XXXVII.—*Theoretical Considerations on the Effect of Pressure in Lowering the Freezing Point of Water.* By JAMES THOMSON, Esq., of Glasgow. Communicated by Professor WILLIAM THOMSON.

(Read 2d January 1849.)

Some time ago my brother, Professor WILLIAM THOMSON, pointed out to me a curious conclusion to which he had been led, by reasoning on principles similar to those developed by CARNOT, with reference to the motive power of heat. It was, that *water at the freezing point may be converted into ice by a process solely mechanical, and yet without the final expenditure of any mechanical work.* This at first appeared to me to involve an impossibility, because water expands while freezing; and, therefore, it seemed to follow, that if a quantity of it were merely enclosed in a vessel with a moveable piston, and frozen, the motion of the piston, consequent on the expansion, being resisted by pressure, mechanical work would be given out without any corresponding expenditure; or, in other words, a perpetual source of mechanical work, commonly called a perpetual motion, would be possible. After farther consideration, however, the former conclusion appeared to be incontrovertible; but then, to avoid the absurdity of supposing that mechanical work could be got out of nothing, it occurred to me that it is necessary farther to conclude, that *the freezing point becomes lower as the pressure to which the water is subjected is increased.*

The following is the reasoning by which these conclusions are proved. Let there be supposed to be a cylinder, and a piston fitting water-tight to it, and capable of moving without friction. Let these be supposed to be formed of a substance which is a perfect non-conductor of heat; also, let the bottom of the cylinder be closed by a plate, supposed to be a perfect conductor, and to possess no capacity for heat. Now, to convert a given mass of ice into water without the expenditure of mechanical work, let this imaginary vessel be partly filled with air at 0° C., and let the end of it be placed in contact with an indefinite mass of water, a lake for instance, at the same temperature. Now, let the piston be pushed towards the bottom of the cylinder by pressure from some external reservoir of mechanical work, which, for the sake of fixing our ideas, may be supposed to be the hand of an operator. During this process the air in the cylinder would tend to become heated on account of the compression, but it is constrained to remain at 0° by being in communication with the lake at that temperature. The change, then, which takes place is, that a certain amount of work is given from the hand to the air, and a certain amount of heat is given from the air to the water of the lake. In the next place, let the bottom of the cylinder be placed in contact with the mass of water at 0°, which is proposed to be converted into ice, and let the piston be allowed to move back to the position it had at the commencement of the first process. During this second process, the temperature of the air would tend to sink on account of the expansion, but it is constrained to remain constant at 0° by the air being in communication with the freezing water, which cannot change its temperature so long as any of it remains unfrozen. Hence, so far as the air and the hand are concerned, this process has been exactly the converse of the former one. Thus the air has expanded through the same distance through which it was formerly compressed; and, since it has been constantly at the same temperature during both processes, the law of the variation of its pressure with its volume must have been the same in both. From this it follows, that the hand has received back exactly the same amount of mechanical work in the second process as it gave out in the first. By an analogous reason it is easily shewn, that the air also has received again exactly the same amount of heat as it gave out during its compression; and, hence, it is now left in a condition the same as that in which it was at the commencement of the first process. *The only change which has been produced, then, is, that a certain quantity of heat has been abstracted from a small mass of water at* 0°, *and dispersed through an indefinite mass at the same temperature, the small mass having thus been converted into ice.* This conclusion, it may be remarked, might be deduced at once by the application, to the freezing of water, of the general principle developed by CARNOT, that no work is given out when heat passes from one body to another without a fall of temperature; or rather by the application of the converse of this, which of course equally holds good, namely, that no work requires to be expended to make heat pass from one body to another at the same temperature.

Next, to prove that the freezing point of water is lowered by an increase of the pressure to which the water is subjected:—Let a cylinder, of the same imaginary construction as that used in the foregoing demonstration, contain some air at 0° C. Let the bottom of the cylinder be placed in contact with the water of an indefinitely large lake, of which the temperature is above 0° by an infinitely small quantity; and let the air be subjected to compression by pressure applied by the hand to the piston. A certain amount of work is thus given from the hand to the air, and a certain amount of heat is given out from the air to the lake. Next, let the bottom of the cylinder be placed in communication with a small quantity of water at 0°, enclosed in a second imaginary cylinder similar in character to the first; and let this water be, at the commencement, subject merely to the atmospheric pressure. Let, however, resistance be offered by the hand to any motion of the piston of this second cylinder which may take place. Things being in this state, let the piston of the cylinder containing the air move back to its original position. During this process part of the heat of the air becomes latent on account of the increase of volume. Thus the temperature of the air, from being above 0°, by an infinitely small quantity, instantly becomes absolutely 0°; and afterwards, as the motion of the piston continues, the air absorbs heat from the mass of water in the second cylinder, part of the mass passing at the same time into the state of ice. Hence the whole mass expands; and therefore, on account of the resistance offered by the hand to the motion of the piston of the cylinder containing the mass, the internal pressure is increased, and a quantity of work, not infinitely small, is given out by the piston, and is received by the hand. Towards the end of this process, let the resistance offered by the hand gradually decrease till, just at the end (that is, when the piston of the air-cylinder has resumed its first position) it becomes nothing, and the pressure within the water-cylinder thus becomes again equal to that of the atmosphere. The temperature of the mass of partly frozen water must now be 0°, and the air in the other cylinder being in communication with this, must have the same temperature. The air is therefore, infinitely nearly at its original temperature, and it has its original volume. Hence it is now left in a state infinitely nearly the same as that in which it was at first. Farther, let the ice, which has been formed by the freezing of the water, be placed in contact with the lake till it melts, which it will really do since the lake is warmer than 0°, though only by an infinitely small quantity. Thus the mass of water is left in its original state, and it has been already shewn that the air is left infinitely nearly in its original state. Hence no work, except an infinitely small quantity, can have been absorbed or developed by any change on the air and water, which have been used. But a quantity of work not infinitely small has been given out by the piston of the water-cylinder to the hand; and therefore an equal quantity* of work must have been given from the hand to the air-piston, as there is no other way in which the work developed could have been introduced into the apparatus. Now, the only way in which this can have taken place is by the air having been colder, while it was expanding in the second process, than it was while it was undergoing compression during the first. Hence it was colder than 0° during the course of the second process; or, in other words, *while the water was freezing, under a pressure greater than that of the atmosphere, its temperature was lower than 0°.*

The fact of the lowering of the freezing point being thus demonstrated, it becomes desirable, in the next place, to find what is the freezing point of water for any given pressure. The most obvious way to determine this would be by direct experiment with freezing water. I have not, however, made any attempt to do so in this way. The variation to be appreciated is extremely small, so small, in fact, as to afford sufficient reason for its existence never having been observed by any experimenter. Even to detect its existence, much more to arrive at its exact amount by direct experiment, would require very delicate apparatus which would

* In saying "an equal quantity" I, of course, neglect infinitely small quantities in comparison to quantities not infinitely small.

not be easily planned out or procured. Another, and a better, mode of proceeding has, however, occurred to me: and by it we can deduce, from the known expansion of water in freezing, together with data founded on the experiments of REGNAULT on steam at the freezing point, a formula which gives the freezing point in terms of the pressure; and which may be applied for any pressure, from nothing up to many atmospheres. The following is the investigation of this formula:—

Let us suppose that we have a cylinder of the same imaginary construction as that of the one described at the commencement of this paper; and let us use it as an ice-engine analogous to the imaginary steam-engine conceived by CARNOT, and employed in his investigations. For this purpose, let the entire space enclosed within the cylinder by the piston be filled at first with as much ice as would, if melted, form rather more than a cubic foot of water, and let the ice be subject merely to one atmosphere of pressure, no force being applied to the piston. Now, let the following four processes, forming one complete stroke of the ice-engine be performed.

Process 1. Place the bottom of the cylinder in contact with an indefinite lake of water at 0°, and push down the piston. The effect of the motion of the piston is to convert ice at 0° into water at 0°, and to abstract from the lake at 0° the heat which becomes latent during this change. Continue the compression till one cubic foot of water is melted from ice.

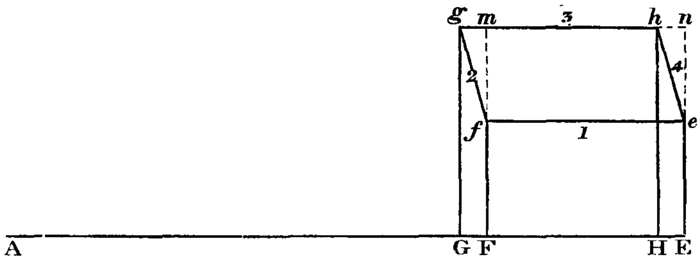
Process 2. Remove the cylinder from the lake, and place it with its bottom on a stand which is a perfect non-conductor of heat. Push the piston a very little farther down, till the pressure inside is increased by any desired quantity which may be denoted, in pounds on the square foot, by p. During this motion of the piston, since the cylinder contains ice and water, the temperature of the mixture must vary with the pressure, being at any instant the freezing point which corresponds to the pressure at that instant. Let the temperature at the end of this process be denoted by $-t°$ C.

Process 3. Place the bottom of the cylinder in contact with a second indefinitely large lake at $-t°$, and move the piston upwards. During this motion the pressure must remain constant at p above that of the atmosphere, the water in the cylinder increasing its volume by freezing, since, if it did not freeze, its pressure would diminish, and therefore its temperature would increase, which is impossible, since the whole mass of water and ice is constrained by the lake to remain at $-t°$. Continue the motion till all the heat has been given out to the second lake at $-t°$, which was taken in during Process 2, from the first lake at 0°.*

* This step, as well as the corresponding one in CARNOT's investigation, it must be observed, involves difficult questions, which cannot as yet be satisfactorily answered, regarding the possibility of the absolute formation or destruction of heat as an equivalent for the destruction or formation of other agencies, such as mechanical work; but, in taking it, I go on the almost universally adopted supposition of the perfect conservation of heat.

Process 4. Remove the cylinder from the lake at $-t^\circ$, and place its bottom again on the non-conducing stand. Move the piston back to the position it occupied at the commencement of Process 1. The temperature and pressure, during this process, must vary with one another, as they did in Process 2. Also, since as much heat has been given out as was taken in; and since the volume is the same as at the commencement of Process 1, the physical state of the mass contained in the cylinder must be now in every respect the same as it was at that time.

By representing graphically in a diagram the various volumes and corresponding pressures, at all the stages of the four processes which have just been laid down, we shall arrive, in a simple and easy manner, at the quantity of work which is developed in one complete stroke by the heat which is transferred during that stroke from the lake at 0° to the lake at $-t^\circ$. For this purpose, let E be the position of the piston at the beginning of Process 1; and let some distance, such as E G, represent its stroke in feet, its area being made a square foot, so that the numbers expressing, in feet, distances along E G may also express, in cubic feet, the changes in the contents of the cylinder produced by the motion of the piston.



Now, when 1·087 cubic feet of ice are melted, one cubic foot of water is formed. Hence, if E F be taken equal to ·087 feet, F will be the position of the piston when one cubic foot of water has been melted from ice, that is, the position at the end of Process 1, the bottom of the cylinder being at a point A distant from F by rather more than a foot. Let ef be parallel to E F, and let E e represent one atmosphere of pressure; that is, let the units of length for the vertical ordinates be taken such that the number of them in Ee may be equal to the number which expresses an atmosphere of pressure. Also let gh be parallel to E F, and let fm represent the increase of pressure produced during Process 2. Then the straight lines ef and gh will be the lines of pressure for Processes 1 and 2; and for the other two processes, the lines of pressure will be some curves which would extremely nearly coincide with the straight lines fg and he. For want of experimental data, the nature of these two curves cannot be precisely determined; but, for our present purpose, it is not necessary that they should be so, as we merely require to find the area of the figure $efgh$, which represents the work developed by the engine during one complete stroke, and this can readily be obtained with sufficient accuracy. For, even though we should adopt a very large value for fm, the change of pressure during Process 2, still the changes of volume $g\,m$ and $h\,n$ in Process 2 and Process 4 would be extremely small compared to the expansion during the freezing of the water; and from this it follows evidently that the area of the figure $efgh$ is extremely nearly equal to that of the rectangle $efmn$, but fe is equal to F E, which is ·087 feet. Hence the work developed during an entire stroke is $\cdot087 \times p$ foot-pounds. Now this is developed by the descent from $0°$ to $-t°$ of the quantity of heat necessary to melt a cubic foot of ice; that is, by 4925 thermic units, the unit being the quantity of heat required to raise a pound of water from 0° to 1° centigrade. Next we can obtain another expression for the same quantity of work; for, by the tables deduced in the preceding paper from the experiments of REGNAULT, we find that the quantity of work developed by one of the same thermic units descending through one degree about the freezing point, is 4·97 foot-pounds. Hence, the work due to 4925 thermic units descending from $0°$ to $-t°$ is $4925 \times 4{\cdot}97 \times t$ foot-pounds. Putting this equal to the expression which was formerly obtained for the work due to the same quantity of heat falling through the same number of degrees, we obtain

$$4925 \times 4{\cdot}97 \times t = \cdot087 \times p.$$

Hence,

$$t = \cdot00000355\, p. \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

This, then, is the desired formula for giving the freezing point $-t°$ centigrade, which corresponds to a pressure exceeding that of the atmosphere by a quantity p, estimated in pounds on a square foot.

To put this result in another form, let us suppose water to be subjected to one additional atmosphere, and let it be required to find the freezing point. Here p = one atmosphere = 2120 pounds on a square foot; and, therefore, by

$$(1.) \qquad t = \cdot00000355 \times 2120.$$

or

$$t = \cdot0075.$$

That is, the freezing point of water, under the pressure of one additional atmosphere, is $-\cdot0075°$ centigrade; and, hence, if the pressure above one atmosphere be now denoted in atmospheres,* as units by n, we obtain t, the lowering of the freezing point in degrees centigrade, by the following formula—

$$t = \cdot0075\, n. \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

* The atmosphere is here taken as being the pressure of a column of mercury of 760 millimetres; that is 29·92, or very nearly 30 English inches.