

# A Study of Ice Sintering

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## *Abstract*

Adhesion of ice, or ice-bonding phenomenon, at temperatures below  $0^{\circ}\text{C}$  was studied from the viewpoint of sintering. The growth rate of necks between ice spheres having radii  $R < 100\ \mu$  was measured in both saturated air and kerosene environments. The results showed that ice-bonding, or adhesion, takes place as a result of solid diffusion. Many photomicrographs of ice-bonds were taken by making use of thin-section technique.

## 1. Introduction

Snow crystals deposited as a loose cover gradually change their shapes and join together to form a mantle of coherent structure. Such a phenomenon takes place in the snow cover even if air temperature is below  $0^{\circ}\text{C}$ . In polar regions, the deposited snow turns into firm without ever being subjected to thawing and finally into ice after the lapse of a long time. It has been an important problem for glaciologists and snow-engineers to know the mechanism of ice-bonding between snow particles. The fact that two ice pieces when brought into contact tend to stick to each other has been demonstrated by a number of investigators since the times of Faraday and Tyndall, who made experiments concerning the "regelation" of ice, as they called it. In order to explain the phenomenon of adhesion of ice, Faraday and Tyndall suggested the hypothesis that, while a thin layer of water bounded by ice only on one side does not freeze, it would freeze if bounded by ice on both sides. J. Thomson and W. Thomson, on the other hand, interpreted the phenomenon as due to surface melting of ice when pressure is applied (melting point lowering of ice with pressure) and resolidification upon removal of pressure. NAKAYA and MATSUMOTO (1950) conducted experiments on the adhesion of ice in the temperature range of  $0^{\circ}\text{C} \sim -16.0^{\circ}\text{C}$ , and measured the force required to separate two ice spheres brought into

contact. They observed that the adhesive force of ice increases with increasing temperature and found that two ice spheres suspended by thin filaments are caused to rotate before separation as the inclination of the filaments from vertical is increased. From these facts, they attributed the adhesion of ice to a liquid-water film assumed to be existent on the ice surface even at temperatures below  $0^{\circ}\text{C}$ . HOSLER et al. (1956) conducted another experiment on the adhesion of ice spheres after Nakaya and Matsumoto's method and obtained similar results, supporting the liquid film hypothesis. They also found that the adhesive force of ice is strongly dependent on ambient vapor pressure; for instance, in the case of ice saturation no adhesion took place at temperatures below  $-25.0^{\circ}\text{C}$ , while when the vapor pressure was less than ice saturation no adhesion was observed below  $-4.0^{\circ}\text{C}$ . H. H. G. JELLINEK (1956) measured adhesive force between ice and various kinds of material such as metals, quartz, and high-polymeric substances, and he explained the adhesive phenomenon of ice in terms of "liquid-like film" at the surface. It is noticed that the pressure melting theory is incapable of explaining the adhesion of ice-bonding which is actually observed when no pressure is applied, and that the liquid-film

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hypothesis at the temperature below  $0^{\circ}\text{C}$  has no rigorous thermodynamical justification.

Recently W. D. KINGERY (1960) treated this problem from the viewpoint of sintering, well known in powder metallurgy. He observed the growth rate of the ice-bond between ice spheres having radii  $R > 100\ \mu$  as a function of temperature and analyzed the ice-bonding mechanism by means of determining the sort of sintering process involved. He concluded, in contrast to the liquid-film hypothesis, that ice-bonding or ice-adhesion takes place as a result of mass transfer to the contact area arising from surface diffusion. The author has performed another experiment on ice spheres having radii  $R < 100\ \mu$  in environments of kerosene and of air saturated with respect to ice, making combined use of thin-section technique with the aim of observing the internal structure of sintered ice-bonds.

## 2. The Sintering Process

When a compacted powder is heated to a temperature near the melting point, its hardness and density increase. This is the so-called sintering process. It is known that every metal shows appreciable sintering at a temperature roughly three fourths of its melting point on the absolute temperature scale. Therefore, seemingly "low" temperatures of  $0^{\circ}\text{C} \sim -20^{\circ}\text{C}$  in a natural environment may be considered as sufficiently "high" temperatures for ice, so that whenever ice particles are brought together they will show a tendency to stick to one another, forming necks (ice-bonds) which grow as time elapses. The growth of necks is accompanied by a decrease in surface area, therefore sintering may thus be defined as a process of decreasing surface area of a porous solid at a temperature near the melting point. The question is now to inquire into the mechanism of sintering which gives rise to the neck growth.

Consider that two spherical particles are brought into contact (as illustrated in Fig. 1), then the rate of neck-growth ( $x/R$ ) is, in general, given by the formula:

$$\left(\frac{R}{x}\right)^n = \frac{F(T)}{R^{n-m}} t \quad (\text{I})$$

where  $x$  is the radius of neck,  $R$  the radius of sphere,  $t$  sintering time,  $n$  and  $m$  constants

Tellus XIII (1961), 2

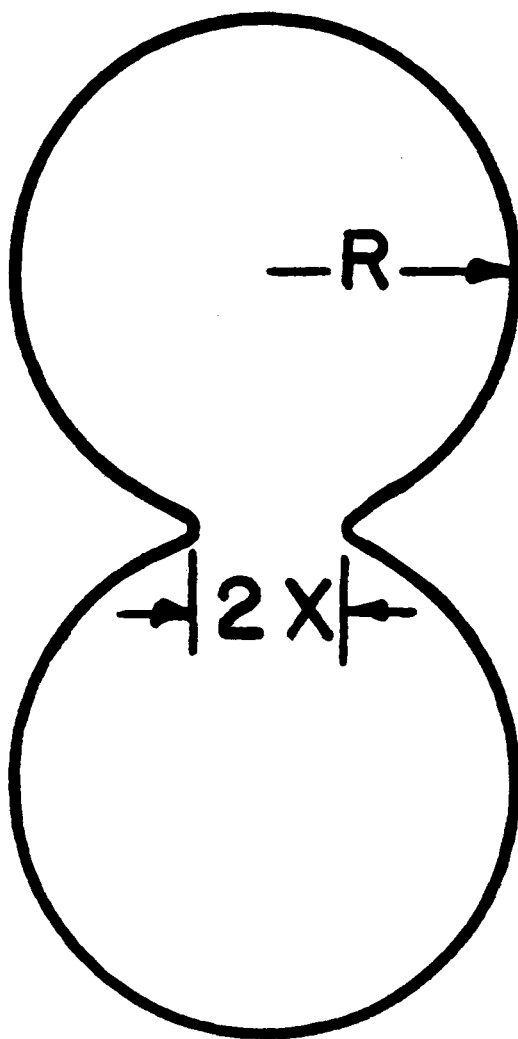


Fig. 1. Scheme of sintered ice spheres.

peculiar to a given sintering mechanism,  $F(T)$  function of the surface energy and temperature. There are four types of sintering mechanism; namely, viscous flow, evaporation-condensation, volume diffusion, and surface diffusion. The characteristic constants  $n$  and  $m$  have been discussed by various authors for a long time, with the result that their numerical values are:

- |       |                |                                 |
|-------|----------------|---------------------------------|
| (I)   | $n = 2, m = 1$ | for viscous flow,               |
| (II)  | $n = 3, m = 1$ | » evaporation-<br>condensation, |
| (III) | $n = 5, m = 2$ | » volume-diffusion,             |
| (IV)  | $n = 7, m = 3$ | » surface-diffusion.            |
- (2)

Viscous flow (I) implies that the neck growth is accomplished by a shrinkage between particles in contact under an applied stress or a driving force arising from surface tension. The chemical potential gradient coming from differences in curvature of the surfaces causes a continuous material flow into the neck area. The evaporation-condensation mechanism (II) describes the neck growth as being achieved by the transport of molecules through the vapor phase. Mechanisms (III) and (IV) mean that the continuous mass flow into the neck is caused by the flow of vacancies (vacancy diffusion) moving in a direction opposite to the mass flow. According to the theory, the vacancies are generated continually at the neck (source), and are diffused into sinks located within or at the surface of the particles influenced by the chemical potential gradient. The mechanism (III) means the vacancy diffusion from the neck to the internal-sink, and (IV) the diffusion from the neck to the surface-sink.

Using the above-mentioned relationship, we are now to determine which type of mechanism plays the predominant role during sintering, since the numerical value of  $n$  which characterizes the time dependence of  $(x/R)$  varies from 2 to 7, and particle-size dependence  $(n-m)$  varies from 1 to 4, depending on the mechanism taking place. Kingery made experiments with ice spheres having radii 0.1 mm ~ 3 mm in the temperature range  $0^\circ\text{C} \sim -25.0^\circ\text{C}$ , and obtained  $n = 6.1 \sim 7.1$  (mean  $\cong 6.9$ ), and  $(n-m) \cong 4$ . He concluded that ice sintering occurs as the result of surface diffusion.

### 3. Experimental Procedure and Results

Experiments were carried out in a large cold room. The small ice spheres were made by spraying pure water into liquid oxygen filling a shallow dish. The pure water was prepared by a purification device making use of ion-exchanging resins. The liquid oxygen evaporated rapidly leaving small ice spheres at the bottom of dish. Then several tens of the small ice spheres were transferred with a clean brush to a metallic slide with a 1 cm in diameter aperture at its center, sealed at the base by an attached cover glass (Fig. 2). After the ice spheres were placed in the hole, the top was covered with a cover glass and sealed completely with ice so that the air inside might be kept at

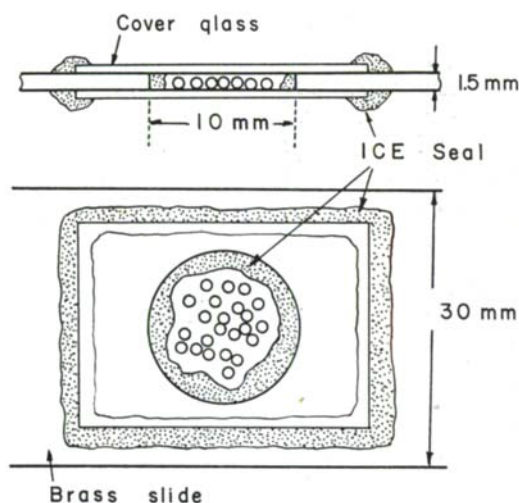


Fig. 2. Microscope slide made of brass plate for sintering test.

saturation vapor pressure with respect to ice. All surfaces which would come into contact with the spheres, the slide and the cover glasses, had previously been thoroughly cleaned by hard rubbing with clean cotton gauze. A slight shock was given to the slide in order to bring the spheres into contact with each other. The slide was then placed on the stage of a microscope located in a constant temperature box regulated to a latitude of  $\pm 0.1^\circ\text{C}$ . The metallic slide minimized the time required for the sample to reach a stationary temperature. A pair of ice spheres which contacted each other were chosen for observation, and photomicrographs of the ice-bonding process were taken at definite time intervals.

The successive stages of sintering obtained in saturated air (at  $-5.0^\circ\text{C}$ ) are shown in Fig. 3. (A) shows the initial stage of the ice spheres brought into contact, (B) the development after 33 minutes, and (C) after 64 minutes. Some typical results as to the time dependence of neck growth are illustrated in Figs. 4, 5 and 6. Sphere radii, sintering temperatures, and numerical values for  $n$  calculated from the slope of the curve are indicated for each curve. As will be seen from Figs. 4 ~ 5, the values of  $n$  are scattered in the range between 4 and 7.7. Curve (1) in Fig. 4 is considered to be a special case, because at temperatures above  $-2.0^\circ\text{C}$  quick ice-bonding takes place due to surface melting and will not be discussed here. It appears that at higher temperatures volume

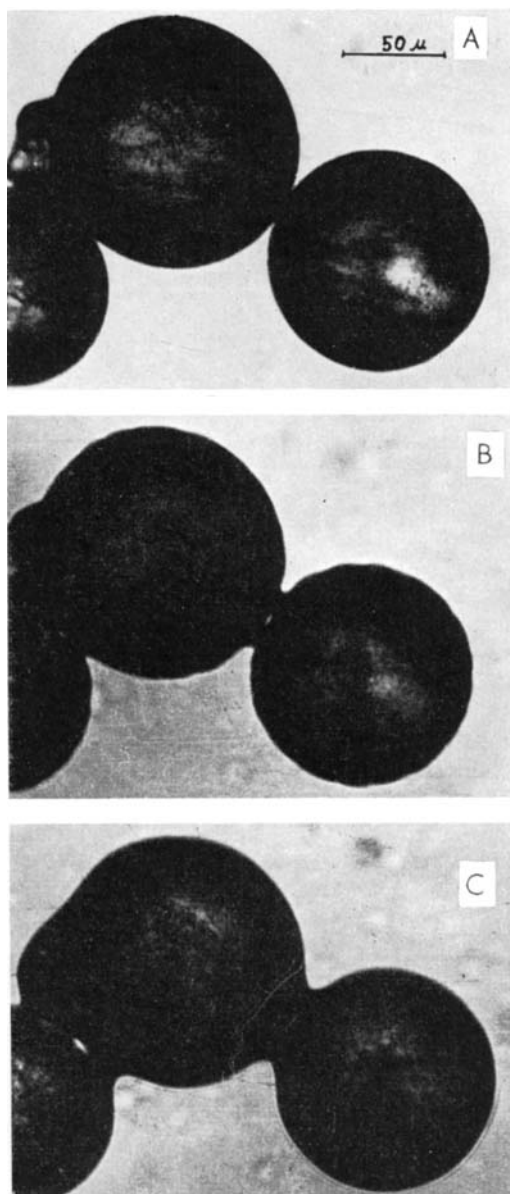


Fig. 3. The successive ice-bonding between ice spheres in air saturated with respect to ice (at  $-5.0^{\circ}\text{C}$ ). (A) initial stage (B) after 33 minutes (C) after 64 minutes

diffusion plays the main role, while as the temperature becomes lower, surface diffusion becomes more predominant; the saturated vapor around ice spheres adding no appreciable contribution in either case. In order to obtain further evidence for support of this statement, an experiment was carried out in a *Tellus* XIII (1961), 2

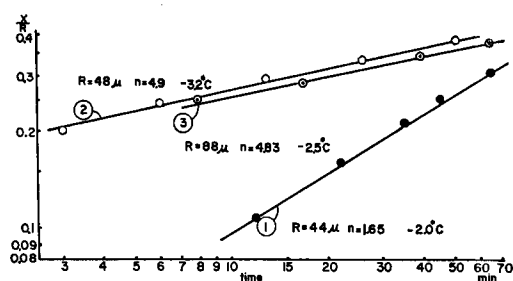


Fig. 4. Neck growth between spheres at different temperatures.

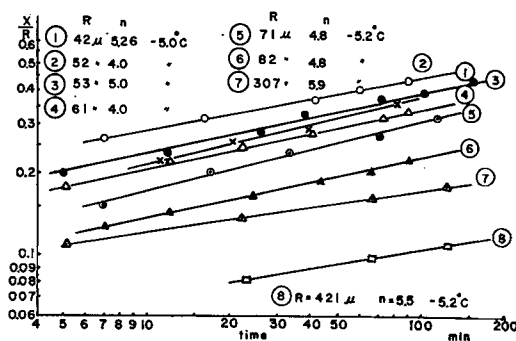


Fig. 5. Neck growth between spheres at different temperatures.

kerosene environment where the vapor phase was completely excluded.

Fig. 7 shows the successive stages of the ice sintering taking place in kerosene at  $-3.5^{\circ}\text{C}$ . (A) is the photograph taken 35 minutes after the specimen was immersed in kerosene, (B) the photograph taken after 279 minutes, and (C) that taken after 1,369 minutes. Fig. 8 represents the time dependence of the neck growth observed in kerosene environment at different temperatures. As can be seen from this figure,  $n$  takes various numerical values ranging from 5 to 7, which means that the ice sintering in kerosene is achieved by volume diffusion or surface diffusion or by both.

Fig. 9 shows the particle-size dependence of the growth rate of an ice-bond in air (at  $-5.0^{\circ}\text{C}$ ) and kerosene (at  $-3.5^{\circ}\text{C}$ ). Here the time required for  $x/R$  to attain the value 0.2 is plotted against  $R$ . The values of  $(n-m)$ , as calculated from the slope of each curve, are found to be roughly equal to 3, which implies that the sintering process in one of volume diffusion. It is to be remarked that the determination of the sintering mechanism always involves some

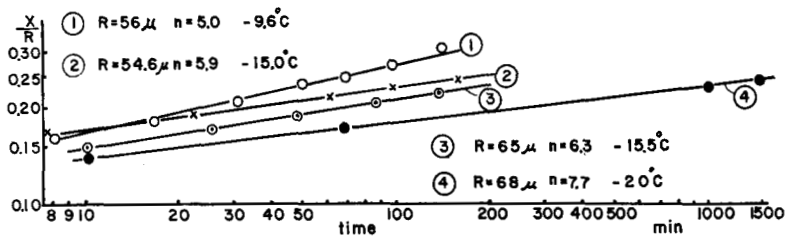


Fig. 6. Neck growth between spheres at different temperatures.

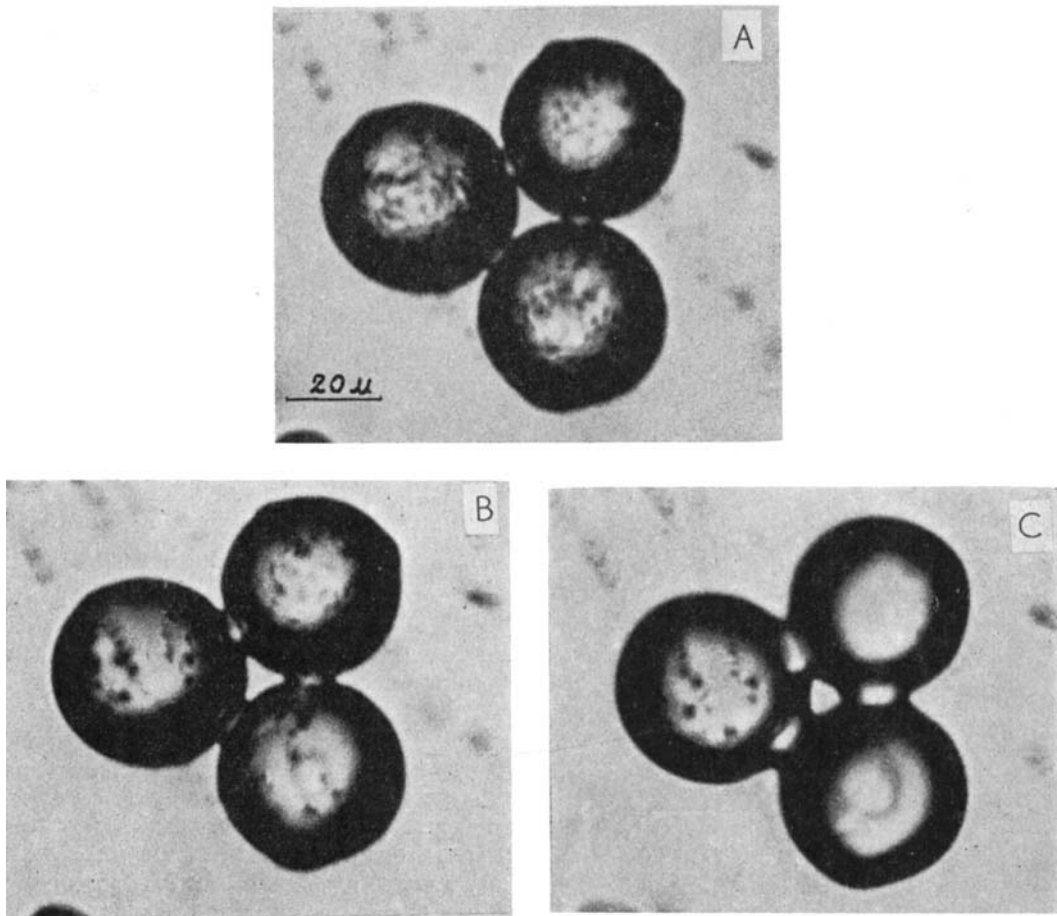


Fig. 7. Successive ice-bonding between ice spheres in kerosene (at  $-3.5^{\circ}\text{C}$ ).  
(A) after 35 minutes, (B) after 279 minutes, (C) after 1,369 minutes

ambiguity, inasmuch as the characteristic constants  $n$  and  $(n-m)$  are obtained from the inclination of the curve on logarithmic scales. Apart from the sintering mechanism of ice, we must emphasize that ice-bonding takes place even in the medium of kerosene where no vapor phase is present and no stress is

applied. The situation is very similar to the case of saturated air: although in kerosene the growth velocity of the neck is lower. The lowering of growth velocity in kerosene may well be accounted for by the decrease in interfacial energy ( $F(T)$  in Eq. (1)) between the ice surface and kerosene.

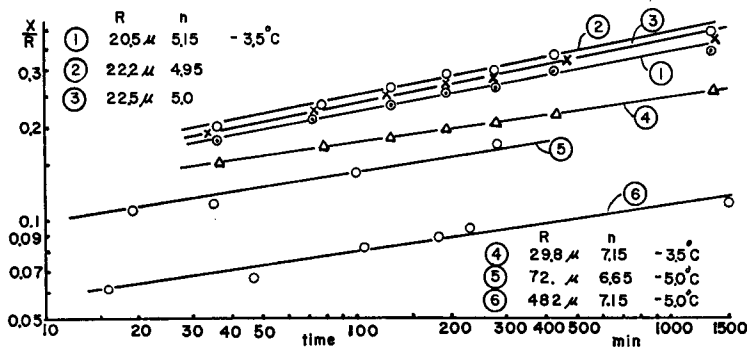


Fig. 8. Neck growth between ice spheres in kerosene.

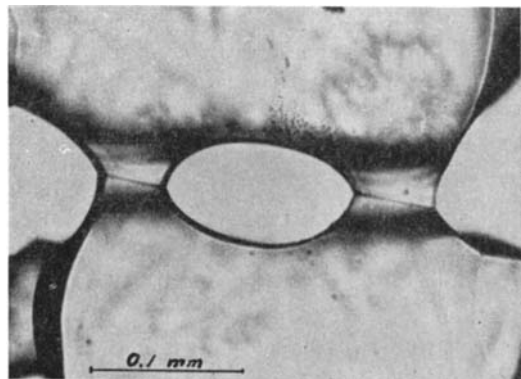
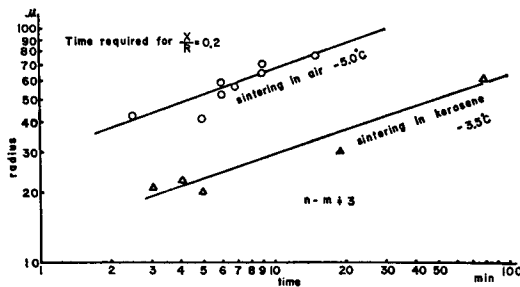
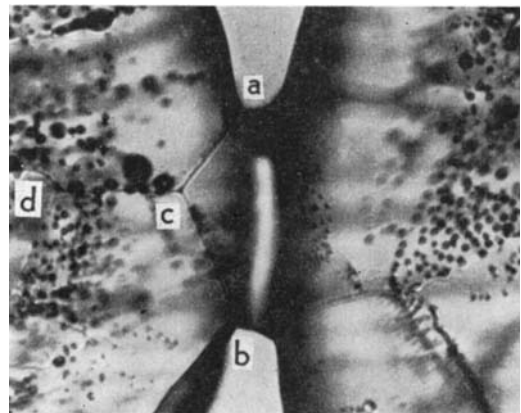
#### 4. The fine Structure of an Ice-Bond

In order to obtain further information as to the sintering mechanism of ice, a thin section of ice-bond was prepared by making use of aniline and was carefully observed under the microscope. A sintered specimen was put into liquid aniline cooled down to  $-5.0^{\circ}\text{C} \sim -10.0^{\circ}\text{C}$ . A short time after, the temperature was lowered below  $-20^{\circ}\text{C}$ , where aniline solidified. The block of solid aniline including the sintered specimen was cut and planed sufficiently thin for taking photomicrographs. When this thin section was warmed up to  $-5.0^{\circ}\text{C}$ , the solid aniline melted and became transparent, KINOSITA and WAKAHAMA (1959).

i) The structure of the neck and the displacement of the neck boundary.

If the mass transfer into the neck occurs at the same rate from both sides, a straight boundary is to be located at the middle of the neck. A typical example, which was observed in the case of natural snow particles sintered at  $-3.0^{\circ}\text{C}$  for 6 days, is shown in Fig. 10. Fig. 11 gives a photograph of the boundary displaced from the neck into the interior of ice

sphere during sintering. This was the case of two pure ice spheres sintered at  $-4.0^{\circ}\text{C}$  for 41 hours. Inference can be drawn from this picture that the boundary a-b-c was straight at initial

Fig. 10. A thin section of ice-bond between snow particles sintered at  $-3.0^{\circ}\text{C}$  for 6 days.Fig. 9. Effect of sphere radius on time required to reach a specific geometry  $x/R = 0.2$ .Fig. 11. A thin section of ice-bond between pure ice spheres sintered at  $-4.0^{\circ}\text{C}$  for 41 hours. a-b-c shows a grain boundary displaced during the sintering process.

stage of contact, but it moved into the sphere on the left in order to minimize the excess of free energy arising from intersection with the grain boundary c-d, which happened to exist in the ice sphere. Each angle of intersection is found equal to  $120^\circ$ . The dispersed spots found in ice spheres are small air voids originally occluded when the water droplet was frozen in liquid oxygen. Fig. 12 shows an example of a curved boundary within the neck.

ii) Ice sintering onto an ice plane.

Fig. 13 represents a thin section of a pure ice sphere sintered onto a plane distilled water ice surface at  $-4.0^\circ\text{C}$  for 3 hours. There is a mound of ice on the plane surface built of the mass which flowed from the lower part of the ice sphere. In the case of sintering between an ice sphere and a plane surface, the material flow takes place from sphere to plane due to the difference in curvature of the surfaces.

The volume of flowing mass was reduced by addition of some chemical impurity to the sphere. Fig. 14 shows a thin section of an impure ice sphere containing 1 %  $\text{NH}_4\text{F}$  sintered

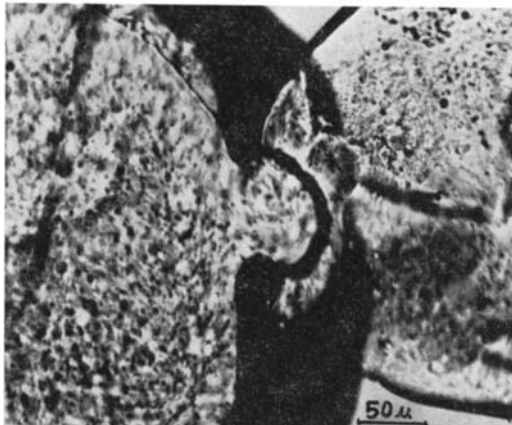


Fig. 12. A thin section illustrating a curved grain boundary within a neck.

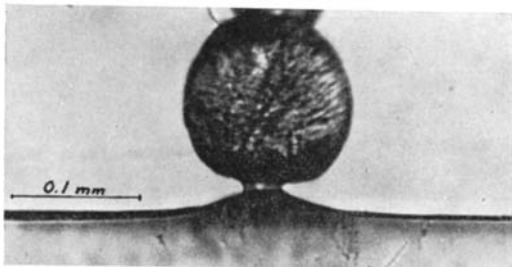


Fig. 13. A thin section of pure ice sphere sintered to pure plane ice surface at  $-4.0^\circ\text{C}$  for 3 hours.



Fig. 14. A thin section of impure ice sphere containing 1 %  $\text{NH}_4\text{F}$  sintered to pure plane ice surface at  $-4.0^\circ\text{C}$  for 19 hours and 30 minutes.

to a plane pure ice surface at  $-4.0^\circ\text{C}$  for 19 hours and 30 minutes.  $\text{NH}_4\text{F}$  is known to be a chemical compound which makes a solid solution with ice. This photograph was taken with the sample between crossed polaroids. No mound of ice is formed on the plane surface, and the crystallographic orientation of the lower part of the impure ice sphere is found to have changed into that of the plane ice.

Fig. 15 (A) shows the case of a pure ice

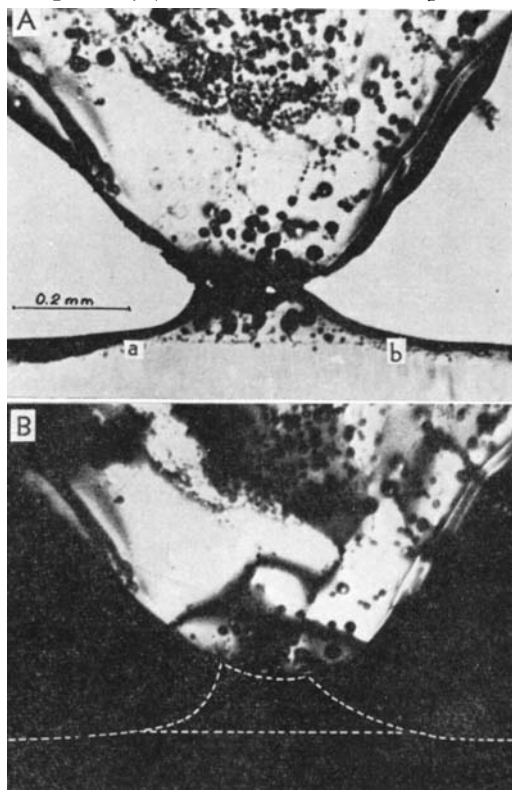


Fig. 15. (A) A thin section of pure ice sphere sintered to impure ice plane containing 0.05 M  $\text{NH}_4\text{F}$  ( $-4.0^\circ\text{C}$ , 45 hours).

(B) Photograph taken with crossed polaroid.

sphere sintered to an impure ice plane 0.05 M  $\text{NH}_4\text{F}$ ) at  $-4.0^\circ\text{C}$  for 45 hours, where conspicuous flow of mass with minute air voids has taken place from the sphere forming a mound of ice on the plane surface. a-b represents the front of the ice mass which flowed. Many air voids crowded together near the neck seem to indicate significant mass transfer. Fig. 15 (B) is a photograph of the same section as (A) taken with crossed polaroids. The crystallographic orientation of the mound of ice (the portion enclosed with white broken curve) is identical to that of the plane ice.

### 5. Summary

The process of sintering of small ice spheres was examined at various temperatures and in different environments by microscopic observation of thin sections. Inference as to the sintering mechanism of small ice spheres was drawn by employing the conventional method used in powder metallurgy. The results obtained indicate that in air saturated with

respect to ice, sintering of ice spheres having radii  $R < 100\ \mu$  is mainly due to volume diffusion (a few specimens showed the surface diffusion). The sintering was also observed in a kerosene environment, where the vapor phase was completely excluded; there the growth rate of an ice-bond was much lower than in air. Further evidence for the occurrence of material flow due to solid diffusion was obtained from the photomicrographs of thin sections of ice-bonds. The phenomena known as regelation, adhesion of ice, and ice-bonding of snow may then all be explained reasonably in terms of sintering.

### Acknowledgements

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