

LIII.—*The Boiling Point of Nitrous Oxide at Atmospheric Pressure, and the Melting Point of Solid Nitrous Oxide.*

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LIQUID nitrous oxide is an admirable substance for producing and maintaining a low temperature. It has the great advantage over solid carbon dioxide, or a mixture of carbon dioxide and ether, of being as transparent as water; and when filtered into a double-walled tube, the space between the walls of which has been exhausted to

a high vacuum, it may be preserved for several hours in the liquid state without serious loss by evaporation.

An investigation recently carried out made it necessary to ascertain accurately its boiling point at atmospheric pressure. The only data on this subject are contained in a paper by Faraday, published in 1845 (*Phil. Trans.*, 172), and one by Wills (*J. Chem. Soc.*, 1874, 27, 21), who gives the boiling point as -92° , and the solidifying point as -99° . Faraday measured the vapour pressures of nitrous oxide at pressures varying from 1 atmosphere to 33.4 atmospheres, by means of an alcohol thermometer. On testing his results, however, by means of the formula $R' = R + c(t' - t)$, where R' is the ratio, between the absolute temperatures of nitrous oxide and some other substance (water for example) of which the vapour pressures are known, at some pressure, the same for both; R , the ratio at some other pressure; c , a constant; and $(t' - t)$, the difference between the absolute temperatures of one of the liquids (e.g., water), the value of c was found to vary within wide limits. As Ramsay and Young have shown that the relation holds with almost absolute accuracy for a great many liquids and solids, including among them dissociable substances, and even such substances as liquid oxygen (*Phil. Mag.*, 1885, 515), it was not to be expected that nitrous oxide should form the only exception to the rule.

It must be remembered that both Faraday and Wills used an alcohol thermometer, of which the scale below 0° was graduated in divisions equal in length to those above 0° ; and that the coefficient of expansion of alcohol is certainly not uniform. Of this, Wills seemed to be aware, as he remarks: "The readings of alcohol thermometers at such low temperatures are, no doubt, somewhat untrustworthy;" hence the necessity of a redetermination.

A thermometer filled with hydrogen, carefully purified and dried, was employed; and readings of pressure were taken at constant volume. But although the stem was of fine capillary tubing, an error is introduced, inasmuch as the stem is not at the same temperature as the bulb; the method of determining the temperature, however, eliminated this source of error.

The plan adopted was to read the position of the mercury in the capillary stem, when the bulb was immersed in water at atmospheric temperature; to raise it to about 100° , by covering it with cotton wool, and exposing it to the steam of boiling water, and to read the increase of pressure of the gas; and then to immerse it in the boiling nitrous oxide, and again to read the pressure, which, of course, is then reduced. Had the stem been at 100° , the pressure would have been higher than that actually read corresponding to the temperature of the steam; and had the stem been at the boiling point of

nitrous oxide, the pressure read would have been lower than that actually read; or in other words, the rise of pressure for the temperature of the steam was not great enough; and the fall of pressure for the temperature of liquid nitrous oxide was not great enough; hence, assuming as accurate the temperature of the steam, that of the nitrous oxide can be calculated with a great approach to accuracy, on the assumption that the coefficient of expansion of hydrogen within these limits of temperature is uniform: an assumption which is exceedingly likely to be true.

The error due to alteration of volume of the bulb by rise or by fall of temperature is also eliminated by this process. For, imagine the volume of the bulb at 100° to be restored to that which it occupied at atmospheric temperature: the pressure would be slightly increased, owing to the contraction of the bulb; and, again, imagine the volume of the bulb at -90° to be restored to its original volume: the expansion would necessitate a slight lowering of pressure to keep volume constant. These corrections have opposite signs, and are proportional to the total differences of temperature between that of the atmosphere and of boiling water, or of boiling nitrous oxide; hence the fall of pressure due to the cooling of the hydrogen can be accurately calculated from the rise of pressure due to its heating.

As this is an important point, and, as we think, indicates a new method of using a hydrogen or air thermometer, we deem it advisable to illustrate it by a numerical example.

Suppose the middle temperature to be 20° , that of steam 100° , and that of boiling nitrous oxide -90° . Let α stand for the coefficient of expansion of hydrogen at 20° ($= 1/293$), and β for the cubical coefficient of expansion of glass, also at 20° supposed to be uniform. Then, as the rise of pressure, due to the expansion of gas from 20° to 100° , is proportional to the increase of temperature, it is proportional to 80α ; and, similarly, the fall of pressure from 20° to -90° is proportional to -110α .

Similarly, the rise of pressure (a minute one) which would be produced by the alteration of the volume of the glass bulb at 100° to its original volume at 20° is proportional to 80β ; and the fall of pressure from 20° to -90° is proportional to -110β .

We therefore get the equation

$$\frac{80\alpha}{-110\alpha} = \frac{80\beta}{-110\beta},$$

or, in words, the alteration of pressure due to expansion and contraction of gas is proportional to the alteration of pressure due to expansion and contraction of glass.

It is obvious that a similar correction might be made for the fact

that the hydrogen in the stem of the thermometer is not heated or cooled; and that such a correction would also be proportional. Hence this method of determining temperature is an absolute one, the accuracy of which is conditioned only by the accuracy of readings of volume and pressure.

The actual measurements are as follow:—

I. *Boiling Point of Nitrous Oxide.*

a. Rise of pressure when bulb was placed in steam	216.0 mm.
Fall of pressure when bulb was placed in liquid	
N ₂ O	277.8 „
Temperature of steam	100.27°
Temperature of atmosphere (bulb in water)....	17.0°
—277.8 × (100.27 — 17)/216 = —107.1; and —107.1 — 17 = —90.1°.	
b. Rise of pressure when bulb was placed in steam	205.9 mm.
Fall of pressure when bulb was placed in liquid	
N ₂ O	282.7 „
Temperature of steam.....	100.0° „
Temperature of atmosphere (bulb in water)....	20.0°
—282.7 × (100 — 20)/205.9 = —109.8; and —109.8 — 20 = —89.8°.	
c. Rise of pressure when bulb was placed in steam	216.8 mm.
Fall of pressure when bulb was placed in liquid	
N ₂ O	278.0 „
Temperature of steam	100.26°
Temperature of atmosphere (bulb in water)....	17.1°
—278 × (100.26 — 17.1)/216.8 = —106.6; and —106.6 — 17.1 = —89.5°.	

The mean result of the three determinations is 89.8°.

It should be observed that it is necessary to keep the nitrous oxide boiling vigorously during the reading of pressure, otherwise the liquid becomes superheated, and the temperature is read too high.

II. *Melting Point of Solid Nitrous Oxide.*

a. Rise of pressure when bulb was placed in steam	259.3 mm.
Fall of pressure when bulb was surrounded with solid N ₂ O	268.2 „
Temperature of air (bulb in melting ice)	0.0°
Temperature of steam	99.13°
—268.2 × 99.13/259.3 = —102.5°.	

b. Rise of pressure when bulb was placed in steam	216·8 mm.
Fall of pressure when bulb was surrounded with solid N ₂ O	310·8 „
Temperature of steam.....	100·26°
Temperature of atmosphere (bulb in water)....	17·1°
$-310·8 \times (100·26 - 17·1)/216·8 = -119·2$; and $-119·2 - 17·1$	
$= -102·1°$.	

The mean result is $-102·3°$.

The solid nitrous oxide was produced by covering the bulb of the hydrogen thermometer with cotton-wool, and dipping it into the liquid. On removing it, and blowing air on the surface, the liquid froze, and temperature fell, pressure falling concurrently. The lowest reading of pressure was taken as equivalent to the melting point of the solid.

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