of liquid hydrogen is to diminish its resistance to one-eleventh.

The approximate density of liquid hydrogen at its boiling point was determined by measuring the volume of the gas obtained by evaporating 10 cc. and is slightly less than 0.07, or about one-sixth that of liquid marsh gas, which has a density of 0.41 and is the lightest liquid at its boiling point hitherto known. It is remarkable that, with so low a density, liquid hydrogen is so easily seen, has so well defined a meniscus, and can be so readily collected and manipulated in vacuum vessels. As hydrogen occluded in palladium has a density of 0.62, it follows that it must be associated with the metal in some other state than that of liquefaction. The atomic volume of liquid hydrogen at the boiling point is about 14.3, atomic volumes of liquid oxygen and nitrogen being 13.7 and 16.6, respectively, at their boiling points. The density of the gas at the boiling point of liquid hydrogen is 0.55, or about one-half that of air, and is eight times that of the gas at ordinary temperatures. The ratio of the density of hydrogen gas at the boiling point to that of the liquid is approximately 1 : 100, as compared with a ratio of 1 : 255 in the case of oxygen.

The specific heat of hydrogen in the gaseous state and in hydrogenized palladium is 3.4, but may very probably be 6.4 in the liquid substance. Such a liquid would be unique in its properties, but as the volume of one gram of liquid hydrogen is about 14–15 cc. the specific heat per unit volume must be nearly 0.5, which is about that of liquid air. It is highly pro-

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bable, therefore, that the remarkable properties of liquid hydrogen predicted by theory will prove to be susceptible of explanation when they are compared with those of liquid air, volume for volume, at corresponding temperatures as defined by van der Waals.

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#### THE SPECIFIC HEAT OF METALS AT LOW TEMPERATURES.

DR. WOLCOTT GIBBS having requested Professor Rood to make some determinations of the specific heat of a few metals, employing liquid air, the matter was finally handed over to me by Professor Rood, and I herewith give a short account of the method used and the results obtained.

Few experiments on the specific heat of substances at low temperatures have been made. The chief cause of this has been the difficulty experienced heretofore in reducing the temperature of bodies to a definite number of degrees sufficiently below zero, Centigrade. Liquid air affords a means of obtaining a very low temperature, and was procured through the kindness of Mr. Charles E. Tripler, who has devised apparatus for making it in considerable quantities.

In a paper on the liquefaction of gases by Professor Charles Olszewski, in the *Philosophical Magazine*, London, February, 1895, Vol. XXXIX., No. CCXXXVII., pp. 188-212, it is stated, that the boiling point of liquefied air under atmospheric pressure is  $-191.4^{\circ}\text{C}.$ , that of liquefied nitrogen  $-194.4^{\circ}\text{C}.$ , and that of liquefied oxygen  $-181.4^{\circ}\text{C}.$  These temperatures were determined with a hydrogen thermometer, and are generally accepted as correct.

Liquefied air changes in composition when in a state of ebullition, the percentage of nitrogen contained in it diminishing, while that of oxygen increases.

This change occurs because liquid nitrogen is the more volatile of the two liquid gases, and boils away at a higher rate than liquid oxygen; consequently liquid air changes in temperature. If it is allowed to boil for a considerable time it becomes almost pure liquid oxygen and its temperature correspondingly approaches near the boiling point of that liquid gas, or  $-181.4^{\circ}\text{C}.$

Such was the case with the liquefied air procured for the experiments on specific heat; therefore, after standing several hours, the cold liquid employed by me was considered to be liquid oxygen and its temperature  $-181.4^{\circ}\text{C}.$

A series of determinations were made of the specific heat of copper, iron and aluminium between the boiling point of liquid oxygen ( $-181.4^{\circ}\text{C}.$ ) and about 13 degrees Centigrade.

The method of mixtures was employed and was applied in a manner suggested by Professor Rood.

The experiments were conducted as follows:

A piece of metal of known weight was immersed in liquid oxygen ( $-181.4^{\circ}\text{C}.$ ); after it had cooled down to the temperature of the liquid, it was lifted out by a silk thread, attached to it, and transferred quickly to a calorimeter containing water of known weight and temperature.

The loss in temperature of the water, due to the insertion of the cold substance, was carefully noted, and the specific heat of the metal computed.

Various precautions were taken to avoid errors in the results, and the usual corrections were applied in the calculations.

Before the determinations of the specific heat of metals between the boiling point of liquid oxygen and normal temperatures (about  $13^{\circ}\text{C}.$ ) were begun, a series of experiments were performed on the specific heat of copper between  $23^{\circ}\text{C}.$  and the boiling point of water ( $100^{\circ}\text{C}.$ ), under condi-