



XLV. On the maximum density of water

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results are given in a paper on the Solubility of Isomeric Organic Compounds &c., published in 1888 (Chem. Soc. Journ. Trans. 1888, pp. 782-802). Their results are by no means concordant, owing no doubt to the method of conducting the experiments, for which reference must be made to the original paper. The general form of the curves representing their results is the same as that given by my experiments, as will be seen by reference to fig. 4, Plate VIII., in which I have plotted my results, and side by side with them the curves given by Carnelley (*loc. cit.*).

Here the subject must be left for the present. For although there are many points of interest raised, and some general conclusions of importance to be deduced, the discussion of these is best deferred until experiments at present in progress on the molecular volumes of such solutions have been completed.

XLV. *On the Maximum Density of Water.*

By H. M. VERNON, *Scholar of Merton College, Oxford*.*.

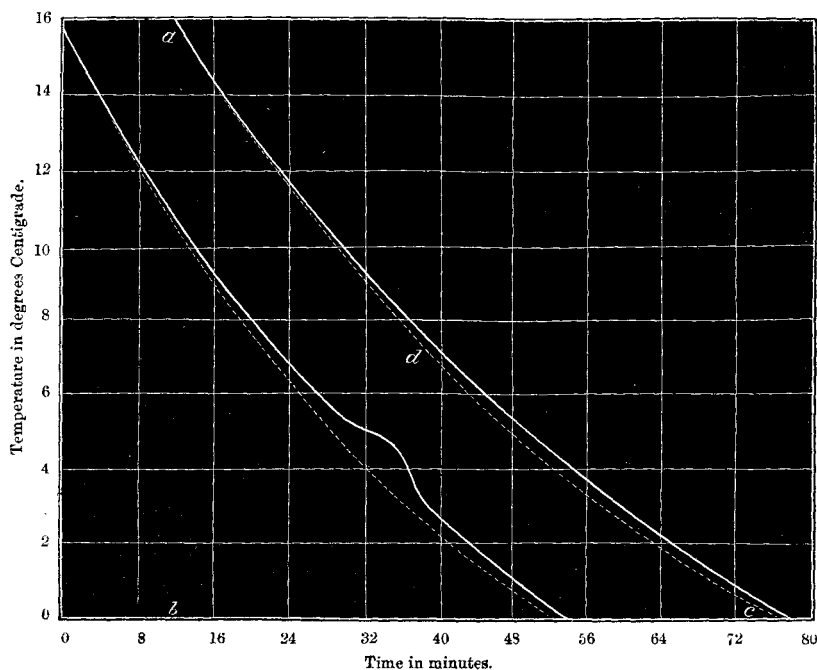
THOUGH the fact that water has not a regular dilatation, but reaches a maximum density at about 4° C., has been universally known for a very long time, apparently no explanation has yet been offered of this seeming anomaly, which is of such vast importance in nature. The object of this paper is to bring forward a few experiments which afford an interpretation of the fact.

If the fact of the irregular dilatation of water be carefully considered, it will be seen that the only possible explanation of it is that some change in the position of the water molecules towards each other takes place at about 4° C., whereby such a considerable variation in the density is caused. It is, therefore, probable that at this temperature some thermal change will also take place. If a volume of water be heated and allowed to cool without being subjected to any external variations of temperature, it is evident that if such a thermal change does occur at 4° C., the rate of cooling of the water will not be regular at this point. To test this, experiments were made on the rate of cooling of water from about 30° C. to slightly below 0° C.

A volume of distilled water, varying in different experiments from 30 cub. centim. to 60 cub. centim., was placed in a glass flask which was suspended inside a large beaker surrounded by a freezing-mixture of ice and salt. The vessel

* Communicated by the Author.

containing the freezing-mixture and the beaker itself were well covered up, and the temperature was found to remain constant throughout the experiment. The thermometer used was a standard one, graduated in tenths of a degree; and as all readings were taken with a cathetometer, it was read to the hundredth of a degree. The water was then warmed to about 30°C. , and readings taken of the thermometer at intervals of a minute, till it had cooled to about -3°C. , when ice began to form. In the figure will be seen the curve for the



rate of cooling which was thus obtained. The curve is only given up to 16°C. , as above this it is quite regular. From about 14°C. the cooling begins to take place slightly less rapidly than would be the case if no internal thermal change were taking place, and continues getting less and less rapid till from about $5^{\circ}\cdot 5\text{C.}$ to $4^{\circ}\cdot 7\text{C.}$ it almost stops. At $4^{\circ}\cdot 7\text{C.}$ it suddenly begins to sink rapidly again till about 3°C. After this point the curve becomes regular again. The part of the curve from 30°C. , if produced on the supposition that the curve is regular, gives the dotted-line curve in the figure.

Water has been found to have its maximum density at

4°·07 C. by Rosetti, at 4°·1 C. by Hällstrom, at 4°·08 C. by Kopp, and at 4°·0 by Despretz ; but here the maximum point of the irregularity in the curve is at 4°·7 C. There can be no doubt that such is the case, as several separate cooling determinations gave this temperature as the maximum, it being also corrected for the thermometer, which gave the freezing-point of water as +·08° C. Also the rate of cooling of oil was taken by the thermometer, and was found to be quite regular ; so the difference could not have been due to a thermometric error.

In these experiments the water was not stirred ; and it is to this fact that the great irregularity in the curve at 4°·7 C. is due. The cooling effect produced in the outer layers of water in the flask mainly reach the inner layers of water and the thermometer-bulb by convection-currents set up by the change in the density of the water with change of temperature. The inside layers will therefore always have a slightly higher temperature than the outside layers. When the temperature of the outside layers has cooled to near 4° C., when the density no longer increases with fall of temperature, the convection-currents will be stopped, and at a slightly lower temperature, when the density decreases, will begin to be set up in an opposite direction. This explains why there is a sudden pause in the curve for the rate of cooling, and also why directly after this the temperature sinks rapidly for a degree or two and then sinks much less rapidly ; for this is due to the cold layers, which had been accumulating while the cooling almost stopped, being suddenly brought into contact with the thermometer-bulb. This experiment, therefore, merely serves to show the change in the density of water at about 4° C., and that the cooling effect reaches from the outside to the inside of the flask mainly through convection-currents, and not by radiation or conduction.

Experiments were then made on the cooling of water when stirred. A beaker containing 100 cub. cent. distilled water was suspended in another large beaker surrounded by a freezing-mixture. The smaller beaker was closed by a tightly-fitting bung, through which passed the thermometer and a light glass-rod stirrer. This was moved up and down regularly at intervals of about four seconds, during the whole period of cooling, by means of a cord passing over two pulleys. The second curve in the figure represents the rate of cooling. The curve above 14° is quite regular ; and this curve, produced on the supposition that the curve is regular, gives the dotted-line curve in the figure. It will be seen that there is no sudden change in the curve at any point, but that the irregularity

seems to be greatest at about 4°C. , though it is only very slightly marked.

The space between the two curves is a measure of the heat evolved in the cooling of the water. By calculating its area, and also the area of the figure $abcd$, it was found that the specific heat of water is increased, on an average, from 12°C. to 0°C. by about 3 per cent. Only a very rough estimate can be arrived at in this way, as it is not possible to calculate the position of the dotted-line curve with any exactness. It is enough, however, to show that there is a material increase in the specific heat of water at temperatures near to that of its maximum density.

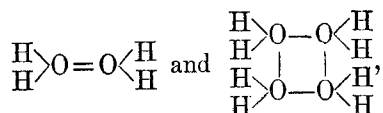
We have now to see to what extent the results obtained by cooling correspond with the variations in the dilatation of water. The density determinations of Rosetti (*Ann. Chim. Phys.* (4) x. p. 47), plotted out as a curve, show that down to about 16°C. the density increases regularly with decrease of temperature. From this point downwards the rate of increase of density begins to gradually get smaller, it getting less and less till at $4^{\circ}\cdot07\text{C.}$ it stops. From this point the density begins to gradually decrease. If the dilatation were regular, the density of water at 4°C. would be much greater than is actually the case; that is, the density of water in the state of molecular aggregation it exists in at 4°C. is considerably less than it would be if the dilatation were regular, and no molecular change took place. This fact serves to explain why water below 4°C. begins to decrease in density.

The change in the density of water, which, as has been shown, is attended by an evolution of heat, can only be due to water molecules aggregating together, and forming more complex molecules than before existed. As, therefore, from 14°C. downwards the aggregated molecules are being formed in larger and larger quantities, whilst fewer and fewer of the unaggregated molecules are left, the lesser density of the aggregated molecules at last at 4°C. counteracts the greater density of the unaggregated molecules; and from this temperature downwards, when fewer still of the unaggregated molecules remain, the density of the water begins to decrease instead of increase. We do not know at what temperature the maximum number of aggregated molecules is formed; but the curve for cooling appears to have a slight maximum at about 4°C. So it may be taken that the density of water begins to decrease when about half of the molecules present have undergone aggregation. It is not necessary, however, that the maximum of the irregularity in

the curve for cooling should correspond with the temperature of maximum density of water.

We see then that, allowing for the effect of temperature, ordinary molecules of water have the greatest density, aggregated molecules have a lesser density, and ice, which must contain molecules in a still greater state of aggregation, has the least density.

Raoult, from his experiments on the molecular lowering of freezing-points (*Ann. Chim. Phys.* (6) ii. p. 66), concluded that while solvents such as acetic acid and benzene had molecular weights expressed by their ordinarily received formulæ, water had a molecular weight four times as great; that is, its molecular formula was $(\text{H}_2\text{O})_4$. From analogy with other liquids, as acetic acid and hydrofluoric acid, and from the fact that at ordinary temperatures water is liquid, while the similarly constituted hydrides of sulphur, selenium, and tellurium are gaseous, it is probable that when water-vapour condenses it undergoes molecular aggregation. Water molecules from 100°C . to about 4°C . will probably, therefore, have the formula $(\text{H}_2\text{O})_2$; and below 4°C . these will condense to $(\text{H}_2\text{O})_4$ molecules. In constitution these condensed molecules may be considered merely as molecular compounds, or, what is really more simple, as atomic compounds linked thus:—



with oxygen in the tetravalent state.

We must now examine whether the evolution of heat taking place when water is cooled to 4°C ., that is to say, the increased specific heat of water at this temperature, shows itself in the determinations of observers on the latent heat of fusion of ice and the specific heat of water. Regnault has determined the specific heat of water from 0° – 40°C ., 0° – 80°C ., 0° – 120°C ., &c., but not for smaller temperature-intervals than these. If, however, these results are calculated out for 20°C ., 60°C ., 100°C ., &c., and a curve plotted out, it will be found that the specific heat of water for the interval 0° – 40°C . is appreciably greater than we should be led to suppose from the specific heats at higher temperatures.

A. W. Velten (*Annalen*, 1884, p. 61) has made two series of determinations of the specific heat of water. By the method of mixing, the specific heat was determined for different intervals from $4^\circ\cdot7\text{C}$. to 100°C . For the interval

4°·7–42°·9 C. the specific heat was found to be ·9943; for the interval 7°·38–41°·1 C. it was ·9863; again, for the interval 8°·24–93°·6 C. it was ·9873, and for the interval 11°·78–93°·0 C. it was ·9837. Several other determinations showed that for temperatures near to 4° C. the specific heat was greater than the normal. By means of the ice-calorimeter the specific heat was determined for various intervals from 0° C. to 100° C. These results show that the specific heat is about 3 per cent. greater from 0°–7°·31 C. than from 7°·31–10°·81 C., and at higher temperatures. There seemed also to be another slight increase in the specific heat at about 18° C.; but the mixing experiments, in which it is possible to attain greater accuracy, do not show this, so it is probably not the case. If it were so, the curves for the cooling of water would also show an irregularity; they were, however, quite regular at this point.

As the latent heat of fusion of ice is determined by mixing it with water of known temperature, an appreciable difference should be observed in the values obtained, according as the temperature of the mixture is near 4° C. or considerably removed from it. In both Regnault's experiments and those of Provostaye and Desains (*Ann. Chim. Phys.* 1843, pp. 18 and 27), the temperature of the mixture varied from 7°·2 C. to 18° C.; but no regular variations in the values for the latent heat appear. The values vary among themselves from 78·74 to 79·26 units in Regnault's experiments, and from 78·75 to 79·46 in those of Provostaye and Desains; so the variation might be masked by experimental error. In Person's determinations the temperature of the mixture was about 4°·8 C., and the value 80 was obtained. This seems to show that the specific heat of water is increased at about 4° C., as though this heat is evolved in all the determinations; yet in those in which the mixture had a higher temperature, this heat was spread over a greater interval, and so would not produce so appreciably great an effect.

We see, then, that both the specific heat and the heat of fusion of ice determinations confirm the results obtained by cooling. There can be, therefore, no doubt as to the molecular change taking place at 4° C. The method of cooling affords a simple and accurate means for confirming any supposed irregularities in the specific heat of a liquid; and, as the above results show, in the density of a liquid as well, provided it is not stirred during the cooling.

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