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The Sintering and Adhesion of Ice

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ABSTRACT

The current theory of sintering is incomplete and consequently previous experiments on the sintering of ice have been misinterpreted. The evaporation-condensation theory is now extended to include the case where material is transferred by diffusion through an environmental gas. Measurements were made on the rates of growth of the neck formed between single and polycrystalline ice spheres, $50\ \mu$ to $700\ \mu$ in diameter, in the temperature range -3°C to -20°C , in air at atmospheric pressure. The results are in quantitative agreement with the new evaporation-condensation theory, and further confirmation was obtained from experiments with spheres of heavy ice, and by the observed effects of replacing the air by either hydrogen or silicone oil. It is argued that the sintering of ice by either volume or surface diffusion would be slower by almost four orders of magnitude. No evidence is found for the recent suggestion that the sintering and adhesion of pure ice is caused by the existence of a liquid-like surface layer. The ice spheres show symptoms of having such a liquid layer only if they contain dissolved salts or if their surfaces are otherwise contaminated.

§ 1. INTRODUCTION

IN recent years there has been a renewed interest in the mechanism by which ice particles tend to adhere to one another at temperatures well below the freezing point. It is, for example, of particular relevance to the growth of snowflakes by the aggregation of individual ice crystals. An examination of the experimental results relating to this phenomenon reveals the difficulty of explaining all the facts on the basis of the long accepted 'pressure-melting' theory of Thomson (1859). The work of Nakaya and Matsumoto (1954) and of Jensen (1956), for example, shows that the force needed to separate two ice spheres brought lightly into contact decreases with lowering temperature, but even at -20°C , an appreciable force is still needed to part the spheres. Depression of the melting point of ice to -20°C would require a pressure exceeding 1000 atmospheres, but this pressure itself would not cause melting unless accompanied by a flow of heat from a source at a higher temperature than -20°C . No such heat source existed in the adhesion experiments of Nakaya and Matsumoto.

An alternative theory, originally suggested by Faraday (1860), postulates the existence of a liquid-like layer on the surface of ice. This liquid film is not to be regarded as super-cooled, but as being in equilibrium with the solid on one side and the vapour on the other. When two pieces of ice touch, the liquid solidifies at the point of contact to form a solid junction.

This theory has recently received some theoretical support from Fletcher (1962, 1963), who estimates the thickness of the liquid-layer to be about 70 Å at -3°C and to decrease rapidly at lower temperatures, finally disappearing at -12°C . Such a temperature variation might explain the observed decrease in the force of adhesion at lower temperatures, but the existence of the liquid layer has yet to be established experimentally and Fletcher's theory is open to objection (see Watts-Tobin 1963).

A more recent explanation of the adhesion of ice was given by Kingery (1960), who observed that when two ice spheres are pushed together to touch at a point, the area of contact grows with time, even when the original force of contact is removed. He explains this growth on the basis of sintering, a phenomenon well known in the field of powder metallurgy. By measuring the growth rate of the neck between two polycrystalline ice spheres, Kingery claims to show that, for spheres in the size range 0.2 mm to 6 mm diameter and in the temperature range -2°C to -25°C , the mass-transfer is due to surface diffusion. However, from similar experiments with ice spheres less than 100μ in diameter, Kuroiwa (1961) claims that volume diffusion is dominant between 0°C and -10°C with surface diffusion becoming of increasing importance at lower temperatures and dominating below -15°C .

The present paper describes the results of measurements made on the rates of sintering of polycrystalline and single crystals of ice, in the form of spheres of diameter 50μ to 700μ , in the temperature range -3°C to -20°C . For all cases it is found that evaporation-condensation is the principal mechanism by which sintering occurs under clean conditions. It is pointed out that, in some respects, the current theory of sintering is incomplete and, as a result, previous experiments on the sintering of ice have been misinterpreted.

§ 2. THEORY OF SINTERING

Two spheres in point contact form a system which is not in thermodynamic equilibrium because the total surface free energy is not a minimum. Under a sufficient driving force a neck will form between the spheres to decrease the total surface area. The driving force is provided by the gradient of chemical potential existing between the highly stressed region beneath the concave surface of the neck and the remaining parts of the system remote from this region. There are four possible ways in which the neck may receive material from elsewhere in the system: (i) viscous and plastic flow of material under surface tension forces; (ii) evaporation of material from the convex surfaces, its transfer through the environment, and condensation into the sharply curved concave neck; (iii) volume diffusion resulting from a local excess of lattice vacancies that arise from the deficit in pressure produced by the surface tension forces in the neck region; and (iv) surface diffusion of material arising from the difference in concentration of adsorbed molecules existing in the neck and the rest of the system, again set up by the surface tension forces.

Theoretical expressions for the rates of growth of the neck by each of these four mechanisms have been derived by Kuczynski (1949). Corrected for numerical errors arising in his treatment, they read:

Viscous flow:

$$\left(\frac{x}{r}\right)^2 = \frac{3\gamma}{2\eta r} \cdot t, \quad (1)$$

Evaporation–condensation:

$$\left(\frac{x}{r}\right)^3 = \frac{12M\gamma p_0}{\beta^2 RT r^2} \left(\frac{M}{2\pi RT}\right)^{1/2} \cdot t, \quad (2)$$

Volume diffusion:

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3}{kTr^3} D_v t, \quad (3)$$

Surface diffusion:

$$\left(\frac{x}{r}\right)^7 = \frac{112\gamma\delta^4}{\pi kTr^4} D_B t, \quad (4)$$

where $2x$ is the width of the neck after time t (see fig. 1), r the radius of the sphere, γ the surface tension, β the density, and η the viscosity of ice, M the molecular weight, R, k , the universal and Boltzmann gas constants, T the absolute temperature, p_0 the equilibrium vapour pressure over a plane ice surface, δ the intermolecular spacing, D_v the coefficient of volume diffusion and D_B the surface diffusion coefficient as introduced by Kuczynski.

These four expressions can be written in the general form

$$\left(\frac{x}{r}\right)^n = \frac{B(T)}{r^m} t, \quad (5)$$

where $B(T)$ contains the temperature-dependent parameters, and m and n take the following values:

Mechanism	n	m
Plastic or viscous flow	2	1
Evaporation–condensation	3	2
Volume diffusion	5	3
Surface diffusion	7	4

In many investigations of sintering it has been the practice to evaluate m and n from experimental data and to compare these values with those in the above table in order to deduce which mechanism is responsible for sintering. A good deal therefore hinges on eqns. (1) to (4), but their validity may be challenged on two counts.

In the first place, Kuczynski does not treat surface diffusion realistically but rather considers migration of vacancies into the neck through a boundary layer rather than the diffusion of adsorbed molecules across the surface. Kuczynski considers the concentration gradient of vacancies to be derived entirely from the pressure differences due to curvature and to exist across a boundary layer of width equivalent to the intermolecular spacing δ . The

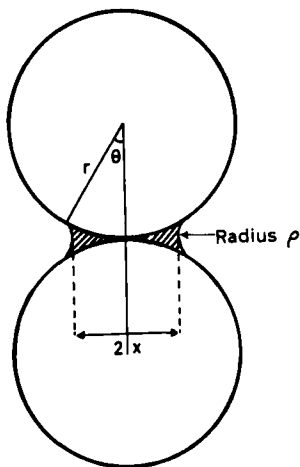
effective coefficient D_B for this 'boundary layer' vacancy diffusion is therefore not equivalent to the coefficient for surface diffusion of molecules. The problem has been treated in a much more satisfactory manner by Cabrera (1950), who considers the migration into the neck of adsorbed molecules whose concentration is maintained either by condensation from the vapour or by evaporation into the surface from kink sites existing on the surface. Cabrera's treatment leads to the following expression:

$$\left(\frac{x}{r}\right)^5 = 80 \frac{\gamma}{kT} \frac{\delta^3}{r^3} \frac{\delta^3}{y_s} n_0 D_s t$$

$$= 80 \frac{\gamma}{kT} \frac{\delta^3}{r^3} \frac{\delta^3}{y_s} \nu [\exp -(W_s + U_s)/kT] \cdot t, \quad . \quad . \quad . \quad (6)$$

where y_s is the mean migration distance of an adsorbed molecule, n_0 the concentration of adsorbed molecules on the surface far from the neck, D_s the surface diffusion coefficient, ν the vibration frequency of a surface molecule, W_s the evaporation energy of an isolated molecule on the crystal surface, and U_s the activation energy for diffusion between two neighbouring equilibrium positions on the surface distance δ apart. It will be noted that eqn. (6) is of similar dimensional form to eqn. (3) for volume diffusion, m and n having identical values.

Fig. 1



The geometry of a pair of sintering spheres.

We also wish to point out that eqn. (2) for the evaporation-condensation mechanism, which employs Langmuir's expression for transfer through a vacuum, will be valid only if the radius, ρ , of the neck is small compared with the mean-free path of the vapour molecules in the environment. It is certainly not valid for ice spheres in air at atmospheric pressure when the mean-free path of the vapour molecules is only about 10^{-5} cm and ρ exceeds

10^{-4} cm. In this case, the molecules will be transferred from the surfaces of the spheres to the neck by diffusion through the environmental gas. An expression for the rate of growth of the neck under these conditions may be derived as follows.

With reference to fig. 1, the equilibrium vapour pressure p over the concave surface of the neck of radius ρ is given by Kelvin's equation, viz:

$$\left. \begin{aligned} p &= p_0 \exp(-\gamma\delta^3/kT\rho) \\ \text{or} \quad p_0 - p &\simeq p_0\gamma\delta^3/kT\rho, \end{aligned} \right\} \dots \dots \dots (7)$$

where p_0 is the equilibrium vapour pressure over a plane surface which, since $r \gg \rho$, may be taken as that over the surface of the spheres of radius r . The difference between the vapour concentration above the surface of the spheres and that in the vicinity of the neck is then $c_0 - c = (p_0 - p)/kT$, and if this fall in concentration is regarded as occurring over a distance ρ equal to the radius of the neck, the concentration gradient is:

$$\frac{c_0 - c}{\rho} = \frac{p_0\gamma\delta^3}{(kT\rho)^2} \dots \dots \dots (8)$$

The flux of molecules into the neck is thus $D_E(c_0 - c)/\rho$ and the rate of increase of volume of the neck is:

$$\frac{dV}{dt} = A\delta^3 D_E \frac{p_0\gamma\delta^3}{(kT\rho)^2}, \dots \dots \dots (9)$$

where D_E is the effective diffusion coefficient and A the surface area of the neck.

From the geometry of the system we have $V = \pi^2 x^4/4r$, $A = \pi^2 x^3/r$, $\rho = x^2/2r$. Substituting these values in eqn. (9) and integrating gives:

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3}{kTr^3} \frac{p_0\delta^3}{kT} \cdot D_E \cdot t. \dots \dots \dots (10)$$

In evaluating D_E , it is important to bear in mind that the growth rate of the neck is controlled not only by the rate of arrival of molecules by diffusion through the surrounding gas, but also by the rate at which the latent heat of sublimation liberated at the surface can be dispersed. In metals this effect may be small because the latent heat may be conducted away quickly through the metal spheres, but with ice, which has a high latent heat and low thermal conductivity, the heat will escape largely by conduction through the air. In this case, Mason (1951) shows that:

$$\frac{p_0\delta^3}{kT} D_E \text{ should be replaced by } \left[\frac{kT\beta}{p_0 m D_G} + \frac{L_s^2 m \beta}{K k T^2} \right]^{-1},$$

where D_G is the diffusion coefficient of water vapour in the gas, L_s the latent heat of sublimation, K the thermal conductivity of the gas and m the mass of a molecule. Equation (10) now becomes:

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3}{kTr^3} \left[\frac{kT\beta}{p_0 m D_G} + \frac{L_s^2 m \beta}{K k T^2} \right]^{-1} \cdot t \dots \dots \dots (11)$$

and is identical in its dependence on t and r with Kuczynski's equation (eqn. 3) for volume diffusion and Cabrera's equation (eqn. 6) for surface diffusion. Hence, it is not possible, with ice spheres in air at atmospheric pressure, to distinguish which of the three possible mechanisms is responsible for sintering merely by determining experimentally x as a function of t and r and evaluating the parameters m and n . The conclusions arrived at by Kingery and by Kuroiwa accordingly appear unsound and a decision must be made on the basis of observed *rates* of sintering and evaluation of the $B(T)$ term of eqn. (5).

The relative rates of sintering by evaporation-condensation, volume diffusion, and surface diffusion are given by:

$$\left[\frac{kT\beta}{p_0 m D_G} + \frac{L_s^2 m \beta}{K k T^2} \right]^{-1}, D_v \quad \text{and} \quad \frac{4\delta^3}{y_s} \nu \exp -(W_s + U_s)/kT,$$

which may be regarded as transport coefficients for the three processes. At -10°C , and for diffusion in air at atmospheric pressure, the numerical value of the first term is $3 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$. The volume diffusion coefficient, from radioactive measurements on the diffusion of tritons in ice, is given by Riehl and Dengel (1962) as $1.5 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ at -10°C . In evaluating the coefficient for surface diffusion, we assume that the removal of an isolated adsorbed atom from the surface involves the breaking of at least one hydrogen bond and therefore the minimum value of $(W_s + U_s)$ is one-half the latent heat of sublimation of ice, or $4.15 \times 10^{-13} \text{ erg}$ per molecule. The mean migration distance, y_s , has been measured on the basal plane of ice by Mason, Bryant and Van den Heuvel (1963), who find $y_s = 4 \times 10^{-4} \text{ cm}$ at -10°C . These values, together with $\nu = 5 \times 10^{12} \text{ sec}^{-1}$, make the third term $1.7 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$.

On the basis of these calculations it appears that, because of the high vapour pressure, sintering of ice spheres in air at atmospheric pressure will take place by evaporation of material from the surface of the spheres, diffusion through the air, and condensation into the concave region of the neck. Growth of the neck by either volume or surface diffusion is likely to be slower by four orders of magnitude.

We shall now describe experiments in which the growth of the neck between two ice spheres was measured and compared with theory in regard to time dependence, the radius of the spheres, temperature, absolute rate of growth, the effect of changing the environmental gas, and the effect of impurities.

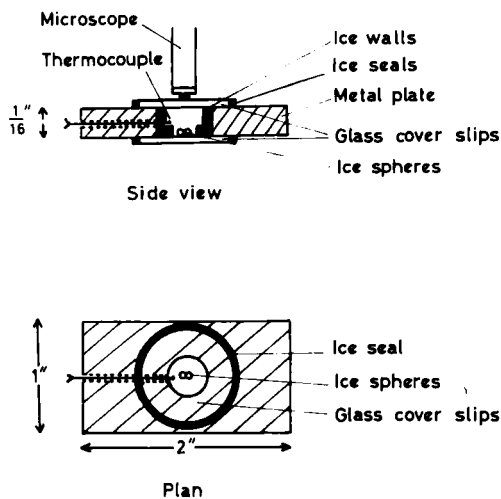
§ 3. EXPERIMENTAL TECHNIQUE

Water drops of uniform size were produced by the resonating hypodermic needle device described by Mason, Jayaratne and Woods (1963). Water was forced under constant pressure through a hypodermic needle rigidly attached to the diaphragm of an earphone. By driving the diaphragm at its resonant frequency, the tip of the needle is made to oscillate and to

throw off stable streams of droplets, each stream consisting of uniformly-spaced droplets constant in diameter to within 1%. Using a $1\frac{1}{2}$ in., 30 gauge needle, it was possible, by varying the resonant frequency and the flow rate of the water, to obtain uniform drops in the diameter range 20μ to 300μ . Drops of diameter greater than 300μ were obtained by passing a fine glass wool fibre through a stream of droplets and allowing these to coalesce to form drops of up to 1 mm diameter.

Drops of diameter $20\text{--}300\mu$ were made to freeze by allowing the stream to fall through a hollow metal tube that was 2 ft long and surrounded by solid carbon dioxide. The drops froze during their passage through the tube and were collected on a clean glass slide at the lower end. In this way it was possible to obtain many hundreds of small, uniform ice spheres. The larger drops, collected on glass wool, were frozen by placing them in a refrigerator. The ice spheres, although usually polycrystalline, were quite often either free of air bubbles or contained just one fairly large air occlusion. It was possible to produce single crystalline spheres by nucleating the drops at temperatures above -5°C with fine particles of silver iodide. When viewed through crossed polaroids, these produced brightly coloured concentric rings which were easily distinguishable from the disordered coloured pattern produced by polycrystalline spheres.

Fig. 2

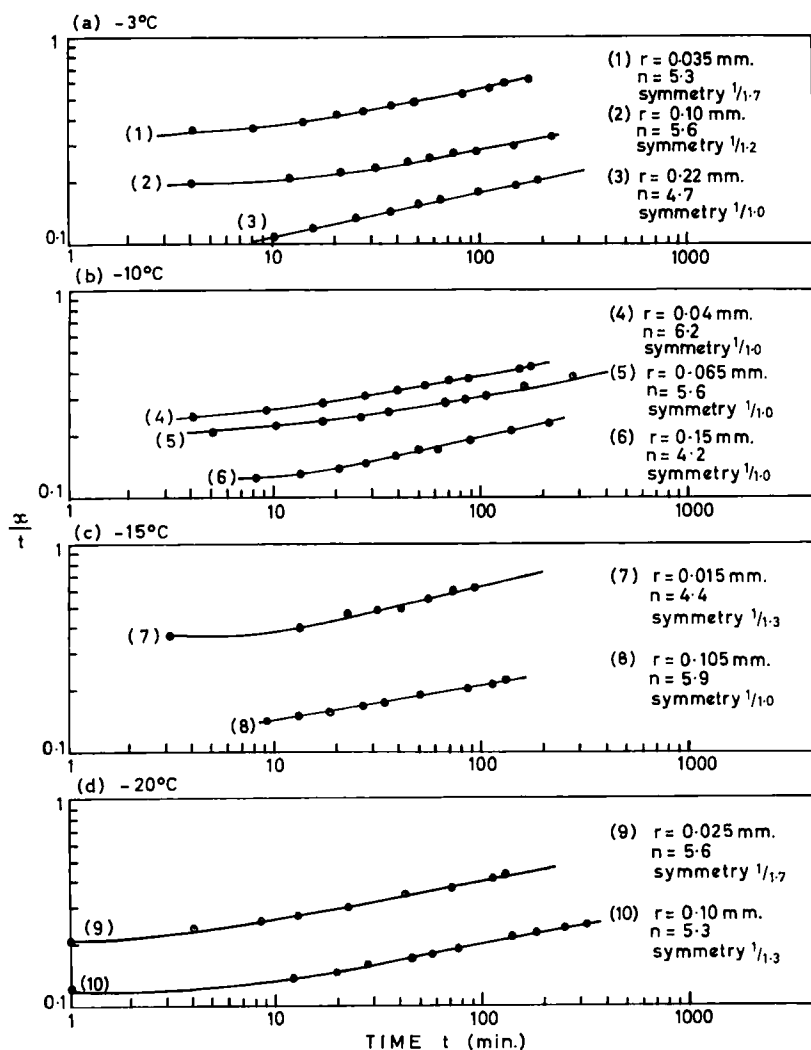


The experimental chamber.

Particular care was taken at all times to keep the ice spheres as clean as possible. After freezing, the spheres came into contact only with the carefully cleaned glass slide and with clean, highly purified gas. Distilled water was used on most occasions, but measurements made on spheres frozen from water which had been distilled and then passed through an ion-exchange column gave very similar results. The ice spheres were

placed in a small sealed chamber (see fig. 2) consisting of a thin glass base and top and metal walls. It could be sealed and partially evacuated, or filled with another gas such as hydrogen. The chamber was attached to the travelling stage of a microscope and placed in a refrigerator controlled in temperature to within $\pm \frac{1}{2}^{\circ}\text{C}$. The inner walls of the chamber were coated with ice to ensure an ice-saturated environment and the temperature was measured by a thermocouple placed close to the ice spheres. Spheres as small as 50μ in diameter could be kept in this chamber for several days without showing any sign of evaporation. Having brought two spheres

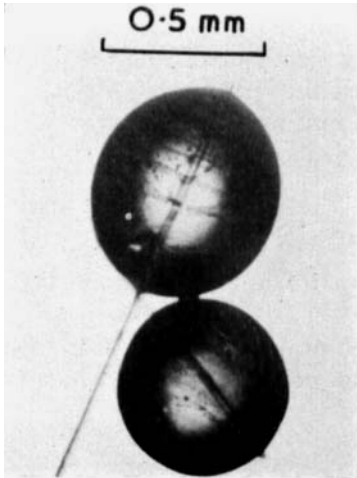
Fig. 3



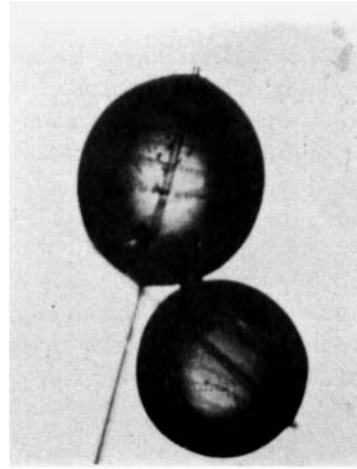
Rates of sintering for polycrystalline ice spheres at different temperatures.

into gentle contact, the growth of the neck between them was measured through a microscope and a $\times 10$ micrometer eyepiece which allowed the width of the neck to be determined with an accuracy of a few microns. The source of illumination for the spheres was filtered by several inches of heat-absorbing glass and was only switched on during the brief periods required to make a measurement.

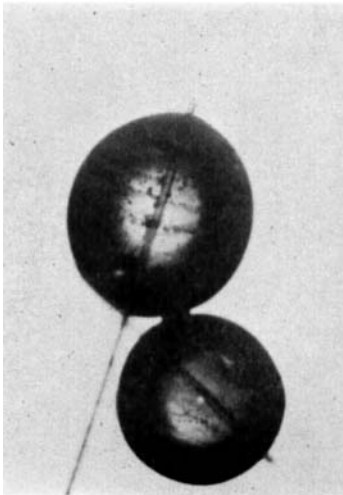
Fig. 4



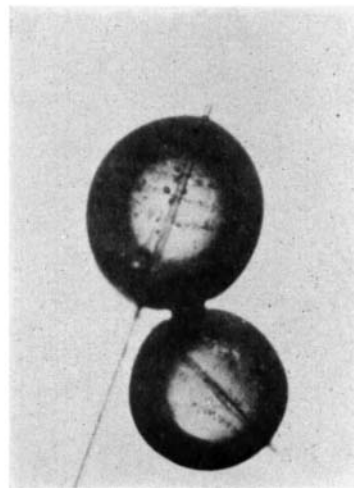
(a) 3 minutes.



(b) 40 minutes.



(c) 153 minutes.



(d) 320 minutes.

Four stages in the growth of the neck between two ice spheres at -5°C .

§ 4. MEASUREMENTS ON POLYCRYSTALLINE SPHERES

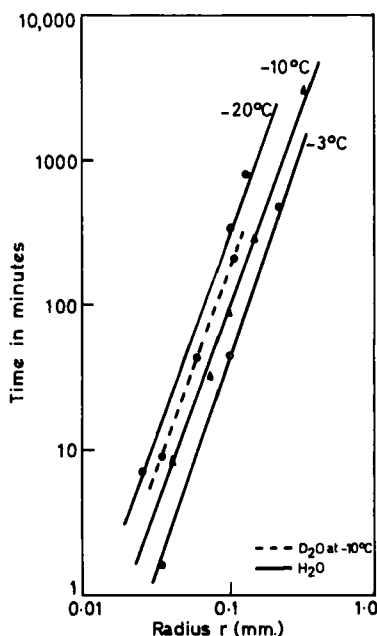
The results of measurements on the growth rate of the neck between two polycrystalline ice spheres, for spheres of 50 to 700 μ in diameter, and temperatures between -3°C and 20°C , are shown in fig. 3, where $\log x/r$ is plotted against $\log t$. The photographs of fig. 4 show the extent to which the neck grew between two spheres at -5°C over a period of about five hours. The graphs show that, after an initial period of about 10 min, the experimental points lie on straight lines having slopes of $n \simeq 5$, the slopes of the individual lines being quoted on the diagrams. The departure from linearity during the first 10 min can be explained by the fact that, while eqn. (5) is derived on the assumption that x is measured from the instant of contact, i.e. $x=0$ when $t=0$, in practice, the spheres were usually in contact for some unknown time before the first measurement was made; the relevant equation is therefore

$$\left(\frac{x}{r}\right)^n - \left(\frac{x_0}{r}\right)^n = \frac{B(T)}{r^m} \cdot t,$$

where $x=x_0$ when $t=0$; this reduces to eqn. (5) when $x \gg x_0$, and $\log x/r$ against $\log t$ is then a straight line of slope n .

Besides measuring the overall diameter of the neck, measurements were also made on either side of the original point of contact, which was

Fig. 5

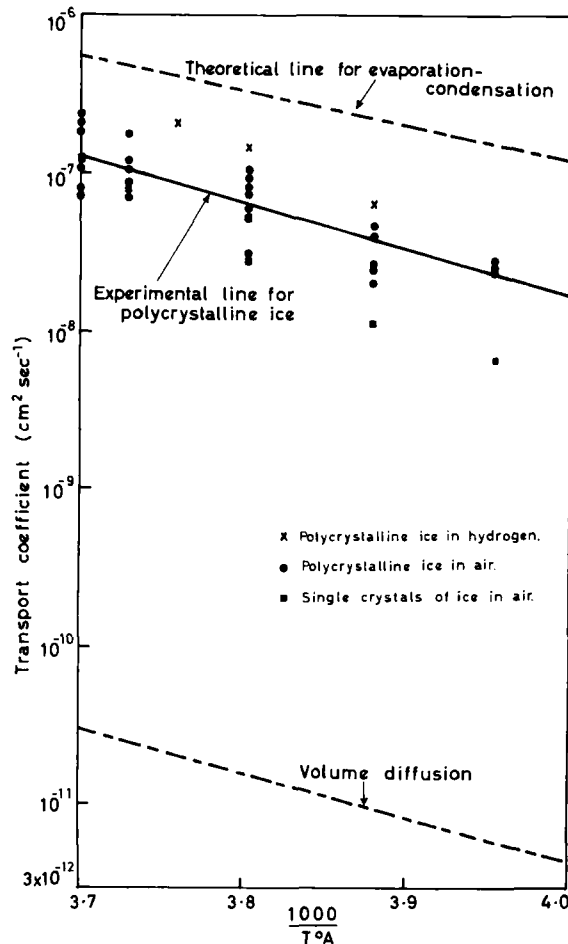


Time required for the necks to grow to the stage at which $x/r=0.25$.

centred on the reference cross-wire of the micrometer, to check the symmetry of the growth. The ratio of the growth on either side of the point of contact is shown in diagrams under the heading 'symmetry'; the figures show that, in the majority of cases, the growth was reasonably symmetrical.

The value of m in eqn. (5) can be found by determining how the size of the spheres influences the time taken to reach a given value of x/r . In fig. 5 the time required for the neck to grow to one-quarter of the sphere diameter ($x/r=0.25$) is plotted against the sphere radius. The slopes of the lines obtained at -3° , -10° and -20°C are respectively 2.9, 2.8 and 2.8, suggesting a value for $m=3$.

Fig. 6



Experimentally determined transport coefficients compared with the values to be expected from the evaporation-condensation theory and by volume diffusion.

Comparison of these experimental results with the theory suggests that there are three possible mechanisms for the sintering of ice, namely, evaporation-condensation, volume diffusion and surface diffusion; in all three cases the theory predicts values of $n=5$ and $m=3$. In order to decide which of these three processes is primarily responsible for sintering, we compare the rates of material transfer as deduced from the experimental data with those computed from eqns. (3), (6) and (11) in which the three transport coefficients

$$\left[\frac{kT\beta}{p_0 m D_G} + \frac{L_s^2 m \beta}{K k T^2} \right]^{-1}, D_v \quad \text{and} \quad \frac{4\delta^3}{y_s} D_s n_0$$

are all equal to $\left(\frac{x}{r}\right)^5 \frac{kT}{20\gamma\delta^3} \frac{r^3}{t}$.

If t is taken as the time required for x/r to reach 0.25, and $\gamma = 100$ dyne/cm, the last expression becomes $2r^3T/t$. It is evaluated from the experimental data given in fig. 4 and plotted against $1/T$ in fig. 6. Each of the points is determined by the time taken for a particular sintering pair to reach a given geometry ($x/r = 0.25$); the scatter arises because r^3T/t is not found to be strictly constant for different pairs at the same temperature. When these experimentally-derived values are compared on the same diagram with the transport coefficients for evaporation-condensation as computed in terms of p_0 , D_G , L_s and K , and with the experimental values of D_v given by Riehl and Dengel (1962), it is clear that the evidence is strongly in favour of evaporation-condensation being the dominant mechanism, volume diffusion being slower by four orders of magnitude. The effective transport coefficient for surface diffusion is more difficult to evaluate but we have shown that this is probably of the same order of magnitude as volume diffusion. In addition, fig. 6 shows that the observed transfer rates vary with temperature in the manner predicted by the evaporation-condensation theory. Also, the actual observed and computed values agree to within a factor of five, which is probably not outside the discrepancy to be expected from the approximations used in the theory and the experimental errors.

§ 5. RESULTS FOR SINGLE CRYSTALS AND HEAVY ICE

The results of experiments on the sintering between ice spheres in the form of single crystals were similar to those for polycrystalline ice spheres in that they also gave $n=5$ and $m=3$. But, below -10°C , the experimental values of $2r^3T/t$ for single crystals fall below those for the polycrystalline spheres of fig. 6; in other words, sintering proceeds less rapidly for the single crystals. The reason may be that a polycrystalline surface retains relatively large areas of high-index faces whereas, on a single crystal, these tend to disappear during evaporation.

Several measurements were made on the rates of sintering of ice spheres frozen from 'heavy' water (D_2O) of 99.7% purity. Again the results were very similar to those for ordinary ice but the actual rates of growth

for D_2O at $-10^\circ C$ corresponded to those for H_2O at about $-14^\circ C$ —see fig. 5. This result is in accord with eqn. (11) for sintering by evaporation-condensation because the equilibrium vapour pressure, p_0 , of D_2O ice at $-10^\circ C$ is very nearly equal to that for H_2O ice at $-13^\circ C$.

§ 6. THE EFFECT OF ENVIRONMENT

All of the results described so far were obtained with ice spheres in air at atmospheric pressure and saturated with respect to a plane ice surface. We now describe the effect of varying the environmental conditions.

The spheres were exposed to air that was unsaturated with respect to ice. Under these conditions the spheres evaporated, but so slowly that a change in diameter was discernible only after about an hour. Sintering was observed to take place during the first 20 min or so, but after this, very little growth of the neck took place. This suggests that, in the initial stages of sintering, the environmental conditions remote from the neck had little effect and that the vapour supply to the neck came from portions of the spheres very close to the neck region which were able, temporarily, to maintain the air in this vicinity near ice saturation. This fact supports the assumption made in deriving eqn. (11), that the fall in vapour pressure ($p_0 - p$) occurs over an effective distance ρ equal to the radius of the neck.

If sintering takes place by a process involving diffusion through the environment, the rate, which is proportional to

$$\left[\frac{kT}{p_0 m D_G} + \frac{L_s^2 m}{K k T^2} \right]^{-1},$$

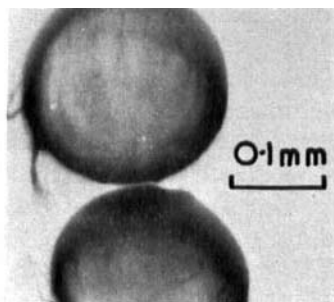
should be affected by changing the diffusivity D_G and the thermal conductivity K of the environmental gas. If the air pressure were reduced to 1/10 atm., D_G would be increased tenfold but K will remain unchanged. The net result is that the time taken for the neck to reach a given value of x/r would be decreased by a factor of only 2.5. Measurements were taken in air at 1/10 atm. pressure but no significant increase of growth rate was detected above the scatter in the experimental data.

In an atmosphere of hydrogen, D_G and K are greater than in air by factors of 3.4 and 7 respectively, and the rates of sintering would be 4 times greater. The experimental results obtained in hydrogen are included in fig. 6, the transfer coefficients being about 2.5 times greater than in air. In view of the experimental error, this result is taken to be in fair agreement with the theory.

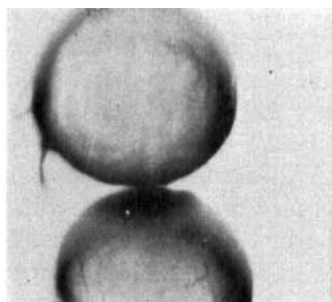
It is well known that if a small piece of ice is immersed in silicone oil very little evaporation takes place even over periods of several weeks; the sintering rate should be correspondingly reduced because the term $p_0 D_G$ is greatly reduced compared with its value for air. Two ice spheres were brought gently into contact beneath silicone oil held at $-3^\circ C$ and the neck was observed at regular intervals for several days. No growth of the neck could be detected during this period. When kerosene was used in

place of silicone oil, the neck grew perceptibly over a period of several days, but only at about one-tenth the rate observed in air. This result may be attributed to water having a higher solubility (larger p_0) in kerosene than in silicone oil.

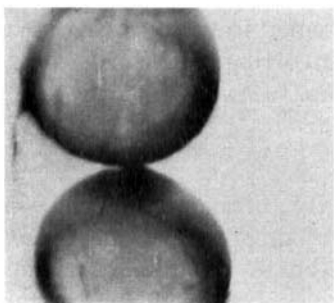
Fig. 7



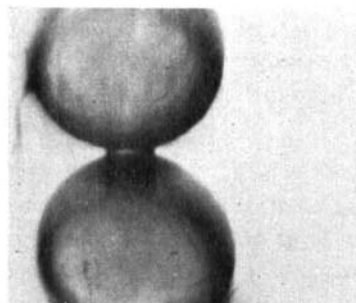
(a) Approach.



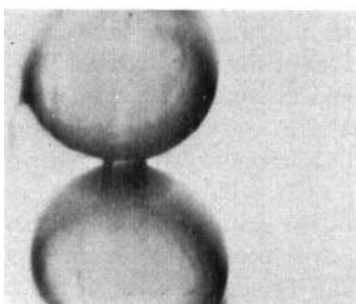
(b) Contact.



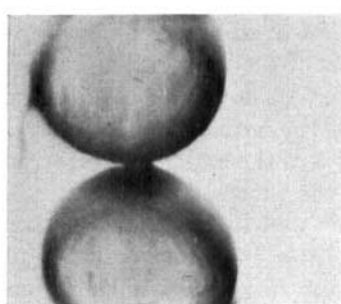
(c) Spheres rotate.



(d) Liquid flows into neck.



(e) 7 sec after (d).



(f) 20 sec after (d).

Flexible adhesion and flow of liquid at -10°C between ice spheres frozen from a 1% NH_4F solution.

If sintering of ice occurred by volume diffusion, the only effect of silicone oil would be to reduce the growth rate by reducing the interfacial tension. Since the surface tension of the silicone oil was 21 dyne/cm, γ would be reduced from 100 to 79 dyne/cm at most, and this would reduce the rate of sintering by a mere 20%. The drastic reduction actually produced by silicone oil therefore strongly supports evaporation-condensation, and not volume diffusion, as the responsible mechanism.

§ 7. EFFECTS OF ADDED IMPURITIES

Measurements on spheres produced by the freezing of 10^{-2} M solutions of NH_4F , HF and NH_3 showed that, in some cases, the rates of sintering were slightly reduced by the presence of these impurities.

An interesting phenomenon was observed with ice spheres produced from 1% solutions of NaCl and NH_4F . When held at -10°C , the spheres appeared, at first sight, to be quite solid, but on bringing two into contact, a neck grew very rapidly between them so that, within a minute or two, it achieved a size that would have taken several hours with pure ice. Figure 7 shows a sequence of time-lapse pictures in which the actual rate of mass transfer into the neck was nearly 300 times faster than with pure ice. This effect was obviously due to the presence of a thin layer of liquid on the surfaces of the spheres. It appears that, during freezing, relatively concentrated salt solution was exuded from cracks in the ice shell and formed a surface layer with freezing point below -10°C . The photographs of fig. 7 illustrate a phenomenon that was often observed with spheres frozen from 1% salt solutions. When a sphere, suspended from a fibre, was brought into contact with a similar stationary sphere, it tended to roll slightly, and rotation was followed by a rapid flow of liquid into the region of contact. A similar effect was observed by Nakaya and Matsumoto (1954) who found that, when two suspended spheres frozen from a 0.1% NaCl solution were brought into contact, this type of 'stick-slip' motion occurred far more frequently than it did with 'pure' ice spheres. The cohesion of the former, even at -14°C , was greater than that of the latter at -3°C .

§ 8. CONCLUDING REMARKS

The conclusions reached in this paper differ from those in the two previous papers on the sintering of ice by Kingery (1960) and Kuroiwa (1961).

Kingery found that his measurements on the growth of necks between pairs of polycrystalline spheres, 0.2 to 6 mm in diameter, followed the relationship $(x/r)^7 \propto t/r^4$ and, on the basis of Kuczynski's analysis, concluded that sintering was occurring by surface diffusion. Kingery deduced the diffusion coefficient to be given by

$$D = D_0 \exp(-W/kT)$$

with

$$D_0 = 10^{22} \text{ cm}^2 \text{ sec}^{-1}$$

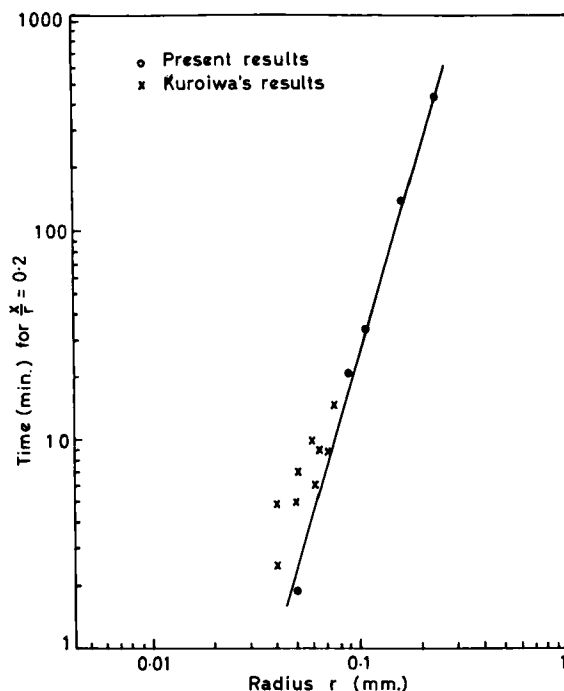
and

$$W = 27.5 \text{ kcal/mole,}$$

both of which seem very high, even for ice, the value of the activation energy W being more than twice the latent heat of sublimation! The reason for the discrepancy between the present results and those of Kingery may be due to the fact that Kingery's ice spheres were not contained in an ice-saturated enclosure. Consequently, after 30 min or so, no further growth of the neck took place, and his measurements were therefore confined to the first ten minutes or so when, as we have seen in fig. 3, the growth rates are less than those predicted by eqn. (5). We therefore question Kingery's use of these measurements to determine m and n and his conclusion that surface diffusion was the responsible mechanism.

Kuroiwa's measurements on small ice spheres, taken over several hours in an ice-saturated environment, agree quite well with those of the present work—see fig. 8. Kuroiwa found that his results followed a relationship of the form $(x/r)^5 \propto t/r^3$ and, comparing these with Kuczynski's theoretical treatment, concluded that volume diffusion was responsible. He did not, however, compute the empirical diffusion coefficient which, as shown above, is three orders of magnitude larger than the volume diffusion coefficient measured by radioactive-trace techniques. We believe that the results can be explained much more satisfactorily in terms of evaporation-condensation.

Fig. 8



Comparison of sintering rates with those of Kuroiwa at -3°C .

We find no evidence to support the view of Jellinek (1961) that the sintering and adhesion of pure ice is caused by the existence of a liquid-like layer on the surface. The spheres show symptoms of having a liquid layer only if they contain dissolved salts or if their surfaces become otherwise contaminated; in such cases, the neck grows rapidly by the flow of liquid into the neck, a phenomenon not observed with the very slow growth associated with pure ice.

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