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Studies on the Freezing of Water

(II) Formation of Disc Crystals

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Various methods were devised for the production of disc crystals. The one is to make seeding ice particles grow into disc crystals on the surface of water or inside the water. The other is to produce many dispersed ice particles from mother ice. The mother ice is formed instantaneously by crystallization of supercooled water, and the dispersed ice particles are obtained by mechanical method or produced spontaneously. Besides, a special experimental method based on Clausius-Clapeyron's formula was devised for the production of disc crystals. In this case the water temperature very slightly below ice point can be determined accurately.

By these methods the physical conditions are determined under which the disc crystals are produced. Also, observations were carried out with respect to crystal forms and surface phenomena of growing crystals. The mechanism of anchor-ice formation is discussed in relation to the formation of disc crystals in the dispersed state.

It is suggested that the effect of interfacial tension between ice crystal and supercooled water is important in the dispersion process, and also in the growing process of ice crystals.

§ 1. Introdcution

In the prvious paper[1] the ice crystals formed in water were classified according to their crystal forms. In hydrology, the classification is based on their modes of formation under natural conditions; for example, anchor ice, frazil ice, etc. Recently LAMBOR[2] presented detailed results based on such a grouping. ALTBERG[3] reported that anchor ice was comprised of disc crystals in early stage of growing, and SCHAEFER[4] also stated that in his observations disc crystals were recognized in the frazil ice made in rivers. With regards the formation of disc crystals, it is necessary to find the relation between the disc crystal and the anchor ice or the frazil ice.

The problem of formation of disc crystals can be considered in two processes. The one is their appearance, and the other is

their growth. In the followings different methods of producing disc crystals are described.

§ 2. Experiments and Results

(a) Formation of disc crystals on water surface by seeding.

(i) *Method of seeding.*

SCHAEFER[4] and KUMAI and ITAGAKI[5] reported on the experimental procedures for producing ice crystals on the surface of supercooled water by seeding with minute ice particles. The author also used the same method. When a metal block which had been cooled by immersing in liquid air was suddenly exposed to the air in the cold chamber, a stream of white cloud is produced. This stream contains numerous minute ice crystals. When this white cloud falls on the surface of the supercooled water, the minute ice particles grow into myriad small ice crystals.

To determine the shape and size of cloud particles, they were trapped in cedar oil by aspiration method,[6] and photomicrographs were taken as shown in Photo. 1 in Pl. I.

Air temperature in the cold chamber was about $-27°C$. The distance of fall of those particles was 56 cm. A small copper cylinder, 2 cm in diameter and 2.5 cm in height, was used for the seeding.

In Photo. 1, excepting one large particle near the lower right margin, all particles are comparatively uniform in size, being about the order of 10^{-4} cm in diameter. Under a polarization microscope with crossed Nicols, two kinds of particles were distinguishable, bright ones and dark ones. It seems probable that those particles consist of ice crystals and supercooled droplets. The roundly hexagonal particle in the right part of Photo. 1 is probably an ice crystal of plate form.

Other observations on this kind of particles were carried out with the temperatures of $-19°C$ and $-15°C$. In any of these three cases, no crystal of distinctly columnar or needle form was found in the field of microscope. All the particles appear to be round plates or spheres. In the latter two cases, the size of the particle was of the same order of magnitude as in the previously described observation.

(ii) *Seeding on water surface at ice point temperature* (Series I).

The first experiment was carried out on the growth of disc crystals produced by seeding the water surface whose temperature was kept at ice point. The apparatus is shown in Fig. 1. V is a shallow glass tray, 7 cm in diameter, and 3 cm in height, which contains about 20 cc of distilled water to be seeded. To keep the water at ice point, the glass tray was divided coaxially into two parts with a circular glass wall. The space between two walls was filled with a mixture of ice and water. W_1 is a large cylindrical vessel containing a mixture of water and snow. W_2 is a double-walled cylindrical vessel, 51 cm in height and 24 cm in outer diameter. The space between the coaxial walls was 5.5 cm and this space is filled with a mixture of water and snow. L is the light source for the shadow-photograph method.

A sheet of photographic paper P is slipped between the glass tray V and the vessel W. S is a hole through which the seeding particles produced by the cooled copper block are to be poured in.

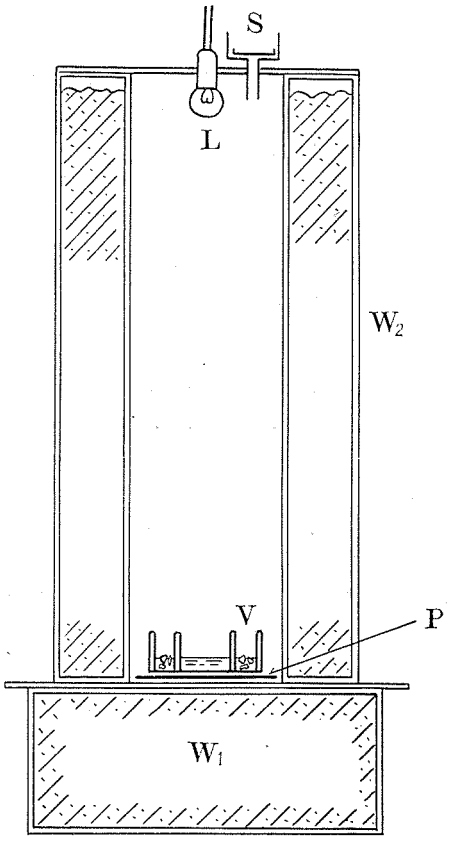

Fig. 1. Apparatus for 0°C-seeding.

The apparatus was placed in a room at the temperature between 1°C and 2°C. Seeding was carried out at half an hour or more after the apparatus was set. Photographs were taken at varying values of the time T_p which measures the interval between the beginning of seeding and the moment of exposure of the photographic paper. T_s means the time during which the seeding

is continued. The results are summerized in TABLE I.

TABLE I.

Series No.	Exp. No.	T_s	T_p	Size (L) Disc	Semi-circle	Needle	Mean rate of growth of disc crystal (L/T_p)
		sec	sec	mm	mm	mm	mm/sec
	19	60	60	0.3	0.3	0.35	5.0×10^{-3}
	20	30	30	0.2	0.15	0.5	6.7
	21	40	40	0.75	0.8	0.8	19
	23	60	60	0.35	0.35	0.25	5.8
	24	60	120	0.45	0.55	0.4	3.7
I	26	30	120	0.35	0.6	0.5	2.9
	27	30	60	0.25	0.4	0.5	4.2
	29	30	240	0.25	0.25	0.2	1.0
	33	30	60	0.15	0.15	0.15	2.5
	34	30	60	0.1	0.15	0.15	1.7
	35	30	180	0.4	0.7	0.7	2.2
	41	60	240	0.25	0.6	0.45	1.0

One of the original photographic papers is reproduced in natural size in Photo. 2, Pl. I. The circular black part in the middle of the picture is the free surface of water in the tray. The outside part of a thick ring form represents the mixture of water and ice fragments. The small white image in the black part is the shadow of a cloud given in the course of the seeding. In the original photographic papers, ice crystals are very minute in size and it is difficult to observe by a naked eye. For the study of the form and structure of ice crystals, a photograph of this original picture is taken, and it is enlarged. Photos. 3, 4, 5 and 6, show the crystals thus enlarged. Usually the distribution of ice crystals is not uniform, and the number of ice crystals observable in one picture shows a considerable fluctuation ranging between ten and several hundreds. However, the size of crystals is comparatively uniform as shown in these photographs. Characteristic types of crystal form are disc, semicircular and needle. Besides, there are several intermediate forms. The respective numbers of ice crystals of these three typical forms are obtained by counting them of five photographs and the results are shown in Table II. Informations

TABLE II.

Series No.	Exp. No.	Number of crystals		
		Disc	Semicircle	Needle
I	21	30	8	3
	23	169	40	10
	24	59	19	3
	26	42	20	9
	35	98	26	13

on the growing processes of these three types of ice crystals were obtained by taking many photographs at various stages of growth. The most probable process of the growth of each crystal is shown in Fig. 2. For each of the crystal types, the largest sample is

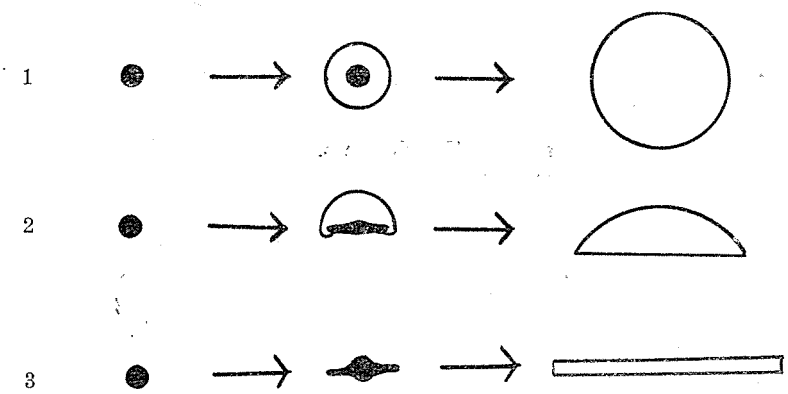

Fig. 2. Growth process of a seed particle into three typical forms.

chosen among numerous crystals of this kind observable in one picture, and the dimension of this sample is measured and shown by L in TABLE I. Measurement was done with respecct to the longer diameter in case of disc crystals, the length of the cord for semicircular crystals, the length for needle crystals. Disc crystals are usually slightly smaller than the other two types. In Fig. 3 the largest size of disc crystals in TABLE I is plotted against T_p, assuming that each crystal begins to grow at the moment of seeding. The curve in Fig. 3 has only a statistical meaning. Under the experimental conditions above described, crystals sometimes

increase in size rapidly in the early stage of growth. The fastest rate of growth was observed in the case of Exp. No. 21 in TABLE I. The average rate of growth is seen from Fig. 3 to be 1.9×10^{-3} cm/sec or 1.1 mm/min during the initial 40 seconds.

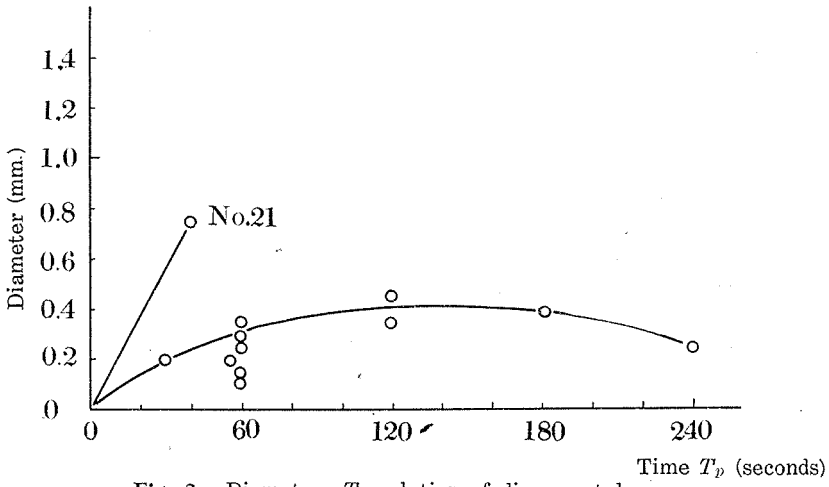

Fig. 3. Diameter—T_p relation of disc crystals, when the water is 0°C.

Sometimes at the beginning of seeding, a sizzling noise was heard in the apparatus. This is due to the small droplets of liquid air falling on water surface. In such a case, ice particles of a complicated form was observed. One example is shown in Photo. 7, Pl. III. This ice particle looks to be composed of a bundle of needle crystals spreading out from the spherical surface of an initially formed ice ball. The rate of growth of this ice particle is very much greater than that of the three regular types of crystals.

(iii) *Seeding on supercooled water surface* (Series II).

The previous method was applied for seeding on supercooled water surface. Experiments were carried out in a cold chamber with air temperature at about −10°C. The same tray (V in Fig. 1) containing 20 cc of distilled water was placed in a wooden box with a temperature controlling device. The air in the box had been stirred by a motor-fan, and the air temperature was kept nearly constant by regulating the heater. The shadow photograph

method was also applied in this case. Four photographs of successive stages were taken by sliding along a sheet of photographic paper beneath the tray. Air temperature in the box and water temperature of the tray were measured by thin alcohol thermometers. A fine copper wire cooled in liquid air was used for seeding.

Just before the seeding, water temperature t_1 and air temperature t_2 were observed. Then the fan was stopped so that the motion of crystals on the water surface was prevented. Seeding was carried out during a few tenths of a second by inserting the copper wire into the box. After seeding, four successive photographs were taken within one minute; just after the fourth photograph had been taken the water temperature t_1' and air temperature t_2' were again observed.

Experiments were carried out on the surface of water at various temperatures between −0.1°C and −3.2°C. In TABLE III,

TABLE III.

Seires No.	Exp. No.	Initial t_1 °C	Initial t_2 °C	Final t_1' °C	Final t_2' °C	Crystal form T_1	T_2	T_3	T_4
II	26	−0.1	−0.1	0.0	0.0	*D,S,N,* (5)	*D,S,N,* (10)	*D,S,N,F,H,* (30)	*D,S,N,F,H,* (60)
	21	−0.4	0.0	0.0	−0.4	*D,N,* (5)	*D,N,H,* (10)	*D,N,F,H* (30)	*D,N,F,H* (60)
	10	−0.9	−0.7	0.0	−0.7	*D,N,F,* (5)	*D,N,F,H* (10)	*D,N,F,H* (30)	*D,N,F,H* (60)
	2	−2.5	−2.3	0.0	−2.9	*N,F,H,* (5)	*N,F,H,* (15)	*N,F,H,* (45)	*N,F,H,* (75)
	25	−3.0	−3.1	−0.2	−3.0	*N,F,H,* (5)	*N,F,H,* (10)	*N,F,H,* (20)	*N,N,H,* (30)

experimental conditions and the mode of growth of crystal forms are tabulated. In the last four columns, crystal forms are discribed by the letters *D, S, N, F* and *H,* which correspond respectively to disc crystals, semicircular crystals, needle crystals, feather-like crystals and stellar crystals. Numbers in parentheses show the time moments T_1, T_2, T_3, T_4 in seconds at which each photograph was taken in each series of the experiments, the time having been measured by taking the moment of start of seeding as zero.

In Exp. No. 26 of TABLE III when the initial temperature was about −0.1°C, the crystals in the early stage were with forms of disc, semicircle and needle, coinciding respectively with those

obtained in Exp. I. Disc crystals and semicircular crystals were found solely in the regions of high concentration of seeding particles. In the regions of low concentration, all crystals were needle or semicircular in shape. In later stages, some of the disc crystals grew into stellar crystals, and the semicircular into feather forms. Photo. 9, Pl. IV, shows the crystal form at one minute after the seeding. In Photo. 8, Pl. IV, a magnified photograph of disc crystals is reproduced which is taken from a portion of Photo. 9. In the early stage, there is no marked difference in size among the crystals of different forms. In later stages, however, needle crystals and feather crystals grew at a larger rate than disc crystals.

In Exp. No. 10, Table III, the initial water temperature being $-0.9°C$, disc crystals are found only in the part of considerably high concentration of seeded particles, as shown in Photo. 10, Pl. IV. These disc crystals are so densely scattered that no further growth is noticed. In the part of low concentration, large feather crystals and a few needle crystals are observed, as shown in Photo. 11, Pl. IV.

Crystals of dendritic form grow at a rapid rate. In the early stage stellar crystals of fern-like structure are often observed, as shown in Photos. 12 and 13, Pl. V. These two pictures show the shape of crystals at $T_1=5$ sec. and the initial temperature of water is $-0.9°C$. In later stages it is impossible to discriminate between feather-like crystals and stellar crystals.

When the water is further more supercooled than $-0.9°C$, no disc crystal is observed even in the parts of high concentration of seeding particles.

The dimension of the disc crystal of the largest size observable

Table IV.

Series No.	Exp. No.	Dimension of the disc crystal of the largest size observable in one picture.			
		T_1	T_2	T_3	T_4
II	7	— (5 sec)	0.9 mm (10 sec)	1.7 mm (*H*) (30 sec)	2.0mm (*H*) (60 sec)
	8	0.6 (5)	1.2 (*H*) (15)	2.1 (*H*) (30)	3.0 (*H*) (60)
	14	0.25 (5)	0.5 (10)	1.5 (*H*) (30)	2.5 (*H*) (60)
	15	0.3 (5)	0.5 (10)	1.5 (*H*) (30)	— — —
	16	0.3 (5)	0.7 (10)	1.0 (30)	1.2 (60)

in each of the pictures is measured in the case when the water is supercooled to −0.1°C. The results are shown in TABLE IV and Fig. 4. Excepting No. 16, the disc crystals grew into stellar forms in the later stages, as marked with a letter *H* in parentheses in TABLE IV. In Fig. 4 broken lines indicate the growth into a stellar form. The solid straight line represents the mode of growth of Exp. No. 21 in Series I, when the water temperature is kept at 0°C. Exp. No. 21 in Series I is the example of an exceptionally rapid growth when the water temprature is 0°C, as seen in Fig. 3. However, compared with the curves when the water is supercooled to −0.1°C, it is decidedly slower in its rate of growth.

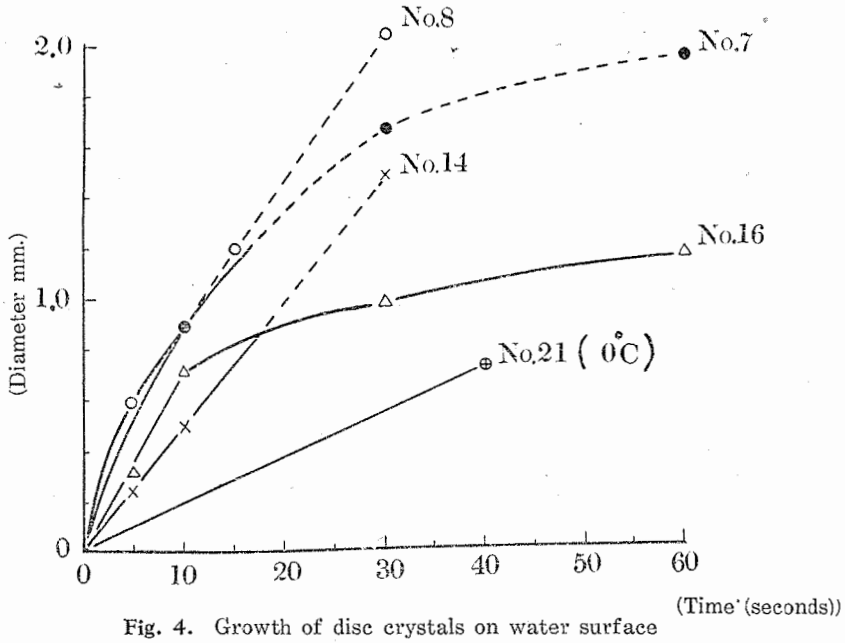

Fig. 4. Growth of disc crystals on water surface supercooled to −0.1°C.

Usually disc crystals transform into stellar type in the later stage. The condition controlling this transformation is not yet clarified. The size of crystal can not be a criterion, because an extraordinarily large disc is sometimes observed. In order to study this point, further experiments were carried out with respect to the rate of growth. Many disc crystals were produced by the above mentioned method of seeding, and successive shadow photo-

graphs were taken during their growth. The mean growth rate between successive stages was obtained. The results are plotted in Fig. 5, in which the abscissa represents the diameter of disc crystal at a certain time interval, and the ordinate shows the mean rate of growth in this time interval. The black circle marked by shows the case when this disc crystal grows into a notched form in the next stage of time interval. The white circle marked by indicates that no variation occurred in the crystal form, that is, the circular disc grows in size but remains as a circular disc in the next picture. General tendency is that the rate of growth

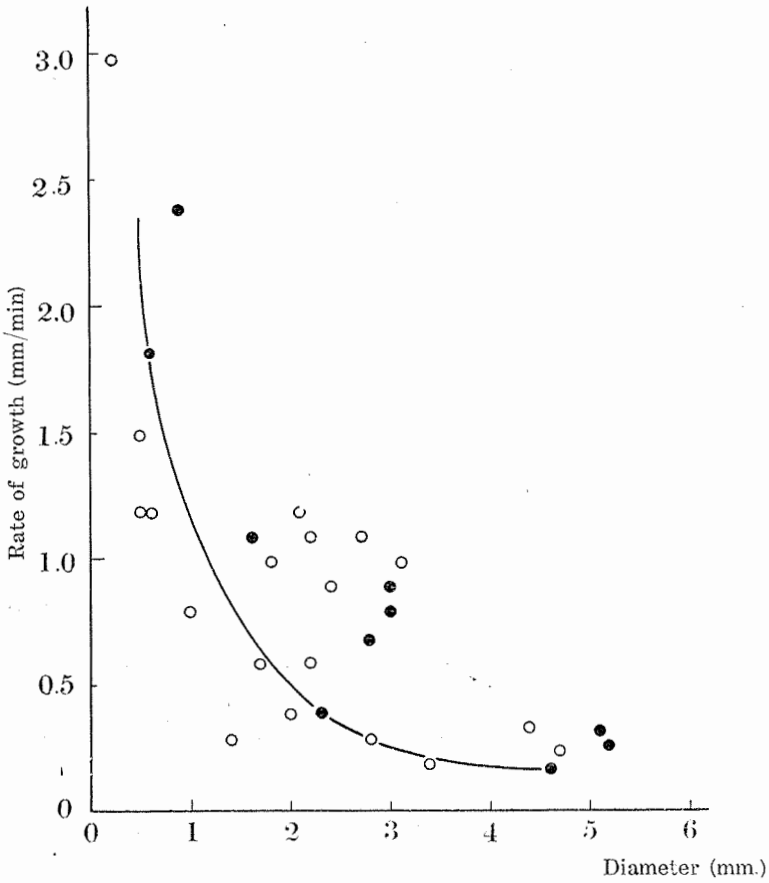

Fig. 5. Rate of growth–Diameter Relationship of disc crystals.

decreases with the diameter in both cases. Further it is noticed in Fig. 5 that the black circles are as a whole situated higher than the white circles. This means that for a certain size of disc crystals the probability of growing as a disc without transforming into a notched form is larger when the rate of growth is smaller. The curve in Fig. 5 shows the limit of the rate of growth under which disc crystals can grow as a disc form.

When the seeding is carried out on supercooled water surface, the resultant disc crystal usually shows a marked white periphery and a complicated pattern on its surface. Two examples are shown in Photos. 8, Pl. IV and 14, Pl. V. Other types of structure of crystal surface are observed at the later stages of growth of disc crystals. Several examples are shown in Photos. 15–18, Pl. VI. It appears that some of the patterns are made of boundaries between wet parts and dry parts of crystal surface. The disc is floating on the water surface and it often happens that the top surface is partly covered with a water films. Photos. 17a and b reveal some rounded patterns which appear to be similar to the steps of the layer growth.

(iv) *Observations by a binocular microscope* (Series III).

Growing crystals on water surface were observed by means of a binocular microscope in the cold chamber. In the course of continuous seeding on water surface at a temperature slightly above ice point, ice crystals are observed to appear in the field instantaneously, and in a few seconds they develop into a certain size. When the seeding is too dense; say, the concentration of seeds on the water surface amounts to about 10^2 particles per square cm, the crystals grow at a very slow rate. This condition is most convinient for the observation of growing crystals of various forms. Disc crystals, semicircular crystals and needle crystals are also observed in this case, which are similar in forms to those shown in the photographs of the previous experiments of ice point seeding. It was found that the orientation of disc crystals is perfectly in parallel with water surface. The semicircular crystals are in an inclined attitude, to the water surface. The needle crystals are found to be not in the form of a simple needles, but actually they were the side view of thin elongate plates floating

with the edges perpendicular to the water surface. In the further development ice crystals grow at a slower rate, and in this stage also no marked change is observed in their relative position to the water surface.

(b) **Formation of disc crystals in supercooled water by scratching** (Series IV).

The growth process of disc crystals was observed in slightly supercooled water. The tray containing 20 cc of distilled water was set in the cold chamber with the air temperature at −8°C∼−10°C, and it was cooled gradually on the stage of a microscope. Under this condition crystals of needle form grow on the inner glass surface of the bottom of the tray. They develop very fast in the early stage, but their growth rate diminishes rapidly. In this state, the surface of those needle crystals is scratched with the tip of a fine needle. By this process many small ice particles are produced in water. Photo. 19 a, Pl. VII, shows the state of ice crystals scratched at two points. Some of the ice particles are adhered to the mother needle crystal and others ascend slowly towards the water surface, Photo. 19 b. As time passed, some of the adhered particles are also detached and ascend in the water one after another. Variation of shape during the growth of disc crystals is observed while the crystals are ascending in water, and the results are shown schematically is Fig. 6, in which the succesive stages of the front and side views are reproduced. In the first stage *A*, immediately after the ice particles are dispersed, they were spherical in form with a diameter of about 10^{-3} cm. On ascending, sudden appearance of a pair of flat surfaces is noticed on the spherical surface of ice particle, as shown in stage *B*. After

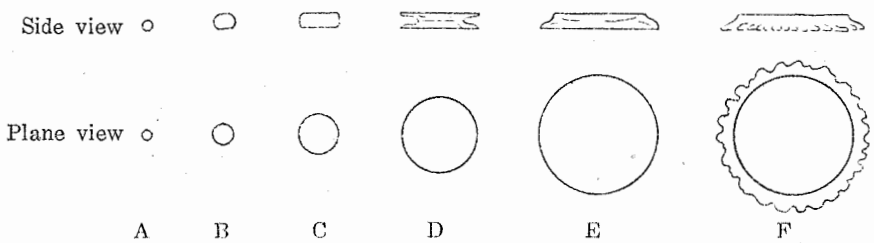

Fig. 6. Growth process of a seed particle into a notched-disc crystal.

this stage, the particles take a disc form and the further growth is facilitated mainly in the lateral direction. In stage *C*, the ratio of diameter to thickness is estimated roughly to be between 5 and 100. This observation was carried out with respect to many disc crystals with diameters varying between 0.5 mm and 3 mm. The next stage *D* is sometimes not observable. Usually the process of growth is directly from stage *C* to stage *E*. When the disc crystals reach the water surface, some of them take the position in parallel with water surface. This tendency is more enhanced as the size of crystal increases. After this stage, disc crystals grow into a notched form, growing more rapidly in the lower part than in the upper, as indicated in stage *F*.

Some of these stages are shown in Photos. 20 a, 20 b, 21 and 22, Pl. VII. Photo. 20 a corresponds to stage *D*, and Photo. 20 b to stage *E*. Photo. 21 is the initial stage of the notched form. The example of the last stage *F* is shown in Photo. 22.

After the disc crystals reached water surface and took a horizontal position, their surfaces are usually covered with a thin water film. For the later reference this state will be called as the wet condition. Waiting for a while, the water film on the upper surface of the disc gets frozen. This ice surface will be called "dry". During the course of transition from wet condition to dry, some interesting phenomena are observed. Photo. 23, Pl. VIII, shows an intermediate or transitional state. In Photo. 23, a small portion at the upper rim looks white, and the other part is grey. This white portion is dry, while the greater area is covered with water film. There is another type of transition shown in Photo. 24. In this case a thin water film is dispersed in the form of lens-like droplets on the crystal surface, after having attained dry condition. These lens-like droplets often show a peculiar phenomenon; they migrate slowly on the surface of ice and it looks that there is some definite direction in this motion. In the course of their migration, droplets leave some traces on the ice surface which are similar in shape to ripple marks on sand beach. The shematical sketch of Photo. 24 is shown in Fig. 7, in which the "ripple marks" and the direction of motion is illustrated. These droplets somtimes coalesce with each other by moving on the surface, as shown in Photos. 25 a–25 d, Pl. VIII.

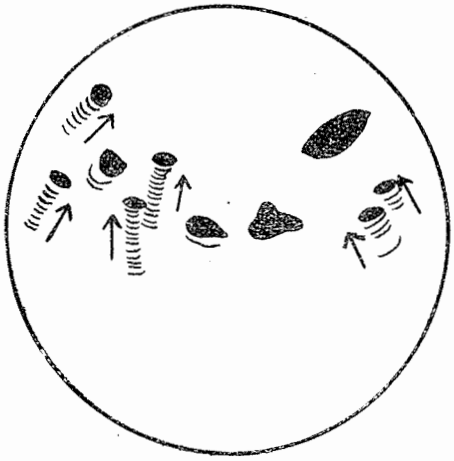

Fig. 7. (Photo. 24)

With respect to the surface condition of crystals, some further experiments were carried out. In some cases crystals grow always in dry condition. In such a case a sort of network pattern is usually observed on the upper surface of the crystal. One example is shown in Photo. 26, Pl. VIII, and its sketch in Fig. 8. Black dot *D* in Fig. 8 is a dust particle. This dust was originally at the position *A*. During the course of the growth of crystal, this dust is always kept at a point on the edge, and the trace of its motion is left on the crystal surface.

In order to detect the surface conditions, ice crystals were exposed to alcohol vapor. When the surface is wet, no change is observed. In the case of dry surface, however, a remarkable phenomenon takes place; that is, many droplets appear on the ice surface by simply exposing the surface to alcohol vapor. One example of this "dew formation" is shown in Photo. 27, Pl. VIII. These dews are observable only for a short time, and the whole surface is suddenly covered with a water film completely. This method of exposing the ice surface to alcohol vapor can be used as a criterion to determine whether the ice surface is wet or dry. Photos. 28 a and b, Pl. IX, show two stages before and after the alcohol vapor treatment for the same sample. Portions of the crystals which

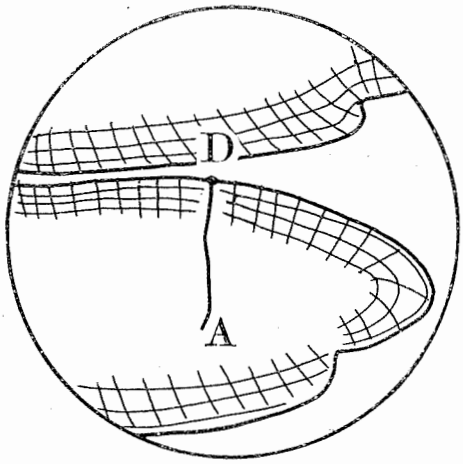

Fig. 8. Growing ice crystal in dry condition.

present different appearance in these two photographs are understood to be in dry condition.

(c) **Formation of disc crystals by instantaneous contact of supercooled water with ice** (Series V).

As the results of the preceding experiments show, the temperature range most favorable for the growth of disc crystals is between 0°C and −1°C. A simple method was devised in order to keep water at slightly supercooled temperature with high accuracy. Experimental procedure is as follows. A cubic metal vessel, $15 \times 15 \times 15\ cm^3$ in volume, is filled with water, and cooled very slowly in the cold chamber. After two days, a cubic ice block containing a spherical portion of unfrozen water inside is obtained. This ice block is taken out of the vessel, and further cooling of the block is continued. When the internal pressure reaches to the limit of strength of the ice wall, a sudden break takes place in the wall, resulting in the sudden release of the internal pressure. This action causes an instantaneous formation of numerous air bubbles near the bottom of the water in the ice cube. After those air bubbles went up to the surface, there were found some disc crystals ascending in the water. They are very thin, and shine brilliantly with interference colours under a suitable illumination.

In later experiments, in order to obtain high internal pressure, an iron case of volume $20 \times 20 \times 20\ cm^3$ was used, which has four circular windows in the four side-walls, and one on the upper side for insertion of a manometer into the water. Photo. 29 shows an ice block containing a manometer suspended in the water inside the ice cube.

The water temperature just before the breaking is obtained by the measurement of internal

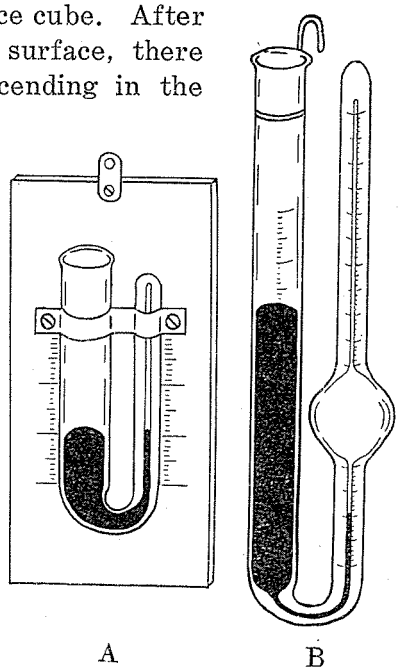

Fig. 9. The manometers.

pressure. The depression of the freezing point by pressure is calculated from Clausius-Clapeyron formula of thermodynamics. Two types of manometers are used. They are illustrated in Fig. 9. One end of a U-tube of the manometer is open and the other end is closed, where a suitable amount of air space is left. The internal presure is calculated from the decrease in volume. In the calculation of supercooled temperature, the equation $dT/dp = -0.0099$ degree/atm/cm^2 was used.[7]

TABLE V.

Exp. No.	Hydrostatic pressure at the breaking	Degree of supercooling	Crystal form	Condition of ice block
1	8.8 atm	− 0.077°C	$D \to D$	without iron case
2	1.3	− 0.003	$D \to D$	"
3	5.1	− 0.041	no crystal	"
4	25	− 0.24	$D \to$ notched discs $D \to D$	with iron case

Experimental results are shown in TABLE V. In the fourth column, the change in crystal form is shown by arrows. In the cases of Exp. Nos. 1 and 2, there was no further change in crystal form; that is, disc crystals remained as they were. In Exp. No. 4, however, disc crystals initially originated grew into a slightly notched form in the course of ascent. Appearance of disc crystals continues for some time, and in later stages crystals do not show the change in form and remain as disc crystals. In Exp. No. 3, ice crystals were not observed but it seems that this will be due to oversight. Ascending velocities of those disc crystals are all nearly the same, being about 0.2 cm/sec. While ascending, they show usually no definite orientation, but it often happens that they take a horizontal position in the later stages of ascent. The crystals grow into a size about 2 or 3 mm in diameter after ascending about 10 cm through the water.

As the preliminary experiments, surface structure inside the ice wall was examined in the course of freezing. One day after the beginning of freezing, the ice cube was cut vertically into three equal portions. The photograph shows the side view of the middle portion is shown in Photo. 30, Pl. X. The bottom side of

the inner ice wall is rugged with projecting ice crystals. An ice crystal marked by an arrow is semicircular in form and the periphery is slightly notched. Other parts of the inner surface are perfectly flat without projecting ice crystals. Detailed examination also proved that there was the same preferred orientation of flat ice plates of minute sizes along the whole lower part of the inner surface.

In all the experiments above described (Series V), when the wall of the ice block had grown into a certain thickness, the old water inside the cube was changed with fresh water at the temperature slightly above ice point; then the manometer was inserted into it.

(d) Disc crystal formation inside the supercooled water by seeding (Series VI).

In this Series of experiments, the supercooled water was seeded with ice through a capillary tube near the bottom of the crystallizing vessel. In Fig. 10 two apparatuses are shown. First apparatus A was used, but after two sets of experiments it was broken. In Fig. 10 A, *G* is the crystallizing tube made of glass, 5.2 cm in diameter and 40 cm in length. A rubber stopper *R* is put into its lower end, through which a capillary tube *C* is inserted. The crystallizing tube is immersed in a large glass vessel *V* containing dilute solution of potassium chloride. *S* is a stirrer. *M* is an open end through which an ice particle is dropped for seeding.

In apparatus B, the crystallizing tube *G* and the capillary tube *C* are fused together. In both apparatuses, water temperature was measured by a mercury thermometer with divisions of 1/10°C.

The apparatus is slowly cooled in the cold chamber. The cooling rate of water is about 0.24°C/hour at the temperatures below 4°C. The solution is continuously stirred with the stirrer *S*. Water in the crystallizing tube *G* is also stirred gently with the thermometer stem. When the water temperature reaches the predetermined supercooled temperature, an ice particle is put into the open end *M*. Then the crystallization of water proceeds through the water in the capillary tube *C*.

In the case of apparatus A, when growing ice crystals in the capillary tube reach the point *P*, some ice crystals appear separately in the water slightly above the end point *P* of the capillary tube.

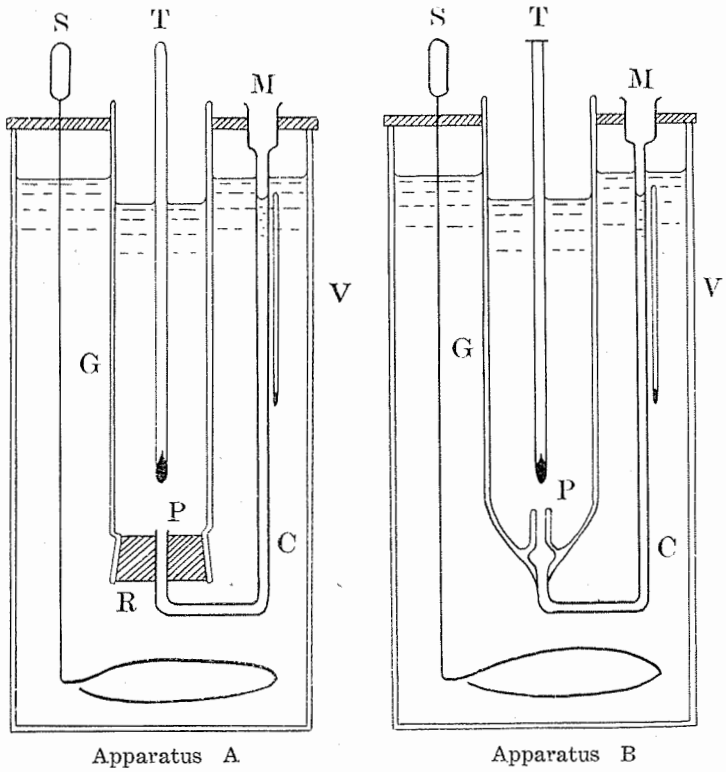

Fig. 10. Apparatus for the formation of disc crystals with seeding at the bottom of vessel.

In apparatus B, however, a fine feathery crystal is observed to grow from the capillary end *P*, no separate ice crystals being detected. This feathery crystal is very fragile and is easily broken by touching with the thermometer bulb. In this case several minute ice crystals are produced in the water above the end point *P*. The results of measurements in this Series of experiments are given in TABLE VI. In Exp. Nos. 3, 4 and 5, the crystals are notched disc type from the beginning being about 1 mm in diameter. They transform into stellar type while ascending in water. In Exp. No. 1, the ice crystals are disc-like in their initial stage and grow into the notched form in the course of rising water. In Exp. No. 2 no disc crystal was observed. The initiation of ice crystals continues for a considerable time, and in the later stage of each

TABLE VI.

Exp. No.	Apparatus	Degree of supercooling	Crystal form	Seeding
1	A	− 0.32°C	*D*→notched disc	only seeding with ice
2	A	− 0.01	no crystal	
3	B	− 0.36	notched disc→stellar	seeding with ice and broken with the thermometer bulb
4	B	− 1.04	notched disc→stellar	
5	B	− 0.46	notched disc→stellar	

experiment all ascending crystals become disc form, as the water temperature in the crystallizing tube gradually reach to ice point by the liberation of latent heat of crystallization. In TABLE VI, "crystal form" refers to the crystals in the early period of the experiment.

(e) **Spontaneous formation of disc crystals in supercooled water** (Series VII).

In this Series of experiments, sudden freezing of supercooled water is a cause of formation of dispersed ice crystals, no seeding used. Two kinds of apparatus are designed for this purpose. They are shown in Figs. 11 and 12 respectively. In Fig. 11, *V* is a crystallizing vessel made of glass tube, 3.3 cm in diameter and 21 cm in height. *B* is brass rod, 2 cm in diameter and 10 cm in length, which is inserted into a hole in the middle of the rubber stopper *R*. *C* is a beaker containing cooled alcohol for cooling the rod *B*. A large glass vessel *G* covers the entire crystallizing vessel *V* in order to prevent the intrusion of ice particles from the air. Water

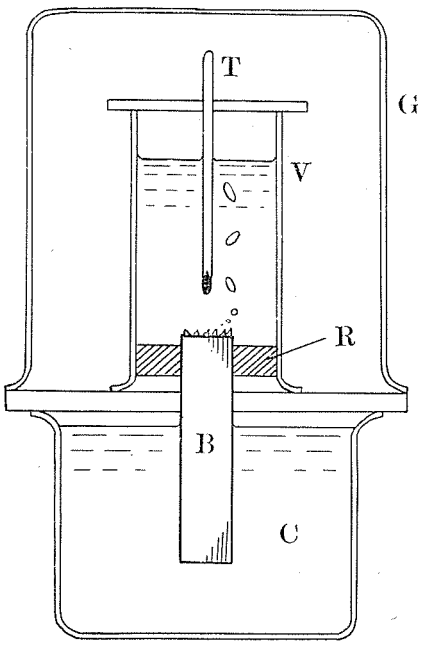

Fig. 11. Apparatus for the instantaneous formation of disc crystals.

temperature in the vessel was measured by a thin alcohol thermometer *T*. In the first Series of experiments, the brass rod *B* was covered with a finger-stall. In the second Series, a thin mercury layer was added to the bottom of the crystallizing vessel so that the finger-stall and the rubber stopper is covered with mercury.

First the beaker *C* only was set in the cold chamber, and was cooled to about −20°C. Then the crystallizing vessel *V* containing water at ice point temperature was placed on this beaker, as shown in the Fig. 11. Water temperature decreases gradually, and at a certain temperature the crystallization takes place suddenly on the rubber film. This crystal is feather-like type and has a very fine structure. In a moment, minute disc crystals appear in the water slightly above the rubber film. They grow rapidly into stellar crystals through the stage of notched form during their ascent. This process continues for several tens seconds or a few minutes and in the later period all ascending crystals become disc type. Results are shown in TABLE VII. In the second Series of experiments, the dispersed ice crystals are formed above the mercury layer. The third Series was carried out by using a simpler apparatus shown in Fig. 12. In this case, the crystallizing vessel

TABLE VII.

Series No.	Exp. No.	Water temperature at the initiation of crystallization	Duration of production of crystals	Number of crystals observed	Water used	Condition of surface
I	1	− 2.5°C	60 sec	about 10	not distilled	rubber film
	2	− 2.5	40	10	" "	
	3	− 2.2	360	100	" "	
	4	− 2.4	210	100	distilled	
	5	− 1.3	240	100	"	
	6	− 3.0	210	10	"	
II	7	− 3.2	120	20	distilled	mercury
III	8	− 1.5	60	10	not distilled	bottom glass of the beaker
	9	− 3.2	60	20	" "	
	10	− 3.0	50	30	" "	
	11	− 3.3	10	10	" "	

is a large beaker *V*. It was cooled down with a cylindrical brass block *B*, which had been cooled to −20°C in the cold chamber. Experimental procedure is the same as in the previous cases. In this case, formation of dispersed ice crystals is also observed slightly above the bottom of the beaker. Results are shown in TABLE VII. In the early period of each Series of experiments, notched crystals of the size less than about 2 mm in diameter are observed, but they were observable for a very short time, because they always grow rapidly into stellar form. In the later period, ascending crystals are all disc type and sometimes they show interference colours in their early stage of growing.

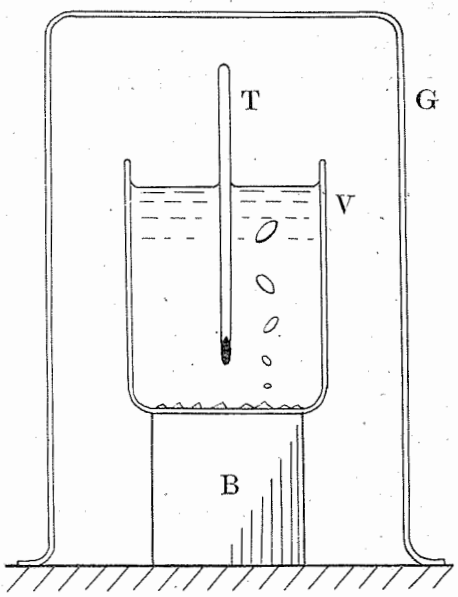

Fig. 12. Simple apparatus for the instantaneous formation of disc crystals.

Detailed obserbations were done at the initiation stage of crystallization. When the feathery ice crystals on the bottom spread out in water to some extent, dispersed ice particles begin to appear in the water above the bottom ice crystals. Detailed descriptions are given in the separate paper.[8]

§ 3. Discussions

(*a*) *External conditions for the growth of disc crystals.*

The first problem in the growth of a disc crystals is to determine the physical conditions under which the crystal continues to grow in the disc form. In the case of growing on the water surface, the controlling factors are water temperature and orientation of the crystal relative to the water surface. The latter was already pointed out by IMAI,[9] and our observations by the binocular microscope and Photos. 3, 4, 5 and 6 substantiated this opinion. The

effect of concentration of disc crystals on the surface of water is probably due to the change of water temperature caused by the heterogeneity of seeding. With respect to the water temperature, the most accurate results are obtained in the experiments of Series V. The lower limit of supercooling lies between $-0.08°C$ and $-0.24°C$ for disc crystals of the size smaller than about 2 mm in diameter. However, it seems that there are two processes causing the variation in water temperature after the sudden drop of hydrostatic pressure. The one is the adiabatic expansion of numerous air bubbles adhering the inner side of ice wall, and the other is heat liberation caused by the crystallization of ice block. These two processes act thermally in opposite directions. In the foregoing calculation of water temperature, they were neglected, because the interval between the moment of pressure release and the time of appearance of the first disc crystal was very short, and also the heat capacity of those air bubbles is very small.

With the water temperature at $-0.24°C$ in Series *V* and $-0.32°C$ in Series VI, gradual growth of disc crystals into notched form was observed. In the case of growth of ice crystals by seeding on the water surface, Series II, the initial water temperature at $-0.9°C$ was suitable for the growth of disc crystals when they were very tiny. Those evidences suggest that the condition for keeping the disc form is not determined by the temperature only but it is also a function of the size. Disc crystals grow easily into the notched form as they increase in size. Results obtained in Figs. 4 and 5 suggest that there is some relationship between the rate of growth and the size of the disc crystals. The rate of growth is closely connected to the degree of supercooling. When a disc crystal is small, comparatively large rate of growth is allowable. Further discussions will be summarized in the later paragraph.

(*b*) *Initial conditions for growing of disc crystals.*

In this Series of experiments, disc crystals were developed from two kinds of ice particles. In case of seeding experiments, the initial ice particles in the stream of cloud from a rod cooled with liquid air are about 10^{-4} cm in diameter. The other is of the spherical ice particles of size about 10^{-3} cm in diameter. This

is produced by means of scratching. The water temperature at the initial stage is between ice point and $-0.9°C$ for the growth of seed particles. For the growth of the latter ice particles made by scratching, the water temperature is probably very close to ice point.

There is a distinct difference between the initial water temperature above mentioned and the optimum water temperature for the continuous growth of a disc crystal. This fact suggests that the suitable water temperature depends upon the size of ice particles.

The orientation of seeding particles relative to the water surface is also a controlling factor determining the crystal form. The predominance of disc crystals on water surface, as shown in TABLE II, suggests that there may be some factor to prevent the growth of other types; that is, semicircular crystals and needles. When water temperature is at ice point, the seeding ice particles are not in the state of equilibrium. According to THOMSON's formula, it is necessary for those particles to coexist with supercooled water, and the degree of supercooling depends on the crystal size—strictly speaking, it depends on the radius of curvature of the ice particle. It is estimated that a disc crystal has the largest radius of curvature, a needle crystal has the smallest value at the two ends, and semicircular crystal a middle value. If above considerations are applicable, one would expect that all seeding particles should grow into disc form, when water temperature is very close to ice point.

(*c*) *Formation of disc crystals in dispersed state.*

The most interesting phenomenon of disc crystals is their formation in dispersed state. Frazil ice and anchor ice formed in rivers are the ice of this type appearing in large quantity.

In the present paper, this phenomenon is treated in the experiments carried out with the apparatus *A* in Series VI and those in Series V and VII.

In the experiments of Series V, the pressure of water is released abruptly. It seems that some mechanical shock accompanied by cracking in ice wall would produce minute ice fragments.

Another mechanism of formation of dispersed disc crystals is

as follows. Some photographs obtained in the experiments of Series II show ice crystals of dense ramification, which was reported by WEINBERG[10] in his observation of growing ice crystals in supercooled water. When THOMSON's formula is applied to those growing ice crystals, it seems likely that those dendritic ice crystals may be in contact with supercooled water. Unless removal of latent heat of crystallization is enough to maintain the same interfacial condition, the degree of supercooling would rapidly decrease. When the form of crystal cannot harmonize itself with the temperature increase, thin branches of the dendrite would be dispersed into minute ice fragments by the effect of interfacial tension between water and ice. Then those ice fragments could possibly play a rôle as seeds for the formations of the disc crystals. This mechanism is probably available for explaining the formation of disc crystals in the experiments of Series VI with apparatus A and those of Series VII.

The present author and his collaborator[11] reported two similar phenomena of ice crystal formation in dispersed state. One of them was observed at the initial stage of freezing of aqueous solutions of some organic liquids. The other phenomenon occurred at the moment of seeding supercooled water with ice particles wetted with organic liquids. In both cases, many dispersed ice particles spreaded on supercooled water surface, and soon some of them grew into disc crystals.

Similar phenomena were observed by PAPAPETROU[12] in the crystallization from supersaturated solutions.

(*d*) *Nucleation.*

Recently HOLLOMON and TURNBULL[13] presented a work in which they defined the nucleation as the initiation of transformation at a certain recognizable center, and called the propagation of transformation from the center the growth. In the process observed in the experiments of Series VII, there occurred simultaneously two processes, viz., the growth of mother ice crystals of feathery structure and the formation of dispersed disc crystals. In this case the crystallization of mother crystals is the nucleation process, and the following process of dispersion of disc crystals is a separation process, even if those dispersed ice particles are very minute

in size at initial stages of their formation.

The recent theory of nucleation classifies the initiation of crystallization into two kinds; namely, the homogeneous nucleation and the heterogeneous nucleation. The latter process is likely to occur in the crystallization of not so purified water. The water used in the present experiments belongs to this kind.

In the forgoing experiments, initiation of crystallization always occurred on the surface of some foreign substance, including ice, in contact with the supercooled water. No evidence was obtained of initiation of crystallization from a point inside the specimen water. Sometimes freezing started from a certain point on the free surface of supercooled water, as shown in Photos. 2 and 3 a in the previous paper.[1] In these cases, however, the probable cause was the seeding of ice particles which fell on the water surface. In the experiments of Series VII, the water temperature at which initiation took place was between −1.3°C and −3.3°C. These values, however, are not accurate and further supercooling might have taken place.

Several years ago LAMBOR[2] reported his observations of frazil ice in rivers, in which some photographs of foreign nuclei suspended in water were reproduced. As for the degree of supercooling of river water, Altberg reported its limit to be from minus one-thousandth to −0.05°C. After reviewing the literatures, it may be said, there has been until now no report of foreign nuclei which were proved to be effective in nucleation under such a slight supercooled condition.

Besides foreign nuclei, mechanical stimuli were found to be effective for the initiation of crystallization in slightly supercooled water as reported by YOUNG and VAN SICKLEN.[14] They could initiate the crystallization even in a water at −0.02°C. The effect of ultrasonic irradiation studied by TURNER and VAN HOOK[15] is especially significant.

(*e*) *Anchor-ice formation.*

As for the water temperature under which disc crystals grow, there is a good agreement between the experimental results reported above and ALTBERG's observations under natural conditions. The most important problem of the formation of anchor-ice is the

initial stage thereof; in other words, whether anchor-ice originates from preceding mother ice or not. When the existence of mother ice is assumed, the problem of production of massive anchor-ice is led to the mechanism of separation of ice particles in the case of still water and a more active breaking process of ice crystals by turbulent flow in the rapids. The appearance of mother ice under natural condition could be caused by means of any of many possible processes, such as introduction of ice particles to water surface from the air, mechanical stimulus, or heterogeneous nucleation. Regarding the heterogenous nucleation, thermal conditions are more suitable for its occurrence at the water surface than in deep water. In the process of anchor-ice formation, the early stage of ice crystals in the running water is in the form of frazil ice, and afterwards those ice crystals would adhere to the river bottom. Further growth and accelerated accumulation of those frazil ice crystals would result in a large scale anchor-ice formation on the bottom.

Regarding the problem of anchor-ice formation by the process of pure heterogenous nucleation, there are some difficulties in explaining effectiveness of foreign nuclei, and further observations under natural conditions and more detailed experiments under controlled laboratory conditions are desirable.

(*f*) *Rate of growth and dendrite formation.*

Thermal conditions as related to a growing disc crystal should be taken into consideration more carefully. The water temperature in contact with a growing crystal is one factor. Another factor is the rate of removal of latent heat liberated by the crystallization. The removal of latent heat takes place mainly in two ways; that is, heat conduction and covection. The rate of heat removal is in principle obtainable from the measurement of the growth rate, but the amount of heat removed by conduction or convection cannot be separated.

Disc crystals grow in disc shape in a limited range of water temperature. This range of temperature is a function of crystal size. The maximum rate at which they can grow in keeping disc form, decreases as the size of crystal increases. A similar result was obtained also by KUMAI and ITAGAKI.[5] These two facts are

closely related to the mechanism of the dendritic growth of disc crystals. Dendritic growth is generally attributed to the occurrence of spatial fluctuation in the growth rate of a growing crystal.

Regarding the growth of a disc crystal, the most peculiar phenomonon is the large difference of the growth rate in two directions, perpendicular and parallel to the principal axis. Also each individual disc crystal shows a different ratio of diameter to thickness. The disc crystals grown in the experiments of Series V and VII show interference colours. In other cases, however, crystal are far thicker, and no interference colour is observed. The preferred orientation observed in the experiments of Series V could be reduced to the difference of the growth rate in two directions.

In the process of growth shown in Fig. 6, the ice particle of stage A reveals no definite crystalline facet. At stage B a pair of parallel planes perpendicular to c-axis is observed. In further growing, the side plane of the disc crystal is not a simple crystal plane, showing a large rate of growth. It seems that there is no disctinct heterogeneity in thermal condition surrounding the ice particle until these two parallel planes appear. This is one of the evidences to suggest the existence of some controlling factor other than the thermal condition.

CHALMERS[16] proposed that the equilibrium temperature between crystal and liquid varies with the crystallographic orientation of the interface, and may be different for different faces of the same crystal. It seems that this view is applicable to some extent for the explanation of the phenomenon above mentioned.

However, there is some discrepancy between this point of view and the consideration based on the macrocopic interfacial tension between ice crystal and supercooled water. The macroscopic consideration takes into account the radius of curvature only and does not deal with the interfacial energy between the individual surface and water. Furthermore, this process does not take place in the state of equilibrium ; then, it seems that the simple thermodynamical consideration cannot provide a definite basis for explaining this sort of growth.

The course of transition of a disc crystal to a stellar type is classified into the following steps :

a) disc transforms into a notched form,
b) Six "buds" of branches appear on the notched periphery,
c) "buds" develop into branches, giving a stellar crystal.

As for the step c), the explanation based on the thermal heterogeneity surrounding the crystal would seem reasonable. Regarding the step b), however, this conception cannot be applied, because there will not be a sensible thermal heterogeneity arround the circular crystal. This point looks to be very important and further researches are desirable, especially with reference to the surface properties of growing crystals.

In the present experiments, some observations were made of the surface phenomena, such as the surface migration of small droplets on disc crystals, wet or dry condition of growing crystals, the strange net-work patterns on the dry surfaces of disc crystals, etc. With respect to snow-crystal formation in the air, the surface condition of a growing snow-crystal would play an important rôle. NAKAYA[17] in his recent publication, suggested the possibility of the diffusion of H_2O molecules on the surface of snow crystals. Furthermore, NAKAYA and MATSUMOTO[18] reported the existence of the "liquid water film" on ice surface.

§ 4. Concluding remarks.

In the present paper, disc-crystal formation was studied with regard to the form of the crystals during the process of their growth. The effect of the interfacial tension between water and ice crystals should be taken into account, because the process of separation of minute ice particles from the mother crystal suggests that it plays an important rôle in the process of freezing of water. The initial stage of formation of disc crystals under natural conditions is probably a very complicated process. In the theories of anchor-ice formation in rivers and lakes, there is some confusion which is caused mainly by the lack of detailed accurate observations. It is not difficult to prove one mechanism as probable, but it is impossible to reject other possible mechanisms without confirmed observations. As for the important problem whether anchor-ice grows, in the initial stage of formation, on river bed or not, the present author suggested only some possibilities based on the

present experimental results.

Problems of crystal growth are not simple, and more fundamental properties of surface of *growing* crystals should be studied experimentally.

In conclusion the author wishes to thank the Low Temperature Institute, Hokkaidô University, Sapporo, in which cold chamber the present experiments were carried out. This work is a part of studies on snow and ice in NAKAYA Laboratory of Fac. Sci., Hokkaidô University, and the author's gratitude is expressed to the members of the Laboratory for their kind help and discussions throughout the experiments.

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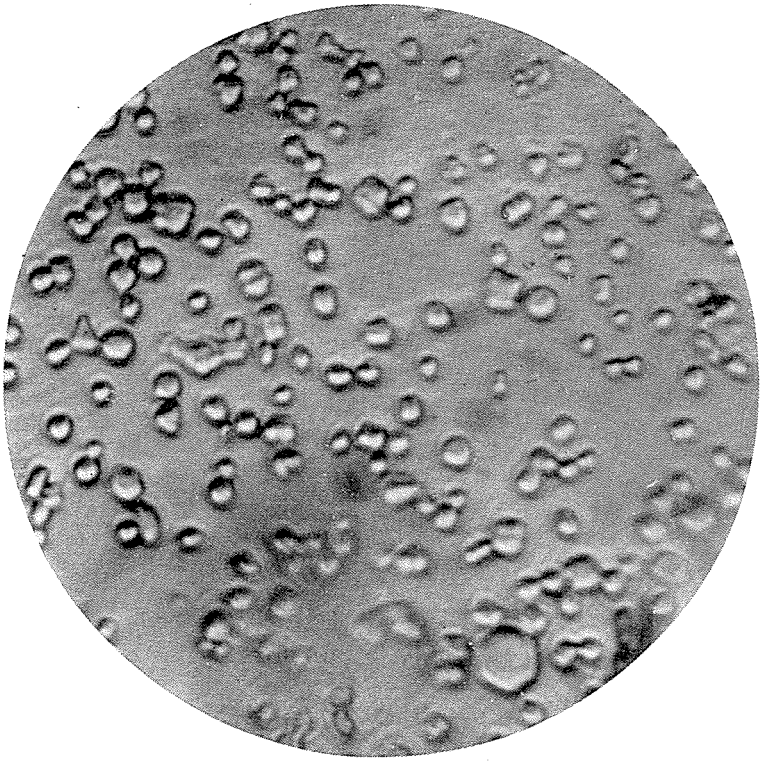

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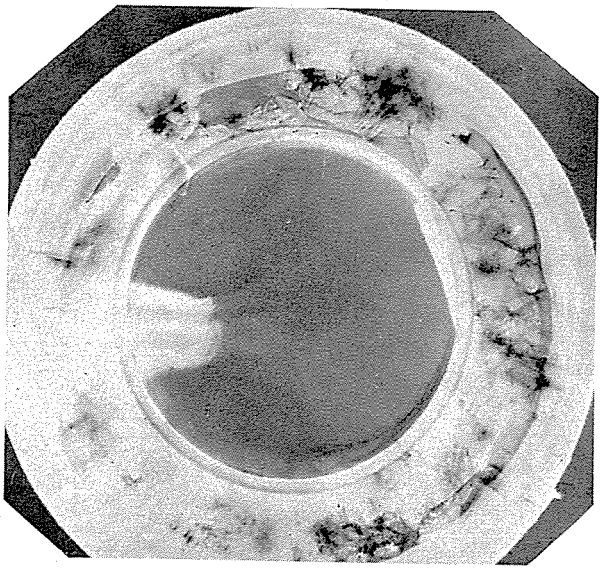
1. Replica of seeding particles.



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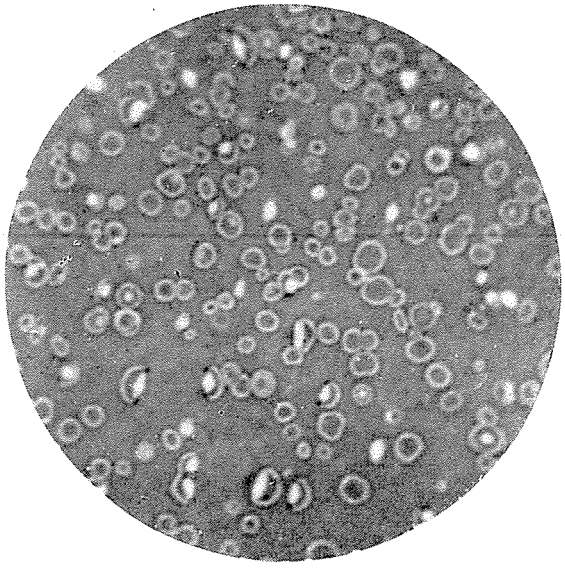
2. Series I, Exp. No. 23, T_s, 60 sec.; T_p, 60 sec.

× 12

3. Series I, Exp. No. 20, T_s, 30 sec.; T_p, 30 sec.



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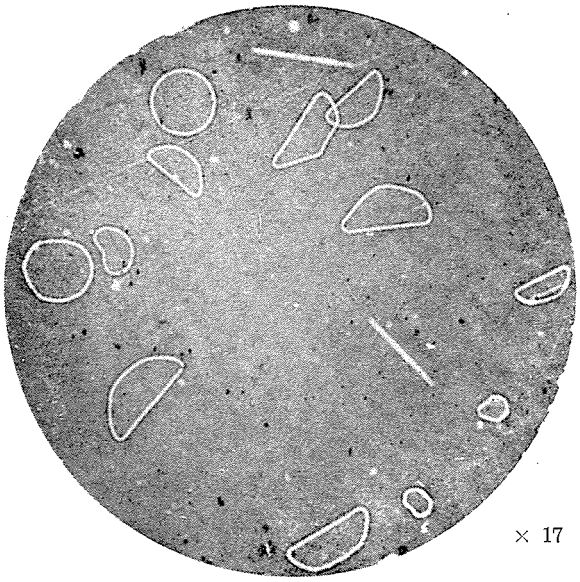

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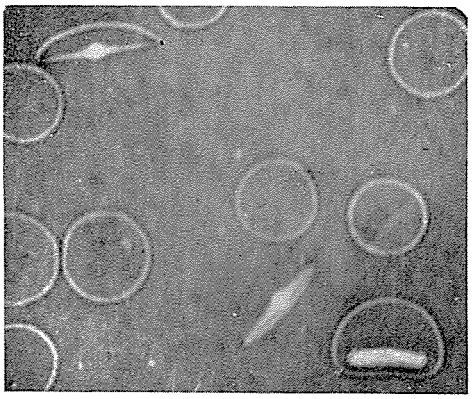
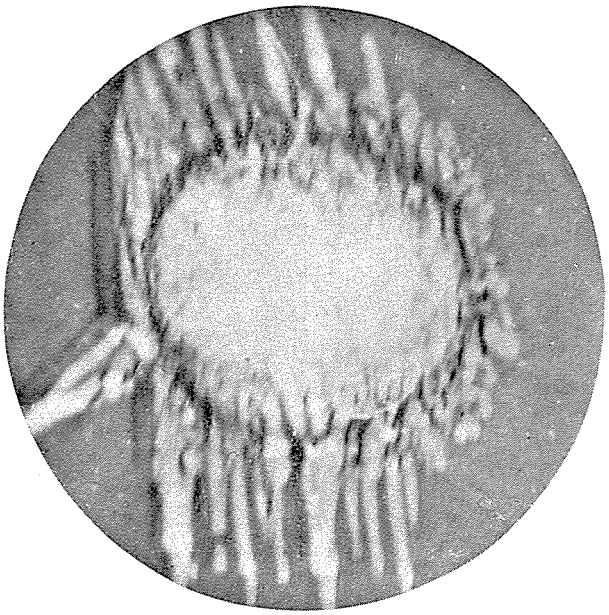
5. Series I, Exp. No. 35, T_s, 30 sec.; T_p, 180 sec.



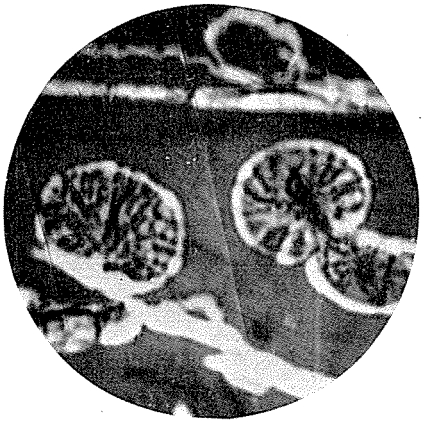
× 23

6. Series I, Exp. No. 21, T_s, 40 sec.; T_p, 40 sec.



× 23

7. Series I, a droplet of liquid air fell on the surface of water at 0°C.



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8. Series II, Exp. No. 26 ; $T_4 = 60$ sec.

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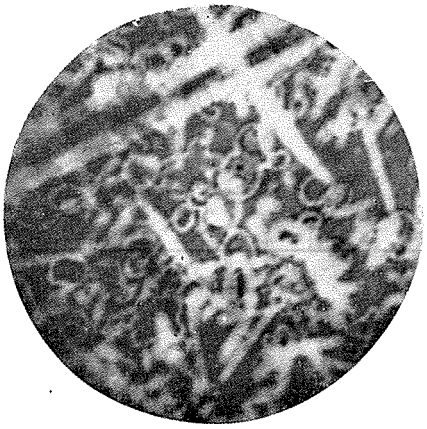
9. Series II, Exp. No. 26 ; $T_4 = 60$ sec.



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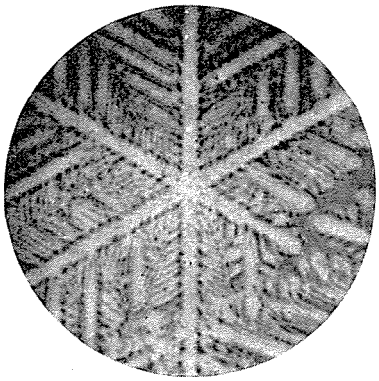
10. Series II, Exp. No. 10 ; $T_4 = 60$ sec.

× 1.8

11. Series II, Exp. No. 10 ; $T_4 = 60$sec.



12. Series II. Exp. No. 25 ;
$T_1 = 5$ sec.

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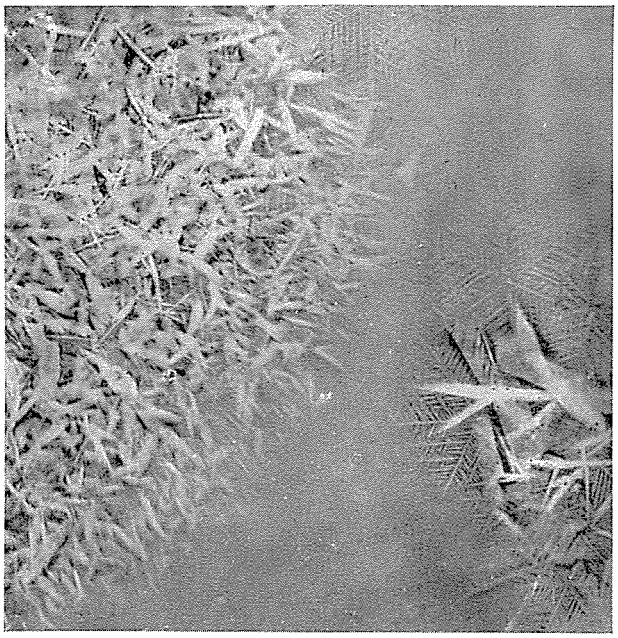

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13. Series II, Exp. No. 25 ; $T_1 = 5$ sec.

14. Series II, Exp. No. 21 ;
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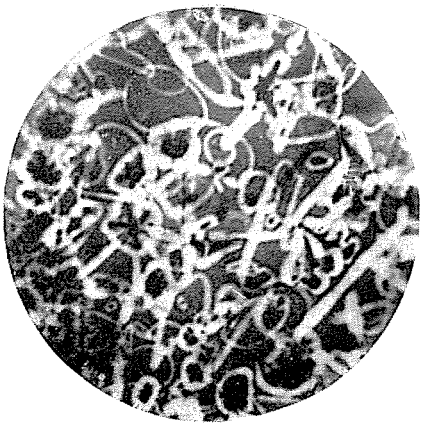
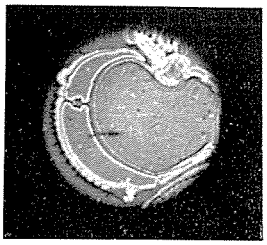


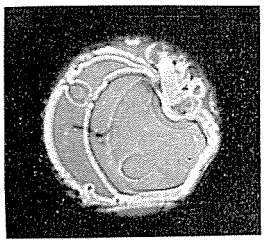
× 17

Interesting patterns on disc crystals. (magnified)



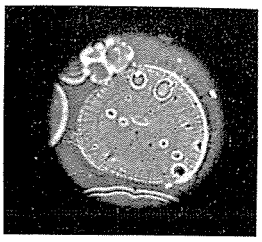
× 4.3

15 a.



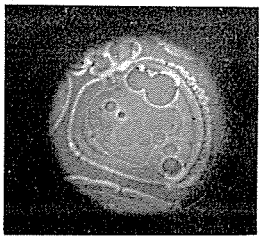
× 4.3

15 b. after five minutes.



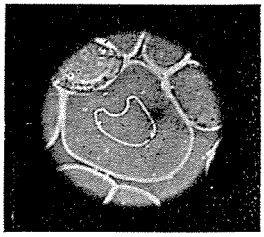
× 4.3

16 a.



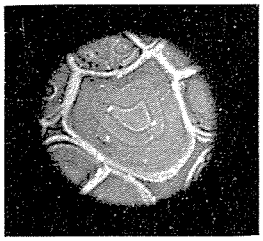
× 4.3

16 b. after five minutes.



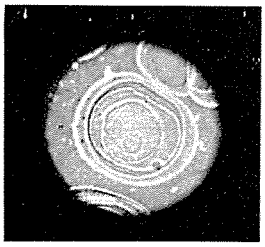
× 4.3

17 a.



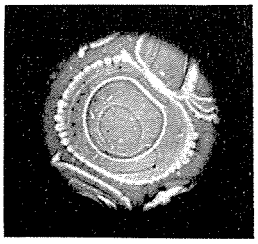
× 4.3

17 b. after five minutes.



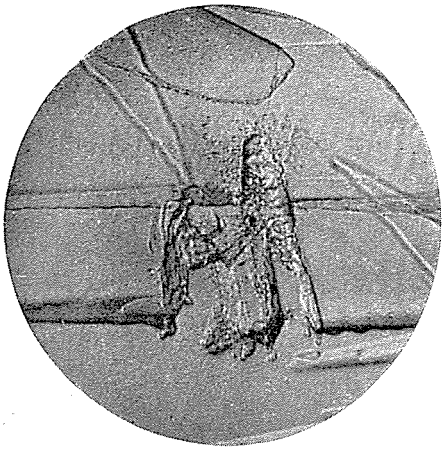
× 4.3

18 a.



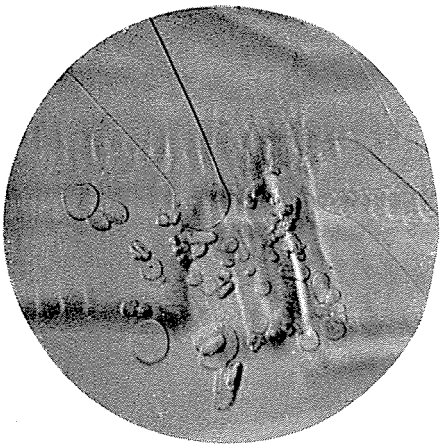
× 4.3

18 b. after five minutes.



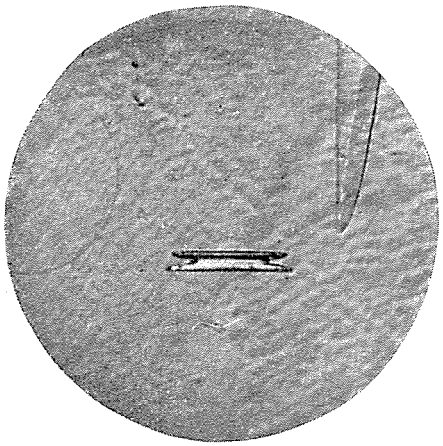
× 26

19 a.



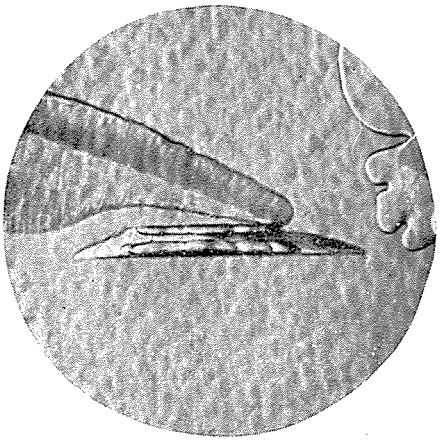
× 26

19 b.



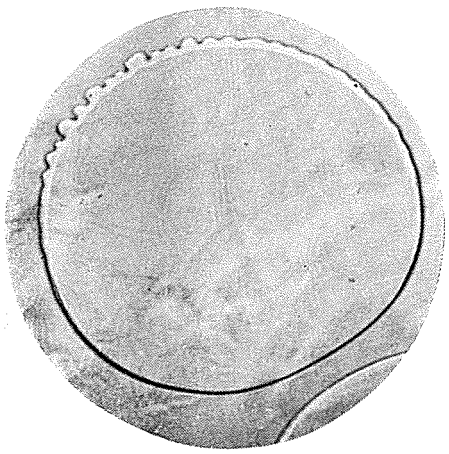
× 26

20 a.



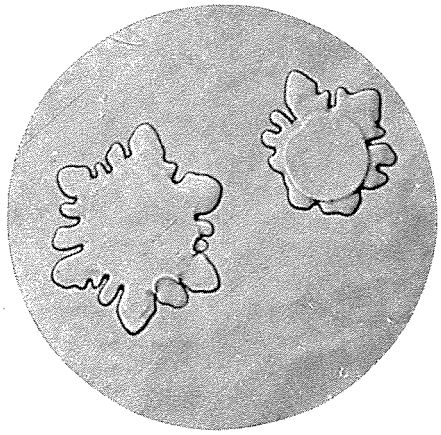
× 26

20 b.



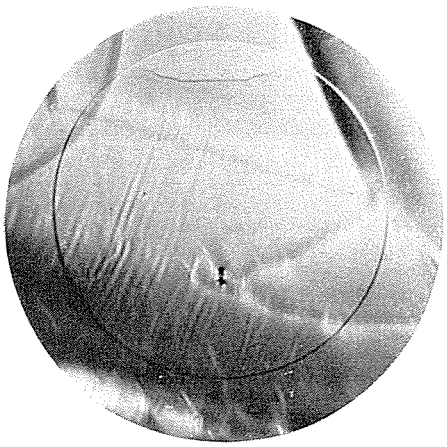
× 23

21.



× 26

22.

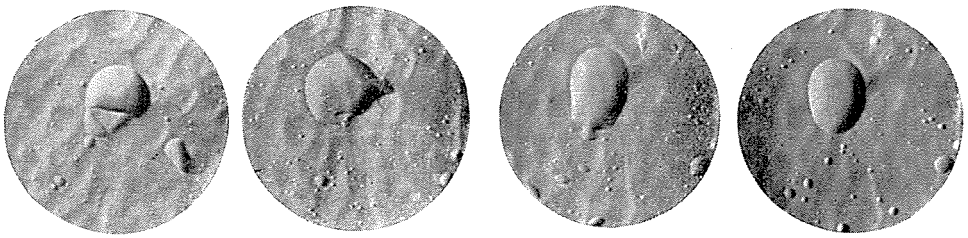


× 12

23.

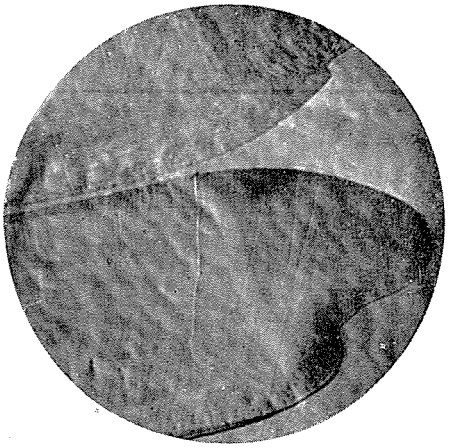
× 26

24.



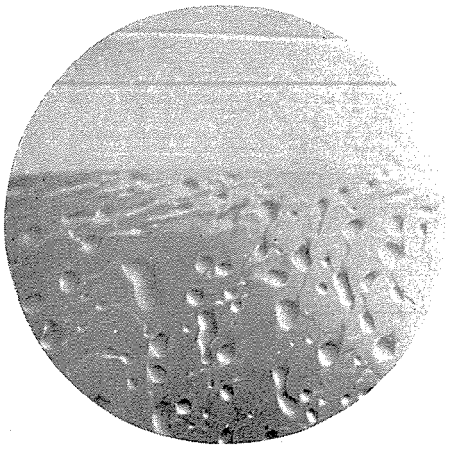
× 26

25 a. 25 b. 1 min. 25 c. 2 min. 25 d. 3 min.



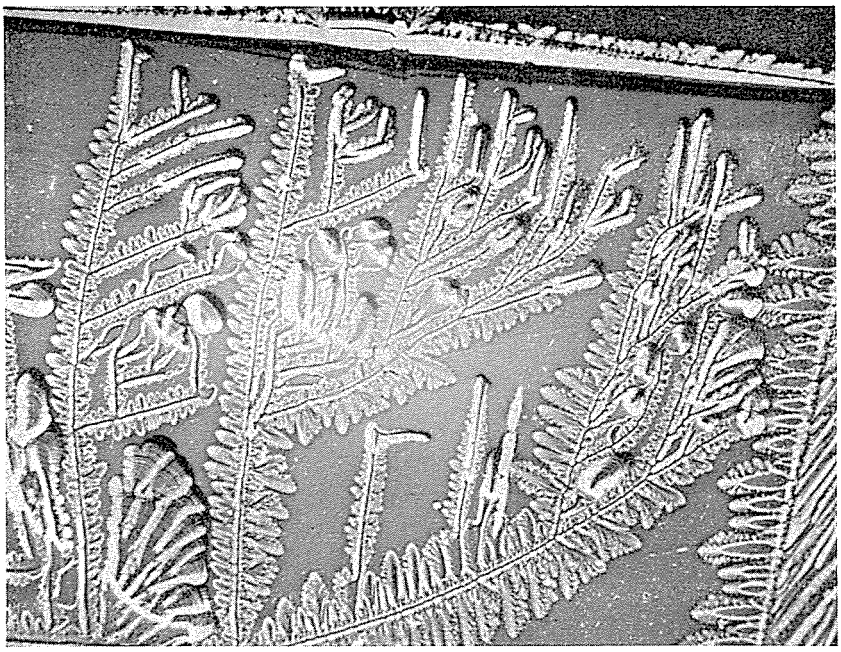
× 26

26.



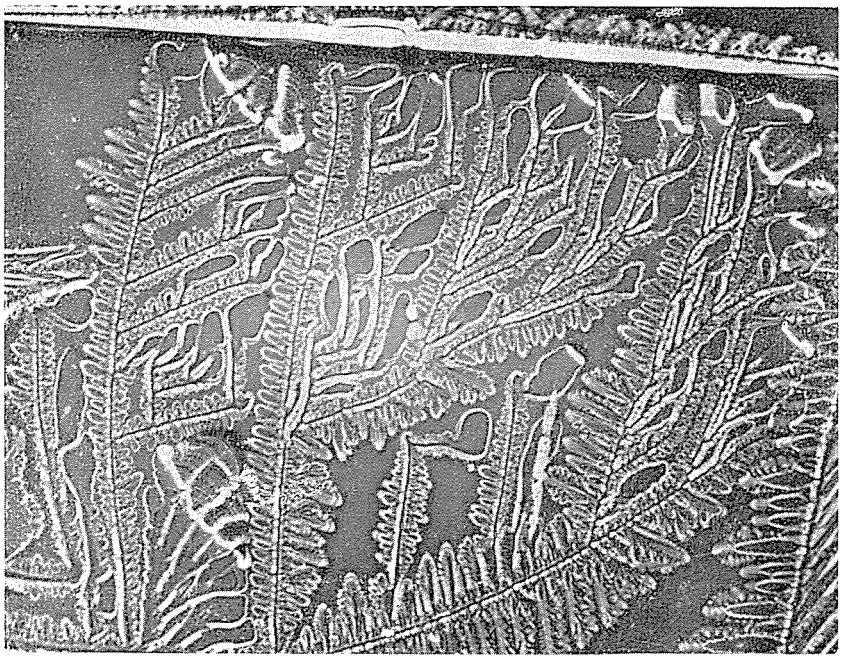
× 26

27.



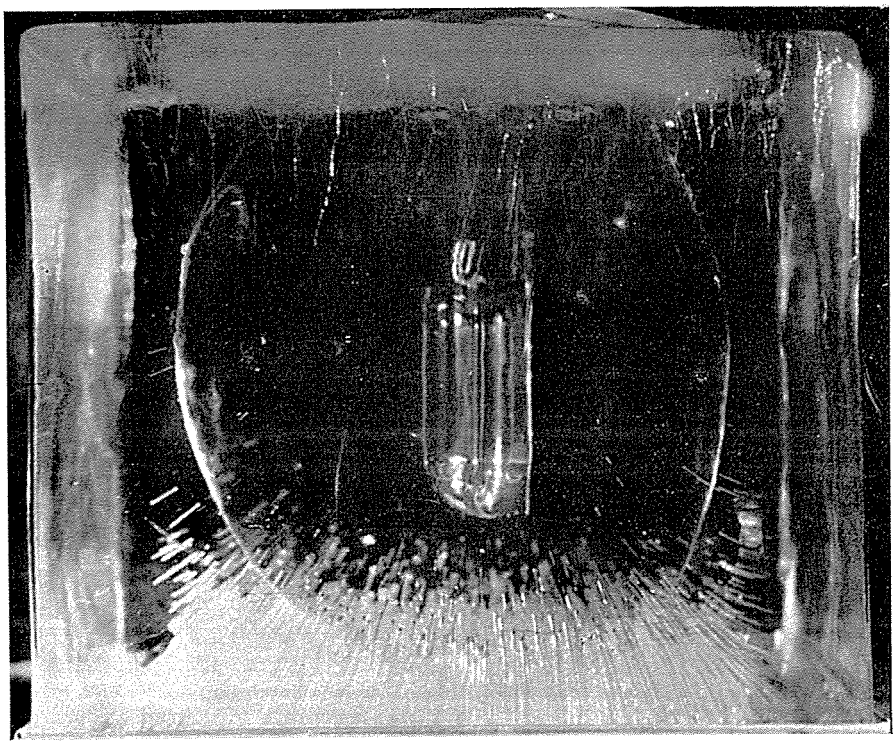
× 5

28 a. Before the Alcohol vapour Treatment.



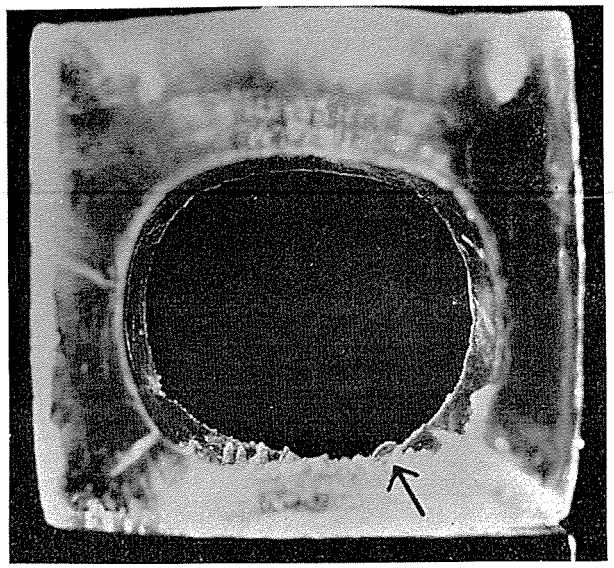
× 5

28 b. After the Treatment.



× 1.4

29. An ice block containing a manometer of A type.



× 0.7

30. Structure of inner surface of an ice block.