

ART. XXIII.—*The Boiling Point of Liquid Hydrogen, determined by Hydrogen and Helium Gas Thermometers*;* by JAMES DEWAR, M.A., LL.D., Professor of Chemistry at the Royal Institution.

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IN a former paper† it was shown that a platinum-resistance thermometer gave for the boiling point of hydrogen $-238^{\circ}\cdot4$ C., or $34^{\circ}\cdot6$ absolute. As this value depended on an empirical law correlating temperature and resistance which might break down at such an exceptional temperature, and was in any case deduced by a large extrapolation, it became necessary to have recourse to the gas thermometer.

In the present investigation the advantage claimed for the constant-pressure gas thermometer over the constant-volume thermometer is absent. The effect of high temperature combined with large increase of pressure does not occur in these experiments, where only very low temperatures and a maximum range of pressure of less than one atmosphere were encountered. At the same time, before dispensing with the effect of pressure upon the capacity of the reservoir of the thermometer, it was carefully estimated and found that it could not affect the volume of the reservoir by as much as $1/60,000$ th part. This being determined a particular advantage results from the use of the constant-volume form, because in its case it is unnecessary to know the actual volume of the reservoir, and of the "outside" space. It is only necessary to know the ratio of these two volumes, and as this ratio appears only in the small terms of the calculation it is not a serious factor in the estimation of such low temperatures.

Two constant-volume thermometers (called No. I and No. II) were employed, in each of which the volume of the reservoir was about 40 c.c., and the ratio of the outside space to the volume of the reservoir was $1/50$ and $1/115$ respectively. A figure of the apparatus is shown in fig. 1 (p. 293), where A is the thermometric bulb covered with a vacuum vessel to hold the liquid hydrogen, and be exhausted when necessary; B is the manometric arrangement for adjusting the mercury at C to constant volume, and D is the barometer. The readings were made on a fixed scale by means of a telescope with cross wires and lever attached. A similar telescope was permanently fixed on the mark to which the volume had to be adjusted. It was found convenient to use both telescopes on the same massive

* From an advance proof sent by the author

† On the Boiling Point of Liquid Hydrogen under Reduced Pressure, Roy. Soc. Proc., 1898.

stand and to read the barometer placed alongside simultaneously.

The formula of reduction used was that given by Chappuis in the *Travaux et Mémoires du Bureau International des Poids et Mesures*, vol. vi, p. 53, namely,

$$\left(V_0 + \frac{v}{1+at}\right)H_0 = \left(\frac{V_0(1+\delta T) + \beta h}{1+\alpha T} + \frac{v}{1+at}\right)(H_0 + h) \quad (1)$$

where V_0 is volume of reservoir at 0°C .

T , temperature of reservoir, measured from 0°C .

v , volume of "outside" space at the temperature of the room.

t , temperature of the room.

α , coefficient of expansion of the thermometric gas.

β , coefficient of alteration of volume of reservoir, due to change of pressure.

δ , coefficient of expansion of substance of reservoir.

H_0 , initial pressure (in these experiments always reduced to 0°C).

$H_0 + h$, pressure at temperature T , after all corrections have been made.

On putting $\beta = 0$ as already explained, equation (1), by algebraic transformation and without any approximation, was altered into the form.

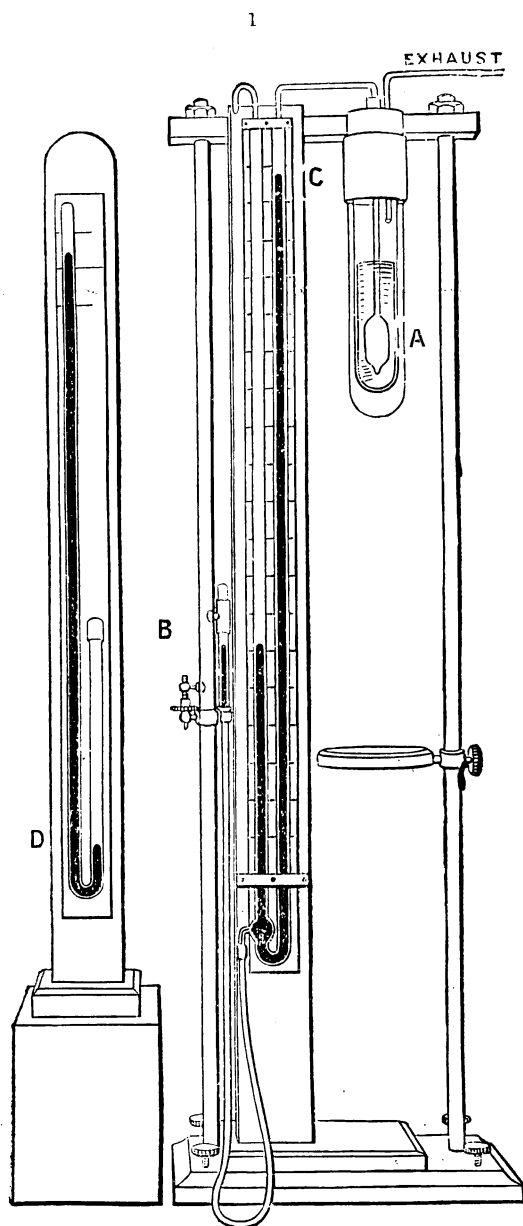
$$\text{Where} \quad T = T_1 \frac{273+t+x273}{273+t-xT_1}, \text{ (say) } = T_1\theta \quad (2)$$

$$T_1 = \frac{P-P_0}{\alpha P_0 - \delta P} \quad (3)$$

in which P_0 and P replace H_0 and $H_0 + h$ and $x = \frac{v}{V_0(1+at)}$.

The gases used as thermometric substances were hydrogen, oxygen, helium, and carbonic acid. The values of α adopted in equation (3) were taken from Chappuis' memoir, and were 0.00366254 for the first three and 0.00371634 for carbonic acid. The reciprocals of these coefficients are 273.035 and 269.083. The number "273" which appears in θ is so nearly equal to the reciprocal of the former value for α that it was allowed to remain for the first three gases; but in dealing with carbonic acid it was replaced by 269.083.

In these experiments T_1 is always negative, and numerically less than 273, so that the value of θ is always greater than unity; nevertheless it differs from it but slightly, its value being unity when $T_1 = -273^\circ \text{C}$., and rising to 1.02 when $T_1 = 0^\circ \text{C}$. in the case of thermometer No. 1, where $x = 1/50$. It may be noted that when δ is neglected, T_1 is the usual value



given by Boyle's law; there is a convenience, therefore, in this form of Chappuis' formula for approximation, because T_1 can quickly be calculated, and the correcting factor θ can be applied later if desired.

In the first experiment (No. 1 of subjoined Table I) thermometer No. 1 was filled with electrolytic hydrogen. The initial pressure, (the pressure at 0°C.) was almost three-eighths of an atmosphere, and was taken low in order to obviate any complication from condensation on the walls of the reservoir. Two other possible causes might abnormally reduce the pressure at very low temperatures; these were polymerisation and the presence as impurity of small quantities of gases liquefying above the boiling point of hydrogen. The measurement of the density of the gas at its boiling point showed that there was no polymerisation, and further proof of this was evident in the constancy of the value of the boiling point when different initial pressures were taken. To guard against the presence of gases with a higher boiling point than hydrogen, the electrolytic hydrogen was allowed to pass continuously for eighteen hours through the thermometric bulb before it was sealed off. It was further calculated that an impurity of oxygen necessary to reduce the boiling point of hydrogen by a degree would amount to 3 per cent, a quantity too large to escape detection. This experiment gave the boiling point of oxygen as $-182^\circ.2$, and that of hydrogen as $-253^\circ.0$.

In the second experiment (No. 2) a new thermometer, No. II, was constructed with a much smaller value of x , and as a further protection against the presence of impurities, palladium-hydrogen was employed as the source of the gas. A rod of palladium, weighing about 120 grams, kindly placed at my disposal by Mr. George Matthey, F.R.S., was charged with hydrogen in the manner described in my paper "On the Absorption of Hydrogen by Palladium at High Temperatures and Pressures,"* and subsequently used as the source of supply to fill the thermometer. The initial pressure was slightly less than that in the first experiment; the corresponding results were $-182^\circ.67$ and $-253^\circ.37$.†

The new thermometer was filled afresh (No. 4) with palladium-hydrogen at an initial pressure rather less than one atmosphere, and gave for the boiling point of hydrogen the temperature $-252^\circ.8$. This result is a confirmation of the absence of polymerisation.

The next step was to compare these results with the results of similar experiments made upon another gas whose boiling point fell within the range of easily determined temperatures;

* Proc. Chem. Soc., 1897.

† This thermometer gave $99^\circ.7$ for the boiling point of water.

and as a further precaution the gas used in the thermometer was the vapor rising from the liquefied gas whose boiling point was to be determined. The gas first selected was oxygen (No. 5), and as an additional condition to be noted, the initial pressure was made slightly more than an atmosphere, so that it would be in a Van der Waal's "corresponding" state with the hydrogen in the first two experiments, namely, the initial pressure in each case was about $1/50$ of the critical pressure. The critical pressure of oxygen was taken about 51 atmospheres, and that of the hydrogen about 18 atmospheres. There are good reasons for believing that the critical pressure of hydrogen is more likely to be about 11 or 12 atmospheres. In the event of the lower value being eventually found the more correct, the effect as between the oxygen thermometer and the hydrogen thermometer will be to make the boiling point of hydrogen a little too high. The result obtained from this experiment was to place the boiling point of oxygen at $-182^{\circ}29$, thus corroborating in a satisfactory manner the reliability of the method of determining the boiling point of hydrogen.

The question still remained, how far is a gas thermometer to be trusted at temperatures in the neighborhood of the boiling point of the gas with which it is filled? To answer this question the oxygen thermometer was used to determine the boiling point of liquid air (No. 7) in which a gold-resistance thermometer was simultaneously immersed. The gold thermometer had been previously tested and found to give correct indications of temperature down to temperatures not only well below the point in question, but lower than those obtainable by any other metal thermometer. In the result the oxygen thermometer gave $-189^{\circ}61$, and the gold thermometer $-189^{\circ}68$, as the temperature of that particular sample of air boiling at atmospheric pressure.

For another method of comparison this oxygen thermometer was practically discharged (No. 8) until its initial pressure was nearly the same as that in the first hydrogen thermometers. In this state it gave the boiling point of oxygen as $-182^{\circ}95$, establishing again the reliability of the method.

As an extreme test of the method, I charged the thermometer No. II with carbonic acid (No. 11) at an initial pressure again a little less than one atmosphere, and used it to determine the boiling point of dry CO_2 ; the result was $-78^{\circ}22$, which is the correct value.

Hence it appears that either a simple or a compound gas at an initial pressure somewhat less than one atmosphere may be relied on to determine temperatures down to its own boiling point.

Another thermometric substance at our disposal as suitable for determining the boiling point of hydrogen, as hydrogen had been in determining that of oxygen, is helium. The early experiments of Olszewski and my own later ones showed that pure helium is less condensible than hydrogen, and that the production of liquid or solid products by cooling Bath helium to the temperatures of boiling and solid hydrogen was only partial, and resulted from the presence of other gases undefined at the time the first experiments were made. The mode of separating the helium from the gases given off by the King's Well at Bath is fully described in my paper on "The Liquefaction of Air and the Detection of Impurities."*

If the neon, present as impurity in the Bath helium which was used, should reach its saturation pressure about the boiling point of hydrogen the values given by this thermometer of the boiling point of hydrogen would be too low. In order to avoid this, the crude helium extracted from the Bath gas was passed through a U-tube cooled by liquid hydrogen to condense out the known impurities, oxygen, nitrogen and argon. In my paper "On the Application of Liquid Hydrogen to the production of High Vacua,"† it was shown that at the temperature of boiling hydrogen, oxygen, nitrogen and argon have no measurable tension of vapor, and that the only known gases uncondensed in air after such cooling were hydrogen, helium, and neon. This same neon material occurs in the gas derived from the Bath wells. A sample of helium prepared as above described, which had been passed over red-hot oxide of copper to remove any hydrogen, was found by Lord Rayleigh to have a refractivity of 0.132. The refractivity of Ramsay's pure helium being 0.1238, and that of neon 0.2345, it results that my helium contained some 7.4 per cent of neon, according to the refractivity measurements. This would make the partial tension of the neon in the helium thermometer cooled in the liquid hydrogen to be about 4 mm., and this being taken as the saturation pressure the boiling point of neon is about 34° absolute. The initial pressure (No. 9) was taken rather less than an atmosphere, and the temperature of the boiling point of hydrogen was given by this thermometer as $-252^{\circ}68$. A further observation was taken on another occasion with the same thermometer, and the value was $-252^{\circ}84$. The fact that the boiling point of hydrogen, as determined by the helium thermometer, is in substantial agreement with the results obtained by the use of hydrogen itself is a conclusive proof that no partial condensation of the neon had occurred.

* Chem. Soc. Proc., 1897.

† Roy. Soc. Proc., 1898.

Of the remaining experiments in Table I, (No. 3) was made in order to show the effect of a very small initial pressure, one-sixth of an atmosphere. The results were unsatisfactory, owing to the sticking of the mercury giving uncertain readings. In this case an error in the reading of a low pressure has six times as great an effect as if the initial pressure had been about an atmosphere. If the temperature deduced for the boiling point of oxygen is corrected, and the same factor of correction applied to the observed liquid hydrogen boiling point, then it becomes $-251^{\circ}4$.

It is of particular moment to have some estimate of how far errors in the observed quantities employed in Chappuis' formula affect the final value of T .

In the case of an error in t , on differentiating equation (2) we get

$$dT = T \cdot \frac{-x(273 + T_1)}{(273 + t - xT_1)^2} dt \quad (4)$$

If $x = 1/50$, $t = 13^{\circ}$, $T_1 = -180^{\circ}$; then $dT = 0.00339 dt$, or it would need an alteration of $2\frac{1}{2}^{\circ}$ in t to alter T by 1/100th of a degree at the boiling point of oxygen. In the same circumstances when $T_1 = -250$, $dT = 0.00136 dt$, so that an alteration of between 7° and 8° in the value of t would only affect the boiling point of hydrogen by 1/100th of a degree.

From equation (4) the error in T varies with x very nearly. This for the second thermometer where $x = 1/115$, a variation of t to the extent of 6° , would only affect the boiling point of oxygen by 1/100th of a degree; and it would require an alteration of 17° in t to affect the boiling point of hydrogen to the same extent.

In Table I the values of t enclosed in brackets are assumed values; this investigation shows that no serious error is involved in these assumptions.

In the case of an error in P , a similar process gives

$$dT = \theta \frac{(a - \delta)P}{(aP_0 - \delta P)^2} - \frac{273 + t}{273 + t - xT_1} dP \quad (5)$$

If $x = 1/50$, $t = 13^{\circ}$. $P_0 = 760$ mm.; $T_1 = -180^{\circ}$; $dT = 0.3563 dP$, so that an error of 1 mm. in P would only alter the boiling point of oxygen by a third of a degree. In the same circumstances at -250° , $dT = 0.3516 dP$, which is practically the same result at the boiling point of hydrogen as at that of oxygen.

For the second thermometer these two equations become

$$\begin{aligned} \text{At } -180^{\circ}, dT &= 0.3575 dP. \\ \text{At } -250^{\circ}, dT &= 0.3548 dP. \end{aligned}$$

TABLE I.

Thermometer. $\frac{v_0}{x = \frac{v_0}{V_0}}$	1	2	3	4	5	6	7	8	9	10	11
	No. I. $\frac{1}{30}$	No. II. $\frac{1}{115}$	No. II. $\frac{1}{115}$	No. II. $\frac{1}{115}$	No. I. $\frac{1}{30}$	No. I. $\frac{1}{30}$	No. I. $\frac{1}{30}$	No. I. $\frac{1}{30}$	No. II. $\frac{1}{115}$	No. II. $\frac{1}{115}$	No. II. $\frac{1}{115}$
Substance.	Electrol. Hydrogen.	Palladium Hydrogen.	Palladium Hydrogen.	Palladium Hydrogen.	Oxygen.	Oxygen.	Oxygen.	Oxygen.	Helium (Bath).	Helium (Bath).	Carbonic Acid..
Barometer -----	760·4	764·4	759·5	770·5	772·5	756·0	766·0	753·5	765·0	770·0	759·0
Temperature of Room -----	13°	13°	13°	21°	12°	13° 6	12°	13° 3	15°	15°	13°
Pressures at 0° C. -----	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
B. P. of Carbonic Acid -----	286·6	269·8	127·0	739·0	806·0	806·0	807·0	290·5	728·0	728·0	619·0
" " Oxygen -----	204·3	193·6	91·0	—	—	—	—	—	—	—	441·0
" " Air -----	97·0	90·2	43·0	—	272·5	269·0	—	95·5	—	—	—
" " Hydrogen -----	—	—	—	55·5	—	—	251·0	—	55·0	—	—
" " Hydrogen Solid -----	21·5	19·7	10·7	—	—	—	—	—	—	54·6	—
(30 to 40 mm.) -----	—	14·4	8·2	—	—	—	—	—	—	—	—
Calculated Temperatures.											
B. P. of Carbonic Acid -----	—	77°·95	78°·22	—	—	—	—	—	—	—	—78° 24†
" " Oxygen -----	—182°·20	—182°·67	—181°·52	—	—182°·29	—183°·46	—	—182°·95	—	—	—
" " Air -----	—	—	—	—	—	—	—189°·62	—	—	—	—
" " Hydrogen -----	—253°·03	—253°·37	—250° 81*	—252°·81	—	—	—	—	—252° 68	—252°·84	—
" " Hydrogen Solid -----	—	—258°·66	—255°·67†	—	—	—	—	—	—	—	—
(30 to 40 mm.) -----											

* Corrected for Oxygen error —257°·1.

† Corrected for Oxygen error —251°·8.

No value is attached to second place of decimals.

† Dry Carbonic Acid.

In each of the last four results if $P_0 = \frac{1}{n} \times 760^{\text{mm}}$ the formulæ become respectively

$$\begin{aligned} dT &= n \times 0.3563 \, dP, \text{ and } dT = n \times 0.3516 \, dP, \\ dT &= n \times 0.3575 \, dP, \text{ and } dT = n \times 0.3548 \, dP; \end{aligned}$$

in other words, any error in reading P is magnified in its effect on T , directly in proportion as P_0 is diminished. This affords some explanation of the weakness of the results in Experiment (No. 3).

In like manner, from an error in P_0 , we get

$$dT = - \frac{P}{P_0} \frac{dT}{dP} dP_0. \quad (6)$$

Here if $x = 1/50$, $t = 13^\circ$, $P_0 = 760 \text{ mm.}$, $T_1 = -180^\circ$; $dT = -0.1188 \, dP_0$, or an error of 1 mm. in P_0 would only alter the boiling point of oxygen by a ninth of a degree; but with the same data at -250° , $dT = -0.0264 \, dP_0$, so that the boiling point of hydrogen would only be altered by a tenth of a degree for a change of 4 mm. on an initial pressure of about one atmosphere.

In this case also if $P_0 = \frac{1}{n} \times 760^{\text{mm.}}$ we get similar results to those in the case of P , namely,

For $x = 1/50$, $dT = -n \times 0.1188 \, dP_0$ and $dT = -n \times 0.0264 \, dP_0$.
For $x = 1/115$, $dT = -n \times 0.1192 \, dP_0$ and $dT = -n \times 0.0266 \, dP_0$.

The general results of an error in either P_0 or P is, that the more reliable experiments are those in which the initial pressure is as high as possible. Hence Nos. 4, 9, 10 are in this respect the most reliable for hydrogen. Also it is of much more importance that P should be accurate than that P_0 should be so; in fact, for hydrogen an error in P has 14 times as much effect as the same error in P_0 .

We can verify these results from Table I. In Experiment (No. 2), where $P_0 = \frac{1}{3} \times 760$ nearly, we have two readings—one at the boiling point, the other in solid hydrogen, namely, 19.7 mm. and 14.4 mm., whose difference is 5.3 mm. This corresponds to $dT = 3 \times 0.3516$ (-5.3) degrees, or $5^\circ.59$. The calculated temperatures for these pressures are $-253^\circ.37$ and $-258^\circ.66$, whose difference is $5^\circ.29$, a satisfactory agreement.

If we compare Experiments Nos. 4 and 9, in both of which the same value of α is used, we can pass from the former to the latter by the formula

$$dT = -0.0266 dP_0 + 0.3548 dP,$$

in which $dP_0 = -11$ mm. and $dP_0 = -0.5$ mm. whence $dT = 0.152$; the observed result is $-252^{\circ}.683 + 252^{\circ}.806$ or 0.123 , which is also satisfactory and explains how so great a drop as 11 mm. in P_0 has, nevertheless, so slight an effect on the result.

An alteration in the value of x has but little relative effect on the results. As before we have

$$dT = T_1 \frac{(273+t)(273+T_1)}{(273+t-xT_1)^2} dx \quad (7)$$

If $x = 1/50$, $t = 13^{\circ}$, then

$$\begin{aligned} \text{At } T_1 = -180^{\circ}, \quad dT &= -57.085 \, dx, \\ \text{At } T_1 = -250^{\circ}, \quad dT &= -19.4205 \, dx, \end{aligned}$$

and for the second thermometer ($x = 1/115$) in like circumstances,

$$dT = -57.895 \, dx.$$

and

$$dT = -19.802 \, dx.$$

For instance, if x were altered from $1/50$ to $1/80$ the result would be to raise the boiling point of oxygen by $0^{\circ}.43$ and that of hydrogen by $0^{\circ}.15$.

Finally, the alteration of a for any particular gas being in any case small affects the value of T practically only in its main factor T_1 . To hundredths of a degree, therefore, the change in T is inversely proportional to the change in a , or, in other words, is directly proportional to the corresponding absolute zero.

For instance, in Experiment (No. 11) had we used the same value of a as for hydrogen the boiling point of dry CO_2 would have been $-79^{\circ}.35$.

The following table shows what alterations would be required for each of the thermometers, in the values of t , P , P_0 , and x to alter the boiling point of oxygen or that of hydrogen by $1/10$ or $1/100$ of a degree. The table is calculated for $t=13^{\circ}$; and in the cases of P and P_0 the initial pressure is taken to be about $1/n$ th of an atmosphere.

Thus, for example, if the initial pressure in either thermometer were about half an atmosphere an error of $1/7$ mm. in reading P would alter T by a tenth of a degree.

If we take the average values given by these experiments as being the most probable, then the boiling point of oxygen is $-182^{\circ}.5$ and that of hydrogen is $-252^{\circ}.5$. The temperature found for the boiling point of oxygen agrees with the mean results of Wroblewski, Olszewski, and others. If the boiling point of oxygen is made -182° , which is the highest value it

TABLE II.

	Thermometer No. 1.	Thermometer No. 2.	Alteration of T.
t { at B.P. of O at B.P. of H	$2\frac{1}{2}^{\circ}$ $7\frac{1}{2}^{\circ}$	6° 17°	$\frac{1}{100}^{\circ}$
P { at B.P. of O at B.P. of H	$\frac{0.280}{n}$ mm. $\frac{0.285}{n}$ mm.	$\frac{0.280}{n}$ mm. $\frac{0.282}{n}$ mm.	$\frac{1}{10}^{\circ}$
P_0 { at B.P. of O at B.P. of H	$\frac{0.842}{n}$ mm. $\frac{3.79}{n}$ mm.	$\frac{0.839}{n}$ mm. $\frac{3.76}{n}$ mm.	$\frac{1}{10}^{\circ}$
x { at B.P. of O at B.P. of H	0.88 per cent. 2.57 “	2.00 per cent. 5.81 “	$\frac{1}{100}^{\circ}$

can have then an equal addition to the hydrogen value must follow, making it then -252° or 21° absolute. In a future communication the temperature of solid hydrogen will be discussed.

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