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The Density and Coefficient of Cubical Expansion of Ice

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XI. *The Density and Coefficient of Cubical Expansion of Ice.*

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Communicated by Professor J. J. THOMSON, *F.R.S.*

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THERE are perhaps no subjects in the domain of experimental physics which call more urgently for attention, than investigations into the properties of water in its various states of aggregation. And of the various points which still need study, the latent heat of fusion is without doubt the most pressing. The method which promises to yield a reliable result for this determination, requires a knowledge of the density of ice at 0° C.

The Bunsen Ice Calorimeter has, in the hands of DIETERICI and other Continental physicists, recently become an instrument of precision, but the results which this apparatus is capable in itself of yielding, are unavailable to Science owing to the lack of an accurate knowledge of the density and latent heat of ice.

But as GRIFFITHS remarks, "There can be but little doubt that the mass of mercury expelled from a Bunsen Calorimeter by the subtraction of a definite thermal unit, is a quantity that can be and doubtless will be determined with accuracy." (GRIFFITHS, 'Phil. Trans.,' A, vol. 186, 1895, p. 265.) It was with the object of contributing something to the solution of this problem that the investigation to be detailed subsequently was undertaken.

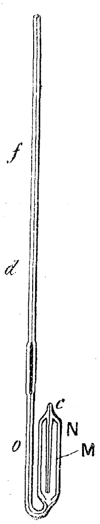
Previous Methods and Results.

The first paper of importance, as regards scientific accuracy, on these subjects was published by BRUNNER in 1845 ('Pogg. Ann.,' vol. 140, p. 113, 1845), but before treating of his paper, we may glance at the state of knowledge on the subject when he attacked it. He was led to take up the research by the fact that PETZHOLDT (PETZHOLDT, 'Beiträge zur Geognosie von Tyrol,' 1843) had announced that ice expanded when its temperature was lowered. PETZHOLDT obtained this result experimentally, and proceeded to found thereon a new theory of glacier action which had the effect of bringing his paper into prominent notice. The idea that ice contracted on warming was an old one, and had been originally mooted by MUSSCHENBROEK, a hundred years previously. (MUSSCHENBROEK, 'Essai de Physique,' Leyden, 1739.) MAIRAN also supported it by experiments published ten years later. (MAIRAN, 'Dissertations sur la Glace,' Paris, 1749.) But HEINRICH in 1807 had obtained a positive coefficient. (HEINRICH, 'Gilbert's Annalen,' vol. 26, p. 228, 1807.) His result, obtained by the direct determination of the change in length of a bar of ice, yields the value ·000024 as the linear coefficient for a degree centigrade. This observer also found the density of ice to be ·905. Thus the subject stood when BRUNNER commenced his experiments.

BRUNNER started experimenting in the direction of preparing air-free ice from boiled distilled water, but failed to obtain it free from air bubbles. Even when he covered the surface of the water with turpentine immediately after boiling, the product had still to be rejected owing to its being full of small cracks; so that he was led to use selected pieces of river ice.

The method consisted in weighing the ice in air, and in either turpentine or petroleum, which latter liquid had the advantages: 1. Of its smaller density; 2. Its freedom from solvent action. He determined the density of the liquid by weighing a piece of glass in it immediately before and after weighing the ice, and he subsequently weighed the same piece of glass in water at different temperatures. He satisfied himself by direct experiment that by determining the temperature of the oil he also obtained the temperature of the ice suspended in it. The whole of the operations were conducted in a laboratory, the temperature of which never rose above freezing point. After making due allowance for the buoyancy of air, the result for the specific gravity of ice at 0° C., referred to water at 0° C., was ·9180, or ·9179 as the density in grammes per cub. centim. The linear coefficient of expansion was ·0000375, which BRUNNER remarks was greater than that previously found for any other solid.

Fig. 1.



The paper of PETZHOLDT also set STRUVE to work about the same time (STRUVE, 'Pogg. Ann.,' vol. 66, p. 298). He obtained the value ·0000531 for the linear coefficient per 0° C., using long bars of artificial ice in his experiments.

MARCHAND ('Journ. f. prakt. Chemie,' vol. 35, p. 254), using a dilatometer of glass containing mercury and the ice to be experimented on, obtained ·0000350 for the linear coefficient, but did not state the kind of ice used.

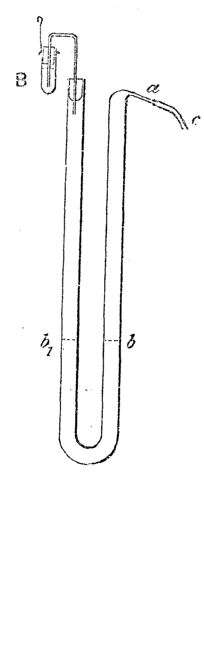
The dilatometric method was also employed in 1852 by PLÜCKER and GEISSLER ('Pogg. Ann.,' vol. 86, p. 265, 1852), who determined the density and dilatation of artificial ice. They used a dilatometer of a remarkably elegant design (see fig. 1). The cylinder, M, of thin glass is open at the bottom, and has a capillary tube, c, inside it. This tube is sealed into the cylinder, M, and also into the outer cylinder, N, at one end. At the other end of the outer cylinder was another capillary tube, and in the preliminary part of the experiment, this tube reached as far as *o* only. The coefficient of expansion of the glass was first determined by preliminary experiments with mercury. To partially fill the inner cylinder with water, a bulb provided with a small opening at the top was sealed on at *c*. This bulb was filled with distilled water, and after this had been boiled for some time the upper orifice ot the bulb was sealed. During this operation the opening at *o* had been closed, but, after cooling, both the upper sealed point in the bulb and *o* were simultaneously opened. Water flowed into M, expressing an equal volume of mercury. The tube at *o* was again closed, and the water in the fine capillary at *c* was displaced by slightly warming the apparatus. This caused the mercury in which the central capillary dipped to rise, and the bulb was then removed by sealing off at *c*. Finally the capillary tube *f d o* was sealed on at *o*, and the position of the end of the column of mercury marked on the tube after the whole apparatus had been reduced to 0° C. On freezing, the water in the inner glass vessel expanded, and breaking the inner cylinder, relieved itself from constraint.

The mean result for the increment in volume of unit of volume of water at 0° C., on changing to ice at 0°, was ·09195, which is equivalent to ·91567 for the density at 0°, while ·0001585 was obtained for the coefficient of cubical expansion.

The next observations with which it is necessary to deal are those of DUFOUR ('Comptes Rendus,' vol. 54, p. 1080). Having previously experimented by finding the density of a mixture of alcohol and water in which ice floated in neutral equilibrium, he published in 1862 an account of experiments in which a mixture of chloroform and petroleum was used in preference to the former liquid, which dissolves ice. By taking the mean of 16 experiments, he obtained ·9178, with a probable error of ·0005, as the specific gravity referred to water at 0° C. He employed the value ·000158 for the coefficient of expansion for reducing his results. The ice used was prepared from water boiled *in vacuo*, and although free from air bubbles was "opaline" in appearance.

BUNSEN's celebrated paper on Calorimetry appeared in 1870 ('Pogg. Ann.,' vol. 141, p. 1, 1870). Amongst other researches included in this memoir is a determination of the density of ice at 0° C., by a dilatometric method which, according to the illustrious author, completely eliminated the errors which had rendered previous estimations uncertain.

Fig. 2.

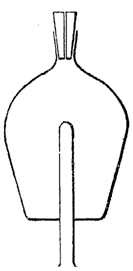


BUNSEN's dilatometer is shown in fig. 2. It consisted of a thick-walled U-tube of hard glass drawn out at *a*, and this was filled with mercury up to the level, b_1 *b*, which was boiled for some time. Boiled water was sucked into the apparatus, and rested on the mercury at *b*. This water was then boiled in the tube for half an hour, the end *a* being, by means of a rubber tube *c*, led under the surface of water, which was also kept boiling. The dilatometer was allowed to cool, while the vessel into which c dipped was kept boiling; the side of the tube $a\,b$ then became completely filled with air-free water, and the point a was then sealed off. By weighing before and after filling with water, the mass of water taken was obtained. The other limb of the U-tube was now filled with mercury, and the water was frozen by subjecting it to cold in such a way that the water froze from above downwards. The ice thus formed was absolutely clear. The cork and capillary tube shown in the figure were then inserted, and the whole apparatus surrounded with dry snow. The mass of the vessel B and its contained mercury was noted. On melting and again reducing to 0°, re-weighing the vessel B provides the other datum requisite to compute the density of ice at 0° C. BUNSEN's mean value was ·91674.

No experiments on these subjects seem to have been published again until quite recent times, when NICHOLS brought out his paper on the density of ice in 1899 ('Physic. Review,' vol. 8, January, 1899). Leaving the theoretical portion of this memoir out of consideration for the present, we find that NICHOLS determined the density of artificial and natural ice by several methods.

Method 1. *Specific Gravity Bottle.*—The apparatus consisted of a specific gravity bottle fitted with a tube (see fig. 3), round which a cylinder of ice was formed. The unfrozen water was shaken out, and the whole again subjected to cold; by weighing in a laboratory, whose temperature was below freezing point, the mass of ice taken was found. The bottle was now filled up with cold mercury, the stopper inserted, and the whole left in an ice bath overnight with the stopper dipping in mercury. Finally, the stopper was dipped into a weighed quantity of mercury, the ice permitted to melt, and the whole apparatus again reduced to 0° C. The loss of weight of the mercury into which the stopper dipped, gave the means of computing the density of the ice mantle at 0° C. free from any error due to deformation of the flask on filling with mercury. The result for the density from a single experiment was ·91619.

Fig. 3.



Method 2. BRUNNER'S *Method.*—NICHOLS employed refined petroleum, and weighed several varieties in it, again working in a laboratory below freezing point. The results were reduced to 0° C., by employing the value ·00015 for the coefficient of cubical expansion. The results obtained were :—

Kind of ice.	Density at 0° C.	Kind of ice.	Density at 0° C.
Artificial	·91603	Natural . . . . . (new pond ice)	·91792
Natural . . . . . (icicles)	·91795	Natural . . . . . (pond ice, 1 year old)	·91632

Method 3. *Determination of the Volume of the Ice by Displacement.*—NICHOLS next attacked the question by the employment of an absolutely original method. An iron box of special construction, having a capacity of about 2 litres, and rectangular in shape, was nearly filled by means of a regular block of new pond ice, and the rest of its interior was filled up with mercury. From the weighings of this mercury and the ice, and a knowledge of the volume of the box, the density of the ice at 0° C. was computed. The ice contained a small quantity of air, the amount of which was separately determined and allowed for. The final value for the density came out at ·91760.

NICHOLS next turned his attention to the determination of the linear coefficient of expansion of ice. No work had been done on the dilatation of ice since 1852. The method employed (' Physic. Review,' vol. 8, p. 184, 1899) was similar to that used by STRUVE in 1845. A bar of commercial artificial ice, which had been manufactured some months previously, was used, and NICHOLS again had the felicity of working in a laboratory which was never warmer than − 3° C. during the work. The readings were obtained by measuring, by means of a dividing engine, the distance between the centres of two tiny drops of mercury resting in depressions in the ice about 40 centims. apart. The range of temperature was from −8° to −12° C. Four sets of readings were taken, with the mean result ·0000540 for the linear coefficient.

NICHOLS's *Theory.*

In order to explain the remarkable discrepancies between the values obtained by previous observers, NICHOLS put forward the theory that in reality there are two kinds of ice which have been under experiment; the density of artificial ice being about ·916, and that of natural ice more than one part in a thousand greater. This immediately throws the subject into a more tangible form, but the serious consequences of such a dual character for ice demand most careful consideration. It seems to me that if there are really two kinds of ice, differing in density so largely, these varieties would also have different latent heats, and, what is perhaps more important still, different melting points.

NICHOLS's theory is, however, supported entirely by his own work, and also by most of the results of previous observers. In this connection it must be pointed out that, according to one of NICHOLS's experiments, natural ice assumes a density approaching to that of artificial ice if the natural ice has been kept some time.

The value obtained for the density by DUFOUR for artificial ice is larger than that of other observers using the same variety. But the method of neutral equilibrium is far inferior in exactitude to the methods employed by PLÜCKER and GEISSLER, BUNSEN, and NICHOLS. Neither must the results of BUNSEN be accepted as being of extraordinary reliability in spite of his assurance that he had eliminated all error. The U-tube dilatometer suffers from the disability that any small difference in the method of holding it may cause considerable change in its voluminal contents. It must also be remembered that the ice in BUNSEN's experiment was probably under considerable pressure, since each new layer as it was formed became the vehicle of transference of heat upwards from the underlying water. Ice is one of the most contractible of solids by fall of temperature, and thus when the whole of the water was frozen, it must have been considerably denser than it would be at 0° C. The sides of the somewhat narrow tube would tend to prevent the ice assuming its proper density as the temperature rose to 0° C. It should be noted that if the mean temperature of BUNSEN's ice column was 4° or 5° below zero, this would suffice for the somewhat high value which he obtained. There is another and more serious objection to BUNSEN's method. Any attempt to get ice exactly at 0° C. by surrounding it with an ice jacket may result either in the resulting temperature being lower than 0° C., through the observer not allowing a sufficiently long time for the equalisation of temperature or, on the other hand, may result in some of the ice melting. In either case the value obtained for the density will be too high. None of these objections apply to PLÜCKER and GEISSLER's work.

BARNES ('Physic. Review,' July, 1901) has recently determined the density of natural ice by weighing selected specimens in water. His results give the same density for old and new ice. The mean value obtained (expressed in grammes per cub. centim.) was ·91649.

Synopsis of Previous Work.

In order to facilitate reference, the results of previous workers have been set out in Table I., which gives the methods adopted, the variety of ice used, and the results obtained by different observers.

In Table II. the results for the two kinds of ice are separately set forth. The work of MARCHAND is omitted altogether from this table, as he did not state what kind of ice he used. The value of the density obtained for old pond ice by NICHOLS is also not included. The mean result for the density of *natural* ice at freezing point is ·9176 gramme per cub. centim., while that of *artificial* ice is ·9165 gramme per cub. centim.

If, however, we neglect DUFOUR's value, we obtain the result ·9162 gramme per cub. centim. for artificial ice.

Only one estimation of the dilatation of natural ice is available. It is ·0001125 for the cubical coefficient of dilatation for 1° C., while three results are available for artificial ice. The mean value is ·000160 for the cubical coefficient of dilatation for 1° C.

Only one direct determination of the cubical expansion of artificial ice is to hand. This was obtained by PLÜCKER and GEISSLER, and is ·0001585 for the cubical coefficient of dilatation for 1° C.

In both Tables I. and II. the cubical coefficient only has been tabulated. In those cases in which the linear coefficient was actually determined, the cubical coefficient

TABLE I.

Date.	Observer.	Method.	Kind of ice.	Density.	Coefficient of cubical expansion.
				(grammes per cub. centim.)	
1845	BRUNNER	Weighing in liquid	Natural	·9179	·0001125
1845	STRUVE	Direct measurement of linear co-efficient	Artificial	—	·0001593
1845	MARCHAND	Dilatometric	?	—	·0001050
1852	PLÜCKER and GEISSLER	Dilatometric	Artificial	·91567	·0001585
1862	DUFOUR	Neutral equilibrium in liquid	Artificial	·9177	—
1870	BUNSEN	Dilatometric	Artificial	·91674	—
1899	NICHOLS	Dilatometric	Artificial	·91619	—
		Weighing in liquid	Artificial	·91603	—
			Natural (icicles)	·91795	—
			Natural (new pond ice)	·91792	—
			Natural (old pond ice)	·91632	—
		Volume by displacement	Natural (new pond ice)	·91760	—
1899	NICHOLS	Direct measurement of linear co-efficient	Artificial	—	·0001620
1901	BARNES	Weighing in water	Natural	·91649	—

TABLE II.

Observer.	Natural.		Artificial.	
	Density.	Co. of Cub. Exp.	Density.	Co. of Cub. Exp.
BRUNNER	·9179	·0001125	—	—
STRUVE	—	—	—	·0001593
PLÜCKER and GEISSLER	—	—	·91567	·0001585
DUFOUR	—	—	·9177	—
BUNSEN	—	—	·91674	—
NICHOLS	—	—	·91619	—
	—	—	·91603	—
	·91795	—	—	—
	·91792	—	—	—
	·91760	—	—	—
	—	—	—	·0001620
BARNES	·91649	—	—	—
Mean	·9176	·0001125	·9165 or ·9162 neglecting DUFOUR	·000160

has been tabulated as three times the linear, but the legitimacy of this procedure is open to grave doubt in the case of a body like ice which is endowed with hexagonal symmetry of structure.

Principle of the Method employed.

Since the question of the density of ice was still, in spite of all the labour that had been spent upon it, in a far from satisfactory state, and since a direct determination of the Cubical Coefficient of Expansion had not been attempted since 1852, I was desirous of employing a method which should yield both results. In order that the work should have any value, it was necessary to employ some device other than any which had been used previously.

The method of weighing ice in mercury was one which naturally suggested itself. For the purpose of a sinker two metals are available, tungsten and platinum. Tungsten is difficult to work, but is readily procurable in any amount; if mercury attacks tungsten this could be avoided by protecting it by an iron shell. Although this direct method was not employed, I believe that the use of a platinum or tungsten sinker for weighing ice in mercury would be well worth the attention of future workers.

The necessity of a sinker can be done away with if the buoyancy of the ice is obtained by determining the tension of a wire which moors it to the bottom of the vessel. The tension of the wire may be found by passing it through a small hole in the bottom of the mercury-containing vessel, which latter must be closed at the top so that the mercury will not pour out of the hole through which the wire comes. This method obviates the use of a balance, for a scale pan may be hung on the wire, and equilibrium obtained by suitably adjusting the suspended weights. JOLY has used this principle in the construction of a balance (JOLY, 'Phil. Mag.,' September, 1888), and my apparatus differs from his, in that I introduce the material whose density is to be determined and use it as the float.

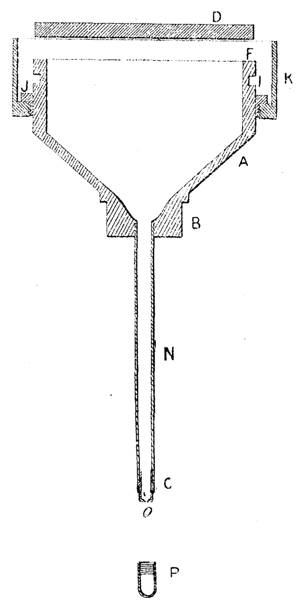
The advantages to be derived from the use of mercury are several. It can easily be obtained quite pure, is without solvent action upon either water or ice, and its coefficient of expansion is of the same order of magnitude as that of ice. Further, this coefficient is known with greater accuracy. The use of a liquid whose coefficient of expansion is near that of ice is helpful in determining the density at 0° C., and also in the determination of the coefficient of cubical expansion.

In order to determine the density at 0° C. it would be sufficient under ideal conditions of temperature to find the buoyancy of an inverted vessel in mercury, to introduce air-free water into this vessel, to determine the buoyancy of the vessel and also that of the water in its liquid and solid state. The experiments were performed by equilibrating the ice at temperatures below zero, and to find the density at these temperatures we must allow for the contraction of the mercury and of the vessel containing the ice. The equilibration of the water was always performed at zero.

Description of Apparatus.

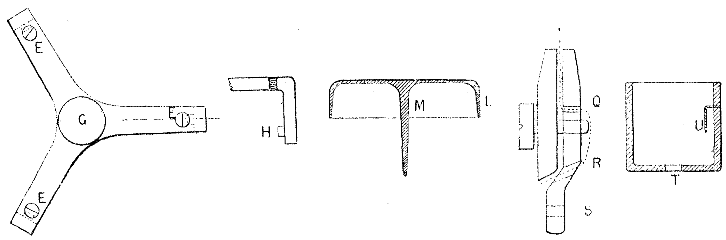
The vessel which constituted the reservoir for the liquid used in the hydrostatic balance is shown in section in fig. 4. It consisted of a funnel-shaped vessel, A, of cast iron. This was turned up in a lathe, and care was taken to have the inside surface quite free from "blow-holes." Into this vessel at B, a tube of steel, N, was driven. The lower end of this tube carried a tightly-fitting screwed piece C, the bottom of which was closed, except for a central hole about ·4 millim. in diameter. This hole was for the wire to pass through downwards to support the scale pan, and upwards to tether the vessel which held the ice or water. The vessel shown in fig. 4 may be called (to save circumlocution) the funnel.

Fig. 4.
($\frac{1}{4}$ size.)



The top of the funnel could be closed by an accurately fitting steel circular plate, shown in section as D. In order to fasten this plate down securely on to the top of the funnel, a three-armed piece of iron, shown in fig. 5*a*, was used. This was provided with three screws, E, the lower ends of which bore directly on the circular plate D, immediately over the annular plane-bearing surface, F. A central screw, G, with a milled head, served to hold the plate D in position in some manipulations which did not require that the surfaces at F should fit very closely. The three-armed piece was provided with three stout pegs, one of which is shown as H in fig. 5*b*, which is a section of one of the portions of the tri-radiate clamp of which fig. 5*a* is a plan. These pegs could traverse round the channel, I, fig. 4, and their pressure on

Figs. 5*a*—8.



5*a* ($\frac{1}{4}$ size.) 5*b* ($\frac{1}{4}$ size.) 6 ($\frac{1}{4}$ size.) 7 (5 times size.) 8 ($\frac{1}{4}$ size.)

the upper roof of this channel, provided reactions for the pressure of the four screws E, E, E, G. In order to place the tri-radiate clamp in position, three small gaps were cut at angular intervals of 120° in the outside of the top rim of the funnel, and three similar gaps were provided in the plate D.

The funnel was provided with a screwed collar, J, which was permanently shrunk on to the cylindrical portion of its outer surface. This collar served to support a removable ring of iron, K. The walls of this ring (which we may call the mercury collar) were higher than the top surface of D, when this latter was in position. The mercury collar served two purposes; it provided a means of sealing the whole of the top of the funnel by flooding with mercury when the closing plate D was in position, the mercury it contained surrounded the bulb of the thermometer which was used to find the temperature of the contents of the funnel. When the funnel was not in position for the actual determinations of buoyancy, it could be held in a vice by the flat surfaces cut in the thick metal at B.

The vessel which served to contain the water or ice, while it and its contents floated in the mercury in the funnel, is shown in fig. 6. It was somewhat of an umbrella shape, and was cut out of a solid block of mild steel in the lathe. It was perfectly smooth, and provided no lurking places for air. The sides, L, were made of decreasing thickness downwards as also was the central stem, M, which was pierced at its lower end with a hole which served to attach the wire by which the scale pan was supported.

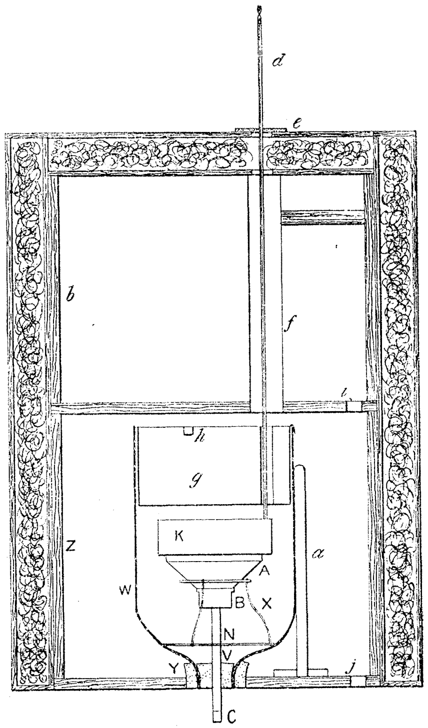
Steel wires of two diameters were used in the experiments—one, about ·17 mm. in diameter, was used in the preliminary investigation of the dilatation of the umbrella, the other, about ·2 mm. in diameter, was used in the actual experiments when the umbrella held ice or water. The wire passed through the mercury in the funnel, down the centre of the tube, N, through the small hole in C, and had a specially constructed clamp attached to the end outside C. This clamp was made so that when held up close to the hole *o* by the buoyancy of the umbrella and its contents, it could be enveloped by the screwed closed tube, P (fig. 4). The clamp is shown in fig. 7. The peculiarity in the construction of this clamp was that it was pierced by the holes Q and R, through which the wire passed as well as being held by the jaws. This arrangement made the chance of the wire slipping very small. The course of the wire is indicated by a broken line in fig. 7. The lower portion of the clamp was also drilled with a screwed hole, S. This hole served to receive a hook by which the scale pan used to hold the weights in the equilibrations was supported, and was screwed inside so as to enable the clamp to be attached to the piece C (fig. 4) always at a definite distance by means of a second screwed piece which could be attached to C. The object of this arrangement was to ensure always that the wire was the same length.

In fig. 8 an iron cylindrical vessel is shown in section. This reservoir could be put on the tube N (fig. 4), which was made slightly conical at its lower end in order to fit into the hole T. A bent wire, U, was fixed into the side of the reservoir, and served to keep the stopper, P, submerged when the reservoir was full of mercury. The use of this portion of the apparatus will be referred to in describing the process of filling the funnel with pure, dry, air-free mercury.

The method of holding the funnel during the determinations, and the arrangements for surrounding it with ice or freezing mixture, are shown in fig. 9.

The tube, C N, of the funnel, A, passed through an india-rubber bung, V, which closed the lower orifice of a large glass jar, W. The funnel was supported by a framework of iron, X, which consisted of two rings joined by three bent wires. The lower ring rested in the concavity of the glass jar and bore the weight of the funnel. The jar in turn was supported by a larger rubber bung, Y, which fitted into a hole in the bottom of the lower wooden box, Z. Three stout brass pieces, *a*, only one of which is shown in the drawing, prevented the jar from tipping sideways.

Fig. 9.
($\frac{1}{9}$ size.)



The upper wooden box, *b*, rested on the lower box, Z, while the whole was surrounded on five sides by the non-conducting cases, *c*. These cases were removable boxes of wood loosely filled with cotton wool.

The thermometer, *d*, passed through a piece of ebonite, *e*, which rested on the top of the non-conducting case, through a hole in the case, down a wide brass tube, *f*, in the upper wooden box, and rested with its bulb in the mercury in the collar, K. The removable thin metal vessel, *g*, was supported by three lugs, *h*, which were bent over so as to engage the rim of the glass jar. The upper and lower boxes were fitted with the holes *i*, *j*, which could be closed by bungs.

The whole of the apparatus shown in fig. 9 rested on three levelling screws, which in turn were supported by a strong table having a hole in its centre through which the wire from the funnel passed.

The lower surface of the lower box was protected from the access of heat by filling in the space between it and the table with loosely packed cloth. The description of any other parts of the apparatus which may be necessary will be more conveniently given when dealing with the conduct of the experiments.

Determination of the Buoyancy of the Umbrella.—In order to find the buoyancy of the ice and water, it was necessary to determine that of the umbrella at different temperatures. If we know the load on the scale pan necessary to obtain equilibrium when the umbrella only is tending to float in the mercury, then the weights added when the umbrella and its contents are equilibrated, gives us the buoyancy of the contents. The funnel was taken and a thin steel wire (·17 millim. in diameter) passed upwards through the hole *o* (fig. 4) until it could be threaded through the hole in the stem of the umbrella, when it was fixed by twisting the end round itself. This

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operation was done in such a manner as to ensure that the length of wire thus used in the fastening was the same in each experiment. The wire was then pulled tight and the little clamp attached with its jaws about 1 centim. distant from *o* by the method previously mentioned. The whole length of wire used was thus always the same. The stopper, P (fig. 4), was then screwed on C and mercury poured into the funnel.

The mercury used throughout these experiments was first cleaned by the ordinary chemical methods, then boiled in air, and distilled twice in a vacuum. After being used in one experiment it was filtered, boiled and distilled twice again before being used in a fresh determination.

The plate D was placed on the funnel and the whole was turned on one side to enable any air imprisoned under the umbrella to escape. This was repeated until no more mercury could be poured into the funnel, when the latter was heaped up with mercury and the plate D was slid on to the top of the funnel and firmly screwed into position by means of the tri-radiate clamp. It was found necessary to carefully grind the bearing surfaces of the closing plate and of the funnel together before each experiment in order to obtain a perfect fit.

After thus filling with mercury, the funnel was removed from the vice and placed in an inverted position on a tripod. The stopper was then unscrewed from the tube, when the little clamp could be seen supported on the top of a straight piece of wire projecting a few millimetres through the hole at the end of the tube. The mercury reservoir (fig. 8) was slipped on to the conical tube and the mercury in the funnel was then boiled by applying the flame of a large Bunsen burner to the closing plate. The mercury which came out of the small hole in this process, partially filled the reservoir, which on removing the flame was filled with mercury boiled in another vessel. The whole was left to assume the ordinary temperature, and then the stopper was inverted and plunged beneath the mercury in the reservoir, where it was prevented from rising to the surface by the wire U.

The boiling was again performed, and then the mercury in the tube and reservoir was also boiled. Operations of alternate heating and cooling were continued until I felt satisfied that no air or water remained in the funnel. The stopper was then taken from the wire in the reservoir, and manipulating it so as never to permit the fingers to come beneath its orifice, it was screwed on to the piece C, and the funnel was thus closed.

The reservoir was then removed, and the funnel was again put in the vice; this time with the mercury collar round it ready to be screwed on. The tri-radiate clamp and the closing plate were removed and the bearing surfaces were covered with a thin film of vaseline before pouring an excess of recently boiled mercury into the funnel and sliding the closing plate again into position. The plate was then fastened down securely and the mercury collar screwed on.

The funnel was then installed in the apparatus shown in fig. 9, when the collar was filled with mercury and the top of the funnel thus completely sealed. The stopper was then unscrewed and a small vessel of hot recently boiled mercury was placed so that the hole *o* dipped beneath its surface. This caused the mercury in the tube to expand and to displace any air from about the orifice of the tube as the exuded mercury flowed through it.

The funnel was now levelled by adjusting the screws on which the bottom box rested, the level being placed with its legs on the top of the closing plate. The wire mooring the umbrella down then coincided with the axis of the tube. In order to find the buoyancy of the umbrella at 0° C., the vessel *g* was not used, but the jar and the boxes were filled with table ice, and the cases *c* placed round the apparatus. Cloths were packed under the lower box, and the whole was left overnight.

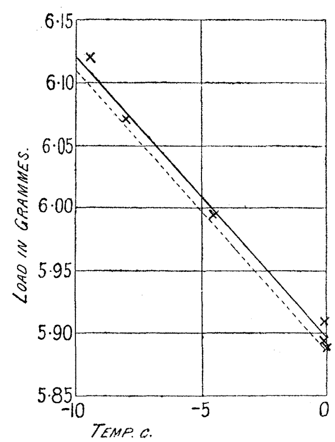
When the equilibration was to be performed, the small mercury vessel into which C dipped was removed, the scale pan attached, and the weights adjusted so that equilibrium was attained when the wire projected 4 millims. from the hole. The reading having been taken, the pan was removed and the hole was again closed with hot mercury.

In order to get readings below 0° C., the ice was all removed, *g* was put in position filled with ice and salt, and the boxes were filled with the same mixture. Then the thermometer was inserted so as to have its bulb in the mercury collar.

The space round the funnel was clear of the freezing mixture, and the funnel thus changed in temperature so slowly that the thermometer readings could be relied on as giving the temperature of the funnel and its contents. All readings were taken with the thermometer slowly rising.

The thermometer used in these experiments was made by HICKS, and had the portion which projected above the cotton wool case graduated from 1° C. to 10° C. in tenths of a degree. I tested its accuracy at 0° C., and could find no error. The temperature rose (after the apparatus had been left a day or so) about a degree in three hours, and readings of the buoyancy could be obtained at intervals.

Fig. 10.



The results for the weights necessary to be added to the pan, which itself weighed about 60 grammes, are set out in Table III., and shown also in fig. 10.

It will be seen that the last weighing taken after five others agrees closely with the first, showing that no air gained access to the umbrella in the process of equilibration.

A new set of platinized weights by OERTLING was used in these experiments. They were tested after the experiments, and were found to be consistent with themselves. Their absolute mass is not involved in the determination.

TABLE III.—Buoyancy of Umbrella.

Order of Weighing.	Circumstances.	Temperature.	Weights in grammes.
1st	After 15 hours in ice	0°	5·890
2nd	After 21 hours in 1st freezing mixture	−8°	6·071
3rd	After 33 hours in 1st freezing mixture	−4°·48	5·995
4th	After 45 hours in 1st freezing mixture	−0°·1	5·895
5th	After 45 hours in 2nd freezing mixture	−9°·42	6·120
6th	After 72 hours in 2nd freezing mixture	−0°·1	5·910

Determination of the Density of Ice at different Temperatures.

The wire and clamp used in equilibrating the water and ice were not the same as those used with the empty umbrella. The values for the buoyancy of the umbrella as read from the unbroken straight line on fig. 10 are thus subject to a correction of ·012 gramme, which must be subtracted from the values thus found. The results for the buoyancy of the umbrella are thus taken from the broken line in this figure.

Let W = the number of grammes necessary to equilibrate the water at 0° C.; *i.e.*, the load in the pan less the corrected buoyancy of the umbrella,

I = the number of grammes to equilibrate the ice at $-t$° C.,

i_{-t} = the density of ice at $-t$° C.,

w_0 = the density of water at 0° C.,

h_0 = the density of mercury at 0° C.,

h_{-t} = the density of mercury at $-t$° C.

Then equating the two values obtained from the above for M, the mass in grammes of the material taken, we have

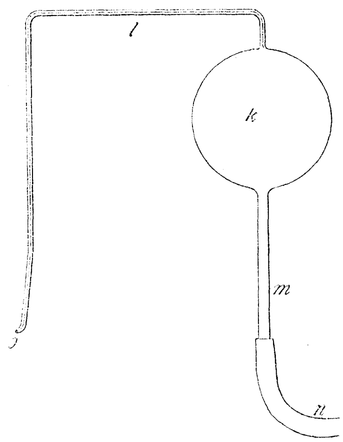
$$\frac{\mathrm{M}}{w_0} h_0 - \mathrm{M} = \mathrm{W} \quad \text{and} \quad \frac{\mathrm{M}}{i_{-t}} . h_{-t} - \mathrm{M} = \mathrm{I}; \qquad \text{therefore } \frac{w_0}{h_0 - w_0} \mathrm{W} = \frac{i_{-t}}{h_{-t} - i_{-t}} \mathrm{I}.$$

Let $\mathrm{K} = \frac{\mathrm{I}}{\mathrm{W}}$ and $\frac{w_0}{h_0 - w_0} = q$; then $i_{-t} = \frac{q h_{-t}}{\mathrm{K} + q}$,

which was the formula used in computing the results. Since the number K only depends on the ratio of the weights, no correction for the effect of the buoyancy of the air is necessary.

The density of water at 0° C. was taken as ·999884, and that of mercury at the same temperature as ·135956, while the density of mercury at lower temperatures was found from the formula of CHAPPUIS ('Procès-verbaux des Séances du Comité International,' 1891, p. 37). The results needed were read off from a plotted curve.

Fig. 11.
($\frac{1}{4}$ size.)



The funnel having been filled with pure dry air-free mercury in the manner already described, the closing plate was removed and air-free water introduced under the umbrella. This was accomplished by means of the apparatus shown in fig. 11.

This consisted of a glass bulb, k, which had a capillary tube, l, sealed into it above, and which terminated in a stout tube, m, below. The whole could be supported by fixing this tube in a clamp. A flexible rubber tube, n, communicated with the bulb and with a somewhat larger reservoir not shown in the figure.

Mercury was poured into this reservoir, and it was raised until the mercury poured out of the orifice, o, in the capillary tube, which was plunged into a beaker of water which had been kept boiling for half an hour. The reservoir was then lowered, and the boiled water rushed into the bulb, k. On again raising the reservoir, this water was expelled, and boiled water was then introduced in its place. This was repeated seven or eight times, when the mercury reservoir was raised and the beaker removed. The water spurted out of o in a rapid stream, so that no air could pass back into the bulb. The point o was then dipped into the mercury of the funnel, and as the water was ejected from the capillary tube it floated up and occupied the upper portion of the inside of the umbrella. This was kept in position during filling by a set of three stout iron wires fixed in a wooden board, which was fixed on the rim of the funnel so that the lower ends of the wires pressed on the flat top of the umbrella. This was necessary because the umbrella was only stable when it contained more than a certain quantity of water. The point o was so made that although the water was projected upwards, the point offered no projection for the rim of the umbrella to catch upon, so that when sufficient water had been introduced, the tube could be removed.

The water used in these experiments was prepared from ordinary distilled water by re-distilling in a new block-tin still, the earlier products of the second distillation being rejected.

After filling, the funnel and its contents were allowed to cool; the funnel was then closed with the closing plate as already described, and was placed in the apparatus, fig. 9, the boxes having been previously washed out to get rid of the salt from the freezing mixture. The mercury to seal the top was poured into the collar, and the

TABLE IV.

I.	Equilibrations. II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Experiment.	Water at 0° C.	Ice at $-t^\circ$ C.	Temp. $= -t^\circ$ C.	W by subtracting 5·886 from numbers in column II.	Buoyancy of umbrella at $-t^\circ$ C., from fig. 10.	I by subtracting numbers in column VI from those in column III.	K $= \frac{I}{W}$.	K + q. q = ·07938.	h_{-t} from fig. 11.	$i_{-t} = \frac{qh_{-t}}{K+q}$.
1	(a) 646·225	(b) 709·350	−1·95	640·354	5·930	703·420	1·09849	1·17787	13·6004	·916603
	(e) 646·255	(c) 709·675	−10·02	—	6·112	703·563	1·09871	1·17809	13·6204	·917780
	Mean of (a) and (e) = 643·240	(d) 709·300	−1·01	—	5·909	703·391	1·09844	1·17782	13·5981	·916487
2	(a) 860·055	(b) 945·235	−2·90	854·169	5·952	939·283	1·09965	1·17903	13·6028	·915863
		(c) 945·100	− ·37	—	5·894	939·206	1·09956	1·17894	13·5965	·915509
3	(a) 822·495	(b) 903·450	−8·37	816·609	6·074	897·376	1·09890	1·17828	13·6163	·917355
		(c) 903·080	−1·02	—	5·909	897·171	1·09865	1·17803	13·5981	·916324
4	(a) 792·690	(b) 871·060	−2·60	786·804	5·945	865·115	1·09953	1·17891	13·6020	·915903
		(c) 870·760	−6·59	—	6·034	864·726	1·09904	1·17842	13·6119	·916950
		(d) 870·580	−3·15	—	5·957	864·623	1·09890	1·17828	13·6034	·916487

funnel was then levelled. The jar and boxes were filled with ice, and the equilibration of the water was performed after waiting about eighteen hours.

The ice in the boxes was then exchanged for freezing mixture, the glass jar was emptied of its ice, and the metal vessel g was filled with freezing mixture and put into the jar. After leaving for two days, the ice was equilibrated, and this could be done at different temperatures, as the ice very gradually rose in temperature. The ice could then be examined, or a new equilibration of the water could be obtained, by allowing the ice to melt and bringing the whole again to 0° C.

The results of the different equilibrations and the computation of the density of ice for different temperatures below 0° C. are set out in Table IV.

In this table the letters prefixed to the equilibrations in columns II. and III., indicate the order in which these numbers were obtained. In finding the numbers in column IX., the values of q is only needed to four significant figures; but to compute the density of ice at different temperatures (column XI.) this same quantity q is ·0793829.

The whole of the equilibrations performed with the final form of apparatus are given in the table. An improvement of the filler was introduced subsequently and anomalous results were obtained for the only experiment carried out. This was traced to the fact that the wire had become damaged during the filling, and the results for this experiment were rejected.

In the case of the first experiment the water was equilibrated at the beginning and end, and the mean value was used for computation. The ice in this experiment was not examined. In Experiments 2 and 3, the ice was taken out after the last equilibration and was found to be free from milkiness and air bubbles, but it had fine circular cracks running round it concentric with the central stem of the umbrella.

The fourth experiment was conducted differently from the others, and the values obtained proved unmistakably that the same specimen of water may assume different densities on freezing. After the value b had been obtained, the ice was permitted to melt either partially or completely. A fresh freezing mixture was put in the apparatus, and two subsequent equilibrations of the new specimen of ice were performed. The second specimen of ice had a considerably greater density than the first although it was made from identically the same water.

The results given in column IX. are plotted in fig. 12. The points are marked with numbers indicating the experiment. The unbroken straight lines drawn through the points give us, by extra-polation, four values for the density of ice at 0° C., while a broken line drawn parallel to the straight line for Experiment 2 through the point given by the first specimen of ice in Experiment 4 furnishes a fifth value. The numbers thus obtained and the weights to be assigned to them in computing the mean are set out in Table V., the weight assigned in each case being equal to the number of equilibrations of the ice.

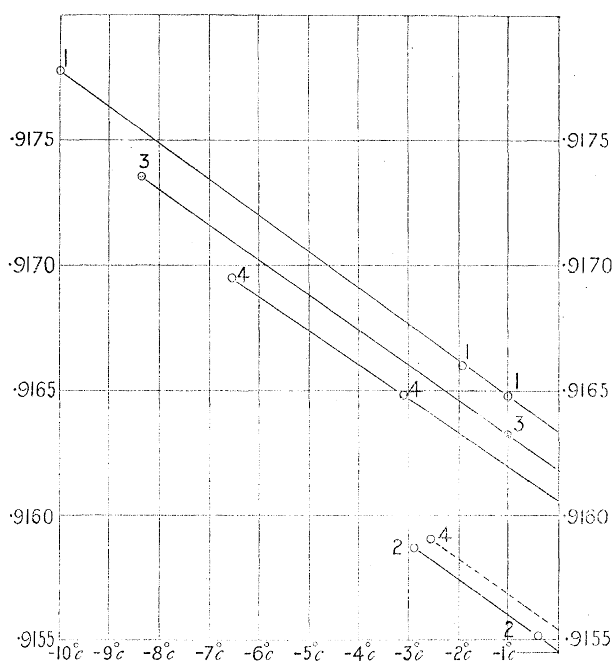
TABLE V.

Experiment.	Density of Ice at 0° C.	Weight Assigned.
1	·916335	3
2	·915460	2
3	·916180	2
4	·915540	1
	·916060	2
Weighted mean . . .	·9160	

We thus obtain ·9160 gramme per cub. centim. as the density of the ice at 0° C.

This result depends upon the assumption that the density of ice is a linear function of the temperature on a mercury-in-glass thermometer. Systematic error in the

Fig 12.



thermometer, so long as the zero is correct, is eliminated. The result likewise depends on the values assumed for the density of water and of mercury at zero, but is independent of the absolute mass of the weights employed.

The Coefficient of Cubical Expansion of Ice.

The errors of the thermometer are, however, involved in computing the coefficient of cubical expansion which also depends upon the particular law of dilatation of mercury used, but these errors are probably such as will not affect the result to the accuracy with which it is given below. The four values which can be found from the data available are set out in Table VI.

TABLE VI.

Experiment.	Coefficient of cubical expansion.	
1	·000155	
2	·000152	Mean ·000152
3	·000153	
4	·000148	

Comparison of Results.

The value ·9160 for the density of ice at 0° C., is lower by two parts in 10,000 than the mean of the results obtained by PLÜCKER and GEISSLER, BUNSEN, and NICHOLS. It is 1 part in 10,000 less than the mean of NICHOLS's values, but is 7 parts in 10,000 lower than BUNSEN's value. The value ·000152 for the coefficient of cubical expansion is 4 per cent. lower than that of PLÜCKER and GEISSLER, the last published value for the directly determined cubical coefficient of artifical ice. It is 5 per cent. lower than the mean value given in Table II.

Conclusion.

The results of this determination of the density and coefficient of cubical expansion of ice are, that NICHOLS's value for the density is confirmed, and that BUNSEN's value is probably too high; but as the same specimen of water can freeze into specimens of ice having different density, the use of the Bunsen ice calorimeter in absolute determinations must be limited to an accuracy of probably about 1 in 1,000.

The coefficient of cubical expansion seems to be 4 or 5 per cent. less than the mean of previous determinations.

The expenses of this research have been in part defrayed by a Government grant from the Royal Society, and in part by the Cavendish Laboratory. I wish to thank Professor J. J. THOMSON, F.R.S., for his kind encouragement, and my thanks are also due to Mr. GRIFFITHS, F.R.S., through whom I was led to undertake the investigation.