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THE FREEZING OF PURE LIQUIDS AND SOLUTIONS
UNDER VARIOUS KINDS OF POSITIVE AND
NEGATIVE PRESSURE AND THE SIMI-
LARITY BETWEEN OSMOTIC AND
NEGATIVE PRESSURE.

By C. S. HUDSON.

I. INTRODUCTORY NOTE.

IN a recent article concerning the relation between osmotic pressure and negative pressure Professor Geo. A. Hulett¹ has shown that the lower vapor-pressure of solutions indicates that the solutions are under a negative pressure, and a calculation of the negative pressure that would cause the observed depression shows that this negative pressure is exactly equal to the osmotic pressure of the solution. This important conclusion is to my knowledge the first evidence that osmotic pressure has the same effect on liquids as does negative pressure.

The question occurred to me on reading Professor Hulett's article whether the lower freezing-temperatures of solutions can also be the result of osmotic pressure acting as a negative pressure. At first sight this does not appear probable, because, since it is known that a positive pressure causes the freezing-temperature of water to sink, it would seem that a negative pressure would cause a rise of freezing temperature and that solutions should freeze above zero rather than below. This reasoning is not correct, however, because the ice which freezes from a solution is under atmospheric pressure,

¹ *Zeitschrift für physikalische Chemie*, 42, 361, 1903.

not negative pressure, and only the solution may properly be regarded as being under a negative pressure. The freezing-temperature of a liquid under such peculiar conditions of pressure is not known, and in order to calculate it I have investigated by thermodynamic methods the freezing of liquids under various kinds of pressure and this article presents the results of this inquiry. These results support without exception the view that osmotic pressure acts as a negative pressure.

2. INTRODUCTION.

In 1849 and 1850 James Thomson and Lord Kelvin showed by thermodynamic theory and by experiment that the freezing-temperature of water is lowered by a uniform pressure on the water and the ice to the extent of 0.00748° C. per atmosphere increase of pressure.

In 1881 J. H. Poynting¹ calculated from a thermodynamic cycle the change of freezing-temperature that is caused by an increase of pressure on the ice alone, such as might be realized for instance by the use of a rigid sieve in compressing the ice. Poynting showed that an increase of pressure of one atmosphere on the ice alone causes the freezing-temperature to sink 0.0899° C., a depression which is twelve times greater than that which is observed when the pressure is exerted uniformly on the water and the ice.

Recently it has been shown by G. N. Lewis² that if ice which is in equilibrium with water be subjected to a pressing³ of dP , there will be no change of freezing-temperature provided the water is also subjected to the pressing dp that is fixed by the relation $dp/dP = V_i/V_w$, where V_i and V_w are the specific volumes of ice and water respectively. If these volumes are 1.0909 and 1.0001 cubic centimeters at 0° , $dp/dP = 1.09$; or, the increased pressing on the water must be nine per cent. greater than the increased pressing on the ice if the freezing-temperature is to remain unchanged. This relation can also be shown to result directly from a combination of

¹ Philosophical Magazine, (5), 12, 32.

² Zeitschrift für physikalische Chemie, 38, 207, 1901.

³ I use the word *pressing* to signify a pressure that is exerted on one phase alone, in conformity with the use by Professor Ostwald of the German word *Pressung* to express the same idea.

the calculations of Thomson and Poynting. First, let the water and the ice be subjected to the pressing dp , on account of which the freezing-temperature sinks $(0.00748) dp$ degrees. Let the pressing on the ice be now diminished by d_1p , the pressing on the water being meanwhile kept constant, as a result of which the freezing-temperature rises $(0.0899) d_1p$ degrees. If the rise of the freezing-temperature be made equal to its previous fall there is finally no change of freezing-temperature and therefore $(0.0899)d_1p = (0.00748)dp$. The total increase of pressing on the ice is $dp - d_1p = dP$, and the elimination of d_1p from the two equations gives $dp/dP = 1.09$, which is the relation that has been stated by Lewis.

Our present knowledge of the change of freezing-temperature with change of pressure can be condensed to Thomson's and Poynting's statements, which include, as I have just shown, Lewis' statement; and it is possible to calculate from the two coefficients 0.00748 and 0.0899 alone the freezing-temperature of water under all conditions of small pressure. To illustrate by an example the method of such a calculation let us find what is the freezing-temperature of water that is under the pressing of two atmospheres when its ice is under the pressing of six atmospheres. Ice and water are in equilibrium under a uniform pressure of two atmospheres at $-2(0.00748)$ degrees, and if the pressing of four atmospheres in addition be applied to the ice alone the freezing temperature will sink $4(0.0899)$ degrees farther; and therefore the final freezing-temperature is 0.375° C. below zero.

On the other hand it is also possible in case the freezing-temperature and the pressing on either the solid or the liquid phase are known to calculate the unknown pressing on the other phase. Let us consider in this connection the following calculation concerning the freezing-temperatures of dilute aqueous solutions. The exact experiments of Raoult and others have agreed in showing that the molecular depression of the freezing-temperature of water is very nearly 1.84 degrees. As we know that the pure ice which freezes from such solutions is under atmospheric pressure we can calculate what mechanical pressing on pure water would cause it to freeze at -1.84 degrees, or in other words to behave exactly as the dilute solution does in so far as freezing is concerned. If the pressure p is applied

uniformly to the ice and the water the freezing temperature sinks p (0.00748) degrees. If this pressure is removed from the ice but kept on the water the freezing-temperature rises p (0.0899) degrees. If the final depression of the freezing-temperature is 1.84 degrees we can write p (0.00748) - p (0.0899) = 1.84, and hence $p = -22.3$ ¹ atmospheres. For comparison with this value let us calculate the pressure that would be exerted by a perfect gas if its volume, temperature, and molal concentration were those of the solution. One mol of a perfect gas occupying the volume of one liter at zero degrees would exert the pressure of 22.4 atmospheres, and if its temperature were lowered 1.84 degrees its pressure would decrease to 22.3 atmospheres. The identity of this pressure which a perfect gas would exert if its volume, temperature, and molal concentration were those of the solution with the mechanical pressure that must be exerted on pure water to make it freeze at the same temperature as does the solution is a striking and instructive fact. It is evident from this simple calculation that the freezing-temperatures of solutions indicate that the solutions are under a negative pressure.

But before discussing this subject further I wish to examine the reasoning which has led to the accepted values of the coefficients of Thomson and Poynting in order to make certain that the use of them in studying the properties of solutions is valid. I shall now describe a thermodynamic cyclic process which shows the change of freezing-temperature that accompanies any change of pressure on the ice and the water. This cyclic process is not different in principle from those described by Thomson and Poynting, but it is of wider application.

3. THERMODYNAMIC INVESTIGATION OF THE PROCESS OF FREEZING.

Let the following cycle of operations be performed on a system which at the beginning is in the following condition: One gram of ice at the absolute temperature T is pressed upon with a pressing

¹The physical interpretation of the negative sign of this pressure obviously is that the pressure is exerted in a direction tending to dilate the liquid. Such pressures as these, which are called negative pressures, have been realized and the behavior of water when subjected to them has been accurately determined by experiment. For a critical summary of our present knowledge of negative pressure in liquids the reader is referred to the previously mentioned article by Professor Hulett.

of P by a piston which is permeable for water-vapor, but not for ice. Separate from this ice is a trace of water which is under the pressing p that is exerted by a piston that is permeable for water-vapor, but not for water. There is free communication for water-vapor throughout the system and its pressure is p' . It is obvious that the pressings P and p must be so selected that it is possible to have the common vapor pressure p' throughout. In such a system the total pressure on the ice is $P + p'$ and on the water $p + p'$.

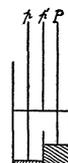


Fig. 1.

Let the piston on the ice move down and the piston on the water move up until all the ice is evaporated at constant temperature and pressure. During this evaporation and condensation the piston on the ice moves through the volume V_i , the specific volume of ice, and the piston on the water moves through a volume that is slightly less than V_w , the specific volume of water, because the loss of volume resulting from the evaporation of the ice is slightly larger than the gain of volume resulting from the liquefaction of an equal mass of water-vapor. In order therefore to condense all the vapor that is formed from the ice it is necessary to move a piston that exerts the pressure p' on the vapor through the volume $V_i - V_w$. The total work that is obtained from the system during this first portion of the cycle is $pV_w - PV_i - p'(V_i - V_w)$, and the heat which must be supplied to the system in order to keep its temperature constant during the changes is L , the specific heat of fusion of ice.

Let the temperature of the system now sink dT degrees and let either p or P be reduced by an infinitesimal amount. The three pressures now are $p - dp$, $P - dP$, and $p' - dp'$. The work that is done in changing these three pressures is so small on account of the very slight compressibility of water and ice that it may be neglected. At this lower temperature $T - dT$ let the pistons move in a manner reverse to that indicated before, thus doing the work $-(p - dp)V_w + (P - dP)V_i + (p' - dp')(V_i - V_w)$, while heat is abstracted from the system to keep its temperature constant. Let the temperature be now raised to its original value T and the pressures on the pistons be changed back to p , P , and p' , respectively, the work done in changing then being again neglected.

The cyclic process is now complete, and since it is at every stage

reversible, the second law of thermodynamics requires that the total gain in work divided by the fall in temperature equal the heat absorbed at the higher temperature divided by that temperature; or,

$$(dP/dT)V_i - (dp/dT)V_w + (dp'/dT)(V_i - V_w) = -L/T. \quad (1)$$

With the aid of this general relation let us now calculate the effect on the freezing-temperature of various typical changes of pressure.

4. CALCULATION OF THE CHANGES OF FREEZING TEMPERATURE THAT ACCOMPANY TYPICAL CHANGES OF PRESSURE.

CASE 1. *The total change of pressure on the ice remains equal to the total change of pressure on the water.* In this case $dP + dp' = dp + dp'$, and the general equation (1) becomes $(dP + dp')/dT = -L/T(V_i - V_w)$. This is the well known relation that was shown by James Thomson. In the case of water and ice an increase of pressure of one atmosphere lowers the freezing-temperature 0.00748°C .¹

CASE 2. *The pressing on the water remains constant while the pressing on the ice is changed.* In this case $dp/dT = 0$ and therefore $dP/dT = -L/TV_i - (dp'/dT)(1 - V_w/V_i)$. Since one of the terms on the right of this equation is ten thousand times smaller than the other it can be neglected and the equation written $dP/dT = -L/TV_i$. This is the relation that was first shown by Poynting, and in the case of water it expresses the relation that an increase of pressing of one atmosphere on the ice alone lowers the freezing-temperature 0.0899°C .

CASE 3. *The changes of pressing on the ice and the water are so related that the freezing-temperature remains constant.* In this case $dT = 0$, and therefore $(dp + dp')/(dP + dp') = V_i/V_w$. This is the equation that was derived by Lewis, which has been discussed in the introduction to this article.

CASE 4. *The pressing on the ice remains constant while the pressing on the water is changed.* In this case $dP/dT = 0$, and therefore $dp/dT = L/TV_w + dp'/dT(V_i/V_w - 1)$; or, neglecting the small

¹ In this calculation and in the succeeding similar ones, the following data are used: latent heat of fusion of ice, 80.1 calories; mechanical equivalent of the calorie, $4.19(10)^7$ ergs; atmospheric pressure, 1,013,200 dynes/cm.²; specific volumes of ice and water at 0° , 1.0909 and 1.0001 cm.³ respectively.

term as was done in case two, $dp/dT = L/TV_w$. This coefficient shows that if ice be kept under constant pressing while the pressing on the water is increased one atmosphere the freezing-temperature rises 0.0824° .

It seems to me that this fourth type of freezing, which to my knowledge has not been previously investigated, may occur in the natural freezings of winter weather whenever the conditions that are illustrated by the accompanying figure occur. The closed vessel *A* is supposed to contain air at atmospheric pressure and to be pierced by an open capillary tube whose lower end is immersed in water *W*. A piece of ice *I* is in the vessel and it is obvious that this ice is under the pressing of one atmosphere. Now it has been shown by Lord Kelvin¹ that the vapor-pressure of water which is in a capillary tube is less than that of a plane surface of water; from this fact we may conclude that the system shown in the figure



Fig. 2.

will not be in equilibrium at zero degrees, but that at that temperature the ice will distil over to the water in the capillary tube. The temperature of equilibrium may be calculated as follows: The water in the capillary tube is under a pressing that is less than atmospheric by the hydrostatic pressure of the column of water. If the tube is so small that the capillary rise is (76×13.6) centimeters the pressing on the surface in the tube is decreased one atmosphere, and therefore according to the relation shown above the system will be in equilibrium at 0.0824° below zero. If the capillary rise is h centimeters the freezing-temperature is $(h \times 0.0824)/(76 \times 13.6)$ degrees below zero.

I wish now to show that this fourth case of freezing is also realized in the freezing of aqueous solutions. The reasoning by which this may be shown has already been given in an elementary form in the introduction to this article. It is obvious that in the freezing of solutions the ice is under atmospheric pressing and that the water is under atmospheric pressing altered by whatever pressing the dissolved substance may exert. If we assume that the dissolved substance exerts the same pressing as a perfect gas, the pressing p is

¹ Proceedings of the Royal Society of Edinburgh, 7; 63 (1870); Maxwell's Heat, 1877, 287.

given by the relation $p = -cRT$, where R is the gas-constant and c is the concentration of the solution expressed in mols of dissolved substance per liter of solution. If this value of p is substituted in the coefficient of case four, we obtain $dT/dc = -(RT^2V_w)/L$. This expression is identical with the well known relation that Van't Hoff¹ first calculated from the osmotic theory of solution, and which has been repeatedly verified by exact experiments. From the agreement of these two expressions for the molecular depression of the freezing temperature with each other and with experiment we must therefore conclude that the freezing-temperatures of solutions indicate clearly that the solutions are under a negative pressure, comparable with a positive mechanical tension, and that this negative pressure or tension is caused by the dissolved substance and is identical with the osmotic pressure of the solution.

PHYSICAL LABORATORY,
UNIVERSITY OF ILLINOIS,
CHAMPAIGN-URBANA, ILLINOIS.

¹ Lectures on Theoretical and Physical Chemistry. Volume 2.