Physics.— *The ice-point of the Thermometer scale.* (19th communication of results obtained by the aid of the "VAN DER WAALS Fund".) By A. MICHELS and F. COETERIER. (Preliminary communication.) (Communicated by Prof. J. D. VAN DER WAALS.)

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A difficulty arising in connection with the determination of isotherms, was the impossibility of determining the 0° (Celsius) point of the thermometer scale with sufficient reproducibility by means of the methods in ordinary use. A greater constancy than 1/100, corresponding at 0° to a temperature accuracy of 1/27300, could not be obtained with certainty, whilst the volume and pressure measurements were susceptible to a much higher reproducibility. The cause of the inconstancy of the ice point has been traced, and a search made for a further point to serve better as the fixed point of the temperature scale.

One of the chief causes of the irregularity is that the ice point is never in a truly unary system, for even if ice from very pure distilled water is available, dissolved gases would still remain as impurities.

A block of commercial ice usually consists of a transparent mass surrounding an opaque core and this core has much the higher gas content.

Nitrogen and Oxygen are the most likely gases to be present, and the saturation of water by these gases at atmospheric pressure results in the freezing point being lowered by 2.5×10^{-3}. Other gases which are always present in a laboratory atmosphere will also be dissolved. Every mm. of Carbon dioxide, for example, will, when the dissociation of dissolved H_2CO_3 is considered, result in a depression of the freezing point of 0.6×10^{-3}.

The products of the combustion of coal gas will also add to the impurities of the atmosphere and, therefore, of the water from the melting ice.

The handling of ice during crushing and contact with a machine may also lead to the picking up of slight impurities.

The constancy given by the triple point of water has therefore been investigated, as all these difficulties may then be avoided and a clearly defined unary system adopted.

Preliminary determinations.

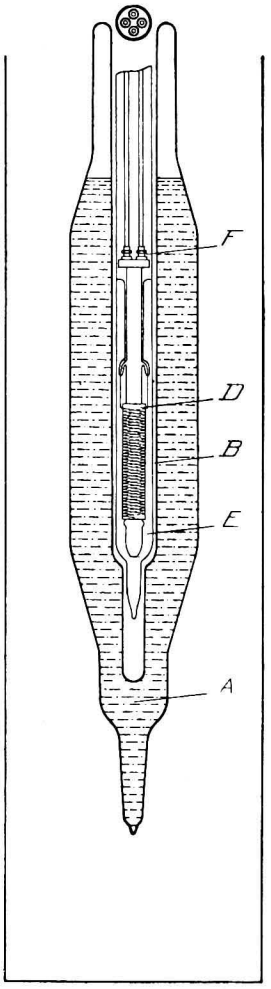
In order to see whether the use of the triple point was practicable, a glass vessel was made in the form of a Dewar-vessel, and the space between the two walls filled with distilled and gas-free water.

The water in the space was supercooled and then crystallised by touching the outside wall with a piece of solid carbon dioxide.

This method of supercooling appeared to possess a great advantage over direct crystallisation. The water was supercooled at every point and, during the crystallisation, the ice needles shot from all sides simultaneously towards the inside of the vessel.

A quantity of mercury was poured into the inner vessel in order to obtain a better temperature exchange, and the bulb of a BECKMANN thermometer was placed in the mercury.

The first experiments gave a temperature variation of only 1/500°. Some of the needles showed that the ice began to melt soon after crystallisation, and the temperature did not remain constant for more than ten minutes.



Further observations.

As the results obtained were favourable, an improved and more definite apparatus was constructed.

A much larger vessel was made, again in the form of a Dewar glass, as shown in the figure (capacity about 1 litre). The space *A* contained gas-free distilled water, and *B* mercury.

The vessel was made large enough to hold a BECKMANN thermometer with the whole length of the Hg thread in the vessel.

The vessel was supercooled by about 4° and, after the water had been crystallised as before, surrounded by a jacket (C) containing crushed ice.

As the temperature between *C* and *A* only differed by 1/100°, the heat exchange between *A* and its surroundings was reduced to a minimum.

It was possible by this means to maintain the temperature in *B* constant for several hours.

Observations with the BECKMANN thermometer divided in hundredths of a degree, and therefore readable to a thousandth, showed no observable variations during the course of one crystallisation and, when the experiment was repeated on different days, the same result was obtained within the accuracy of observation.

Although this accuracy was more than enough for the immediate researches, it appeared advisable to investigate how far the accuracy extended by another method and observations were therefore made with a platinum thermometer.

The platinum thermometer, which was specially made for the purpose, consisted of a platinum wire loosely wound on a porcelain tube D, contained in a sealed glass vessel E, filled with distilled paraffin (Boiling point 210°).

In order to reduce thermal currents, the points F, where the platinum was connected to copper wire, were made so that they were in the constant temperature zone.

The insulation resistance of the platinum thermometer was greater than 10^9 Ohms, and the lag to 1/4000° was two minutes.

The resistance of the platinum thermometer was measured with a potentiometer, and was about 16.3 Ohms at 0°.

The sensitivity of the electrical circuit was so adjusted that a variation of 1.5×10^{-5} Ω gave a deflection of the galvanometer of 0.1 mm on the scale.

A greater accuracy of the electrical measurements could not be obtained.

A series of readings, taken on different days, gave a resistance of

16.28838
39
36
36

The vessel was then opened and refilled with fresh gas-free distilled water.

Two different readings gave 16.28839
38

giving a total mean of $16.28837 \pm 1^5 \times 10^{-5}$,

which is exactly the maximum reproducibility of the electrical measurements, and which corresponds to a constancy of the temperature of within 2.3×10^{-4}°.

The two samples of water used were distilled three times. A good criterion of the purity of the water could be obtained during the measurements from the ease with which the water could be supercooled.

Both the samples of water used remained supercooled despite the reversing of the vessel and the rather violent movement during the removal of the freezing mixture.

The influence of the solubility of silicates from the glass walls on the freezing point still remains to be investigated.

No precautions were taken to choose a special glass, and ordinary laboratory glass was used, the vessel being well steamed out before filling.

The solid residues from the two samples of water used were determined, and the authors are indebted to Prof. J. B. WIBAUT for his kindness in allowing these determinations to be made in his laboratory.

The first sample gave a dry residue of 12.5 and the second of 8.4 milligrams per litre. As the form in which these silicates were present was unknown, it is not possible to say how far the lowering of the freezing point

will be influenced, but, in the most unfavourable case, the lowering of the triple point must be much less than 1/1000°.

Although the water used had remained sealed in glass for one year, it thus appears that the influence of dissolved silica is small.

It will be necessary to repeat the determination with other kinds of glass that have a special resistance to the etching action of water, and with a platinum thermometer of still greater sensitivity.

The influence of the degree of super-cooling on the readings of the thermometer must also be investigated.

An indication that such an influence may exist arose from the fact that a third filling, in which the super cooling did not once go smoothly, gave a temperature difference of 1/1500 degrees. It is not impossible that this result was influenced by a slight impurity.

As a result of the above, it appears desirable to make the triple point of water the fixed point of the temperature scale in place of the icepoint.

In order to obtain an easier connection with the existing scale, it is suggested that *the 0° Celsius point be defined as that point lying 0.007° lower than the triple point of water.*

From the course of the melting point curve of H_2O, this will then be the temperature difference between the freezing and triple points.