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## SUPERCOOLING AND FREEZING OF WATER

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## ABSTRACT

This is a strictly preliminary report, rendered necessary by a temporary suspension of the work. No doubt attaches to the observations reported, but the setting of limits within which they are valid, and the determining of the most satisfactory way in which to explain them, should await further work. Contrary to current opinions, it has been found that the extreme supercooling of water (at least down to  $-21^{\circ}\text{C}$ ) is not dependent upon either extreme quiescence or upon the use of a minute volume, and that motes in the water exert a strong non-specific effect. For each specimen there is a definite temperature (the spontaneous-freezing-point), characteristic of the specimen, at which ice suddenly appears, at which the water freezes spontaneously. The well-known fact that a preheating of the water may facilitate its supercooling has been found to depend upon a lasting change so produced in the water—a change that persists at room temperatures for at least 6 months, and that seems to be permanent. By sedimentation, the spontaneous-freezing-points of the extreme layers of a column of water become different, that of the bottom ones becoming higher than that of the top ones. All the observations are consistent with the idea that the spontaneous-freezing-point of a specimen is determined, within undetermined limits, by the size of the largest mote that it contains; the smaller the mote, the lower the spontaneous-freezing-point. The effect of agitation has been considered, and three distinct types of freezing have been recognized.

## CONTENTS

	Page
I. Introduction.....	799
II. Theories and beliefs.....	800
III. Method and results.....	801
1. Method.....	801
2. Glass.....	801
3. Spontaneous-freezing-points.....	801
4. Motes are effective.....	803
5. Heating.....	804
6. Effect of size of motes.....	805
7. Sedimentation.....	805
8. Agitation.....	807
9. Types of freezing.....	807
IV. Summary.....	807

## I. INTRODUCTION

A study of the supercooling and freezing of water has been under way at the National Bureau of Standards for about a year. It was undertaken for the purpose of getting first-hand information as to the way water behaves when supercooled, and as to how one specimen may differ from another, the numerous published reports on the subject being frequently unconvincing and in part conflicting.

As it has become necessary to lay this work aside for a time, it seems well, although the study is still in the exploratory stage, to publish now a brief statement of some of the observations that have

been made and of the inferences drawn therefrom, especially as they are in part contrary to widely held beliefs. Detailed publication must await the completion of the work.

## II. THEORIES AND BELIEFS

The theories of crystallization that have found favor and are being upheld are of two types.

According to one type of theory, freezing is initiated by certain molecular aggregates of  $\text{H}_2\text{O}$ , often called ice molecules, which are supposed to exist in water even at scores of degrees above the normal melting point of ice. The number of such ice molecules, relative to the other molecules, is small at the higher temperatures and increases as the temperature is lowered; at each temperature it has a fixed value when equilibrium exists. But opinions differ regarding the time that is required for reestablishing equilibrium after an abrupt change in temperature. Some think that adjustment occurs with great rapidity, practically instantaneously; others have claimed that it requires hours, or perhaps days. These ice molecules tend to cohere, forming aggregates that grow with a finite velocity which increases with the temperature, until a certain size, determined by the temperature, is reached, or until the size becomes such that the aggregate can appropriate to itself the adjacent liquid molecules, converting them into ice molecules in the process. Then freezing proceeds apace.

According to the other type of theory, freezing is initiated by foreign solids—by the walls of the vessel or by motes suspended in the water. The initiation is a boundary phenomenon. The motes or isolated spots on the walls serve as nuclei about which ice is built up until presently a stage is reached at which ordinary rapid freezing begins. The details differ from those of the other type of theory mainly in that in this the initial nuclei are solids foreign to the water, whereas in that they are ice molecules formed from the water itself.

Many observations, mainly on organic compounds, have been cited in confirmation of each type of theory, and it seems not impossible that the two theories may correspond to the opposite sides of a single shield, each being satisfactory under certain conditions. Unfortunately, advocates of the ice-molecule type of theory, at least as applied to water, have seldom, if ever, given sufficient consideration to the possible effect of motes.

Each of these types of theory suggests that the duration of cooling plays an important part in determining the temperature at which spontaneous freezing occurs, and that the same may be true of the immediately preceding thermal history of the water. Observations, not entirely convincing, have been advanced in support of each of these conclusions; and each is widely believed. It is also commonly believed that it is difficult to supercool water by more than a few degrees, and that if any considerable supercooling is to be obtained it is necessary to work with very small volumes (not over a few cubic millimeters) and to protect the water from all kinds of mechanical disturbances. Not a few also believe that the effect of motes is largely a specific one, determined by some chemical or crystalline relation between the mote and ice.

Under the conditions of the present work, none of these widely held beliefs is true, unless it be the last, which has been considered only incidentally. But the results obtained indicate that specificity need not be the determining factor.

### III. METHOD AND RESULTS

#### 1. METHOD

The present work was done in this manner: Each specimen of water to be studied was contained in a cylindrical glass bulb with hemispherical ends, from one of which extended axially a 7-mm tube through which the water was introduced. This tube was then sealed by fusion at a point a centimeter or two above the bulb. The bulb proper was 2 cm in diameter by 4 cm long, and was about half filled by the specimen. Total volume of a bulb is 16 to 17 cm.<sup>3</sup> The bulbs were carefully cleaned before the water was placed in them. The sealed bulb was placed in a harness of light copper wire, and was suspended in alcohol which was cooled as desired. The temperature of the alcohol was determined by a mercury thermometer (1° C corresponding to 1.7 mm), and was varied not faster than a few tenths of a degree per minute during the several minutes immediately preceding the freezing of the water. It is assumed that under such conditions the significant temperature of the water at the initiation of freezing may be taken as that of the alcohol.

#### 2. GLASS

Both soft glass and Pyrex have been used for the bulbs. There was no indication that the nature of the glass affected the phenomenon.

#### 3. SPONTANEOUS-FREEZING-POINTS

As the temperature of the water is gradually lowered, a point is reached at which a new phase (ice) suddenly appears. The presence of this new phase profoundly affects the behavior of the system. It causes freezing to proceed at all temperatures below 0° C, even though they are higher than that at which the new phase first appeared; but at these higher temperatures the freezing occurs solely at the interface between the ice and the liquid, the ice grows into the liquid. At the lower temperature the liquid specimen freezes spontaneously; at the higher one it is frozen by the ice. The distinction between the active and the passive attitudes of the liquid specimen seems to be worth maintaining. In view of the great latent heat of fusion of ice, it is obvious that the amount of ice initially formed—more exactly, that present a fraction of a second after the specimen has spontaneously frozen—represents only a fraction of the specimen, a fraction depending upon the extent of the supercooling.

In this work our prime concern is with the behavior of the system up to and including the initial appearance of ice.

It has been found that each definite specimen has in general a characteristic temperature, below 0° C, at which it freezes spontaneously. That characteristic temperature will be called the spontaneous-freezing-point of the specimen. It is quite reproducible, and within a fraction of a degree is the same whether: (1) The bulb at room temperature is cooled slowly to 0° C, held at that temperature for 2 or 3 hours, and then cooled to its spontaneous-freezing-point at such a rate as to insure that the temperature of the water never differs materially from that of the bath, or (2) the bulb with frozen water is removed from the bath, the ice melted by suspending the bulb in a bath at +3° C, and the bulb at once returned to the cold bath, now a little

above the spontaneous-freezing-point of the specimen, and cooled to freezing, or (3) the bulb at room temperature is plunged at once into a bath that is only slightly above the spontaneous-freezing-point of the specimen, and then cooled to freezing. The spontaneous-freezing-point of the specimen remains the same not only for successive freezings on the same day, but for day after day, for weeks or even months, except that there may be a slow progressive change, usually downwards, extending over long periods. See table 1. Such results have been obtained for specimens of water from many sources, both natural and artificial, freezing at various temperatures throughout the range  $-3$  to  $-15^{\circ}\text{C}$ , and may be regarded as representing the normal behavior of water under the conditions realized in this work. Some of the specimens were air-free; most of them were saturated with air at atmospheric-pressure. The difference is not of present significance.

TABLE 1.—*Illustrating the regularity of the spontaneous-freezing-point*[Temperature of spontaneous freezing is  $t^{\circ}\text{C}$ ]

Bulb C111				Bulb C23			
Date	$t$	Date	$t$	Date	$t$	Date	$t$
Jan. 5....	-14.9	Mar. 10....	-15.4	Feb. 17....	-5.8	Mar. 9....	-5.9
Do.....	-15.0	Do.....	-15.9	Do.....	-5.9	Do.....	-5.9
Jan. 29....	-15.5	May 14....	-16.9	Do.....	-6.0	Mar. 22....	-6.0
Do.....	-15.3	Do.....	-16.8	Do.....	-6.0	Do.....	-5.9
Feb. 25....	-15.7	Do.....	-16.8	Feb. 24....	-6.1	Apr. 22....	-5.8
Do.....	-15.7			Do.....	-6.1	Do.....	-5.9
Do.....	-15.5			Mar. 9....	-6.0		

Furthermore, such bulbs of water have been kept continuously below  $0^{\circ}\text{C}$  for 30 days without freezing, the temperature varying between  $-3$  and  $-12^{\circ}\text{C}$ , and averaging about  $-6^{\circ}\text{C}$ .

Whence, it is evident that neither the length of time that a specimen is held at a low temperature nor the recently past thermal history of the water within the range from room temperature to the specimen's spontaneous-freezing-point is of any prime importance in the freezing of these specimens. Also, in an attempt to supercool water it is unnecessary either to limit one's self to excessively small volumes of water or to protect the water carefully from mechanical disturbances, for without such protection and with volumes as large as  $8\text{ cm}^3$  supercooling to  $-21^{\circ}\text{C}$  has been observed in this study.

Although the spontaneous freezing of a specimen normally occurs at a definite, fixed, characteristic temperature, departures from that rule are not infrequent. They are of the following four main types, which may be superposed: (1) The first few freezings after the sealing of the bulb may be discordant with later freezings; the specimen may not at once settle down to its normal condition. (2) When studied over a period of weeks, it may be found that the spontaneous-freezing-point of a specimen slowly drifts, usually downwards. In some cases the direction of drift reverses after a time, and later on it may reverse again. (3) A specimen may exhibit an abrupt and permanent change in its spontaneous-freezing-point. In observations extending over weeks, several such abrupt changes, each lasting for several days, may be observed; they may, or may not, be cumulative. (4) The



spontaneous-freezing-point of a specimen may be essentially erratic over a long period, and such a period of irregularity may be, but is not necessarily, adjacent to a period during which the spontaneous-freezing-point remains constant. Erratic behavior seems to be peculiar to those specimens that at some stage of their history have been capable of being supercooled to a low temperature, such as  $-16^{\circ}\text{C}$  or lower.

#### 4. MOTES ARE EFFECTIVE

The existence of such abnormalities indicates that the behavior with which we are dealing depends greatly upon something other than the water itself, upon what we may call motes, contained in the water. And the fact that the spontaneous-freezing-point of a given specimen may change abruptly as well as drift, shows that the spontaneous-freezing-point is affected by something other than the mere chemical composition and the gross mass of all the mote material contained in the specimen. But without other evidence one can draw no valid conclusion as to whether the spontaneous-freezing-point is also affected by the chemical or the crystalline state of the motes.

TABLE 2.—*Spontaneous-freezing-points of various waters*

With three exceptions, which are noted, each entry refers to a different specimen of water. The water spontaneously freezes at  $t^{\circ}\text{C}$ .

Source or kind of water	<i>t</i>	Source or kind of water	<i>t</i>
Pool, alga-covered, bottom layer.....	-3.3	Aquarium, midlayers, away from walls and weeds.....	<sup>b</sup> -11.5
Pool, alga-covered, midlayer.....	-3.4	Distilled water, ordinary.....	-11.8
Brook, swift and clear.....	-3.9	Do.....	-12.0
Pool, stagnant.....	-4.1	Residue from glass boiler (No. 1).....	-12.2
Spring, small, not recently cleaned.....	-4.3	Conductivity water.....	-13.1
Snow-water of winter of 1935-36.....	-4.6	Residue from glass boiler (No. 2).....	-13.9
River, clear.....	-4.8	Vacuum distilled, no ebullition.....	-14.3
Spring, large, strong flow, fairly clean.....	-5.1	Hot-water supply, country, heated by water-back stove.....	-14.4
Snow-water, Feb. 1937, many surface motes.....	-5.9	Distilled water, ordinary, heated to $97^{\circ}\text{C}$ for 36 hr.....	-15.0
Washington City water, cold-water faucet.....	-6.0	Conductivity water, heated to $97^{\circ}\text{C}$ for 36 hr.....	-15.4
Pool, alga-covered, surface layer.....	-6.0	Vacuum distilled, no ebullition.....	-15.6
Washington City water, hot-water faucet <sup>a</sup> .....	-6.2	Distilled water, ordinary, old stock.....	-15.8
Do. <sup>a</sup> .....	-6.5	Conductivity water.....	-16.0
Ice-water, melted commercial ice.....	-7.0	Vacuum distilled from chromic solution, no ebullition.....	-18.0
Aquarium, from surface of wall and of weeds.....	-7.4	Vacuum distilled, no ebullition.....	<sup>c</sup> -18.5
Water tank, country, cold.....	-7.5	Do.....	<sup>c</sup> -20.2
Distilled water, ordinary, new stock.....	-7.6	Vacuum distilled from chromic solution (same as -18.0°).....	-21.1
Snow-water, Feb. 1937, few surface motes.....	-7.7		
Well, deep, iron pump.....	-7.9		
Aquarium, midlayers, away from walls and weeds.....	<sup>b</sup> -10.6		
Conductivity water.....	-10.7		
Distilled water, ordinary, old stock.....	-10.8		
Snow-water, Feb. 1937, midlayers.....	-10.9		

<sup>a</sup> The water from this faucet is never really hot.

<sup>b</sup> One freezing of this specimen gave  $-10.6^{\circ}\text{C}$ , a following one gave  $-11.5^{\circ}\text{C}$ ; each is entered in the table.

<sup>c</sup> These two entries refer to the same specimen.

Some light, however, is thrown upon this question by the observations assembled in a study of 37 specimens of water obtained from various sources, and freezing at temperatures ranging from  $-3.3$  to  $-21.1^{\circ}\text{C}$ . These specimens arranged in the order of their spontaneous-freezing-points, each on the day of the last observation preceding the tabulation, are briefly described in table 2. For three of the specimens the observations on that day were widely spread; for them each of the individual determinations is tabulated. If the action of a mote were a specific one—depending upon its relation,

chemical or crystalline, to ice—then one might expect to find that the spontaneous-freezing-points of the several specimens form a discontinuous series, being grouped about a few widely separated temperatures. In table 2 there is no clear evidence of any such grouping. This does not justify one in concluding that no specific effect is involved, but it does indicate that if it is involved, then in this work it is quite completely overshadowed by one or more other effects, probably those responsible for the abnormal behaviors already mentioned.

## 5. HEATING

It has long been known that the extent to which a substance can be supercooled may in certain cases be increased by a preliminary heating of the melt to a temperature well above the melting point; and that the increased supercooling so obtained increases, within limits, with the maximum temperature to which the melt is heated, and survives several successive freezings and meltings. There seems to be no generally accepted explanation of this effect, and although I have not looked into the subject as carefully as I desire, I am of the impression that it is commonly believed that this effect of heating is temporary, that it will ultimately vanish if the substance is held at a temperature somewhat above its melting point. Such a belief is entirely rational if the effect be due (1) to a destruction of preexisting ice molecules, or (2) to a change in the adsorption, either of the moles on the walls or of the water on the moles or on the walls, or (3) to a complete melting or solution of some of the moles of certain crystal forms.

In each of those three cases, it is entirely thinkable that the time required for ice to begin to form after the specimen has been cooled to its spontaneous-freezing-point, assumed to be a definite temperature, may be increased by the partial destruction, by heating, of the corresponding condition, and may increase progressively with that destruction. But it is not clear how that temperature can depend upon the mere extent of any one of those conditions. It seems more reasonable to expect that the spontaneous-freezing-point would remain unchanged until the pertinent condition shall have completely vanished, and that it then would jump abruptly to its new value.

TABLE 3.—*Effect of heating on the spontaneous-freezing-point*

Each heating is indicated in its proper chronological position, and by the maximum temperature and the length of time that that temperature was maintained. Except while being heated or frozen, the bulb (C35) was at room temperature; the water froze spontaneously at  $t^\circ\text{C}$ .

Date	$t$	Date	$t$	Date	$t$	Date	$t$
Mar. 4	-6.2	Mar. 27	-6.9	97° C, 2 hr		June 29	-14.0
Mar. 8	-6.1	Do...	-7.2	Apr. 3	-13.8	Nov. 16	-14.1
Do...	-6.0	Mar. 29	-6.8	Apr. 7	-13.7	Do...	-13.7
Mar. 22	-6.2	97° C, 2 hr		97° C, 5.5 hr		Dec. 11	-13.4
Do...	-6.2	Mar. 30	-13.0	Apr. 10	-13.8	Do...	-13.4
54° C, 8 hr		Do...	-12.9	Do...	-14.0		

But observations, both old and new, indicate that the spontaneous-freezing-point changes progressively with the heating—within limits, heating to a lower temperature produces less effect than does heating to a higher one, and heating for a shorter time produces less effect than does heating for a longer one. This is illustrated by the data contained in table 3, which also show that the effect of heating is

largely a permanent one, and that after the specimen has been heated to a certain temperature for some time, additional heating to that same temperature may produce no additional effect, a steady state having been reached. Such a progressive change is difficult to explain if it arises from any of the three effects of heat already mentioned, and the same is true of the permanency of the change.

#### 6. EFFECT OF SIZE OF MOTES

But there is a fourth possible effect. Heating the melt may cause the motes to dissolve in it. That will reduce their number and their size. As before, it is hard to see how a change in the mere number of motes per unit of volume can affect the spontaneous-freezing-point. And that it actually does not, seems to be indicated by the fact that the observed spontaneous-freezing-point of a mixture is the same as that of the higher-freezing constituent; e. g., one containing 10 percent of water freezing at  $-7^{\circ}\text{C}$ , and 90 percent of water freezing at  $-15^{\circ}\text{C}$  froze at  $-7^{\circ}\text{C}$ .

But a change in the size of the motes may cause a change in the spontaneous-freezing-point; and the size will vary progressively, and so does the spontaneous-freezing-point. The idea that the spontaneous-freezing-point may be closely associated with the size of the motes and, within limits, may vary progressively with it, is consistent not only with the observed effect of preheating the melt, but also with the observed tendency of the spontaneous-freezing-point of a specimen to drift slowly to lower temperatures, the motes presumably dissolving slowly while the bulb is kept at room temperatures. The same idea offers an explanation of the erratic behavior of certain of the specimens, as the size of the motes may increase by coalescence, and decrease by dispersion, and be varied by solution and precipitation. It also offers a ready explanation of the almost continuous distribution of the spontaneous-freezing-points listed in table 2. The idea that the size of the motes may be the significant variable in this work is very alluring and deserves careful consideration.

#### 7. SEDIMENTATION

If the size of the motes is the significant variable, then the spontaneous-freezing-point of a given lot of water should be subject to change by sedimentation. Indeed, in table 2 it may be seen that a new stock of distilled water, well stirred by drawing it from the still into the stock bottle, had a spontaneous-freezing-point of  $-7.6^{\circ}\text{C}$ , whereas old stocks that had been undisturbed for some days or perhaps weeks froze at  $-10.8^{\circ}\text{C}$  in one case, and at  $-15.8^{\circ}\text{C}$  in another. Although very suggestive this is not conclusive, as there is no evidence that the old stocks would have frozen at a higher temperature before they had settled; the observations having been made for another purpose, the records are not sufficient for our present one. But other experiments were made. Sedimentation tubes from which water could be drawn from various levels without stirring the remainder of the water were set up. The spontaneous-freezing-point of the stirred distilled water placed in them was determined, and after the tubes had remained undisturbed at room temperatures for 2 or 3 weeks, samples were drawn and frozen. Bulbs of the same kind as those already described were used, but the necks were closed by ground-on caps, not by fusion. Several experiments were made, and in some cases no evidence of any

change due to sedimentation was found. But in view of the very significant observations recorded in table 4, it is believed that faulty technique is responsible for the negative results. That will be investigated when the work is renewed.

TABLE 4.—*Effect of sedimentation*

In the first section of the table are given the observed values of the spontaneous-freezing-point of the water that was placed in the sedimentation tube. Two weeks later a sample was drawn from the topmost layers and another from the very bottom of the tube, and their spontaneous-freezing-points ( $t^{\circ}$  C) were determined. These are given in the other two sections of the table.

Initial		Top		Bottom	
Time	$t$	Time	$t$	Time	$t$
May 21, 2:19 p. m.	-12.0	June 3, 3:34 p. m.	-12.7	June 4, 3:17 p. m.	-7.8
2:37 p. m.	-12.7	3:49 p. m.	-12.6	3:24 p. m.	-7.3
2:50 p. m.	-12.0	June 4, 9:56 a. m.	-13.0	4:21 p. m.	-9.1
May 22, 11:34 a. m.	-12.2	10:05 a. m.	-12.7	4:35 p. m.	-10.5
11:46 a. m.	-12.2			4:44 p. m.	-10.8
Mean-----	-12.2	Mean-----	-12.8	June 8, 1:26 p. m.	-11.7
				1:36 p. m.	-12.0
				1:47 p. m.	-12.1

From table 4 it may be seen that after settling for 2 weeks the spontaneous-freezing-point of the topmost layers is only slightly lower than that of the initial water. Considered alone, this might be taken as an indication that no settling has occurred. But such a conclusion is inconsistent with the values obtained for the bottom layers. For them the spontaneous-freezing-point is at first nearly  $5^{\circ}$  C higher than that of the initial water, and the difference between the two decreases with successive freezings until it finally becomes zero. This entirely unexpected behavior is in complete accord with the idea that the spontaneous-freezing-point is determined by the size of the motes. As the motes settle on the bottom of the tube, they cohere, forming larger aggregates. The size of these aggregates in the sample drawn from the bottom was at first almost that which corresponds to a spontaneous-freezing-point of  $-7.5^{\circ}$  C. With successive freezings, these loosely bound aggregates were gradually broken up, and the spontaneous-freezing-point fell, continuously approaching the value characteristic of the original water. The close accord between the spontaneous-freezing-points of the topmost layers and of the initial water does not indicate that there has been no sedimentation, but merely that sedimentation had not progressed so far as to have removed from those layers all motes of such a size as to cause spontaneous freezing at  $-12.8^{\circ}$  C.

Much of the preceding has been written as though the motes in a given specimen of water are all of the same size. Obviously, such will not in general be the case; they will differ greatly in size. But according to the idea being developed, the spontaneous-freezing-point will be determined, insofar as the size of the motes is the significant quantity, by the size of the largest mote present, provided that that size does not exceed a value still to be determined. The actual number of such motes that is present in a unit volume of the water is of little or no importance, as has already been shown.



## 8. AGITATION

That it has been found unnecessary to take any special precaution to protect these bulbs from mechanical disturbances while in the supercooled condition, has been mentioned. But one can go much further. For example, if a bulb containing water that freezes at  $-15^{\circ}\text{C}$  be cooled to  $-14^{\circ}\text{C}$ , it can at that temperature be tipped about with impunity, pouring the cold water over all its interior surface, without causing the water to freeze. But the water will freeze instantly if the bulb be treated thus: Holding the top of the neck of the bulb between the thumb and index finger of the right hand, the bulb being vertical and neck up, strike the right hand sharply downward against the left.

Even sharp strokes of a cold metal rod against the outside of a stationary supercooled bulb have failed to cause the water to freeze. On the other hand, an exceedingly gentle wiping of the glass-water interface, well below the free surface of the water, may sweep off tiny flakes of ice—that is, may initiate freezing—when the temperature is only a few degrees below  $0^{\circ}\text{C}$  and well above the spontaneous-freezing-point of the water, which in these tests was contained in an open test tube. In neither case are my experiments extensive enough to justify a more definite statement.

## 9. TYPES OF FREEZING

If a bulb of water at room temperature be plunged into a bath cooled well below the spontaneous-freezing-point of the water, then freezing will begin at the walls before the entire volume of water shall have been reduced to its spontaneous-freezing-point, and will proceed gradually from the walls inward. The resulting ice may be quite clear.

If the bulb be placed in a bath at a temperature above the spontaneous-freezing-point of the water, and if the temperature be progressively lowered in such a manner that when the spontaneous-freezing-point shall have been reached the temperature of the water will be essentially the same throughout, then the water will freeze throughout in the twinkling of an eye, forming a solid translucent mass. Although only a small fraction of the water is actually ice at the instant after freezing sets in, the ice crystals are so numerous and intermingled and are distributed so uniformly throughout the volume that the whole is locked together into a single solid mass. Such is the behavior of the bulbs so far studied. The freezing might proceed more slowly and the ice might be clearer if the number of the motes responsible for the freezing at that temperature were small, say if only one were present.

An approximation to the case of a single mote may be obtained by placing into the water a well washed bit of a suitable solid. For example, such a bit of solid was placed in water that froze at  $-13.6^{\circ}\text{C}$ ; freezing then began at the solid at  $-6.7^{\circ}\text{C}$ , and visibly progressed from the solid outward into the water.

## IV. SUMMARY

For specimens of water sealed in glass bulbs the following facts have been established:

1. The liquid specimen normally freezes spontaneously at a definite temperature, here called the spontaneous-freezing-point, characteristic of the specimen.

2. For no specimen yet examined has the spontaneous-freezing-point been so high as  $0^{\circ}\text{C}$ .

3. Abnormal behavior, in which the spontaneous-freezing-point is not constant and may even be erratic, is not uncommon.

4. The lowering of the spontaneous-freezing-point by preheating the liquid is a lasting effect, persisting for months.

5. Sedimentation may change the spontaneous-freezing-point.

6. All of these effects are consistent with the idea that the spontaneous-freezing-point is determined by motes suspended in the water, and in particular by the size of the largest mote present, provided that that size does not exceed a value yet to be determined.

7. Extreme supercooling is not dependent upon the use of a diminutive volume of water.

8. Extreme quiescence is not at all essential to supercooling. Indeed, supercooled water may sustain a considerable mechanical disturbance without freezing.

9. A very gentle wiping of a glass-water interface may initiate freezing when the temperature is only slightly below  $0^{\circ}\text{C}$ , although the spontaneous-freezing-point of that specimen of water is much lower.

10. A volume of water as great as  $8\text{ cm}^3$  has been repeatedly cooled, without precautions to avoid mechanical disturbances, to  $-21^{\circ}\text{C}$  without its freezing.

11. Three types of freezing have been distinguished.

Of these items, 1, 4, 5, 7, and 8 are contrary to widely held opinions, although 8 accords with certain Swiss observations recorded nearly 80 years ago.

The work is still in its preliminary stages. Much remains to be done, some of it extremely obvious. We hope that it will be possible to resume the work at no very distant date.

WASHINGTON, January 4, 1938.