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Determination of the Critical and the Boiling Temperature of Hydrogen. *By* Dr. K. OLSZEWSKI, *Professor of Chemistry in the University of Cracow*.*

IN one of my previous papers† I have described a new method of determining the critical pressure of gases, which may be called the "expansion method," depending on the fact that a gas under high pressure and at a temperature not much higher than its critical temperature, assumes for a moment the liquid state when the pressure is slowly diminished, this being manifested by the turbid appearance of the gas always produced when the pressure is lowered to the critical pressure of the gas experimented with. By means of this method I thus showed that the previously unknown critical pressure of hydrogen lies at 20 atm. In order to verify this method I tested it on two other gases, viz. on ethylene and oxygen, the critical pressures of which were accurately known. I also mentioned that, until we know of other cooling agents able to produce still lower temperatures than is possible by means of liquid oxygen or air, the expansion method will be the only one which allows us to determine not only the critical pressure but also the critical temperature of hydrogen. For if we could succeed by means of a very sensitive apparatus in determining the temperature of hydrogen at the moment of its expansion to the critical pressure, at which the ebullition appears, this would doubtless be the critical temperature of hydrogen.

On again undertaking my researches, begun in 1891, I proposed to measure the temperature at the moment of the expansion of hydrogen by means of a thermo-electric junction, composed of very thin copper and German-silver wires. But several experiments performed in that direction soon proved that a thermo-electric junction is not suitable for such experiments, for the following reasons :—First, a junction composed of two wires soldered together can never be thin enough to assume instantaneously the temperature of the surrounding gas. Secondly, at very low temperatures the junction rapidly loses its sensibility, so that the deflexion of the galvanometer cannot serve to measure the temperature in agreement with the hydrogen thermometer. Then the measuring of low temperatures by means of a thermo-electric junction is possible

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† Rozprawy (Transactions) of the Cracow Academy [2] iii. p. 385 (1891); also Phil. Mag. [5] xxxix. p. 199 (1895).

only between those limits in which it has been compared with the hydrogen thermometer ; every extrapolation would lead to quite false results.

After failing in my experiments with the thermo-electric junction, I resolved to measure the critical temperature of hydrogen by means of a platinum thermometer based on the variation of the resistance of a very thin platinum wire with the temperature. This method for measuring very low temperatures was proposed by Messrs. Cailletet and Collardeau*, afterwards also by Dr. Guillaume †, but practically it was used for the first time by Prof. Witkowski ‡. His researches proved that the platinum thermometer is, after the hydrogen thermometer, the most suitable for measuring low temperatures. It is true that it demands an accurate comparison with the hydrogen thermometer, because the variation of the electrical resistance of platinum is not directly proportional to the variation of the temperature ; but between those limits in which it was compared with the hydrogen thermometer it may be used to determine low temperatures very rapidly and accurately. And considering that the curve which represents the relation between the temperatures measured with hydrogen and the electrical resistance of platinum is very nearly a straight line, we may draw the conclusion that by measuring very low temperatures by means of a platinum resistance-thermometer we may venture on an extrapolation to a moderate extent, and that the error which results from the imperfect agreement of the variation of the resistance to the variation of the temperature cannot surpass 0°·5 to 1°.

The platinum thermometer of such a form as given by Prof. Witkowski is suitable for many practical purposes, but it does not follow variations of temperature with such a degree of quickness as is indispensable for the experiments I had to perform. The reason of the insufficient rapidity of Prof. Witkowski's thermometer is the not very thin platinum wire (0·06 millim. diameter), which was insulated with silk, and hermetically enclosed between two concentric copper tubes made of very thin copper foil.

To give my thermometer the greatest possible sensitiveness I endeavoured to remove all that could have any contrary influence upon it. So, for instance, I used a much thinner wire of chemically pure platinum, whose diameter was only

* *Journal de Physique*, 1888.

† *Archives d. Sc. phys. et natur. Genève*; also *L' Industrie électrique*, i. p. 78.

‡ Rozprawy (Transactions) of the Cracow Academy [2] iii. p. 380; Bull. Intern. of the Cracow Academy, 1891.

0·025 millim., and which was not insulated, and in consequence was able instantly to assume the temperature of the surrounding gas. The wire was wound in a spiral on a very delicate frame, made of ebonite or of very thin mica sheets, in such a manner that each single turn of the wire was 1 or 0·5 millim. distant from its neighbours and did not touch them anywhere. Nor was the wire coil enclosed in a copper tube, but it was in direct connexion with the surrounding hydrogen, and thus the rapidity of registration of the thermometer became considerably increased thereby.

The construction of the apparatus used to determine the critical temperature of hydrogen was on the whole the same as was used to determine the critical pressure of this gas, as described in the Philosophical Magazine (*l. c.*). I will therefore describe only those parts of the apparatus which were altered for these experiments.

So far as it was required to determine the critical pressure of hydrogen by means of an expansion method, we could not help using a glass vessel in which the cooled hydrogen was submitted to expansion from a high initial pressure; for these experiments consisted in the observation of the pressure at the moment of the ebullition of the hydrogen, which could only be done in a transparent vessel. But after the critical pressure of hydrogen had been determined, a metal vessel could be substituted for the glass one. This change was advantageous for several reasons. It was possible to perform the experiments very quietly without any fear of an explosion, and without using masks or taking other precautions. The use of a metal vessel instead of a glass one allowed me to employ larger dimensions and to produce expansions from much higher initial pressures, and all this had a very great influence on the efficacy of the expansion and the precision of the measurement of the temperatures at the moment it took place.

The section of the apparatus serving to determine the temperature of the hydrogen during its expansion is represented in the subjoined diagram (fig. 1). In the steel vessel *a*, tested for a pressure of 220 atm., is placed a frame, *b*, of ebonite or mica with the platinum wire wound round it. Fig. 2 represents its vertical projection. One of the ends of the platinum wire is soldered to the tube *c* passing through the cover of the vessel *a*, and provided above with a binding-screw *d′*; the other is soldered to the insulated copper wire *e* which passes through the tube *c*, in which it is closely cemented, and also provided with a binding-screw *d*. In the course of my experiments I used different frames, of various

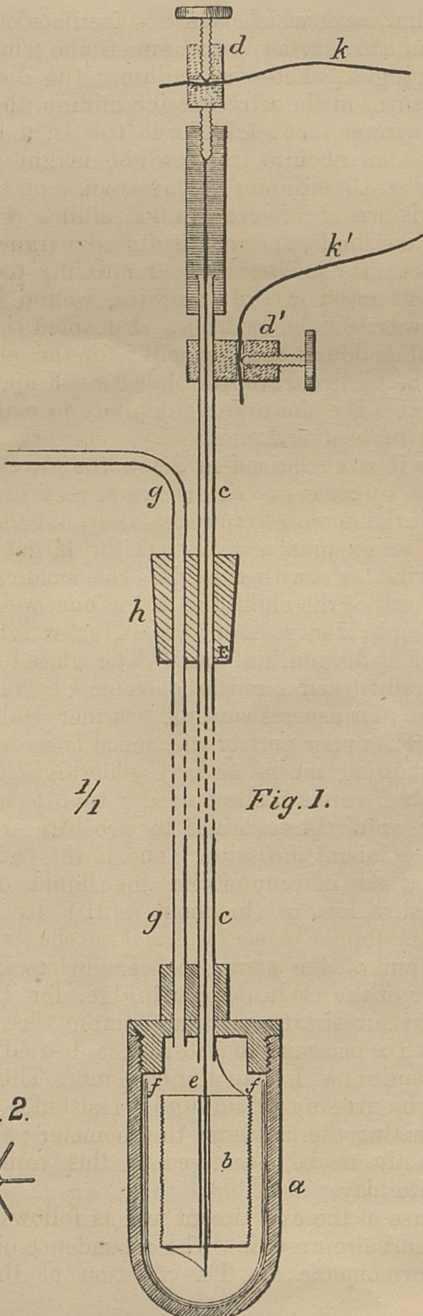
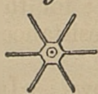


Fig. 1.

Fig. 2.



dimensions, sometimes of ebonite, sometimes of mica. In the first experiments I used an ebonite frame whose height was 20 millim. and diameter 12 millim.; the distance between the single turns of the wire was 0·5 millim., the resistance of the whole wire was 241·4 ohms at 0°. In a further experiment I used an ebonite frame whose height was 11 millim. and diameter 10 millim.; the resistance of the wire, which was wound also at intervals of 0·5 millim., was 117·5 ohms at 0°. In the final experiments I used a frame made of thin mica sheets: its height was 20 millim., the diameter 11 millim.; the resistance of the wire, wound in intervals of 1 millim., was 104·9 ohms at 0°. I devoted the greatest care to the construction of these frames; for the precise determination of the temperatures depended much upon their careful construction. I endeavoured therefore to make them of bad conductors of heat and electricity, and very light and with very thin wings at the edges where the wire touched them, so that the surfaces of contact were very small. The construction of the ebonite frames is easier, but those of mica are considerably less in mass; so that the larger ebonite frame weighed 0·679 gr. with the wire, the smaller ebonite with the wire 0·218 gr., whilst the mica one weighed with the wire 0·177 gr.; the wire of the latter weighed 0·011 gr., and was about 595 millim. long. The glass tube *f* with very thin walls which surrounds the frame *b* served to insulate it during the expansion from the warmer walls of the steel vessel *a*. The upper part of this vessel is screwed into it, and a close adhesion is produced by soldering it by means of an easily fusible bismuth alloy. The tube *g* serves to admit hydrogen, which is contained in a 3-litre iron flask under a pressure of about 170 atm. The lower part of the apparatus described is plunged in the liquid oxygen, whose temperature is lowered to about $-210°$ by pumping; the indiarubber stopper *h* serves to close the whole apparatus whilst the pumping is going on. The wires *k k'* connect the apparatus with a Wheatstone bridge, for the purpose of measuring the resistance of the platinum wire wound on the frame *b*. To measure the resistance I used a very feeble current from one Leclanché element. This current was weakened by passing it through a resistance of 1000 ohms, to avoid heating the platinum thermometer; for the heating was distinctly to be perceived if this resistance was not brought into play.

The course of the experiment was as follows:—In order to draw the curve representing the dependence of the resistance of the thermometer on the variation of the temperature measured with the hydrogen thermometer, I successively plunged the apparatus into melting ice, into a mixture of solid carbonic acid and ether, and into liquid oxygen boiling under atmospheric pressure and at a diminished pressure of 15 millim.; and I thus determined the resistances of the platinum thermometer at these low temperatures which correspond to 0°, −78°·2, −182°·5, and −208°·5 respectively, according to the hydrogen thermometer. It is to be remarked that the temperature of the carbonic acid mixture (−78°·2) is constant only when the carbon dioxide is in excess, and when it has the consistence of butter: as soon as the ether begins to appear separately at the surface, the temperature gradually rises.

The variations of all the three platinum thermometers I used were quite proportional, and, calculated for 1000 ohms of resistance at 0°, were as follows:—

Temperature according to the Hydrogen Thermometer.	Resistance of the Platinum Thermometer.
0°	1000 ohms.
− 78°·2	800 „
−182°·5	523 „
−208°·5	453 „

Thus for each 1° of the hydrogen thermometer between the limits

from	0°	to	− 78°·2	we have a fall of	2·557	ohms.
„	− 78°·2	„	−182°·5	„ „	2·655	„
„	−182°·5	„	−208°·5	„ „	2·692	„

This last number, viz. 2·692 ohms = 1°, I used for the extrapolation in order to measure temperatures lower than −208°·5, at which the platinum temperature could not be compared with that of hydrogen. Assuming that the variation of the resistances is directly proportional to the variation of the temperatures below −208°·5, I committed an apparent error, which, nevertheless, cannot be great on account of the feeble curvature of the line of resistances; for the temperatures extrapolated were not far distant from −208°·5.

To determine the resistance of the platinum thermometer at the moment of the expansion of hydrogen from a high pressure, I brought into the steel vessel *a*, cooled by means of liquid oxygen (at 15 millim. pressure), hydrogen under a pressure of 120 to 160 atm.; in the resistance-box I diminished the resistances, by which means the equilibrium was destroyed, and the galvanometer marked a considerable deflexion.

When the temperature of the hydrogen in the steel vessel became equal to the temperature of the surrounding oxygen, I made a slow expansion of the hydrogen to its critical pressure (20 atm.), if I wished to measure its critical temperature, or to the atmospheric pressure, if I wished to determine its boiling-point. As the cooling of the platinum wire during the expansion continued, the galvanometer returned to the zero-point, *if* the resistance in the resistance-box was chosen so as to be equal to the resistance of the platinum thermometer during the expansion. If in the first experiment the galvanometer did not return precisely to the zero point, I varied the resistances in the resistance-box, and repeated the experiment till that return took place. I thus performed six series of experiments: each of them was composed of about twenty determinations of the critical and the boiling temperature of hydrogen.

As already mentioned, I used in these experiments three platinum thermometers of different dimensions; as cooling agents I employed liquid oxygen boiling under a pressure of 18 to 12 millim.; in one series of experiments I used liquid air, boiling under equally low pressure. The results I obtained were always the same, and relatively very much in agreement with one another, if we consider the great difficulty in performing such experiments. The mean numbers, calculated from many experiments, with reference to 1000 ohms at 0°, were as follows:—

Expansion of Hydrogen from a high pressure to	Resistance of the Platinum Thermometer.	Temperature Extrapolated.
20 atm. (critical pressure)	383 ohms.	−234°·5 (critical temperature)
10 ,,	369 ,,	−239°·7
1 ,, (atmospheric press.)	359 ,,	−243°·5 (boiling temperature)

On the basis of these numbers we can consider −234°·5 as the *critical temperature*, and −243°·5 as the *boiling-point* of hydrogen.

In a preliminary note, published in 'Nature'*, I gave −233° as the critical temperature, and −243° as the boiling-point of this gas. These numbers do not differ much from

* 'Nature,' No. 1325, March 21.

those given now, and were based upon many careful experiments. Considering that the temperatures extrapolated must have been determined a little too low, for the reasons I have stated above, the numbers previously communicated may even be nearer the true data.

I showed above how the expansion method enables us to determine the dependence of the temperature upon the pressure of the gas liquefied, even though the cooling agents do not allow us to reach the critical temperature of the gas experimented with. It would be possible to make the following objections. First, we might ask how it is possible to know whether the gas, expanded from a temperature higher than the critical temperature, to a pressure of 20 atmospheres or of 1 atm., really assumes a temperature equal to the temperature of the liquefied gas, under one or other of these pressures. And then, if this were granted, whether the platinum thermometer described is rapid enough in its indications to assume and to mark the temperature of the surrounding gas at the moment of the expansion.

To ascertain whether these objections had any real foundation, I have done just what I did for the determination of the critical pressure of hydrogen, viz., I performed a series of analogous experiments with oxygen, whose critical and boiling points, and vapour-pressures at several different pressures I have determined in a former paper *, using the hydrogen thermometer. The experiments were performed in a similar manner, with this difference, that for the iron flask containing hydrogen under 170 atm. I substituted another flask, containing oxygen under 110 atm.; to cool the steel vessel containing the platinum thermometer I used liquid ethylene, boiling under atmospheric pressure; then I cooled the oxygen, which was under a pressure of 100 to 110 atm., to a temperature which was about 16° higher than its critical temperature, and expanded it to 50·8 atm. (critical pressure), to 32·6 atm., to 19 atm., to 10·2 atm., and to 1 atm. The measurement of the resistances of the platinum thermometer was done more quickly in these experiments than in those with hydrogen; for, knowing from my former experiments the relation between the temperature and the pressure of liquefied oxygen, I was enabled to determine beforehand with very near approximation the resistances which ought to be inserted in the resistance-box.

* Rozprawy (Transactions) of the Cracow Acad. [1] xiii. p. 27; also *Comptes Rendus*, c. p. 350 (1885).

The results of this experiment are contained in the following table :—

Pressure of the Oxygen.	Temperature of Liquid Oxygen determined by means of a Hydrogen Thermometer.	Temperature of Liquid Oxygen determined by means of the Expansion Method.
50·8 atm. (crit. press.)	−118°·8 (crit. temp.)	from −118° to −119°·2 (crit. temp.)
32·6 „	−130°·3	−130°
19·0 „	......	−140°·5
10·2 „	−151°·6	−152°
1·0 „	from −181°·4 to −182°·7 (boiling temp.)	from −181°·3 to −182°·5 (boiling temp.)

This hardly expected agreement of the results obtained by means of both methods shows that the objections we have stated above are not justified, and that the expansion method is quite suitable for determining the critical and the boiling temperatures of gases. The agreement of these results was doubtless also strengthened by the circumstance that the temperatures of oxygen had not been extrapolated, but were calculated by interpolation. The initial temperature of oxygen was, it is true, only 16° higher than its critical temperature, while the initial temperature of hydrogen was about 26° above its critical point; but I endeavoured to compensate the untoward influence of that circumstance by using a much higher pressure, surpassing by 50 to 60 atm. the initial pressure used in the experiments with oxygen.

In conclusion, I must mention that my colleague Prof. L. Natanson has shown that the expansion method which I have used and described here can be justified theoretically on the basis of thermodynamic considerations*. Shortly before I performed these experiments, Prof. Natanson also calculated and published the probable critical and boiling temperatures of hydrogen† on the basis of the law of corresponding temperatures, and the numbers given by him are sufficiently in agreement with those experimentally found by myself.

* *Bullet. Intern. de l'Acad. de Crac.* April 1895, p. 130.
† *Ibidem,* March 1895, p. 93.