

ART. XVII.—*The Nadir of Temperature and Allied Problems*; by JAMES DEWAR, LL.D., F.R.S. [Bakerian Lecture (abstract) read before the Royal Society,* June 13, 1901.]

1. Physical Properties of Liquid and Solid Hydrogen. 2. Separation of Free Hydrogen and other Gases from Air. 3. Electric Resistance Thermometry at the Boiling Point of Hydrogen. 4. Experiments on the Liquefaction of Helium at the Melting Point of Hydrogen. 5. Pyroelectricity, Phosphorescence, etc.

Details are given in this paper which have led to the following results:—

The helium thermometer which records $20^{\circ}\cdot 5$ absolute as the boiling point of hydrogen, gives as the melting point 16° absolute. This value does not differ greatly from the value previously deduced from the use of hydrogen gas thermometers, viz., $16^{\circ}\cdot 7$. The lowest temperature recorded by gas thermometer is $14^{\circ}\cdot 5$, but with more complete isolation and a lower pressure of exhaustion, it will be possible to reach about 13° absolute, which is the lowest temperature that can be commanded by the use of solid hydrogen. Until the experiments are repeated with a helium gas thermometer filled at different pressures, with the gas previously purified by cooling to the lowest temperature that can be reached by the use of solid hydrogen, no more accurate values can be deduced.

The latent heat of liquid hydrogen about the boiling point as deduced from the vapor pressures and helium-thermometer temperatures, is about 200 units, and the latent heat of solid hydrogen is about 16 units.

The order of the specific heat of liquid hydrogen has been determined by observing the percentage of liquid that has to be quickly evaporated under exhaustion in order to reduce the temperature to the melting point of hydrogen, the vacuum vessel in which the experiment is made being immersed in liquid air. It was found that in the case of hydrogen the amount that had to be evaporated was 15 per cent. This value, along with the latent heat of evaporation, gives an average specific heat of the liquid between freezing and boiling point of about 6. When liquid nitrogen was similarly treated for comparison, the resulting specific heat of the liquid came out $0\cdot 43$ or about 6 per atom. Hydrogen therefore follows the law of Dulong and Petit, and has the greatest specific heat of any known substance.

The same fine tube used in water, liquid air, and liquid hydrogen gave respectively the capillary ascents of $15\cdot 5$, 2 and $5\cdot 5$ divisions. The relative surface tension of water, liquid air, and liquid hydrogen are therefore in the proportion of $15\cdot 5$, 2, $0\cdot 4$. In other words, the surface tension of hydrogen at its

* From an advance proof received from the author.

boiling point is about one-fifth that of liquid air under similar conditions. It does not exceed one thirty-fifth part the surface tension of water at the ordinary temperature.

The refractive index of liquid hydrogen, determined by measuring the relative difference of focus for a parallel beam of light sent through a spherical vacuum vessel filled in succession with water, liquid oxygen, and liquid hydrogen, gave the value 1.12. The theoretical value of the liquid refractive index is 1.11 at the boiling point of the liquid. This result is sufficient to show that hydrogen, like liquid oxygen and nitrogen, has a refractivity in accordance with theory.

Free hydrogen, helium, and neon have been separated from air by two methods. The one depends on the use of liquid hydrogen to boil the dissolved gases out of air kept at a temperature near the melting point of nitrogen; the other on a simple arrangement for keeping the more volatile gases from getting into solution after separation by partial exhaustion. By the latter mode of working something like 1/34000th of the volume of the air liquefied appears as uncondensed gas. The latter method is only a qualitative one for the recognition and separation of a part of the hydrogen in air. In a former paper on the "Liquefaction of Air and the Detection of Impurities,"* it was shown that 100 cc. of liquid air could dissolve 20 cc. of hydrogen at the same temperature. The crude gas separated from air by the second method gave on analysis—hydrogen 32.5 per cent., nitrogen 8 per cent., helium, neon, &c., 60 per cent. After removing the hydrogen and nitrogen the neon can be solidified by cooling in liquid hydrogen and the more volatile portions separated.

There exists in air a gaseous material that may be separated without the liquefaction of the air. For this purpose air has to be sucked through a spiral tube filled with glass wool immersed in liquid air. After a considerable quantity of air has been passed, the spiral is exhausted at the low temperature of the liquid air bath. The spiral tube is now removed and allowed to heat up to the ordinary temperature, and the condensed gas taken out by the pump. After purification by spectroscopic fractionation the gas filled into vacuum tubes gives the chief lines of xenon. The spectroscopic examination of the material will be dealt with in a separate paper by Professor Liveing and myself. A similar experiment made with liquid air kept under exhaustion, the air current allowed to circulate being under a pressure less than the saturation pressure of the liquid to prevent liquefaction, resulted in krypton being deposited along with the xenon.

A study of fifteen electric-resistance thermometers as far as the boiling point of hydrogen, has been made, and the results

* Chem. Soc. Proc., 1897.

reduced by the Callendar and Dickson methods. The table [here omitted] gives the results for seven thermometers, viz., two of platinum, one of gold, silver, copper, and iron, and one of platinum-rhodium alloy. Of these the lowest boiling point for hydrogen was given by the gold thermometer. Next to it came one of the platinum thermometers, and then silver, while copper and the iron differ from the gold value by 26 and 32 degrees respectively. The gold thermometer would make the boiling point $23^{\circ}\cdot 5$ instead of the $20^{\circ}\cdot 5$ given by the gas thermometer. Then the reduction of temperature under exhaustion amounts to only 1° instead of 4° as given by the gas thermometer. The extraordinary reduction in resistance of some of the metals at the boiling point of hydrogen is very remarkable. Thus copper has only $1/105$ th, gold $1/30$ th, platinum $1/35$ th to $1/17$ th, silver $1/24$ th the resistance at melting ice, whereas iron is only reduced to $1/8$ th part of the same initial resistance. The real law correlating electric resistance and temperature within the limits we are considering is unknown, and no thermometer of this kind can be relied on for giving accurate temperatures up to and below the boiling point of hydrogen. The curves are discussed in the paper, and I am indebted to Mr. J. H. D. Dickinson and Mr. J. E. Petavel for help in this part of the work.

Helium separated from the gas of the King's Well, Bath, and purified by passing through a U-tube immersed in liquid hydrogen, was filled directly into the ordinary form of Cailletet gas receiver used with his apparatus, and subjected to a pressure of 80 atmospheres, while a portion of the narrow part of the glass tube was immersed in liquid hydrogen. On sudden expansion from this pressure to atmospheric pressure a mist from the production of some solid body was clearly visible. After several compressions and expansions, the end of the tube contained a small amount of a solid body that passed directly into gas when the liquid hydrogen was removed and the tube kept in the vapor of hydrogen above the liquid. On lowering the temperature of the liquid hydrogen by exhaustion to its melting point, which is about 16° absolute, and repeating the expansions on the gas from which the solid had separated by the previous expansions at the boiling point or $20^{\circ}\cdot 5$, *no mist was seen*. From this it appears the mist was caused by some other material than helium, in all probability neon, and when the latter is removed no mist is seen, when the gas is expanded from 80 to 100 atmospheres, even although the tube is surrounded with solid hydrogen. From experiments made on hydrogen that had been similarly purified like the helium and used in the same apparatus, it appears a mist can be seen in hydrogen (under the same conditions of expansion as applied to the helium sample of gas) when the initial

temperature of the expanding gas was twice the critical temperature, but it was not visible when the initial temperature was about two and a-half times the critical temperature. This experience applied to interpret the helium experiments, would make the critical temperature of the gas under 9° absolute.

Olszewski in his experiments expanded helium from about seven times the critical temperature under a pressure of 125 atmospheres. If the temperature is calculated from the adiabatic expansion starting at 21° absolute, an effective expansion of only 20 to 1 would reach $6^{\circ}\cdot3$, and 10 to 1 of $8^{\circ}\cdot3$. It is now safe to say, helium has been really cooled to 9° or 10° absolute without any appearance of liquefaction. There is one point, however, that must be considered, and that is the small refractivity of helium as compared to hydrogen, which, as Lord Rayleigh has shown, is not more than one-fourth the latter gas. Now as the liquid refractivities are substantially in the same ratio as the gaseous refractivities in the case of hydrogen and oxygen, and the refractive index of liquid hydrogen is about 1.12, then the value for liquid helium should be about 1.03, both taken at their respective boiling points. In other words, liquid helium at its boiling point would have a refractive index of about the same value as liquid hydrogen at its critical point, and as a consequence, small drops of liquid helium forming in the gas near its critical point would be far more difficult to see than in the case of hydrogen similarly situated.

The hope of being able to liquefy helium, which would appear to have a boiling point of about 5° absolute, or one-fourth that of liquid hydrogen, is dependent on subjecting helium to the same process that succeeds with hydrogen; only instead of using liquid air under exhaustion as the primary cooling agent, liquid hydrogen under exhaustion must be employed, and the resulting liquid collected in vacuum vessels surrounded with liquid hydrogen. The following table embodies the results of experience and theory:—

Initial temperature.	Initial temperature.	Critical temperature.	Boiling points.
Liquid helium?-----	$5^{\circ}?$	$2^{\circ}?$	$1^{\circ}?$
Solid hydrogen-----	15	6	4
Liquid "-----	20	8	5 (He?)
Exhausted liquid air-----	75	30	20 (H)
52° C.-----	325	130	86 (Air)
Low Red Heat-----	750	304	195 (CO ₂)

The first column gives the initial temperature before continuous expansion through a generator, the second the critical point of the gas that can be liquefied under such conditions, and the third the boiling point of the resulting liquid. It will

be seen that by the use of liquid or solid hydrogen as a cooling agent we ought to be able to liquefy a body having a critical point of about 6° to 8° absolute and boiling point of about 4° or 5° absolute. Then, if liquid helium could be produced with the probable boiling point of 5° absolute, this substance would not enable us to reach the zero of temperature; another gas must be found that is as much more volatile than helium as it is than hydrogen in order to reach within 1° of the zero of temperature. If the helium group comprises a substance having the atomic weight 2, or half that of helium, such a gas would bring us nearer the desired goal. In the meantime the production of liquid helium is a difficult and expensive enough problem to long occupy the scientific world.

A number of miscellaneous observations have been made in the course of this inquiry, among which the following may be mentioned. Thus the great increase of phosphorescence in the case of organic bodies cooled to the boiling point of hydrogen under light stimulation is very marked, when compared with the same effects brought about by the use of liquid air. A body like sulphide of zinc cooled to 21° absolute and exposed to light shows brilliant phosphorescence on the temperature being allowed to rise. Bodies like radium that exhibit self-luminosity in the dark, cooled in liquid hydrogen maintain their luminosity unimpaired. Photographic action is still active although it is reduced to about half the intensity it bears at the temperature of liquid air. Some crystals when placed in liquid hydrogen become for a time self-luminous, on account of the high electric stimulation brought about by the cooling causing actual electric discharges between the crystal molecules. This is very marked with some platino-cyanides and nitrate of uranium. Even cooling such crystals to the temperature of liquid air is sufficient to develop marked electrical and luminous effects. Considering that both liquid hydrogen and air are highly insulating liquids, the fact of electric discharges taking place under such conditions proves that the electrical potential generated by the cooling must be very high. When the cooled crystal is taken out of either liquid and allowed to increase in temperature, the luminosity and electric discharges take place again during the return to the normal temperature. A crystal of nitrate of uranium gets so highly charged electrically that, although its density is 2.8 and that of liquid air about 1, it refuses to sink, sticking to the side of the vacuum vessel and requiring a marked pull on a silk thread, to which it is attached, to displace it. Such a crystal rapidly removes cloudiness from liquid air by attracting suspended particles to its surface. The study of pyro-electricity at low temperatures will solve some very important problems.