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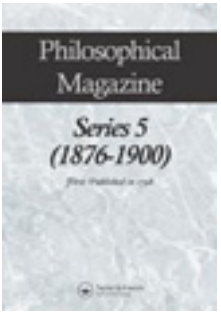

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V. Change of state: Solid-liquid

J.H. Poynting [a] [b]

[a] Trinity College, Cambridge

[b] Mason College, Birmingham

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now took ten seconds less for its ascent. After a day's repose it rose again in the oil with its original velocity.

13. The fundamental formulæ given in this paper admit of easy extension to other cases. I have, for example, found in the ascent of a hollow glass bulb a good indication of the maximum density of water, and of the amount of dissolved matter in saline solutions; and it could obviously be applied to determine the specific gravity of solid bodies.

The experiments which I have recorded show clearly that the rate of ascent of a solid through a liquid depends, not only upon the density of the liquid, but upon some other property —probably the viscosity. When the ascending solid approximates in diameter to the diameter of the reservoir, special retardation occurs, and some new law controls the motion. The commencement of this retardation is earlier with oils than with water, earlier with water than with alcohol and water—earlier, in short, when viscosity is greater. In reservoirs of sufficient diameter, the rate is inversely proportional to the square of the altered condition.

My thanks are due to Messrs. Ellis and Smith for their aid in this investigation.

Glasgow, March 1881.

V. *Change of State: Solid-Liquid.* *By* J. H. Poynting, *Late Fellow of Trinity College, Cambridge, Professor of Physics, Mason College, Birmingham**.

[Plate I.]

TWO distinct types of change of state from solid to liquid have usually been recognized. The most familiar of these is the ice-water type, in which, as the temperature rises, the solid remains quite solid up to the melting-point; when this is reached it begins to melt *at the surface*, and the temperature remains constant till the whole is liquid, when the temperature again rises. Corresponding to this change of state there is a definite latent heat. In the second class of bodies, of which sealing-wax and phosphorus are examples, there is a gradual softening as the temperature rises; and this softening takes place *throughout the mass*. There is no definite arrest of the rise of temperature, and no definite latent heat.

It has sometimes been supposed that the ice-water type is merely a limiting case of the sealing-wax type, where the softening takes place, but through a very small range of temperature. Prof. Forbes held this view, and by it attempted to explain regelation; but subsequent experiments have not

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supported the theory, and I believe it is now generally abandoned.

Since, in the ice-water form of change of state, fusion only takes place at the surface, it seems much more probable that it is an exchange phenomenon analogous to the change which takes place when water is evaporating, according to the kinetic theory. Just as in the case of water-steam, a steady state is reached when the number of molecules escaping from the surface of the water into the gas is equal to the number passing from the gas into the water, so in the case of water-ice a steady state (that is to say, the melting-point of ice) is probably reached when the number of molecules passing from the ice into the water is equal to the number passing from the water to the ice. For the analogue of the sealing-wax type of melting we must probably take the change of state which takes place in a liquid-gas above its critical point, where it changes gradually from a state rather liquid than gaseous to a state certainly gaseous.

In this paper I shall attempt to support this view of solid-liquid change of state. The following is a summary of the argument and the conclusions arrived at.

It is assumed that the maximum vapour-tension of a substance at any temperature is an indication of the number of molecules crossing its surface in a condition to escape. Now Regnault's experiments show that at 0° ice and water have the same vapour-tension; that is, the number of molecules crossing the surface of the ice ready to escape is equal to the number crossing the surface of the water in the same condition. Hence, when the two are in contact at 0°, the interchange of molecules is equal. For temperatures below 0°, Kirchhoff has shown that the vapour-tension of water is greater than that of ice, and above 0° it is less than that of ice—if ice can exist. (Another proof of this theorem is here given.) It is, then, easy to give a general explanation of the phenomena of melting and freezing by supposing that, if the temperature is not at the melting-point, the substance in the state with the greater vapour-tension will lose at the expense of the state with the less vapour-tension.

To explain the alteration of the melting-point by pressure, we must suppose that pressure alters the vapour-tension, and therefore the rate of escape of molecules, and that this alteration is different for the two states. Sir William Thomson has shown that a liquid in a capillary tube is in equilibrium with its vapour at a greater or less tension than at the plane surface according as the surface is convex or concave, upwards, and has given a formula for the difference. Accompanying

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this curvature of surface is a difference of pressure in the liquid; and I suppose the variation of vapour-tension to be due to the difference of pressure. A proof is given of Sir W. Thomson's formula, which seems to bring out more clearly the connexion of the phenomenon with the pressure, and which seems to apply to solids as well as liquids. According to this formula, the steady state (the melting-point) may be reached at any temperature if the pressure can be so adjusted that the vapour-tensions in the two states at that temperature and pressure are equal. The resulting lowering of the melting-point by pressure agrees in amount with that given by the well-known formula of Prof. J. Thomson.

It follows from this mode of regarding the subject, that, if in any way the ice can be subjected to pressure while the water in contact with it is not so subjected, then the lowering of the melting-point per atmosphere is about $11\frac{1}{2}$ times as great as when both are compressed. I give the results of some experiments which I have made to test this, and which certainly seem to indicate that the fall of melting-point is much greater than the amount usually supposed if the ice alone be compressed.

The isothermals for ice-water are then discussed. It has been supposed that, if we could employ a sufficiently low temperature and high pressure, then ice would pass continuously into water; that is, the isothermals would have no horizontal part corresponding to a mixture of ice and water, and we should have a critical point. Assuming, however, that a mixture of ice and water completely freed from foreign gases can be subjected to great negative pressure or tension, it seems probable that there is another critical point at a temperature above 0° and at a high negative pressure; that is, the water-ice line is a closed curve. We know that below 0° the water isothermals can be prolonged below the horizontal portion, since water is unfrozen in certain cases,—and that the ice isothermals can be prolonged above the horizontal portion; for ice, at 0° say, can be suddenly compressed without melting in the interior. This suggests that the true form of the isothermals is a continuous curve, of the nature which Prof. J. Thomson has suggested in the case of liquids and their vapours.

If we suppose that the curves are continuous in the same manner for ice-water above 0°, then Prof. Carnelley's "Hot Ice" would seem to be represented by the prolongations upwards of the ice isothermals beyond the horizontal line to where they meet the line of no pressure. The critical point, which certain assumptions roughly fix at about 14° C., would then be an upper limit, or rather above the limit, to the temperature of hot ice in a vacuum.

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In conclusion, it is pointed out that the sealing-wax type of melting is probably similar to the change of ice into water below the lower, or above the upper, critical points, if these exist.

Melting and Freezing of the Ice-water Type at ordinary Temperatures and Pressures.

It seems to have been conclusively proved by experiment that, in bodies of the ice-water type, change of state, either from solid to liquid, or the reverse, takes place only at the surface, or at a surface separating dissimilar portions. This would also seem to follow from the fact that the change of state always requires a certain finite amount of energy to be abstracted from, or supplied to, the mass without alteration of temperature. In the middle of a homogeneous body, where the temperature varies gradually, we must have the energy per unit of volume a continuous quantity as we pass from point to point. Hence, when at any point there is sufficient energy per unit of volume to change the state, either the surrounding temperature must be far above the ordinary temperature for change of state, or the surrounding substance must occupy an intermediate condition between the two states. On the former supposition we should certainly not have the ordinary change of state, though something of the sort may occur in the case of Dr. Carnelley's "hot ice;" and in the latter we should have the sealing-wax type, and no signs of this have been observed.

Since, then, change of state is a surface phenomenon, we are led at once to connect it with the escape of molecules which we know to be always taking place from the surface, as indicated by the definite vapour-tension which the body possesses, whether solid or liquid. Now Regnault's experiments have shown that at 0° ice and water have the same vapour-tension, and at the same time a mixture of ice and water at that temperature maintains the same proportion between the two constituents as long as no heat is allowed to pass into or out of it; that is, as many molecules escape from the water into the ice as pass in the opposite direction from the ice into the water. We seem, then, to be justified in assuming that *the number of molecules coming up to a given surface with a sufficient velocity to escape is indicated by the maximum vapour-pressure at that temperature.*

Now suppose that we have a mixture of ice and water below 0°. Kirchhoff has shown (Pogg. *Ann.* ciii. p. 206) that below 0° the vapour-tension of water exceeds that of ice by ·044 millim. of mercury per degree; and his reasoning will equally prove that it falls below it by the same amount

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above 0°, if ice can exist at such a temperature. Prof. J. Thomson has subsequently (Brit. Assoc. Report, 1872, p. 24; Proc. Roy. Soc. 1873; 'Nature,' ix. p. 392) arrived at a similar conclusion independently. A proof differing in arrangement from Kirchhoff's, and following out rather the line indicated by Thomson, will be given below.

In a mixture, then, of ice and water below 0°, since the water has the greater vapour-tension, more molecules will cross the surface from the water to the ice than in the opposite direction. The ice will therefore gain, while the water loses. At the same time the molecules will possess less energy when arranged as ice. Hence the temperature of the whole will rise, and this rise will go on till 0° is reached, when there is once more equilibrium—or till the whole is converted to ice, if that condition be previously reached. This seems sufficiently to explain the action of a small piece of ice dropped into water below 0°; and the fact that the change of state is a surface phenomenon seems to show that the presence of some ice is necessary to commence change of state.

If a mixture of ice and water at 0° be supplied with heat, as soon as the temperature rises ever so little above 0° the equilibrium of exchange is destroyed; for the vapour-tension of ice becomes greater than that of water, and therefore the number of molecules entering the water from the ice is greater than the number going in the opposite direction. But since the water arrangement requires more energy, heat is absorbed, and the mixture has a tendency to fall back to 0°.

Before going on to discuss the effect of pressure on the melting-point, I give a proof, with a somewhat more general result, of Kirchhoff's formula,

$$\frac{d\varpi'}{dt} - \frac{d\varpi}{dt} = \cdot 044 \text{ millim. of mercury},$$

where ϖ' is the maximum vapour-tension of ice, and ϖ that of water.

Start with a volume v of water at temperature $-t°$. Let it evaporate, always at the temperature $-t°$, in a cylinder which it does not wet, at its maximum vapour-tension ϖ, which we suppose to be maintained by a piston. Let the ultimate volume of the water-vapour be V. Then the external work done in the expansion is $\varpi(\mathrm{V}-v)$.

Now let the vapour further expand, always at the same temperature and in equilibrium with the pressure, till we have reached a volume V′ at the maximum vapour-tension ϖ' of ice. Assuming Boyle's law to hold, the work done in this expansion is $\varpi'\mathrm{V}'\log\frac{\varpi}{\varpi'}$; and this would be 0 if $\omega=\omega'$.

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Now introduce a particle of ice at $-t°$ into the cylinder, and condensation into ice will go on till all the vapour has disappeared. If the ultimate volume of the ice is v', the work done on the substance is $\varpi'(V'-v')$.

Increase the pressure from ϖ' to $\varpi'+p$ till the melting-point is lowered to $-t°$. If κ' is the coefficient of cubic compressibility of ice, $\frac{p^2}{2}\kappa' v'$ is the work done in the compression.

Introducing a drop of water, allow the whole to melt into water under the pressure $\omega'+p$, the work done during the melting being

$$(\omega'+p)\{v'(1-p\kappa')-v(1-p\kappa)\},$$

where κ is the coefficient of cubic compressibility for water.

Now let the water expand to its original volume v by gradually reducing the pressure to ϖ. The external work done is $\frac{p^2}{2}\kappa v$.

We now have the substance in its original state; and the cycle through which it has been taken was reversible at every step; therefore

$$\int \frac{dQ}{T}=0.$$

But T is constant; therefore

$$\int dQ=0.$$

Then the total external work is zero, or

$$\varpi(V-v)+\varpi' V' \log\frac{\varpi}{\varpi'}-\varpi'(V'-v') \\ -(\varpi'+p)\left\{v'\left(1-\frac{p\kappa'}{2}\right)-v\left(1-\frac{p\kappa}{2}\right)\right\}=0.$$

By means of the equation

$$\varpi V=\varpi' V',$$

and neglecting products of ϖ and κ, this reduces to

$$\varpi V \log\frac{\varpi}{\varpi'}=p\left\{v'\left(1-\frac{p\kappa'}{2}\right)-v\left(1-\frac{p\kappa}{2}\right)\right\}+(\omega-\omega')v. \quad (1)$$

Neglecting the term $(\omega-\omega')v$, and putting for $\varpi' V$ $\omega_0 V_0 \alpha T$, where $\omega_0 V_0$ are the pressure and volume at 0° C., and T the absolute temperature, we have

$$\frac{\varpi}{\varpi'}=e^{\frac{p\left\{v'\left(1-\frac{p\kappa'}{2}\right)-v\left(1-\frac{p\kappa}{2}\right)\right\}}{\omega_0 V_0 \alpha T}}. \quad . \quad . \quad . \quad (2)$$

For temperatures near 0° C. we may neglect products of p

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and κ, and we obtain as an approximation

$$\frac{\omega}{\omega'} = 1 + \frac{p(v'-v)}{\omega' V'},$$

or

$$\omega - \omega' = p\,\frac{v'-v}{V'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

At 0°,

$$v'-v = \cdot 087, \quad V' = 209037,$$

and the pressure required to lower the melting-point $t°$ is $\frac{760\,t}{\cdot 00733}$ millim. by the well-known formula. Substituting in equation (3), we get

$$\omega - \omega' = \cdot 044\,t,$$

or

$$\frac{d\omega'}{dt} - \frac{d\omega}{dt} = \cdot 044 \text{ millim. of mercury,} \quad . \quad . \quad (4)$$

which is Kirchhoff's result.

If the temperature be much below 0° C., we cannot make these approximations without further examination, as the terms containing κ and κ' in (2) may rise into importance.

It may be noticed that (2) could be used as an equation to determine p, the pressure required to produce a fall of the melting-point to T, if there were any accurate experimental method of measuring ϖ and ϖ'.

Effect of Pressure on the Melting-point.

If we are right in regarding the change from the solid to the liquid state as an exchange phenomenon in which the rate of exchange is indicated by the vapour-tension, we ought to be able to show that the pressure which lowers the melting-point to a certain temperature will so alter the rate at which the two states of the substance give off molecules from their surfaces, that at that temperature there will be an equilibrium of exchange. That is, we ought to be able to show that pressure alters the vapour-tensions of the two states, but alters them by different amounts, so that the equality of vapour-tensions now occurs at the new melting-point.

Now in the ordinary case, where the vapour-tension is measured we have the substance only under the pressure of its own vapour; but in the rise or fall of a liquid in a capillary tube we may have a substance in contact with its own vapour when the substance is at a very different pressure from the vapour in contact with it.

Sir William Thomson has shown (Proc. Roy. Soc. Edinb. 1870, vol. vii. p. 63; Maxwell's 'Heat,' 1877, p. 287) that if

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a liquid rises in a capillary tube so that its surface is concave upwards, and (we may add) the pressure of the liquid is less than at the plane surface, then the equilibrium vapour-tension is less than at the plane surface. If the liquid falls in the tube, so that the surface is convex and the pressure greater than at the plane surface, then the equilibrium vapour-tension is greater. It has been supposed that this difference of vapour-tensions is due to the curvature of the surface; and Fitzgerald has suggested that we may thus perhaps obtain a connexion between "two apparently unrelated quantities," the evaporation and the surface-tension (Phil. Mag. [5] viii. p. 384). But while a very slight impurity in a liquid can greatly alter the surface-tension, it has not been shown that it alters the evaporation to the same degree. I think that we must look for the explanation elsewhere than in the curvature of the surface; and I shall endeavour to show that we may account for the effect by the difference of pressures of the liquid at the curved and plane surfaces. The curvature of the surface is then, as it were, an accidental accompaniment of the difference of pressure, and not the cause of the variation in the vapour-tension. We might therefore expect to find the variation taking place also at flat surfaces if the pressure be altered, and with solid as well as with liquid bodies. We cannot directly investigate the vapour-tension of flat surfaces under pressure; but I shall assume that we may here take, instead, the rate at which exchange takes place when the solid and liquid are in contact with each other.

Sir W. Thomson's formula is

$$p=\varpi-\frac{2\mathrm{T}\sigma}{r(\rho-\sigma)}, \quad \ldots\ldots \quad (5)$$

where

p is the vapour-tension in contact with the concave surface,
ϖ is the vapour-tension in contact with the plane surface,
T is the surface-tension of the liquid,
ρ and σ the densities of the liquid and its vapour respectively,
r the radius of curvature of the curved surface.

If P be the difference between the hydrostatic pressures just beneath the curved surface and just beneath the plane surface, equation (5) may easily be put in the form

$$p=\varpi-\mathrm{P}\frac{\sigma}{\rho}, \quad \ldots\ldots\ldots \quad (6)$$

or a pressure P in the liquid increases the vapour-tension by an amount $\mathrm{P}\frac{\sigma}{\rho}$.

The following proof of this formula, $p=\varpi-\mathrm{P}\frac{\sigma}{\rho}$, is, I believe,

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applicable to both solids and liquids, and obtains a more general form for the result.

Let a volume v of a body (solid or liquid) be in a perfectly conducting cylinder (fig. 1, Plate I.) so arranged that the temperature is always constant. A porous plug, which the substance if liquid does not wet, is in the cylinder; and the holes in the plug are to be so fine that any required pressure can be applied to the liquid without forcing it beyond the further surface of the plug, the curved surface of the liquid there withstanding the pressure. A piston to which pressure can be applied is in contact with the substance; and beyond the plug is another movable piston to which any pressure can be applied, the arrows in the figure indicating the direction in which the external pressures are applied to the pistons.

Let the volume of the substance in the denser state at the pressure of its normal vapour-tension ϖ for the given temperature be v. Let V be the volume of the whole as vapour at the pressure ϖ. Let the equilibrium vapour-tension when the denser state is subjected to a greater pressure $\varpi + \mathrm{P}$ be p, and let the volume of the whole as vapour at the pressure p be V′. Let the coefficient of cubic compressibility be κ. Now take the body through the following cycle.

Increase the pressure to $\varpi + \mathrm{P}$ on the left-hand piston, and then let the substance evaporate through the plug to the right hand, pushing out the piston there at pressure p till the whole is evaporated to a volume V′. If p be greater than ϖ, let the vapour expand from V′, always in equilibrium with the pressure, finally arriving at a volume V and pressure ϖ. Now cover the porous plug, and, if necessary, commence condensation by introducing a small amount of the substance. Push in the right-hand piston at the pressure ϖ till the whole is condensed to volume v.

We have now conducted the substance through a cycle each step of which is reversible*. Then

$$\int \frac{d\mathrm{Q}}{\mathrm{T}} = 0.$$

* It seems difficult to imagine a plug which would satisfy the condition of reversibility for the solid under great pressure in contact with its vapour. Perhaps the following would answer the requirements, if an ordinary porous plug is insufficient. Suppose the solid in a finely-divided state, and contained in a liquid which wets it but is of a very slightly greater specific gravity, and whose vapour-tension is negligible. During evaporation turn the cylinder with the vapour-chamber upwards. The particles of solid will rise up through the pores, and a small fraction of their surface will protrude, but they will otherwise be subjected to a pressure $\varpi + p$. For condensation reverse the cylinder. As the solid condenses on the surface it will rise up as fast as it is formed, and so increase the volume of the chamber and force back the piston.

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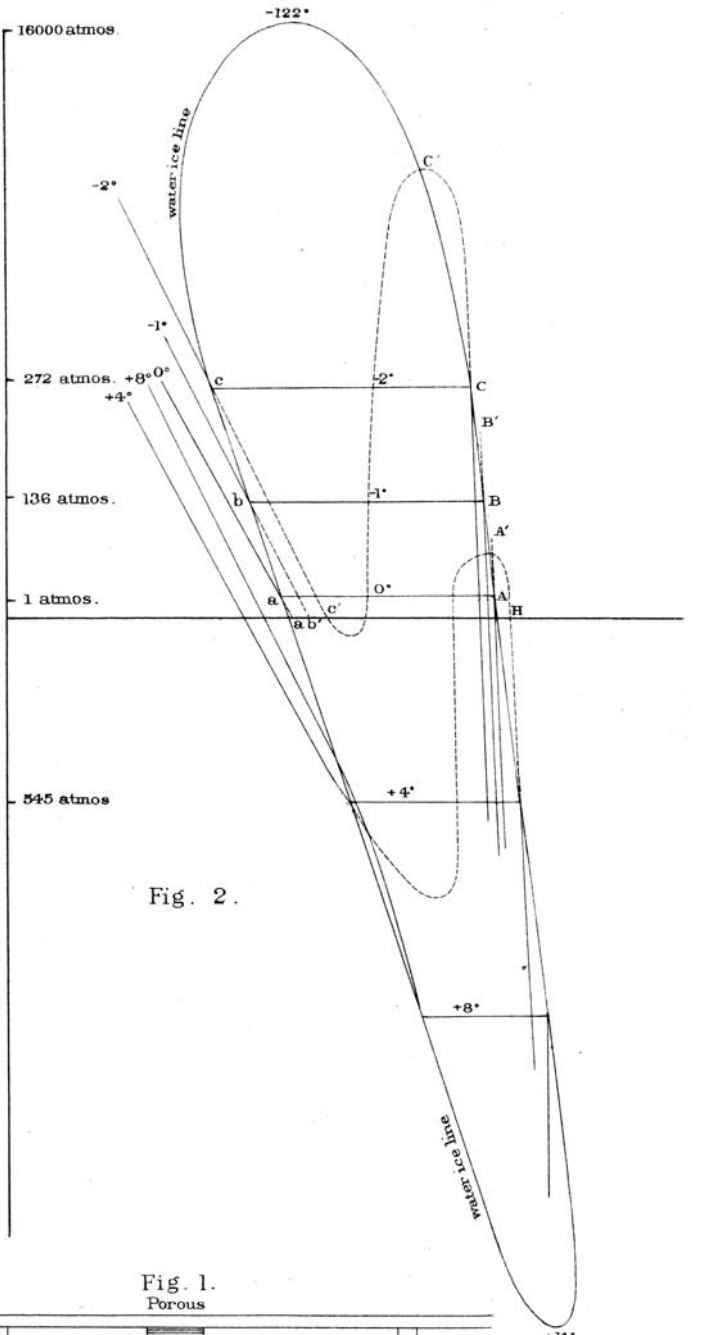

Fig. 2.

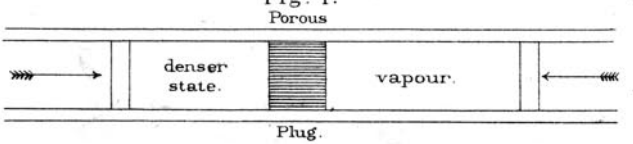

Fig. 1.

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But T is constant; then

$$\int dQ=0,$$

and the external work is, on the whole, zero. This gives us

$$\left(\omega+\frac{P}{2}\right)P\kappa v+(\omega+P)v(1-P\kappa v)-pV'-\varpi V\log\frac{p}{\varpi}+\varpi(V-v)=0. \quad . \quad . \quad (7)$$

But since, at low temperatures such as we are here considering, Boyle's law is almost exact, we have

$$\varpi V=pV'.$$

Then, neglecting terms containing $\varpi\kappa$,

$$\omega V\log\frac{p}{\omega}=Pv\left(1-\frac{P\kappa}{2}\right),$$

or

$$\frac{p}{\omega}=e^{\frac{Pv}{\varpi V}\left(1-\frac{P\kappa}{2}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For ordinary values of P this gives

$$p-\omega=\frac{Pv}{V}=\frac{P\sigma}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

which agrees with Sir W. Thomson's result in equation (6).

It may be worth while to point out the following result of the reasoning on which the above proof is based.

In a quantity of liquid at a uniform temperature, the number of molecules interchanged across a surface will increase as we descend, owing to the increase of pressure. If near the surface the number be proportional to the vapour-tension at the surface, then at any depth the number will be proportional to the pressure in an atmosphere of vapour at that level which, at the level of the surface, has the pressure of the vapour in equilibrium; that is, the liquid will behave as a non-vaporizing solid through whose interspaces the vapour can move freely.

Assuming, then, that equation (9) holds both for solids and liquids, let us apply it to the case of ice and water in contact with each other at a temperature $-t^\circ$ and at a pressure P, such that $-t^\circ$ is the melting-point.

Let ϖ be the normal vapour-tension of water at $-t^\circ$,
ϖ' " " " ice at $-t^\circ$,
p be the altered vapour-tension of water,
p' " " " ice,
ρ the density of water, v its specific volume,
ρ' " " ice, v' " "
σ " " their vapour, V its specific volume.

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Taking σ and V as the same for ice and water as an approximation, then equation (9) gives us

$$\left.\begin{aligned} p &= \varpi + \mathrm{P}\frac{\sigma}{\rho} = \varpi + \frac{\mathrm{P}v}{\mathrm{V}}, \\ p' &= \varpi' + \mathrm{P}\frac{\sigma}{\rho'} = \varpi' + \frac{\mathrm{P}v'}{\mathrm{V}}. \end{aligned}\right\} \quad . \quad . \quad . \quad (10)$$

Subtracting, we have

$$p - p' = \varpi - \varpi' - \mathrm{P}\frac{v - v'}{\mathrm{V}}. \quad . \quad . \quad . \quad . \quad (11)$$

But by equation (3) we have

$$\omega - \omega' = \mathrm{P}\frac{v' - v}{\mathrm{V}};$$

then

$$p - p' = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Or, under the pressure P at the melting-point, the vapour-tension of ice equals that of water, and there is an equal interchange of molecules taking place. According to this, then, we may thus regard the alteration of melting-point by pressure. The pressure increases the number of molecules given off from the surfaces in contact with each other in both states; but the increase is greater in the case of the less dense state. Now, in the case of ice-water, ice is the less dense state, and below 0° it has the less vapour-tension. Hence a sufficiently great increase of pressure, while increasing both vapour-tensions, can make that of ice overtake that of water, or can lower the melting-point. For paraffin, the liquid is the less dense state. Then, increase of pressure can only render the two vapour-tensions equal above the normal melting-point when the liquid vapour-tension is less than that of the solid.

Suppose now only one of the two states (the ice) to be subjected to increase of pressure. For instance, let the ice be compressed on a porous plate through which the water can circulate freely. Then the pressure increases the rate at which molecules escape from the ice into the water, but does not affect the rate of escape of the water-molecules into the ice, and a much less pressure will suffice to produce equilibrium of exchange for a given temperature below 0° than when both ice and water are subjected to the pressure.

To calculate the fall in melting-point produced by a pressure P′ on the ice alone, we have, instead of (10),

$$\left.\begin{aligned} p &= \varpi, \\ p' &= \varpi' + \frac{\mathrm{P}'v'}{\mathrm{V}}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

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If we have $p=p'$, we have the melting-point; and in this case, by subtracting, we obtain

$$\varpi-\varpi'=\frac{P'v'}{V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Now the pressure required to lower the melting-point to the same degree when both ice and water are compressed is given by

$$\varpi-\varpi'=\frac{P\,.\,v'-v}{V}; \quad . \quad . \quad . \quad . \quad . \quad (15)$$

or

$$\frac{P'}{P}=\frac{v'-v}{v}$$

$$=\cdot 087. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Or the fall in melting-point caused by a given pressure on the ice alone is about $11\frac{1}{2}$ times as great as when both ice and water are compressed. That is, 1 atmosphere lowers the melting-point about ·0843° C., and 11·7 atmospheres lower it 1° C. This result may be obtained in the same way as Prof. J. Thomson's formula, on the supposition that the process is reversible; but as I was led to the result by the above considerations, I have given only this proof.

This seems to have an important bearing on ordinary cases of regelation, when two pieces of ice are brought into contact at one or two points. About that point the ice will be subjected to great pressure; but the melted water is not necessarily subject to the pressure, and accordingly the melting-point may be lowered by $11\frac{1}{2}$ times as much as has been formerly supposed. I have made some experiments to test this result; and the best arrangement I have yet devised has been the following:—A block of ice, fitting in a hollow iron cylinder with open ends, was laid on a bed of sand on the top of which was placed one junction of a copper-iron thermopile; the other junction was placed in melting ice. When the two junctions reached the same temperature, as indicated by a galvanometer in the thermopile circuit, pressure was applied to the ice by a hydraulic press. The water from the melting of the ice was able to escape freely through the sand, and was therefore only at atmospheric pressure. The results so far have been very variable, sometimes indicating no greater lowering of the melting-point than that usually assumed—·0073° per atmosphere. But in several cases the lowering has been decidedly greater. The following experiment gives the greatest value I have yet obtained for the lowering of the melting-point. The galvanometer-deflection per

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1° difference in the temperature was determined by separate experiments to be 9·4 divisions.

Time, April 30.	Pressure, in tmospheres.	Galvanometer deflections, in divisions.	Temperature of the cooler junction.	Calculated temperature, at ·0073 per atmosphere.
h m				
12 51	18	4·5	−·48° C.	−·13°
12 53	18	5·3	−·56	−·13
12 57	18	5·0	−·53	−·13
1 30	9	2·5	−·27	−·065
1 32	9	3·3	−·34	−·065

It will be seen, by a comparison of the last two columns, that the lowering here was four or five times that given by the usual formula. I have not thought it necessary to give details of the other results, as I have not yet had time to investigate the causes of failure. I hope to pursue the subject shortly.

Perhaps the following imaginary experiment may serve as a simple illustration of the last two sections. Suppose two cylinders, one containing ice, the other water at the same temperature, to be connected above by a tube through which the vapour can pass, and let them only be in contact with their own vapour.

At 0°, or rather at +·0073, their vapour-tensions being equal, as soon as the pressure reaches 4·6 millim. then the ice and water will remain unaltered in amount as long as no heat is allowed to pass into or out of the cylinders. If the temperature be kept slightly below 0°, then, since the vapour-tension of water is now greater than that of ice, the water will gradually distil over into the ice-vessel and there condense as ice, the average temperature rising. If the temperature be kept constant, however, the whole of the water will in time go over into the ice-vessel. If the temperature be slightly above 0° (supposing it possible still to keep the ice solid), then the ice has the greater vapour-tension and will gradually distil over into the water-vessel, and the average temperature will fall. In time, if the temperature be kept above 0°, the whole of the ice will go over into the water-vessel.

If, now, the ice and water be subjected to pressure by porous pistons which the water does not wet (the pressure in each cylinder being the same), then, if the temperature be 0°, an increase of pressure will cause more evaporation from the ice than from the water; that is, the ice will distil over into the

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water-cylinder and form water there. To obtain equilibrium again, the temperature must be lowered to such a point that the pressure makes the two vapour-tensions once more equal, when the ice and water will remain unaltered in amount—that is, the melting-point will be reached. If now the ice alone be subjected to pressure, its vapour-tension will be increased while that of the water remains the same. And now the pressure required to produce equilibrium of vapour-tensions at a given temperature below 0° will only be about 2-23rds of that required when both are subjected to the same pressure.

The suppositions which I have made amount to this—that if the space filled with vapour be abolished and the ice and water be brought directly into contact with each other, then the rate of escape of molecules will be the same as before in each case, or bear the same proportion to it.

Isothermals of Ice-water: Critical Points.

If we draw the isothermals for ice and water on a pressure-volume diagram, they are of the general form shown in fig. 2, though the figure is entirely out of proportion.

If we may assume that the compressibility of water is considerably greater than that of ice, the horizontal part of the isothermals representing a mixture of ice and water will increase as the temperature falls below 0°, at least just at first. Then, if we call the line passing through the points where the isothermals turn to or from the horizontal part the ice-water line, this line will at first diverge as the temperature falls. Now, while ice contracts on cooling, its coefficient of expansion between −19° and 0° being given as ·000122 by Brunner, Despretz has shown that water expands on cooling below 0° even more than it expands for an equal rise above 8°. Hence the isothermals for ice and water approach each other at ordinary pressures as the temperature falls.

Using Brunner's coefficient for ice, and for water Hällström's formula (Jamin, *Cours de Physique*, vol. ii.),

$$\frac{v_0}{v_t} = 1 + \cdot 000052939\,t - \cdot 0000065322\,t^2 + \cdot 00000001445\,t^3,$$

and supposing that water could be cooled without freezing, it will be found that between −120° and −130° ice and water would have the same specific volume. This might lead us to suspect that the divergence of the two branches of the water-ice line would not continue if we could examine the isothermals at very low temperatures and high pressures, and that, as the temperature fell, the two states would at some point

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begin to approach (that is, the horizontal part of the isothermals would decrease), and that ultimately ice would pass gradually into water without any abrupt change of volume (that is, there would be a critical point). Below this critical point ice and water would probably be identical.

A similar conclusion is arrived at from the latent-heat equation. On the supposition that at the critical point the latent heat vanishes, the temperature given by that equation is $-122°{\cdot}5$, with a pressure of over 16,000 atmospheres (Baynes, 'Thermodynamics,' p. 169).

It is usually assumed that we must stop the isothermal at the base-line of no pressure. But we know that water can be subjected to a negative pressure; as, for instance, when it rises in a capillary tube in a vacuum, or when it adheres to a barometer-tube at a height greater than that of the barometric column. It seems probable that, if perfectly freed from foreign gases, it might even be subjected to a very high negative pressure without the particles being torn asunder. So, too, a mixture of ice and water might probably be subjected to tension. It seems at least worth while to draw the isothermals for ice and water on such a supposition.

Prof. J. Thomson's result for the alteration of the melting-point by pressure would hold for at least a short distance above 0° when we replace pressure by tension. Assuming it to hold for 4°, we should have to put on a tension of $4 \div {\cdot}00733$ atmosphere $= 545$ atmospheres. But if the expansion of water under a tension equals its compression under an equal pressure, the expansion is about $\frac{1}{21000}$ per atmosphere*; so that the volume of the water at 4°, under a tension of 545 atmospheres, will be 1·026. The ice, whose volume at 4° under no pressure would be 1·088, probably will not expand nearly so much under tension. The change of volume on melting will therefore probably be not very far from

$$1{\cdot}088 - 1{\cdot}026 = {\cdot}062,$$

against a change at 0° of ·087. Then the two branches of the ice-line will converge very considerably for temperatures above 0° and with negative pressures. At this rate of convergence the meeting-point is at about 14° C. At higher temperature the ice would pass gradually into water—that is, we should here have another critical point,—the two critical points being at opposite ends of the closed curve which represents the water-ice line.

* Might not the truth of this supposition be tested by the propagation of sound through the water above a barometric column at a negative pressure?

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On considering the isothermals below 0°, it will be noticed that the water-isothermals, at least as far as that for −20°, can be prolonged downwards past the horizontal line to meet the line of no pressure; for Despretz succeeded in cooling water to −20° in thermometer-tubes without freezing. These prolongations are represented by $a\,a'$, $b\,b'$, $c\,c'$ (fig. 2). Similarly the ice-isothermals can be at least slightly prolonged upwards past the horizontal line. For, suppose we take a block of ice at 0° and suddenly subject it to great pressure. Since it expands on heating, then sudden compression produces, if any thing, a slight rise in the temperature. At the same time the melting-point is lowered, and the ice begins to melt at the surface, and in time the whole will be lowered to the new melting-point. But just at first, and until it falls to that temperature, we have the ice on the prolongation of the isothermals upwards as at A A′ or B B′ in fig. 2. In a certain sense, then, we have "hot ice."

Since, then, the water-isothermals may be prolonged downwards and the ice-isothermals upwards, we may probably here adopt Prof. J. Thomson's suggestion as to the true shape of the isothermals in the case of liquid-and-gas mixtures (Brit. Assoc. Report, 1871, p. 30; Maxwell's 'Heat,' p. 125). This is indicated by the dotted line for −2° in the figure. If the isothermals also have this shape above 0° (as indicated by the dotted line for the 4° isothermal), then at first the ice-isothermals will be prolonged upwards to meet the line of no pressure, as, for instance, that of 4° at H. This seems to be the place where we must put Dr. Carnelley's "hot ice," on the diagram, if its temperature be really proved to be above 0°.

But if the critical point for the higher temperature exist, it is evident that, before this temperature is reached, the prolongations of the ice-isothermals will cease to reach up to the line of no pressure, and the limit to the temperature of hot ice in a vacuum is that of the last isothermal which touches the line of no pressure. To obtain ice at still higher temperatures, it would apparently have to be subjected to great tension. If the above calculation for the critical point is at all near the truth, then the highest temperature possible for ice in a vacuum is something below 14° C.

The view here advocated as to the nature of the melting of ice, would show that its fixity is as much a "constant accident" as the fixed boiling-point of water. If we have a piece of ice at any temperature and allow no water to form on its surface, then I see no reason why it should melt if heat be supplied to it by conduction from bodies which, when melted,

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it does not wet. I think, then, we ought to expect its temperature to rise, as Dr. Carnelley has apparently found to be the case.

Dr. Lodge has pointed out ('Nature,' Jan. 20, 1881) that, as far as we know, "there is no definite subliming-point for a solid, any more than there is a definite evaporating-point for a liquid." Hence, with such a mode of supplying the heat as above described, the temperature might perhaps be expected to rise to that of the last isothermal which reaches the line of no pressure. When it has reached this point the whole will be in an unstable state, and we might expect a further supply of heat to cause a sudden change into water. If, however, at any point in this process of raising the temperature the vapour-tension is allowed to rise nearly to its maximum, it will exceed that of water, which has a lower maximum; then a layer of water will be formed on the ice, and we shall have melting with a tendency of the temperature towards 0°.

The Sealing-wax Type of Melting.

We have seen that there is some reason to suppose that ice would pass gradually into water at a sufficiently low temperature and with sufficiently high pressure; that is, there would be no abrupt change of volume at a constant temperature, and no definite latent heat. But these are just the characteristics of the melting of substances of the sealing-wax type; and I think it exceedingly probable that we have such substances at temperatures below their critical points, or at least that they are analogous to water-ice below its critical point. If sealing-wax have a critical point, then if we start with some in the solid state at ordinary temperature, and while raising the temperature we increase the pressure so as always to keep it solid till above the critical point, if we reduce the pressure again to a certain point and at the same time a small amount of liquid sealing-wax be introduced, we ought to have a liquefaction of the whole with a finite expansion of volume; that is to say, we should have changed the ordinary sealing-wax type of melting into the ice-water type. It might, perhaps, be possible to test the truth of this supposition experimentally.

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