On the Anomalous Relation between the Specific Volume of Liquid Water and Temperature

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Abstract

By assuming that liquid water contains tiny ice-crystals having the size of the order of their unit cell, its specific volume, specific heat and coefficient of viscosity are inspected A rough estimate of the amount of such ice-crystals in liquid water shows that it is approximately 0.6% at 0°C.

The presence of a minimum amount in a specific volume of water at 4°C is a strange characteristic of water differentiating it from other liquids whose specific volume increases gradually with the temperature. Water has another peculiarity in that its volume is increased by freezing it into ice. In the following some properties of water are examined by assuming that the above two peculiarities are related to each other. Though the condition of the aggregation of water molecules in the liquid state is not clear, if we assume that ideally they are not held very tightly and that their mutual positions can be displaced easily by thermal agitation, then the specific volume of water will gradually increase with temperature as is usually the case with other liquids and with water as well at the temperature range above 4°C. As the increase of the specific volume of water below 4°C can not be explained by this hypothesis, the writer assumes that some very tiny ice-crystals having the size of the order of their unit cell are present in liquid water even at a temperature above the freezing point : that is, that ordinary liquid water is a mixture of tiny fragments of ice and of ideal liquid water so constituted that the relative positions of its molecules can be moved easily by thermal agitation. Though the existence of each one of such ice-crystals in ordinary liquid water is very unstable, forming and disappearing momentarily here and there, yet a certain fraction of one gramme of ordinary liquid water, which fraction is determined by the temperature, will remain in the frozen state. Let the value of this fraction at the temperature t° C be x, and assume that the manner of the decrease of x with the temperature is expressed roughly by an exponential function, then x is

$$x = x_0 e^{-\alpha t} \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1),$$

where x_0 is the total mass of the ice fragments in one gramme of liquid water at $0°C$.

Let the functional form representing the relation between the specific volume of ideal liquid water and the temperature be $f(t)$, and the specific volume of ice at $0°C$ be 1.0917 ; then, by neglecting the change of the specific volume of the ice fragments according to the temperature, the specific volume V_s of ordinary liquid water at the temperature $t°C$ is

$$V_s = 1.0917x + (1-x)f(t) = f(t) + \{1.0917 - f(t)\}x$$
$$= f(t) + \{1.0917 - f(t)\}x_0 e^{-\alpha t} \qquad \dots\dots\dots\dots\dots(2).$$

The value of $f(t)$ in the bracket ought not be known very accurately in the present case, because the value of x_0 is estimated to be less than 0.01 (as will be seen later). By giving this term a constant value of 0.9998 we obtain

$$V_s = f(t) + 0.0919x_0 e^{-\alpha t} \qquad \dots\dots\dots\dots\dots\dots\dots\dots(3).$$

When the temperature increases from $0°C$, the specific volume of water V_s increases by the thermal expansion of the ideal liquid water, and decreases at the same time by the melting of some ice fragments. Though the occurrence of the minimum specific volume of water at $4°C$ can be understood qualitatively from the above two causes, the presence of the unknown term $f(t)$ in the above equation does not allow us to make even a rough estimation of the values of x_0 and α.

If the above is correct the specific heat of water must also be influenced by the melting of some part of the suspended ice fragments when its temperature is raised. According to Callender[1] the specific heat of water takes a minimum value at $35°-40°C$. But with ideal liquid water, it seems natural to suppose that its specific heat represented by a functional form of $F(t)$ increases gradually with the temperature t as in the case of the specific volume. Let the specific heat of ice and the latent heat of fusion per gramme of ice be 0.5 and 80 calories respectively, then from the above consideration the specific heat c of ordinary liquid water at the temperature t becomes

$$c = 0.5x + (1-x)F(t) + 80\alpha x$$
$$= F(t) + \{80\alpha + 0.5 - F(t)\}x_0 e^{-\alpha t}.$$

If we take the value of $F(t)$ in the bracket as approximately 1, the above expression becomes

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1. Landolt-Börnstein: Physikalisch-chemische Tabellen, p. 1250 (1923)

$$c = F(t) + \{80a - 0.5\}x_0 e^{-\alpha t} \quad \dots\dots\dots\dots\dots\dots(4).$$

By putting $c - F(t) = A$, $\{80a - 0.5\}x_0 = B$, equation (4) becomes

$$A = Be^{-\alpha t} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(5).$$

If we put $V_s - f(t) = E$, $0.0919 x_0 = F$, equation (3) can be written in a similar form

$$E = Fe^{-\alpha t} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6).$$

Equations (5) and (6) are very simple, and we obtain in logarithmic forms

$$\log_{10} A = \log_{10} B - \alpha t \log_{10} e \quad \dots\dots\dots\dots\dots\dots(7),$$
$$\log_{10} E = \log_{10} F - \alpha t \log_{10} e \quad \dots\dots\dots\dots\dots(8).$$

These equations show that $\log_{10} A$ and $\log_{10} E$ decrease linearly with t having the same inclination. In order to get the values of A and E we must know the values of $F(t)$ and $f(t)$; and this is done experimentally by exterpolating the specific heat—temperature curve and the specific volume—temperature curve from the higher temperature range, so that the values of $F(t)$ and $f(t)$ asymptotically approach the actual observations of specific heat and specific volume respectively at the higher temperature range, and always decrease with decreasing temperatures. From these values of $F(t)$ and $f(t)$ those of A and E are immediately obtained by subtracting the values of $F(t)$ and $f(t)$ from the observed values of c and V_s respectively for various values of t. The values of $F(t)$ and $f(t)$ must be so chosen that $\log_{10} A$ and $\log_{10} E$ decrease linearly with t having the same inclination; and this is done by repeating differently several times the manner of exterpolation as stated above. Next the values of B and F are obtained from the graphs showing the linear relations between t and $\log_{10} A$ and $\log_{10} E$ as represented by (7) and (8). The value of x_0 obtained from the values of B and F thus found must be the same if the values of $F(t)$ and $f(t)$ are correct. This condition is almost satisfied by repeated trials at finding the values of $F(t)$ and $f(t)$. After such efforts the writer finally accepted the following values of x_0 and α as the best estimate.

$$x_0 = 0.006, \quad \alpha = 0.0644.$$

From these values of x_0 and α, the total mass of the tiny ice crystals supposed to be suspended in one gramme of ordinary liquid water at the temperature t°C becomes

$$x = 0.006 e^{-0.0644 t} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(9).$$

By using the values of x calculated with (9) for various values of temperature t, $f(t)$ and $F(t)$ are recalculated by means of the equations (3) and (4), and they are represented respectively by the curves drawn

Fig. 1.

Fig. 2.

Fig. 3.
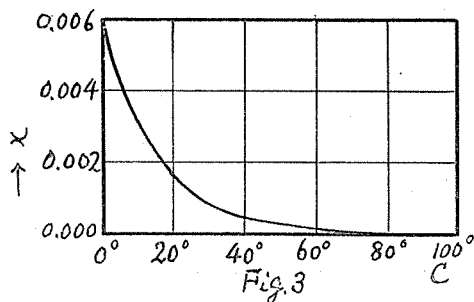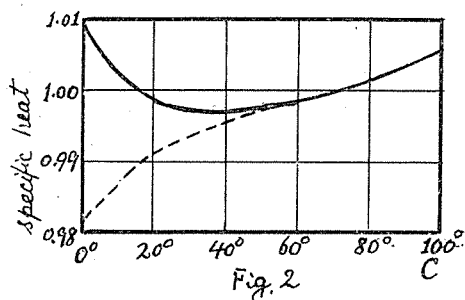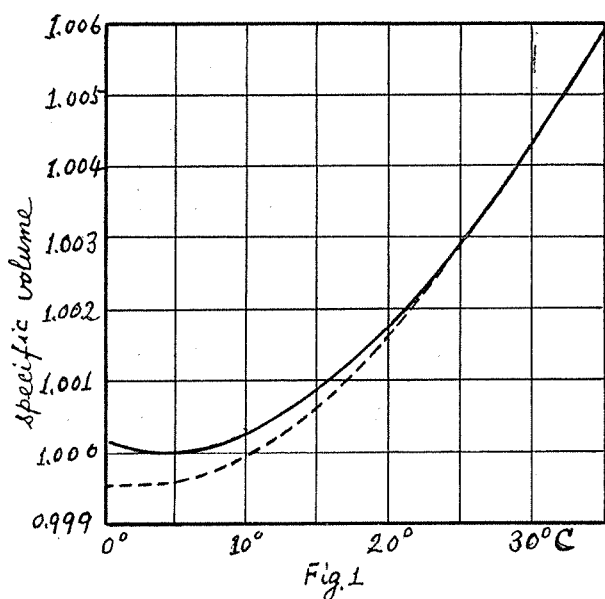
in broken lines in Figs. 1 and 2. The conditions that the specific volume and the specific heat of ideal liquid water increase gradually with increasing temperature, and that they approach asymptotically at the higher temperature range those actually observed with ordinary water respectively seem to be almost satisfied by these two curves in Figs. 1 and 2, where the curves drawn in full lines show the values of the specific volume and the specific heat of ordinary liquid water actually observed. This fact seems to indicate conversely that the above estimate of the amount of tiny ice crystals suspended in liquid water is not inadequate. The amount of floating tiny ice crystals calculated with (9) for various temperatures is shown by the curve in Fig. 3.

The specific volume of ice is larger than that of water, and consequently when the pressure increases by one atmosphere the melting point of ice decreases by about 0.007°C. Thus if ordinary water contains some quantity of ice, as is supposed

above, the amount of ice at a certain temperature must become less when the pressure is increased. Consequently when a sufficiently high pressure is applied to water, the ice crystals suspended in it will almost disappear even at a temperature very near to o°C, resulting in the disappearance of the minimum in the specific volume—temperature curve. This point is ascertained experimentally by Bridgman[1] by raising the pressure above 2000Kg/cm^2. Three curves obtained with the pressures of one atmosphere, 1000 Kg/cm^2, and 2000 Kg/cm^2 are shown in Fig. 4.

Hauser[2] examined the change of the coefficient of viscosity of water with pressure at various temperatures. He measured the coefficients of viscosity of water η_{400} and η_0 at the pressures of 400 atms. and 1 atm. respectively at various temperatures. The relative percentage difference $\{(\eta_{400}-\eta_0)100\}/\eta_0$ for various temperatures are plotted in Fig. 5. As is seen by the curve in Fig. 5, the relative percentage difference becomes negative when the temperature is decreased from about 30°C. This fact seems to conform our view. When the pressure is increased at a certain temperature below 30°C, where the ice content in water is noticeable, some ice crystals melt and disintegrate into much smaller water mole-
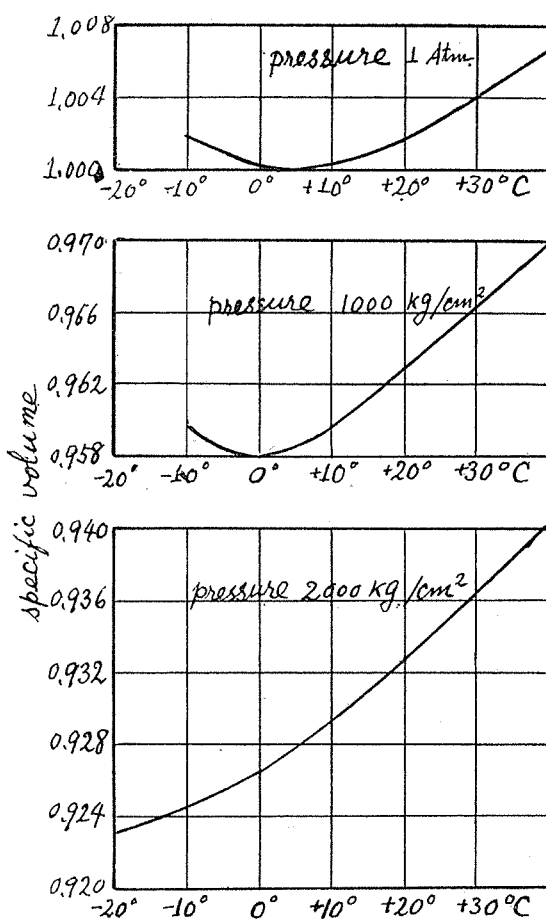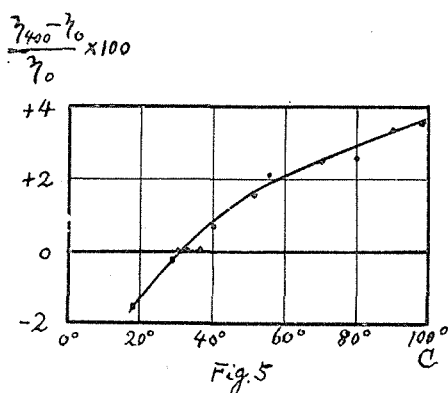

Fig. 4

1 Bridgman: ZS. f. anorg. Ch., **77**, 384–385 (1912)
2 Hauser: Ann. d. Phys., **5**, 597 (1901)

$$\frac{\eta_{400}-\eta_0}{\eta_0}\times 100$$

Fig. 5

cules constituting ideal liquid water ; and as the result of this displacement of the ice crystals by much smaller water molecules the coefficient of viscosity of the water becomes smaller with increasing pressure at a temperature below $30°C$.

Recently the writer and K. Koyanagi[1] found that when a metal was subjected for a long time to a temperature just below its melting point, minute grooves were formed at its crystal boundaries. They attributed the cause of the formation of such grooves to the fact that the metal crystal is easier to melt at its boundaries and also at its contact surface with its melt than in the interior of the crystal. This seems to be due to the irregularity of the intermolecular force at the crystal boundaries and at the contact surface of the crystal with its melt. In the case of a tiny ice crystal having the size of the order of its unit cell, its contact surface with ideal liquid water is very large when compared with its volume : and its tendency to melt is strong even in the temperature range belonging to the supercooled state below $0°C$. Moreover there is a macroscopic force that enables the ice crystal to melt at a temperature above $0°C$ and to grow at a temperature below $0°C$. Influenced by such a macroscopic force the melting tendency of the tiny ice crystal is strengthened above $0°C$ and is weakened below $0°C$. Thus it is thought that the existence of the individual tiny ice crystals is not permanent but momentary. The growth of the ice crystal to a considerable size below $0°C$ is of course governed by the macroscopic force, but a stable nucleus is needed to start it. In the supercooled state, we must of course admit the existence of the tiny ice crystals having the size of the order of their unit cell ; but as the supercooled state persists under suitable conditions, such tiny ice crystals are so unstable that they cannot become the nuclei of the crystal growth except at the extreme low temperature attainable in supercooled water. Thus if the freezing of water is to occur, the existence of nuclei of larger crystal fragments, whose melting tendency is less than that of

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1   U. Yoshida and K. Koyanagi: These Memoirs, **18**, 9 (1935)

the smallest crystal fragments mentioned above, or the proper condition for the formation of such nuclei is necessary. If, in a supercooled state, some minute crystals of the proper size are in some way formed in water, their weak melting tendency will be overcome by the stronger macroscopic force which causes them to grow, and the whole liquid water will freeze immediately. It may be supposed, considered microscopically, that some parts of an ice crystal at a temperature below zero are in the state of liquid water just as ordinary liquid water contains some tiny ice crystals in it. But actually this is inconceivable, and the ice has a definite melting point at $0°C$. This is, of course, due to the presence of a macroscopic force tending to melt the ice at a temperature above $0°C$ and to freeze the water at a temperature below $0°C$. But, according to the writer's view, the other reason for it is that the melting of a crystal usually takes place only at its exterior boundary where the intermolecular force is irregular, and not in its interior where the intermolecular force is regular, even at a temperature which is higher than or equal to its melting point. Thus in the case of ordinary ice at a temperature below $0°C$, if melting occurs spontaneously at some parts of it, it will be confined to a very thin layer at the exterior boundary of the ice. The amount of the liquid water thus formed will be negligible compared with the total mass of the ice, and the whole block of the ice crystal retains its solid state almost perfectly just up to its melting point.

If the consideration above stated that ordinary liquid water contains a small quantity of tiny ice crystals having the size of the order of their unit cell is correct, this is the universal nature of all liquids ; and the liquid of any substance must be regarded as containing similarly some quantity of crystals having the size of the order of their unit cell. The increase in volume by the freezing of water into ice crystals is a peculiar characteristic of water, a peculiarity which causes the occurrence of the minimum value of a specific volume of water at $4°C$. However, with most substances except water, the volume contracts by solidification from the liquid to the crystalline state ; and the specific volume always increases with the rise of the temperature.