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THE SUPERCOOLING CAPACITY OF WATER AND THE LINEAR
CRYSTALLIZATION VELOCITY OF ICE IN AQUEOUS SOLUTIONS

(DIE UNTERKÜHLUNGSFÄHIGKEIT DES WASSERS UND DIE LINEARE
KRISTALLISATIONSGESCHWINDIGKEIT DES EISES IN
WÄSSRIGEN LÖSUNGEN)

BY G. TAMMANN AND A. BÜCHNER

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Approved by: J. H. Parkin,
Director.

SYNOPSIS

Very little is known about the crystallization velocity of water and its solutions. This report serves to draw attention to a field of science which has scarcely been touched upon by research.

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THE SUPERCOOLING CAPACITY OF WATER AND THE
LINEAR CRYSTALLIZATION VELOCITY OF
ICE IN AQUEOUS SOLUTIONS

I THE SUPERCOOLING CAPACITY OF WATER

The crystallization centres of ice arising in supercooled water have - even at small supercoolings - such great linear crystallization velocities that within a short time dendritic ice needles are seen throughout the entire observation vessel. For this reason the observation of the formation of further crystallization centres is impossible. Hence it is not possible (by analogy with other fluids) to determine the supercooling capacity of water as a function of the supercooling, by counting the crystallization centres which form spontaneously within a given time at a given supercooling. It is only possible to determine the appearance of the first crystallization centre as a function of the time and temperature. This may be done in two ways, either by cooling the water slowly and determining the temperature at which the crystallization begins or by cooling a small quantity of water as rapidly as possible to a known temperature and by measuring the time until the first crystallization centre forms. Observations were made using both methods. The results are given below.

For the slow cooling tests glass tubes having an inner diameter of 0.8 mm. and a wall thickness of 0.4 mm. were used. Each tube was filled with 0.4 cc. of water and sealed at both ends. The tubes were put in a bath which was cooled by a copper pipe filled with dry ice. A mechanical stirring rod ensured uniform temperature distribution. In this bath the tubes were cooled with constant velocity beginning at the melting point. The temperature at which spontaneous crystallization began was observed. Normally the cooling rate was approximately 0.7 to 0.8°C per minute. For the tests using the rapid cooling method the tubes were similar but had a smaller wall thickness of only 0.1 mm. The tubes were placed in a bath of alcohol whose temperature was maintained constant to within 0.1°C. The time was measured from the immersion of the tube to the beginning of crystallization.

1. The Supercooling Capacity of Pure Water

The readings taken in the tests with pure water are given in Table I.

TABLE I

Tube	Cooling Rate			Mean in °C	Variation in °C
	1° per min. in °C	1° per min. in °C	0.4° per min. in °C		
1	19.0	18.8	18.4	18.7	± 0.2
2	15.9	15.9	14.3	15.4	0.5
3	16.0	15.2	14.7	15.3	0.4
4	16.0	16.0	15.1	15.7	0.3
a	13.2	13.1	13.1	13.1	0.05
b	14.9	14.8	15.0	14.9	0.07

Tubes 1 to 4 contained ordinary distilled water while tubes a and b were filled with heavy water containing more than 99.5 per cent D₂O^x). The table gives the temperatures of the beginning of crystallization at various cooling rates. There are differences of several degrees between the various tubes, whereas, on repeating the measurement for each individual tube, the variations amount only to a few tenths of a degree, despite the fact that the formation of a crystallization centre is a chance occurrence and consequently a larger variation would have been expected.

The temperature of the beginning of crystallization was independent of the cooling rate over a wide range. The formation of an ice nucleus was nevertheless favoured by sudden cooling. In five tests of tube 1, for example, during the cooling from +20° to -12°C crystallization occurred after 12.0 ± 0.8 seconds, and in tube 3, after 7.3 ± 0.4 seconds. At slow cooling, these two tubes remained at temperatures several degrees below -12°C for 16 and 9 minutes respectively, before crystallization set in. In these tests, too, an unexpectedly good reproducibility was noted.

The supercooling capacity of heavy water was found to be slightly less than that of ordinary water. It was also found that the dependence of the beginning of crystallization on the cooling rate was lower than in ordinary water.

x) G. Tammann and A. Büchner,
Zeitschrift für anorganische und
allgemeine Chemie 222 (1935), p. 12.

2. The Influence of Foreign Substances on the Supercooling Capacity of Water

The investigation of the supercooling capacity of water, which yielded totally different values for the various tubes but gave results that could easily be reproduced for each individual tube, seemed to suggest that the variations may be attributed to the influence of foreign substances, especially since the tests showed that, as a rule, crystallization set in at the same points of the tubes.

It is a known fact that, under otherwise identical conditions, foreign substances in solution have a strong effect on the number of crystallization centres being formed. But even insoluble foreign substances, such as powdered stone and metal wires, influence this number^{x)}; however, no direct dependence of crystallization centre formation on the presence of solid foreign substance was observed. Furthermore, the tests of J. Meyer and W. Pfaff^{xx)} revealed that in materials with low nuclear numbers (such as thymol, salol, benzophenone, and others) the number of crystallization centres may be reduced considerably by filtration.

The tests up to the present were made with substances having low crystallization velocities. Water has not been examined as yet in this respect because of its high crystallization velocity. For that reason the influence of iron wires, powders of rock crystal, quartz-glass, and corundum was investigated in five tubes for each case. In the tests with iron wires (Table II) the temperature of the beginning of crystallization in pure water was first of all determined. Then electrolytic iron wires, 5 cm. long and 0.2 mm. in diameter, after being cleaned with water and alcohol, were placed in the water and readings of the temperature were again taken at which crystallization began spontaneously. Finally the wires were removed and the temperature of the formation of the first nuclei was again determined. It becomes clear that the iron wire raises the temperature of the beginning of ice formation considerably thereby increasing the number of crystallization centres. After the removal of the wires the supercooling

x) G. Tammann, Z. phys. Chem. 25 (1898), p. 456; P. Othmer, Z. anorg. Chem. 91 (1915), p. 241.

xx) J. Meyer and W. Pfaff, Z. anorg. u. allg. Chem. 217 (1934), p. 257.

capacity increased substantially, in contrast with piperonal, where, according to P. Othmer's tests^{x)}, the increased number of nuclei remained even after removal of the wires.

TABLE II

Tube	Pure Water in °C	With Iron in °C	Variation in °C	Number of observations	After the removal of the wires in °C
5	18.1	11.5	-	1	13.4
6	19.3	8.9	±0.2	3	16.8
7	18.3	11.4	0.3	2	18.4
8	12.0	7.7	0.2	2	15.1
9	13.0	8.5	0.1	2	14.8
Mean	16.1	9.6			15.7

The effect of the powders of rock crystal, quartz-glass, and corundum on the supercooling capacity is shown in Table III. Both quartz powders cause a considerable increase in the number of nuclei, whereas the addition of corundum is without effect.

TABLE III

Tube	Pure water in °C	Rock crystal powder in °C	Quartz-glass in °C	Corundum powder in °C
10	20.0	10.3	9.0	18.5
11	18.1	8.8	13.5	18.7
12	18.9	12.5	11.9	19.9
13	15.4	10.1	11.0	19.4
14	15.8	9.1	9.9	13.6
Mean	17.6	10.2	11.2	18.0

The air in solution also affects the supercooling capacity of water. Water containing air crystallizes on an average at a temperature two degrees higher than water cleaned by boiling.

^{x)} P. Othmer, loc. cit.

The results of these tests make it seem probable that as a general rule the spontaneous crystallization observed was caused by foreign substances. Consequently it should be possible, after removing these foreign substances, to supercool the water to a temperature lower than -20°C , the lowest temperature repeatedly observed. The greatest supercooling ever observed to date is 21.5°C ^(*)).

II THE LINEAR CRYSTALLIZATION VELOCITY OF ICE IN AQUEOUS SOLUTIONS

1. The measurement of the crystallization velocity was carried out in U-tubes which had an inner diameter of 1.2 mm. and a wall thickness of 0.5 mm. The temperature bath consisted of alcohol cooled by dry ice and contained in a transparent Dewar flask. A spiral stirring mechanism ensured uniform temperature distribution in the bath. The start of crystallization was effected by inoculation with ice. The progress of the crystallization was timed between two marks which had been made on each arm of the U-tube 80 mm. apart thus ensuring a straight-line measuring distance. At low velocities the time measurement was made by means of a 0.2 second watch, and at velocities higher than 1,000 mm. per minute, by a 0.02 second stop-watch. The time taken by the crystallization boundary to pass upward and downward through the distance between two marks, was determined. For very low crystallization velocities (a few millimetres per minute and less) the U-tube was mounted on a glass scale by means of which the progress of the crystallization was observed. The temperature of the bath was maintained constant during the measurement to within $\pm 0.05^{\circ}$. The ice was added after the U-tubes had remained at the experimental temperature for at least three minutes. To prevent bursting of the tubes, they were removed from the bath before the last few drops of the water could crystallize.

2. The precipitating ice crystallized in the form of well-developed dendrites. The main growth was in the direction of the stem of the dendrite. As a rule, therefore, the growth of the stem coincided with the axis of the tube. The structure of the dendrite is easily recognized, especially at the crystallization boundary formed by one or several dendritic tips. Figure 1 shows the appearance of such a dendritic tip. The branches make an angle of 60 degrees with the stem. The branches in turn have twigs. The thick-

^(*) A. T. Lillenthal, Wiadomości
Instytutu Metalurgji i
Metaloznawstwa 1934, p. 26.

ness of the stem and the branches varies considerably with the concentration of the solution and the supercooling. At slight supercooling, thin, barely recognizable formations arise. At considerable supercooling the branches are often so thick that they collide and the details are no longer distinct. The crystallization front then consists of one or more ice tips which, however, always have the characteristic outline of the dendritic tips, with an angle of approximately 60 degrees at the top. In pure water dendrite stems having a thickness up to 0.5 mm. were observed. Microscopic measurement of individual dendrites, which crystallized at low crystallization velocity from a 50 per cent glycerine solution, revealed a thickness of approximately 0.02 mm. for the stems, 0.005 mm. for the branches, and 0.001 mm. for the finest twigs. The plane of the dendrites lies in the hexagonal group of ice, hence the dendrites correspond to one of the six rays of a snowflake^x). In pure water, at slight supercooling, wide deviations from the tube axis were observed in the direction of the dendrite stems, resulting in a considerably decreased crystallization velocity^{xx}). In dilute sucrose solutions the dendrite stem and the branches sometimes showed a curvature with a radius of a few tenths of a millimetre which resulted in a reduced crystallization velocity. This explains to a certain extent the differences in the values found in the literature for the crystallization velocity of ice from pure water. Up to the present these differences were attributed to varying test conditions (tube diameter, thickness of the tube walls). Lilienthal^{xxx}), who made his measurements under almost the same conditions as the authors of the present report, found values which were smaller by approximately seven per cent, since his tubes were bent three times in order to obtain a longer measuring distance.

3. Figures 2 to 4 show the dependence of the crystallization velocity of ice from various solutions on the supercooling. The numbers given in the figures are the mols of the substances dissolved in 1,000 gm. water. The crystallization velocity was generally followed up as far as the crystallization capacity permitted. The decrease in crystallization velocity effected by the addition differs considerably for

x) G. Tammann and K.L. Dreyer,
Naturwiss. 22 (1934), p. 613.

xx) G. Tammann and A. Büchner, loc.
cit.

xxx) A.T. Lilienthal, loc. cit.

the various substances at identical mol concentration. As yet the available data are not sufficient to give information concerning the effects of these various substances. The decrease in the crystallization velocity of ice caused by sucrose is particularly large. Sucrose far exceeds the other substances in molecular weight and therefore has a particularly low rate of diffusion. This probably explains the strong effect.

It was only possible to attain the maximum crystallization velocity when this was less than 100 mm. per minute. With small values of the maximum crystallization velocity, less than 15 mm. per minute, marked maxima of the crystallization velocity occur. These maxima lie, in the present case, between 7° and 13° of supercooling in agreement with the findings for chemically pure substances.

4. The dependence of the crystallization velocity on the temperature may be represented for pure substances like other reaction velocities by an equation of the form:

$$\log K G_{T_1} = \log K G_{T_2} - A \frac{T_1 - T_2}{T_1 \cdot T_2}$$

where T_1 and T_2 are the temperatures at the crystallization boundary. For small values of the crystallization velocity these temperatures do not differ from that of the bath. If this formula is applied to the dependence of temperature on the crystallization velocity of solutions, then the fact must be taken into account that the crystallization velocity is influenced not only by the temperature at the crystallization boundary, i.e., the equilibrium temperature, but also by the rate of diffusion of the dissolved substance. The rate of diffusion, however, decreases very substantially with decreasing temperature, thus reducing the crystallization velocity. For this reason the formula does not hold for large concentration and temperature intervals. For small ones, however, it is in agreement with the observations. The logarithm of the crystallization velocity is a linear function of the concentration or of the temperature at the crystallization boundary.

The addition of foreign matter usually lowers the melting point. The same applies to the crystallization velocity of the crystals of the solvent at identical supercoolings, although this decrease is substantially larger and satisfies other laws. In a binary series of mixtures the crystallization velocity declines with the distance from the two components, hence for identical supercoolings the

two curves of crystallization velocity in dependence on the concentration must intersect exactly as the curves of fusion do. However, it is not required that the point of intersection of the two curves of crystallization velocity should lie at the eutectic concentration. At this point of intersection the crystallization velocities of the two components are equal if each component crystallizes separately. However, if both crystallize together, then the crystallization velocity will generally increase slightly, compared with the value of the individual component. The reason for this is that the separation of the two substances due to diffusion is facilitated by the existence of both types of crystal at the crystallization front^{x)}. With a mixture of two components, which, in the pure state have very different crystallization velocities, there are concentrations from which even the component of large crystallization velocity crystallizes at a lower rate than the pure component of lower crystallization velocity. The investigation of glycerine-water solutions served as an example. The maximum crystallization velocity of pure glycerine is approximately 0.1 mm. per minute^{xx)}. From a solution containing 60 per cent glycerine the ice crystallizes at a maximum crystallization velocity of 0.093 mm. per minute. However, the crystallization velocity of ice, as well as that of glycerine from 67 and 85 per cent solutions, is at least ten times smaller.

5. The magnitude of the crystallization velocity is important for deciding whether a solution can be transformed to the glass-like state by rapid cooling. Small quantities (approximately 0.1 cc.) of eutectic solutions of KOH, NaOH, HCl, and CaCl₂, whose maximum crystallization velocity is lower than approximately 20 mm. per minute, could be maintained glass-like by cooling in liquid air.

6. In the concentrations investigated to date additions of dissolved foreign matter reduce the crystallization velocity of ice. If, however, the effect of small quantities of dissolved matter (say less than 0.01 mol per litre) is investigated, it is found that a small addition does not have a decreasing effect but, on the contrary, an increasing effect on the crystallization velocity of ice. Consequently, at identical supercoolings, marked maxima can be found on the curves representing the crystallization velocity as a function of the concentration. These curves for solutions of NaOH, HCl, NaCl, and sucrose are given in Figures 5 to 8. The re-

^{x)} G. Tammann and A. Botschwar,
Z. anorg. u. allg. Chem. 157
(1926), p. 27.

^{xx)} G. Tammann and E. Jenckel, Z.
anorg. u. allg. Chem. 193
(1930), p. 76.

spective supercoolings are given at the right-hand side of each curve.

The increase in the crystallization velocity of ice which is evident during the first addition to the water may be interpreted in the following manner. Due to the formation of ice the concentration of the ice forming type of molecule will be reduced. The transition of the other molecule types to the ice forming type is accelerated by the additions. In dilute solutions there is a slightly higher concentration of the ice forming type of molecule than in pure water, causing an increase in the crystallization velocity. In the case of larger additions, however, the decrease of the crystallization velocity caused by the decrease in the equilibrium temperature prevails. With increasing supercooling the maximum crystallization velocity becomes more distinct. The rate of transition of the molecules of water into the ice forming type decreases with dropping temperature and the accelerating effect of the added substance becomes more pronounced. For the addition of NaCl the increasing effect is smaller than for additions of HCl and NaOH, thus shifting the maximum to smaller NaCl concentrations. This shifting is more pronounced in the case of sucrose.

/MJ

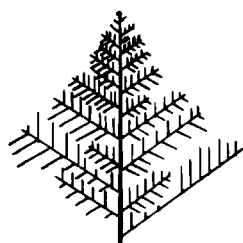


FIG. 1
ICE DENDRITE

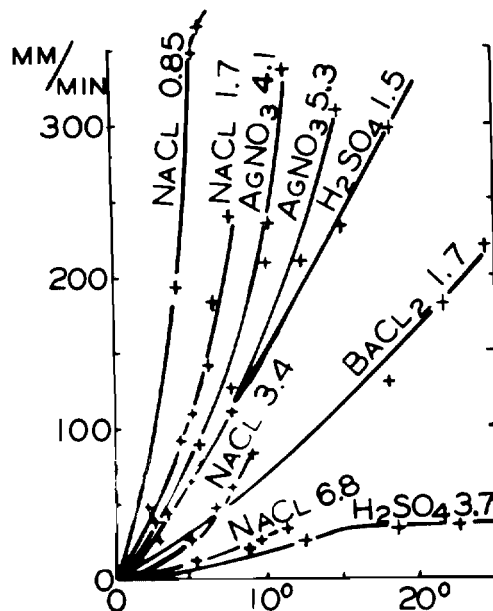


FIG. 2 CRYSTALLIZATION VELOCITY
IN MM/MIN PLOTTED
AGAINST THE SUPERCOOLING.

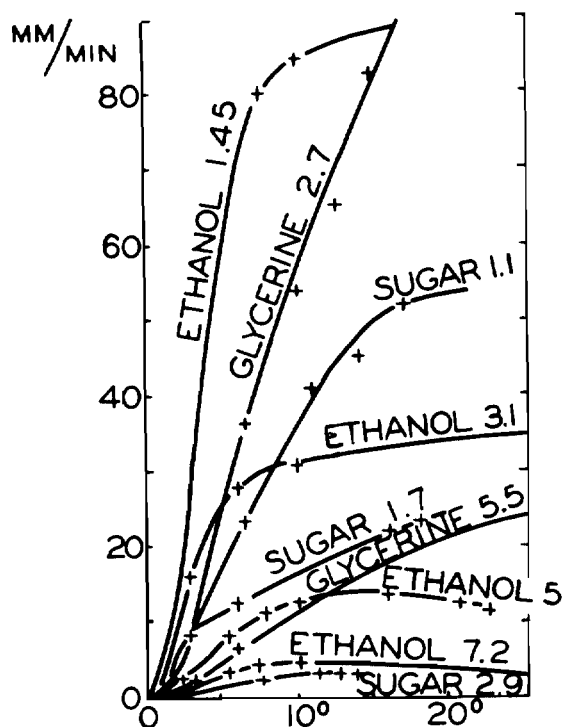


FIG. 3 CRYSTALLIZATION VELOCITY
IN MM/MIN PLOTTED
AGAINST THE SUPERCOOLING.

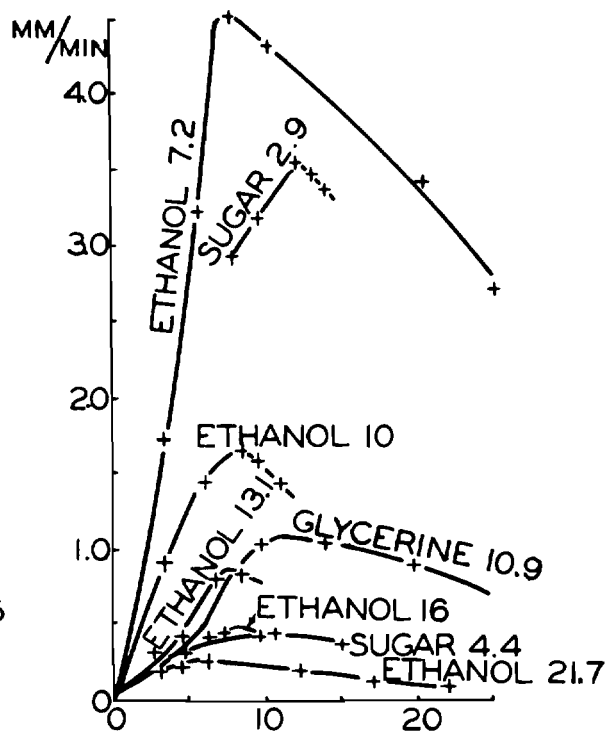


FIG. 4 CRYSTALLIZATION VELOCITY
PLOTTED AGAINST THE
SUPERCOOLING.

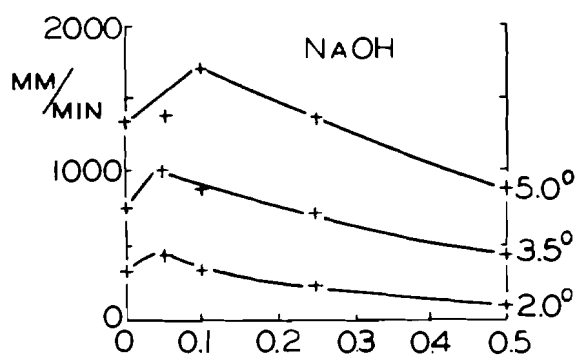


FIG. 5

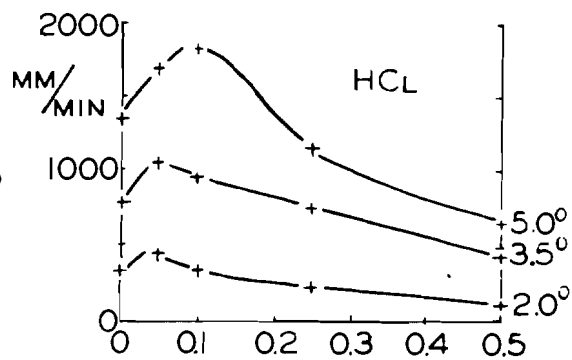


FIG. 6

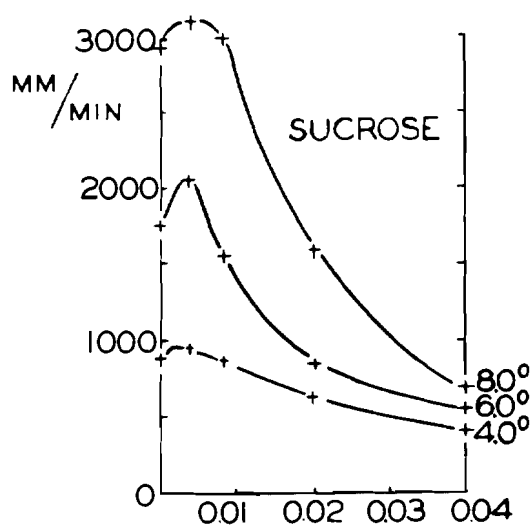


FIG. 7

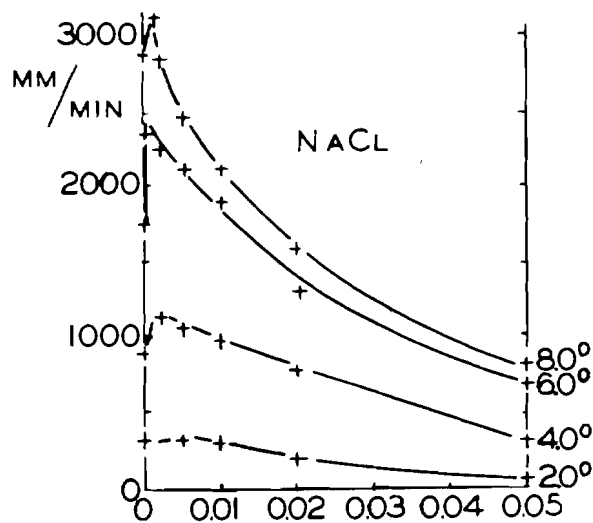


FIG. 8

CURVES OF CRYSTALLIZATION VELOCITY AS
A FUNCTION OF SOLUTION CONCENTRATION.