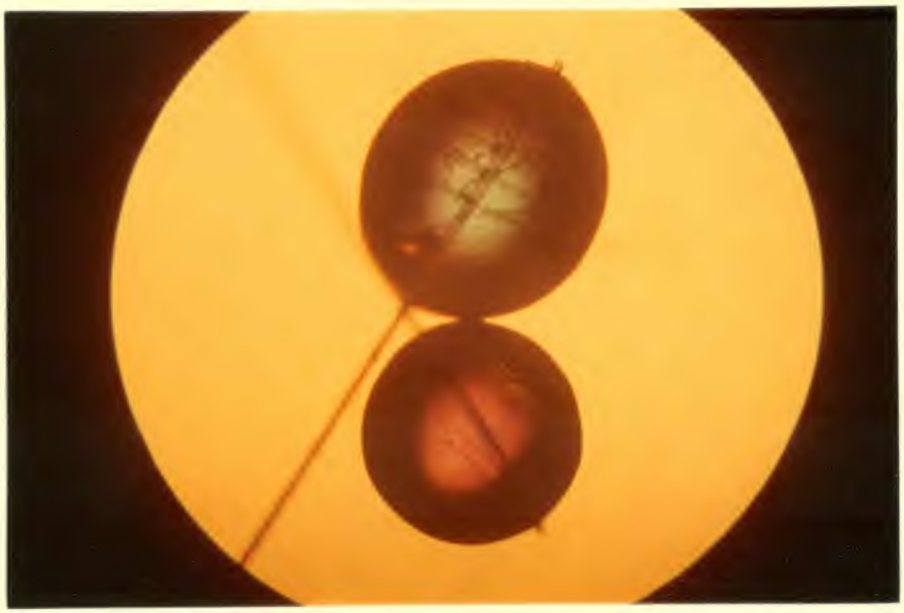
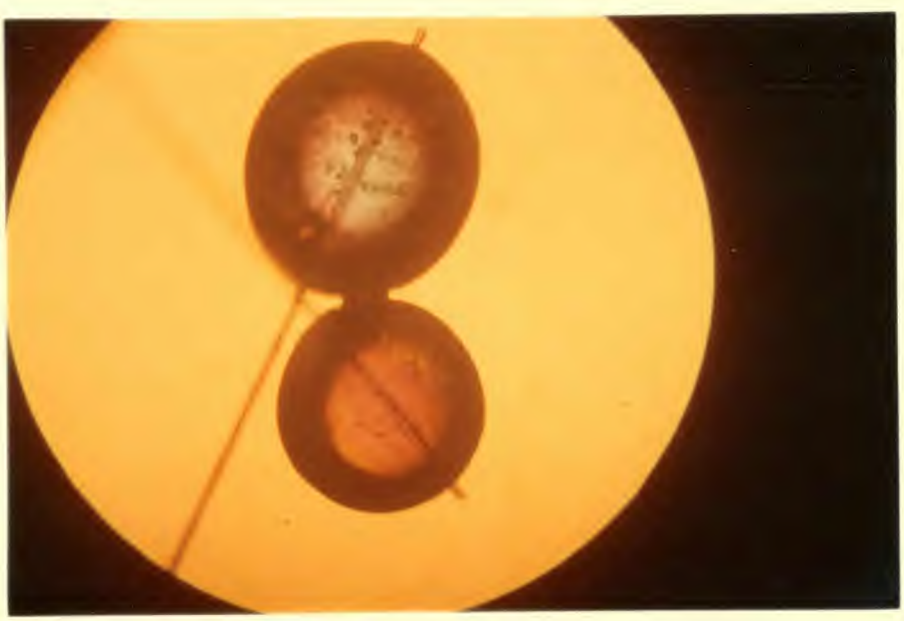
Nothing in nature is more beautiful
than a single crystal of ice, but
unfortunately, they seldom come
like that.

Bill Vaughan.



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2

0.25 mm.

Frontispiece

The sintering of two single crystal ice spheres at $-5^{\circ}C$.

(1) 3 minutes after contact, and

(2) 320 minutes after contact.

THE SINTERING AND ADHESION OF ICE

by

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ABSTRACT

This thesis describes a theoretical and experimental investigation into the sintering of ice. When two ice spheres are brought together to touch at a point, the area of contact is found to increase with time. This phenomenon is well known in the field of powder metallurgy where it is termed sintering. The motivating force for the material transfer is provided by the surface tension forces existing in the sharply concave region of the neck between two particles. The current theory of sintering considers four possible mechanisms for the material transfer: viscous or plastic flow, evaporation-condensation, volume diffusion, and surface diffusion.

A new theory has been developed for sintering involving the transfer of material by diffusion through the environment. Measurements made on the rates of growth of the neck between spheres of polycrystalline ice and single crystals of ice are found to be in quantitative agreement with the new theory. The effect of adding impurities to the ice and changing the environmental conditions has also been investigated and the results interpreted in terms of the proposed theory.

Two previous claims have been made that the sintering of ice occurs by volume diffusion and surface diffusion. These two mechanisms are analysed but the results predicted by each are shown to be at least three orders of magnitude smaller than those observed experimentally. It is concluded that surface diffusion and volume diffusion make negligible contributions to the sintering of ice and that the predominant mechanism for the growth of the neck is provided by the diffusion of water vapour through the environment.

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CHAPTER 1

INTRODUCTION AND REVIEW OF PREVIOUS WORK

When two pieces of ice are brought lightly into contact they tend to adhere to each other even though the temperature may be well below $0^{\circ}C$. For this reason it is unusual to find snowflakes reaching the ground as single crystals; a snowflake usually consists of an aggregate of several individual ice crystals. This aggregation of the ice crystals continues even after they have been deposited on the ground, as the snowflakes, which initially form a loose cover, gradually change their shape and join together to form a more compact layer of snow. The final stage in this metamorphosis is represented by the large single crystals found in pore-free glacial ice. However, equilibrium conditions such as this may not be reached even after hundreds of years.

The work to be described in this thesis is concerned with the initial stages of the bonding between two ice particles and the mechanism by which this takes place.

1.1 The role of ice adhesion in precipitation processes

Clouds form in the atmosphere when air is cooled to below its dew point; condensation of water vapour then takes place

on the numerous foreign nuclei that are present in the air. Initially this produces water droplets a few microns in diameter and, if the temperature is well below $0^{\circ}C$, these will be accompanied by ice crystals. The average life span of a cloud is about one hour, if the cloud is to produce precipitation particles the droplets must grow to about 1 mm diameter in this time. The central problem in the theory of precipitation is to explain how a few of the original cloud droplets grow by two orders of magnitude.

The growth of water droplets by coalescence has received considerable attention during the last decade, and it has been shown that this is one possible mechanism by which a few large droplets may grow at the expense of smaller ones. Another possibility is that raindrops are produced by the melting of clusters of small ice crystals. If supercooled droplets and ice crystals exist together in a cloud, the latter will grow by condensation from the vapour. Houghton (1950) has shown that growth by this mechanism may be as much as one order of magnitude in the first ten minutes, but that subsequent growth will be negligable. However, it is possible for the crystals to continue to increase in size by a process of collision and aggregation to form

conglomerations of ice crystals. Radar studies support the view that such an aggregation of ice crystals plays an important part in the processes leading to precipitation, particularly in higher latitudes.

During the last ten years several laboratory investigations have been reported on ice adhesion. Prior to this the most important work performed on the subject was that of Faraday's more than a hundred years ago. Indeed, it was not until 1954 that it was generally realized that ice can adhere to ice with an appreciable force even though the temperature may be well below the freezing point. There now follows a review of previous work concerned with the adhesion of ice, and an account of the various theories that have been proposed to explain this phenomenon.

1.2 Early work of Faraday and Thomson

The first systematic investigation into the ability of ice to stick to ice was begun by Faraday in 1842. The results of these experiments were described by him in a lecture at the Royal Institute in 1850, and reported in the Athenaeum and Literary Gazette in the same year. Faraday demonstrated that if two pieces of moist ice are

placed in contact they will unite together even when the surrounding temperature is such as to keep them in a thawing state. Provided that the ice was near to its melting point this effect was found to take place in air, in water, or in vacuo. A familiar example of this phenomenon is found in the difficulty in making snowballs when the temperature is well below zero and the snow is very dry, whereas, when the snow has been warmed by the hand it is possible to squeeze it into a hard ball.

To explain these results Faraday suggested that it might be possible for a layer of liquid water to exist in equilibrium on the surface of ice, but on bringing two pieces of ice into contact the liquid solidifies to form a solid ice bond. An alternative explanation of Faraday's experiments was proposed by J. Thomson (1857). It had been shown previously by J. Thomson (1849) that, on thermodynamical grounds, the freezing point of water must vary with pressure, the temperature of freezing being lowered with increase of pressure. This theoretical deduction was subsequently supported experimentally by W. Thomson (1850). J. Thomson argued that in Faraday's experiments the two pieces of ice could not be brought into contact without causing some slight

pressure between them. Also, when two pieces of thawing ice are brought together in air, there will exist a capillary force tending to press the particles together. Small as these forces are, they act over regions which are little more than points and therefore give rise to considerable pressures. In J. Thomson's view these pressures caused melting at the point of contact, followed by a relief of the pressure and then resolidification.

In order to investigate the effect of pressure on the adhesion of ice particles, Faraday (1860) performed the following experiments. Two blocks of ice were totally immersed in water which was maintained at a temperature of $0^{\circ}C$. Each block of ice was moored to a particular place by means of a thread passing through a hole in the ice and attached to the base of the water container. The two ice blocks then took up positions of equilibrium under the action of buoyancy forces. By the use of a rod of wood the blocks of ice could be pushed into any desired position. If brought near to each other and then left unrestrained they returned to their former positions with considerable force. If, however, the slightest contact was made between the ice blocks they remained adhered together despite the

force tending to separate them. Faraday also observed that the force of adhesion appeared to increase with the time of contact. In these experiments, apart from a slight force at the moment of contact, there was no pressure either from capillary action or any other cause. In further experiments Faraday introduced a slip of wood between two adhering ice spheres and attempted to prise them apart. This caused the spheres to move with respect to one another, but they did not part. Instead a flexible adhesion occurred in which the region of contact between the spheres shifted from one point to another, even though the spheres were under a continual force, provided by the attached threads, which tended to separate them.

Faraday concluded that these experiments supported his "liquid-layer" theory of ice adhesion. In the case of the flexible adhesion, he supposed that under the action of the applied force a rupture occurred on one side of the centre of contact, whilst on the other side the two ice surfaces were brought into close enough proximity for adhesion to take place due to the freezing of the "liquid-layers". On the contrary, J. Thomson (1861) thought that these observations could be explained perfectly in terms of his

own pressure-melting theory. Although in Faraday's experiments flexible adhesion appeared to take place under tension, Thomson contended that this was not in fact the condition in the region where union occurred. For, on applying the prising force to one side of the point of contact, the ice junction would act as a fulcrum. This would produce a pressure on the other side of the junction where melting and regelation could then occur. In this manner a rolling motion could take place such as that observed by Faraday.

In the years following this controversy, J. Thomson's theory of pressure-melting and regelation became the generally accepted explanation of the phenomena of ice adhesion. In addition, skiing, skating, the penetration of ice by a weighted wire, and the flow of glaciers were all explained by the pressure-melting theory. However, as a result of recent experiments, to be described later, it is now believed that these phenomena can only be explained by pressure-melting when the temperature is very close to the melting point.

1.3 Friction of ice: skiing and skating

The friction of ice on ice slightly below the melting

point is very small. This may be shown by placing a small block of ice onto a polished ice surface when the smallest inclination of the latter will cause the ice block to slide. As a result of this remarkably low friction of ice, skating and skiing are possible.

On the basis of the pressure-melting theory the explanation offered is as follows. The pressure between the two surfaces causes a depression of the freezing point of the ice, local surface melting then takes place and a thin layer of lubricating water is formed between the two surfaces. If the surface area of a single ski is taken as 2,500 cm^2 the pressure exerted by an average man of weight 75 kg is 15 gm/cm^2. An increase of 1 atmosphere (1.032×10^3 gm/cm^2) in the pressure lowers the melting point of ice by $0.0075^{\circ}C$, therefore, a pressure of 15 gm/cm^2 can only cause melting if the snow is at $-0.00012^{\circ}C$ or a higher temperature. However, for powder snow the ratio of the real area of contact to the apparent area is probably of the order 1/1000, but, even when this is taken into account, the pressure would still only be sufficient to melt snow at $0.12^{\circ}C$. In order to explain skiing at a temperature of $-20^{\circ}C$, one has to assume that the real area of contact is 1/100,000 of the

apparent area, which is unlikely.

Bowden and Hughes (1939) have suggested that, at temperatures more than a few degress below zero, frictional heating is likely to be more effective than pressure in causing surface melting. In the case of a ski sliding on ice at $-20^{\circ}C$, if the coefficient of friction, μ, is taken as 0.05, the amount of frictional heat liberated when the ski moves forward 1 cm under a weight, M kg, is given by

$$Q = \frac{\mu M g}{J} = \frac{0.05 \times 37.5 \times 981 \times 1000}{4.18 \times 10^{7}}$$

$$= 0.044 \text{ calories}$$

If the real area of contact is taken as 1/100 of the ski, then this heat is sufficient to raise the temperature from -20° to $0^{\circ}C$ and to form a layer of water of thickness 2×10^{-4}cm.

To test whether a layer of water was formed during skiing, Bowden and Hughes performed the following experiment. Two electrodes were sealed into the base of an ebonite ski which could be made to slide on an ice surface. With the ski in contact with the ice at $-20^{\circ}C$ the friction was relatively high and the electrical resistance between the electrodes was 2×10^{6} ohms. As the ice was allowed to

warm up, the friction gradually fell, but there was very little variation in the electrical resistance. Near the melting point, however, the resistance suddenly dropped to 2×10^4 ohms, showing that a continuous water film had formed between the surfaces, and the friction then had a low value of $\mu = 0.03$. At the low temperatures the high value of the electrical resistance shows that any surface melting that might have occurred was confined to isolated points, thereby giving rise to the high value of the friction.

In order to determine whether the water layer is formed by pressure-melting or by frictional heating, Bowden and Hughes considered the effect of varying the thermal conductivity of the skis. In the case of pressure-melting, the application of pressure alone is not sufficient to cause the ice to melt, in addition there must be a flow of heat to the ice to provide the latent heat of fusion. Ice itself has a low thermal conductivity, therefore most of this heat flow must take place by conduction through the ski. Under these conditions, skis made from material of high thermal conductivity would give rise to a lower coefficient of friction than those made from a poor conductor. The reverse would be true, however, if frictional heating

were responsible for the melting. For, in this case, the heat evolved at the interface between the sliding surfaces would be carried away more rapidly by a good conducting ski and leave less heat for melting the ice. The results obtained by Bowden and Hughes are shown in Fig. 1. It can be seen that the friction of brass skis on ice is considerably greater than that of ebonite, the effect becoming more marked as the temperature is lowered. These results show that frictional heating plays an important part in the formation of the water layer, particularly at low temperatures.

1.4 Adhesion of ice to ice

It has been shown above that in the case of skiing and skating the mechanism of pressure-melting is ineffective at temperatures more than a degree or so below the melting point. Similarly, in the case of the adhesion of ice to ice, the pressure of contact is unlikely to cause melting unless the temperature is close to $0^{\circ}C$. In Faraday's original experiments, the ice was always kept at the melting point, for this reason the possibility of adhesion by pressure-melting could not be excluded. During the last

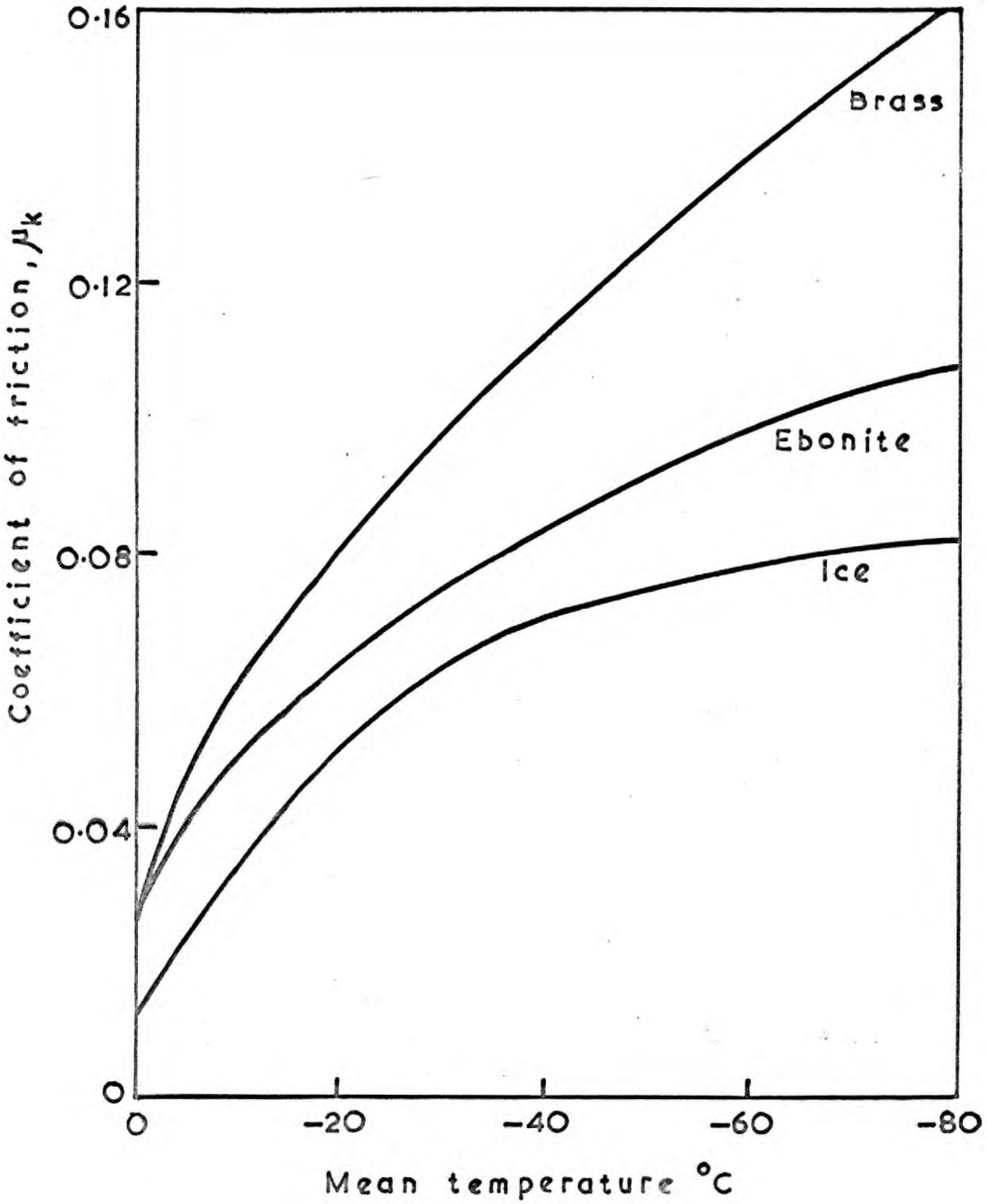


FIG. 1 Effect of temperature on the friction of brass, ebonite and ice sliding on ice (after Bowden and Hughes, 1939)

ten years, however, it has been shown by several workers that ice will adhere to ice at temperatures as low as $-30^{\circ}C$.

The first investigation into the effect of temperature on the adhesion of ice particles was made by Nakaya and Matsumoto (1954). In these experiments the force required to separate two ice spheres of about $1\frac{1}{2}$ mm in diameter was measured as a function of temperature in the range 0° to $-16^{\circ}C$. The spheres were frozen from distilled water and suspended on cotton filaments; one of the spheres could be moved by means of a screw motion. The whole assembly was contained inside a metal box, the temperature of which could be varied between 0° and $-16^{\circ}C$. On bringing the spheres into contact, care was taken to avoid any appreciable pressure between them. The spheres were kept in contact for about a minute and then separated by means of a tension force applied along one of the cotton filaments. The force ofadhesion was calculated from the measured values of the masses of the spheres and the inclination of the filament when the spheres separated. Although the results showed considerable fluctuation, the force of adhesion was found to decrease with temperature from about 5 dynes at $-2^{\circ}C$ to 1 dyne at $-15^{\circ}C$.

Nakaya and Matsumoto also found that on some occasions the spheres exhibited a flexible adhesion similar to that described by Faraday. This consisted of a rotation of the spheres before actual separation took place. This rotation did not always occur, but it was not rare. It took place more frequently at temperatures near the melting point, but on one occasion it was observed at -7°C. When the spheres were frozen from a 0.1% NaCl solution the rotation was observed far more frequently.

Similar results to those of Nakaya and Matsumoto were obtained by Jensen (1956). In these experiments the ice spheres were contained in an ice saturated chamber and forces of adhesion were measured from 0° to -30°C. The results obtained by Jensen for spheres of diameter $1\frac{1}{4}$ cm are shown in Fig. 2. The average value of the forces measured at each temperature is seen to increase in an exponential form from -25° to 0°C.

In an attempt to study the factors governing the amount of aggregation that is likely to occur in a natural ice cloud, Hosler and Hallgren (1960) measured the number of crystals collected by a small ice sphere placed in the path of a moving cloud of ice crystals. The ice sphere was suspended

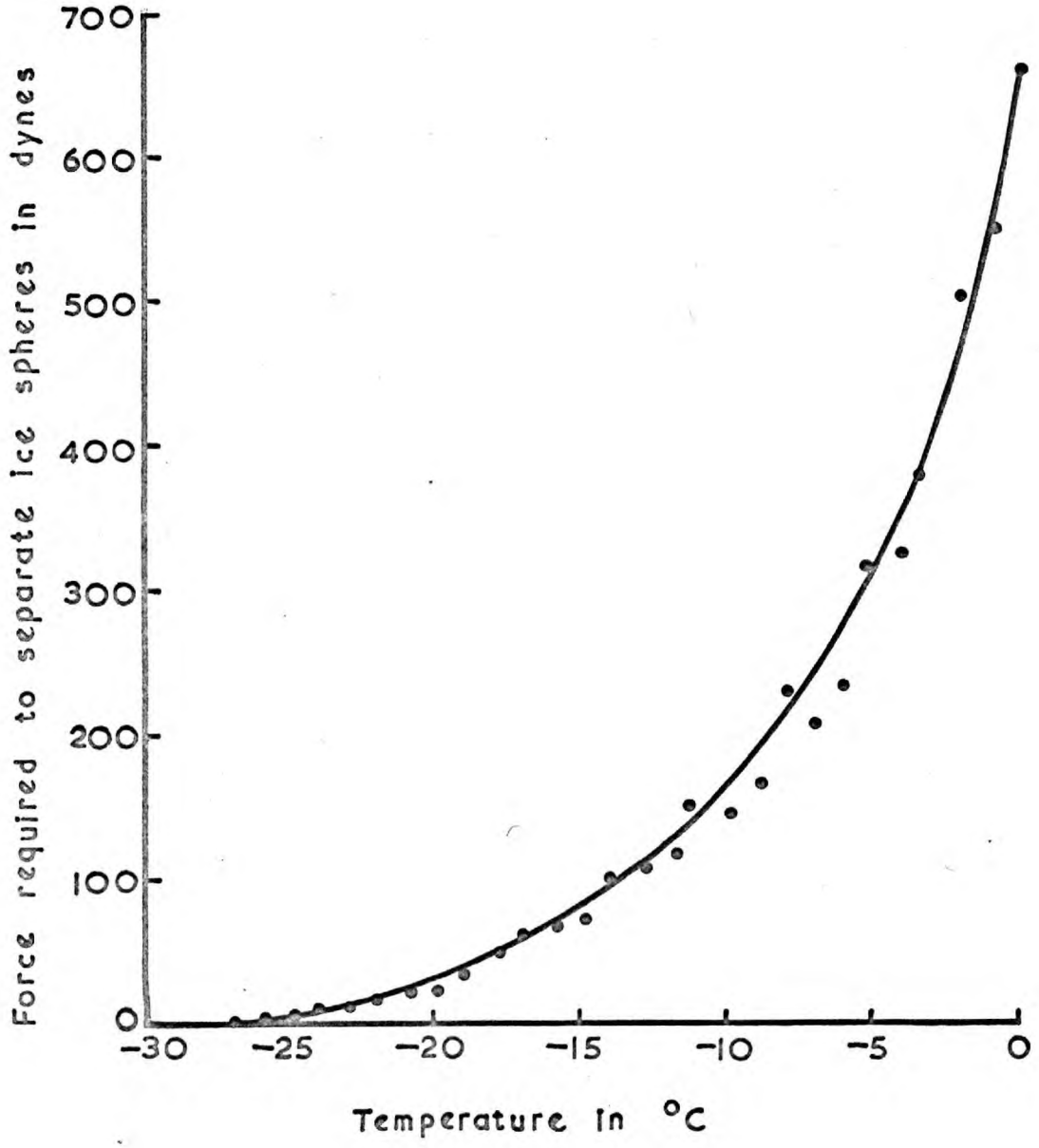


FIG. 2 Force required to separate ice spheres at ice saturation against temperature (after Jensen, 1956)

inside a wind tunnel in which both temperature and vapour pressure could be varied. The ice crystals were drawn past the sphere at speeds approximating to that at which the sphere would encounter the crystals were it falling at its terminal velocity. The crystals were from 7 to 18μ in diameter and existed in concentrations of 3,000 to 20,000 cm^{-3}. The ice sphere was observed during its growth, and its dimensions were measured periodically. By this method it was possible to calculate the percentage of ice crystals in the path of the ice sphere that collided with, and adhered to, the sphere.

The results obtained by Hosler and Hallgren for the collection efficiency of a sphere of 127μ initial diameter are shown in Fig. 3. A similar curve wasobtained in the case of a sphere of diameter 360μ, except that the collection efficiencies were slightly higher. From the measurements of Jensen, described above, one might expect the collection efficiencies to increase continuously with increase in temperature. However, it can be seen from Fig. 3 that this was not found to occur. Below a temperature of $-12^{\circ}C$ the collection efficiency did fall with decreasing temperature, but for temperatures above $-12^{\circ}C$ the collection efficiency

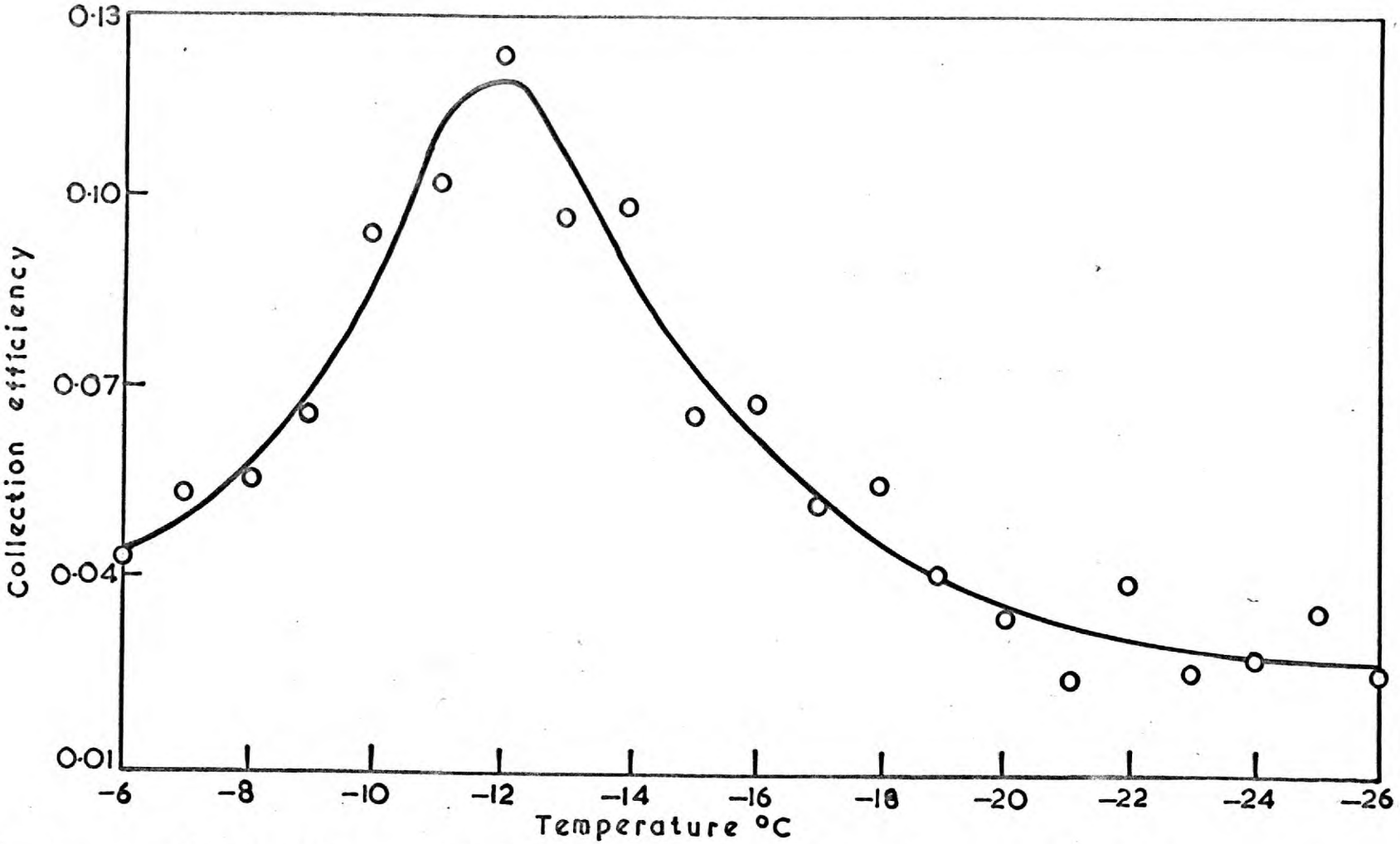


FIG. 3 Collection efficiency of an ice sphere of 127μ initial diameter (after Hosler and Hallgren, 1960)

was found to decrease with increasing temperature. Hosler and Hallgren explain these results on the basis of a change in crystal type at $-12^{\circ}C$. At temperatures between -6° and $-12^{\circ}C$ the ice cloud consisted mainly of prisms, but below $-12^{\circ}C$ hexagonal plates predominated. The decrease in collection efficiencies above $-12^{\circ}C$ was thought by Hosler and Hallgren to be due to the "liquid-layer" being thicker on the basal plane than on the prism face; hence plates would tend to form aggregates at a greater rate than prisms.

This interpretation must, however, be treated with caution for the following reasons. Firstly, at a temperature of $-11^{\circ}C$ the difference in vapour pressure between supercooled water and ice is a maximum; hence, it is possible that the maximum value of the collection efficiency at $-12^{\circ}C$ was due to the presence of supercooled water in the ice cloud. Secondly, the possibility of the ice crystals carrying a net electric charge was not investigated by Hosler and Hallgren. It is quite likely that considerable charges were carried by the ice crystal cloud due to impacts on the lucite walls of the chamber. If this were the case, the collection efficiencies measured in this experiment would bear little relationship to the aggregation of neutral ice crystals.

1.5 The "liquid-layer" theory

In recent years there has been renewed interest in Faraday's concept of an equilibrium "liquid-layer" of water on the surface of ice. In the modern version of this theory, it is postulated that a "liquidlike" layer exists on ice throughout the temperature range 0° to $-30^{\circ}C$. This liquid is supposed not to be supercooled water, for it is in equilibrium on one side with the ice and on the other side with the air. Ice adhesion at temperatures below zero is then explained by the freezing of this "liquid-layer" on bringing two pieces of ice into contact. The decrease in the force of adhesion with temperature (Fig. 2) is accounted for by the decrease in the thickness of the "liquid-layer" as the temperature is lowered.

The first attempt to give theoretical support for the existence of a "liquid-layer" appears to be that of Gurney (1949) who presents the following argument. Consider a stress-free surface of a crystalline solid at a temperature such that appreciable molecular migration is possible. The chemical potential, μ, of the surface molecules will be higher than that of the interior molecules, hence more atoms will leave the surface than enter it. This will give rise

to an increase in the concentration of vacancies near the surface, and also an increase in the entropy of the surface molecules. The chemical potential, however, remains unchanged because $(\partial\mu/\partial s)_{\gamma,T} = 0$. If this state of affairs persisted, no effective tension would be set up in the surface, and molecules would continue to leave the surface: thermal equilibrium would be impossible. To attain thermal equilibrium the departure of the molecules from the surface must set up a force opposing further departure. According to Gurney this arises as follows. When the number of vacancies at the surface reaches a given number the crystalline arrangement of the surface molecules becomes unstable with respect to the liquid phase. The molecules at the surface then melt to form a liquid film a few molecules thick which completely covers the surface. A tension stress is now set up in this liquid such that the chemical potential of molecules in the liquid film is equal to that of the interior molecules. Under these conditions the system is in equilibrium.

Weyl (1951) has argued in support of "liquid-layers" on ice from another standpoint. His hypothesis is that in order to keep the surface-free energy at a minimum, the

surface ions must be polarised and the protons must be slightly recessed to form a dipole layer on the surface. The steps by which this rearrangement takes place are illustrated in Fig. 4 and are as follows:

(a) Due to the asymmetrical environment the ions at the surface of a freshly cleaved solid are acted on by considerable electric fields.

(b) This produces polarisation of the surface ions, and hence some reduction in the net field at the surface takes place.

(c) Further reduction in the field is brought about by a slight recession of the H^+ ions.

Weyl then assumes that this transition layer will retain the characteristics of a liquid at temperatures below the melting point of ice.

Fletcher (1962) has also considered the effect of a surface "liquid-layer" on the total free energy of an ice surface, and claims to demonstrate that such a layer will be thermodynamically stable down to a temperature of $-30^{\circ}C$. The method employed by Fletcher is to derive an expression for the difference in the free energy per surface molecule, ΔG, of a "liquid-layer" structure and that of a simple ice

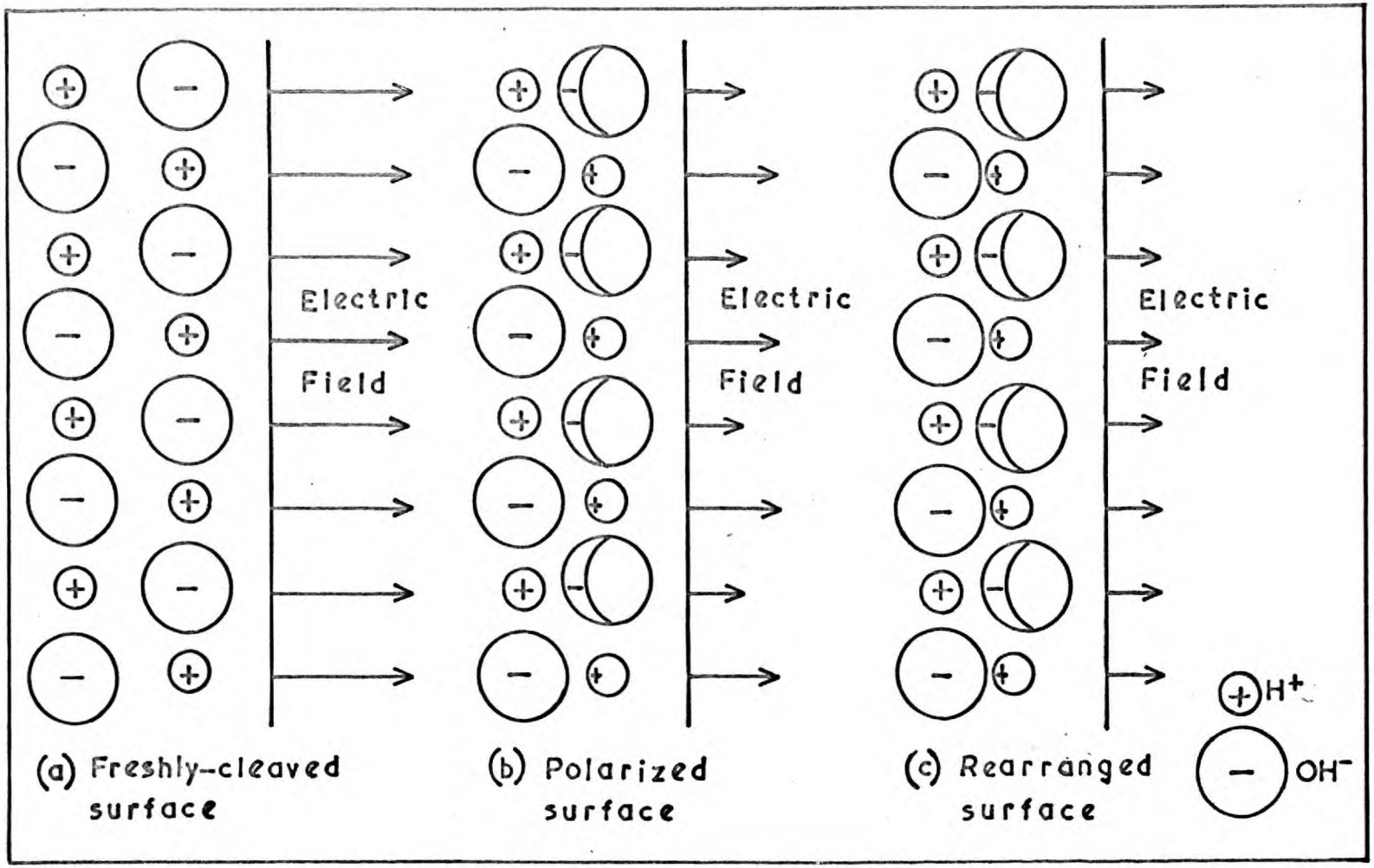


FIG. 4 Ionic rearrangement in an ice surface

structure. The results of this calculation are shown in Fig. 5 where the maximum value of ΔG is plotted against temperature. For temperatures above about $-13^{\circ}C$, ΔG is negative by an amount of the order 10^{-14} erg per molecule (10 erg cm^{-2}), which indicates that the "liquid-layer" is stable. In the region between -13° and $-30^{\circ}C$ ΔG is slightly positive, but, since these calculations give the upper limit to ΔG, it is possible that the film is still stable at these temperatures. Fletcher also estimates the thickness of the "liquid-layer" as a function of temperature (Fig. 6). It can be seen that, on the basis of these calculations, the film exists down to $-30^{\circ}C$, and its thickness is of the order of some tens of angstroms.

Fletcher's calculations have been critized by Watts-Tobin (1963) on the grounds that the dipole-dipole interaction between water molecules was not taken into account in evaluating ΔG. This interaction would produce a strong depolarising field on a molecule in the oriented layer and therefore cause it to be unstable.

If a "liquid-layer" of about thirty molecular layers did exist on the surface of ice, it should be possible to detect it by techniques such as infra-red absorption or

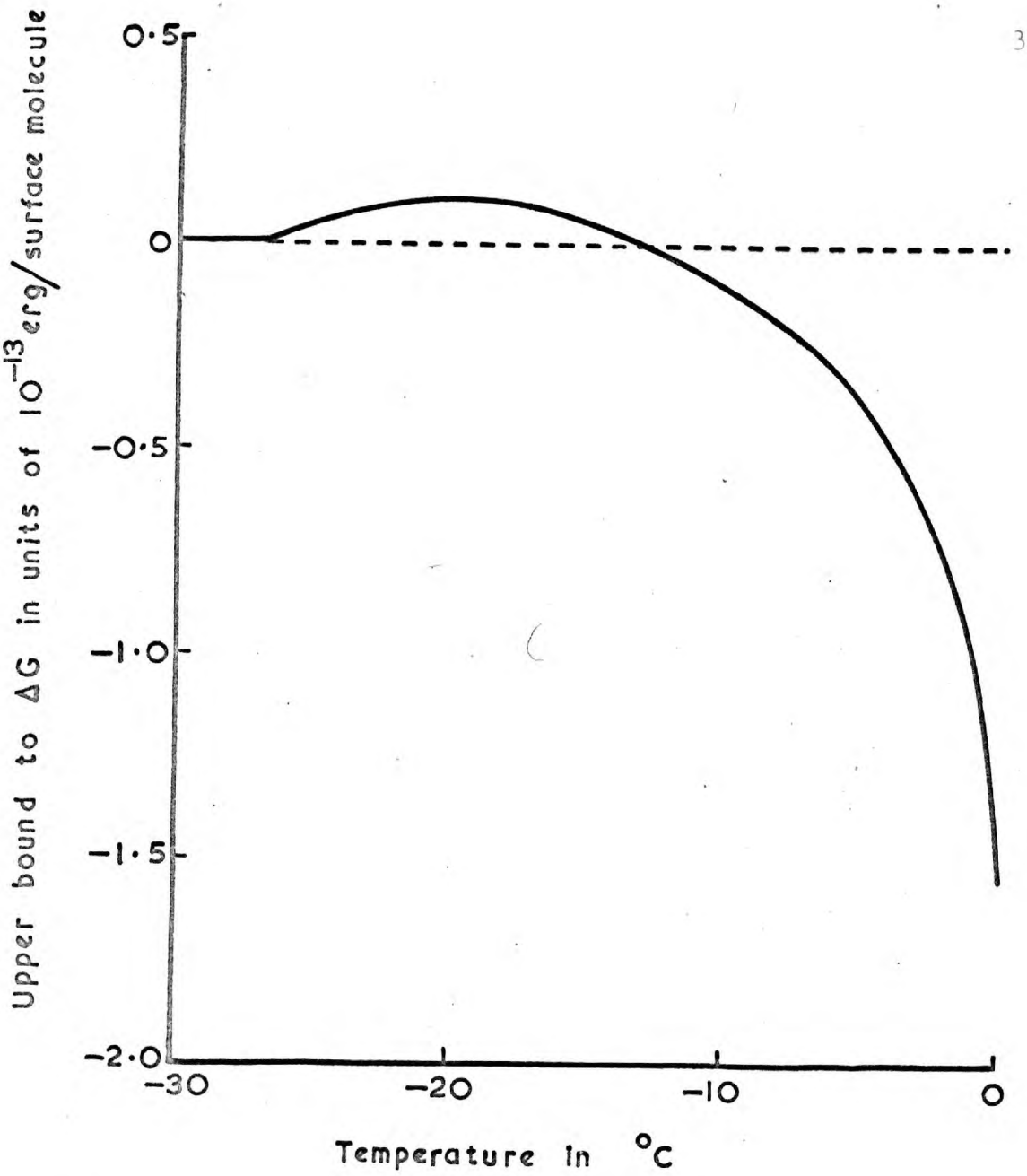


FIG. 5 Upper bound to the amount ΔG by which the free energy of the equilibrium liquid film surface exceeds that of a solid crystalline ice surface (after Fletcher, 1962)

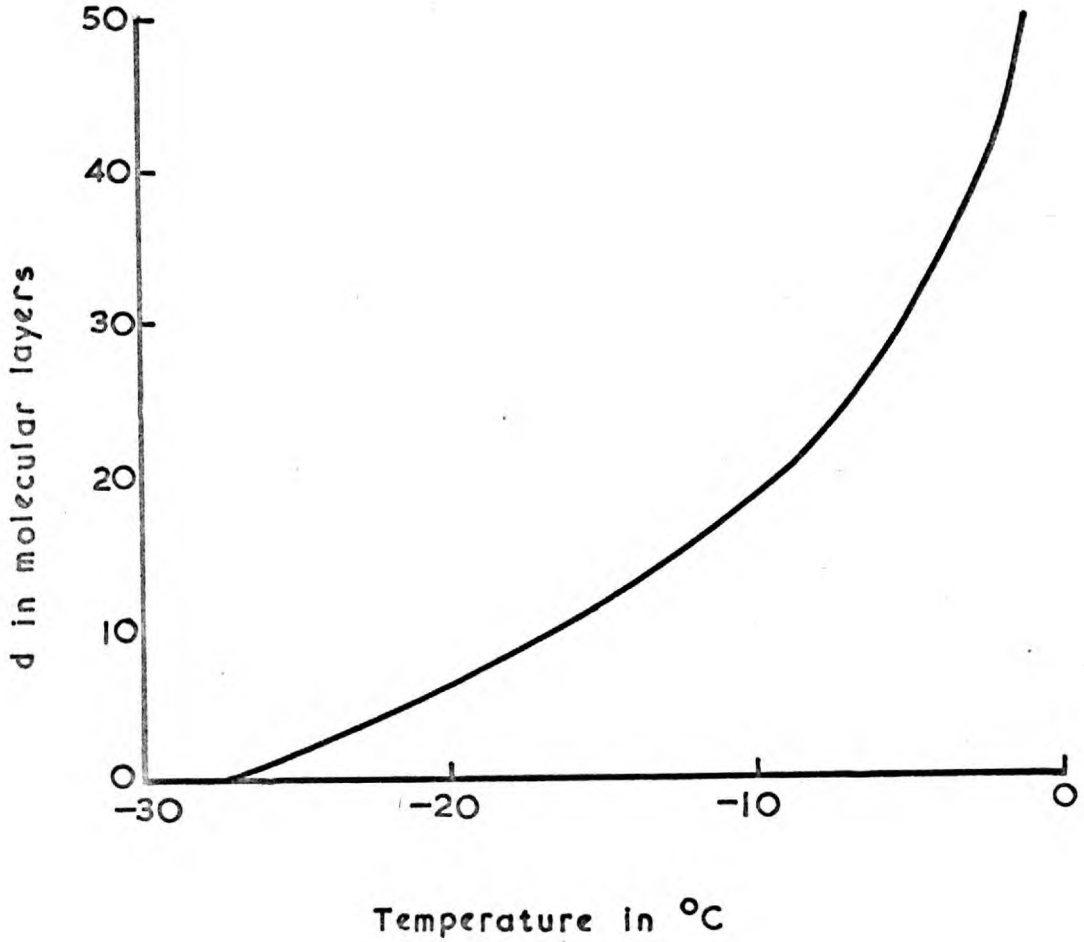


FIG. 6 The thickness d of the equilibrium liquid film on the surface of ice as a function of temperature (after Fletcher, 1962)

proton spin resonance. Until such direct evidence of this type is obtained the "liquid-layer" theory must remain in the nature of a postulate.

1.6 Sintering of ice

Kingery (1960) observed that when two small 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. This phenomenon is well known in the field of powder metallurgy where it is termed sintering. It will be shown in the next chapter that sintering may be explained in a quantitative manner on the basis of material transfer by a number of possible mechanisms. Thus, neither the pressure-melting theory nor the "liquid-layer" hypothesis is necessary to account for the adhesion of ice. For, whenever ice particles are brought together they will show a tendency to stick to one another due to the formation of necks (ice-bonds) which grow as time elapses.

By measuring the growth rate of the neck between two polycrystalline ice spheres, Kingery claims to show that for spheres over the size range 0.2 mm to 6 mm, and for temperatures between -2° and -25°C, the mass-transfer is due to

surface diffusion. However, in similar experiments performed by Kuroiwa (1961) on ice spheres less than 0.1 mm in diameter, volume diffusion was found to be predominant. These two sets of results are inconsistent with the theory of sintering used by both Kingery and Kuroiwa, for it may be shown that if surface diffusion predominates for large spheres it must continue to do so for spheres of smaller size.

This thesis is concerned with a theoretical and experimental investigation into the sintering of ice. In the following chapter the current theory of sintering is re-examined; it is shown that in some aspects the theory is incomplete and as a result many experiments on sintering, including those on ice, have been misinterpreted. In the last two chapters an account is given of experiments which have been performed on the sintering of ice and these are discussed in the light of a revised theory of sintering.

CHAPTER 2

THE THEORY OF SINTERING

2.1 Introduction

Two particles in contact at a point form a system which is not in thermodynamic equilibrium as the total free surface energy is not a minimum. Provided that sufficient motivation exists, bonding will take place to decrease the total surface area, even though the temperature may be lower than the melting point. This phenomenon of bonding between solid particles is termed sintering.

Fine powders of most metals, and many other substances, will sinter when they are heated above about three-quarters of their melting point on the absolute scale. Permanent adhesion between the particles then takes place and the whole mass becomes less porous and, in general, its properties change towards that of the dense material. Most sintering experiments have been performed on powder compacts and consist of measuring the overall density of the compact as a function of time and temperature of sintering. In systems such as this the details of the geometry of the contacts between particles and their effect on the density are so

complex that a quantitative prediction of results becomes impossible. In the present work attention has been concentrated on the relatively simple case of the bonding between two spherical particles. A theoretical analysis of this system will now be given and the results of this will subsequently be compared with experiments on the sintering of two ice spheres.

2.2 Motivation for sintering

Although two spherical particles in contact at a point are thermodynamically unstable, transfer of material into the neck region will only take place if sufficient driving force is available to overcome the activation energy associated with the mechanism of transport. There are two possible motivating forces, they are pressure and surface tension. Two particles which are pressed together by an external force can yield to the force by growing together. However, a comparison of results on the sintering of pressed and unpressed metal powders reveals that the basic course of sintering is not modified by compression. Moreover, in the present experiments only the slightest pressure is applied on bringing the particles into contact,

subsequent rates of sintering are measured in the absence of any applied force. It is, therefore, only necessary to consider the effect of surface tension as the motivating force in sintering.

Before developing the theory in detail it is useful to consider the order of magnitude of some of the quantities involved. Ice has a surface tension, γ, of about 100 erg/cm^2. The interior of a particle of radius r will be under a pressure due to the surface tension of magnitude $2\gamma/r$. For particles of diameter 100μ this gives a pressure of 4×10^4 dynes/cm^2, or approximately 4×10^{-2} atmospheres. Tensions of about two orders of magnitude higher than this might be expected near the neck where the two particles have started to sinter together, since the curvature in this region is concave outward and much sharper. The lowering of the free energy accompanying the complete sintering of two spheres considered above is of the order 10^{-2} ergs. Finally, the vapour pressure, p_ρ, over a concave surface of radius ρ is related to that over a plane surface, p_o, by Kelvin's equation

$$\ln \frac{p_o}{p_\rho} = \frac{2\gamma\delta^3}{kT\rho} \qquad (1)$$

where, δ^3 is the molecular volume, k Boltzmann's constant, and T the temperature. If ρ is taken as $10^{-2}r$, for spheres of diameter 100μ, equation (1) gives p_o/p_ρ equal to 1.003.

The above considerations suggest two possible ways by which material might be transferred into the neck from elsewhere in the system. Firstly, there will be transfer through the vapour phase due to the difference in vapour pressure $(p_o - p_\rho)$ between the ice saturated environment and the region adjacent to the sharply concave neck. Secondly, diffusion will take place through the ice lattice under the influence of the deficit in pressure in the region of the neck produced by the surface tension forces. Both these effects may be described in terms of the gradient in chemical potential existing between various portions of the surface of the particles.

Consider the case of a crystal which is perfect except for occasional interstitial molecules and lattice vacancies. Let N_h and N be the number of lattice defects and the number of molecules respectively in a given volume v. If F is the Helmholtz free energy of a region, the chemical potential μ of the molecules and μ_h of the lattice defects are defined by

$$\mu = \left(\frac{\delta F}{\delta N}\right)_{N_h,T,v,\text{strain}} \qquad (2)$$

and,

$$\mu_h = \left(\frac{\delta F}{\delta N_h}\right)_{N,T,v,\text{strain}} \qquad (3)$$

When vacancies or interstitial molecules migrate into a given region N and N_h change by equal and opposite amounts. The change in the free energy of the region is therefore equal to the number of molecules entering or leaving it multiplied by $(\mu - \mu_h)$. Now, a transport of matter will only occur from one region to another if, as a result, the total free energy of the crystal is lowered. This will only be the case if there exists a gradient of $(\mu - \mu_h)$ within the crystal.

Under the assumption of a free interchange of vacant lattice sites and interstitial molecules between a surface and the region immediately beneath it, Herring (1951) has shown that the difference in chemical potential of a molecule and of a lattice vacancy immediately beneath a curved surface of principal radii of curvature R_1 and R_2 is given by

$$(\mu - \mu_h) - \mu_o = \delta^3 \left[\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{\delta^2\gamma}{\delta n_1^2}\frac{1}{R_1} + \frac{\delta^2\gamma}{\delta n_2^2}\frac{1}{R_2}\right] \qquad (4)$$

where, μ_o is the value of $(\mu - \mu_h)$ corresponding to a flat surface (R_1, $R_2 = \infty$), δ^3 is the volume per molecule and n_1 and n_2 correspond to directions on the surface associated with R_1 and R_2.

If it is now assumed that γ is independent of the orientation ofthe surface, equation (4) reduces to

$$\mu' = \delta^3 \gamma K \qquad (5)$$

where μ' is the value of $(\mu - \mu_h) - \mu_o$ on a surface of curvature K. In equation (5) K is taken as positive when the surface is convex outwards and negative when it is concave outwards.

2.3 Sintering by evaporation-condensation

In deriving an expression for the rate of growth of the neck due to the transfer of vapour through the environment, it is necessary to consider two distinct cases which will now be dealt with in turn.

Case (i): Direct Transfer

In a system in which the mean free path of the molecules, λ, is large compared with the radius of the neck, molecules will be transferred directly from the surface of the spheres to the concave region of the neck. This transfer will take

place under a pressure difference $(p_o - p_\rho)$ at a rate given by Langmuir's equation. These conditions are likely to prevail, for example, when all air is excluded from the environment and the spheres are in contact with their own vapour phase. An expression for the rate of sintering between two spheres under these conditions has been derived by Kuczynski (1949) as follows.

The vapour pressure p_K of an ideal gas in equilibrium with a surface of curvature K, is related to its chemical potential μ_K by the expression

$$p_K = p_o \exp\left(\frac{\mu_K - \mu_o}{kT}\right) \qquad (6)$$

If the gas is in equilibrium with the surface of the crystal there will be no change in the free energy of the system when molecules are removed from the vapour and added to the crystal, therefore

$$\mu_K = \mu - \mu_h \qquad (7)$$

Combining equations (5), (6) and (7)

$$p_K = p_o \exp \frac{\delta^3 \gamma K}{kT} \qquad (8)$$

which is Kelvin's equation.

The geometry of the system under consideration is

illustrated in Fig. 7 where the spheres are taken to be of equal radius, r, and the radii of the neck, after sintering for time t, are x (convex) and ρ (concave). For all practical purposes the spheres themselves may be regarded as plane surfaces in equilibrium with a vapour pressure p_o. Also, since $x >> \rho$, the curvature of the neck may be written as $(1/-\rho)$. If the vapour pressure adjacent to the neck is p_ρ, Kelvin's equation gives.

$$p_\rho = p_o \exp\left(\frac{-\delta^3\gamma}{\rho kT}\right)$$

or,

$$p_o - p_\rho = \frac{p_o \delta^3 \gamma}{\rho kT} \qquad (9)$$

If the rate of transport, G, of material from the surface of the spheres to the concave region of the neck is now assumed to be given by Langmuir's equation, then

$$G = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} (p_o - p_\rho) \qquad (10)$$

where m is the mass of a molecule. From equations (9) and (10)

$$G = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \left(\frac{p_o \delta^3 \gamma}{\rho kT}\right) \qquad (11)$$

The rate of condensation, G, on the area, A, of the neck must be equal to the rate of increase in the mass of

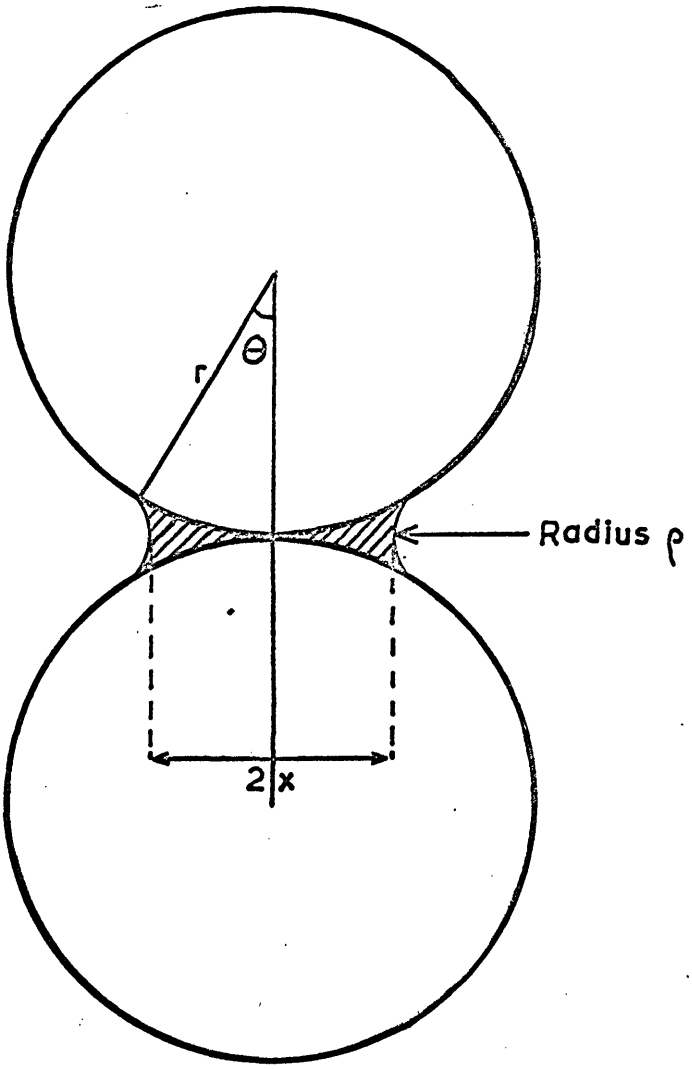


FIG.7 The geometry of the system

the neck. Therefore,

$$AG = \beta \frac{dV}{dt} \tag{12}$$

where β is the density of the solid and V the volume of the neck at time t. Provided that θ (Fig. 7) remains a small angle the following expressions may be derived from the geometry of the system

$$\rho = \frac{x^2}{2r} \tag{13}$$

$$A = \frac{\Pi^2 x^3}{r} \tag{14}$$

and, $$V = \frac{\Pi^2 x^4}{4r} \tag{15}$$

Combining equations (11) to (15) and integrating leads to the following expression for the rate of growth of the neck by evaporation-condensation

$$\left(\frac{x}{r}\right)^3 = \frac{12 M \gamma p_o}{\beta^2 RT r^2} \left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} t \tag{16}$$

where R is the gas constant and M the molecular weight. Equation (16) is that derived by Kuczynski (1949) and also by Kingery and Berg (1955).

In deriving equation (16) it has been assumed that all the molecules that collide with the surface of the neck

remain attached and thereby cause the neck to grow. Some of the impacting molecules, however, may not find a suitable site on the surface of the crystal in which case they will re-evaporate into the environment. The coefficient of condensation, α, is defined as the ratio of the number of molecules condensing on a surface to the total number of molecules colliding with the surface. This effect is taken into account by multiplying the right hand side of equation (16) by α, to give

$$\left(\frac{x}{r}\right)^3 = \frac{12M\delta p_o \alpha}{\beta^2 RTr^2}\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} t \qquad (17)$$

Kuczynski has also shown (see § 2.4) that for sintering by volume diffusion the corresponding expression to equation (17) is of the form

$$\left(\frac{x}{r}\right)^5 = B(T)\,\frac{t}{r^3} \qquad (18)$$

where B(T) is a temperature dependent constant. Kuczynski then claims that it is possible to distinguish between the mechanisms of evaporation-condensation and volume-diffusion by measuring (x/r) as a function of t and r and comparing the results with equations (17) and (18). In the field of powder metallurgy this method has become the standard

way of interpreting experimental results on the sintering of particles. However, it appears to have been overlooked that the derivation of equation (17) is based on Langmuir's equation and is therefore only applicable to systems in which the mean free path of the vapour molecules is large compared with the distance over which transport occurs. Failure to appreciate this fact has led to the application of Kuczynski's equations to systems for which they are not valid.

Case (ii): Transfer by Diffusion

When the mean free path of the molecules is considerably less than the radius of the neck, molecules will be transferred from the surface of the spheres to the neck by a process of diffusion through the environmental gas. Sintering by evaporation-condensation under these conditions has not been previously considered, although this is the case which will normally apply when sintering takes place in air at atmospheric pressure. An expression will now be derived for the rate of growth of the neck by this mechanism of material transfer.

The difference in concentration, ΔC, between the molecules in the vapour phase above the surface of the spheres and those

in the vicinity of the neck is given by the gas equation as

$$\Delta C = \frac{1}{kT}(p_o - p_\rho) \qquad (19)$$

This fall in concentration occurs over a distance of the order of the radius, ρ, of the neck. The concentration gradient is therefore

$$\frac{\Delta C}{\rho} = \frac{1}{kT\rho}(p_o - p_\rho) \qquad (20)$$

and using equation (9) this becomes

$$\frac{\Delta C}{\rho} = \frac{p_o \delta^3 \gamma}{(\rho kT)^2} \qquad (21)$$

The flux of molecules F (per unit area per sec) produced by this gradient is given by Fick's equation as

$$F = D_E \frac{\Delta C}{\rho}$$

or,
$$F = D_E \frac{p_o \delta^3 \gamma}{(\rho kT)^2} \qquad (22)$$

where D_E is the diffusion coefficient in the environment. The rate of increase in the volume, V, of the neck is therefore

$$\frac{dV}{dt} = A\delta^3 \propto D_E \frac{p_o \delta^3 \gamma}{(\rho kT)^2} \qquad (23)$$

where A is the surface area of the neck and α the coefficient of condensation. Substituting the expressions for ρ, A and V from equations (13) to (15) into equation (23) and integrating gives

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3\alpha}{kTr^3}\,\frac{p_o\delta^3 D_E}{kT}\,t \qquad (24)$$

An effect which has not been taken into account in deriving equation (24) is that the surface of the neck will be at a higher temperature than the environment due to the latent heat released by the condensing molecules. For metals this effect will be small as the latent heat will be quickly conducted away through the spheres. In the case of the sintering of ice spheres, however, the rise in temperature of the neck may be considerable, and under some circumstances the maximum rate at which the latent heat can be removed will set an upper limit to the rate of growth of the neck. A correction term for this effect has been derived by Mason (1953) in considering the growth of ice crystals in supercooled water clouds; it is shown that, provided the latent heat of sublimation, L_s, is dispersed solely by conduction through the air, the expression $\frac{p_o\delta^3 D_E}{kT}$ mustbe replaced by $\frac{1}{\beta\left(\frac{kT}{p_o m D_E} + \frac{L_s^2 m}{\mathcal{K}kT^2}\right)}$

where $\mathcal{K}$ is the thermal conductivity of air and m the mass of a water molecule. Equation (24) then becomes

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3}{kTr^3} \frac{\alpha}{\beta\left(\frac{kT}{p_o m D_E} + \frac{L_s^2 m}{\mathcal{K} kT^2}\right)} t \qquad (25)$$

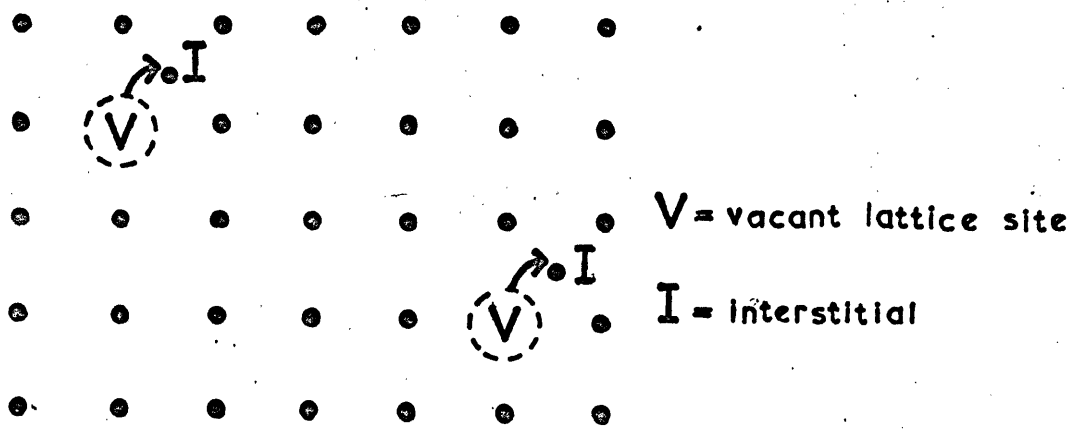
Equation (25) gives the rate of sintering of two ice spheres due to evaporation-condensation when the mean free path of the molecules of the sintering substance is small compared with the radius of the neck. It can be seen that equation (25) is identical in its dependence on t and r with Kuczynski's equation for volume diffusion (equation (18)). Hence, under these conditions, it is not possible to distinguish between evaporation-condensation and volume diffusion merely by determining experimentally x/r as a function of t and r. If the rate of sintering is found to vary as the one-fifth power of the time, the absolute rates of sintering predicted by equations (18) and (25) must be compared with that found experimentally in order to decide whether volume diffusion or evaporation-condensation is predominent. Experiments on the effect of the environment and of added impurities to the spheres may also help in deciding the mechanism of sintering.

2.4 Sintering by volume diffusion

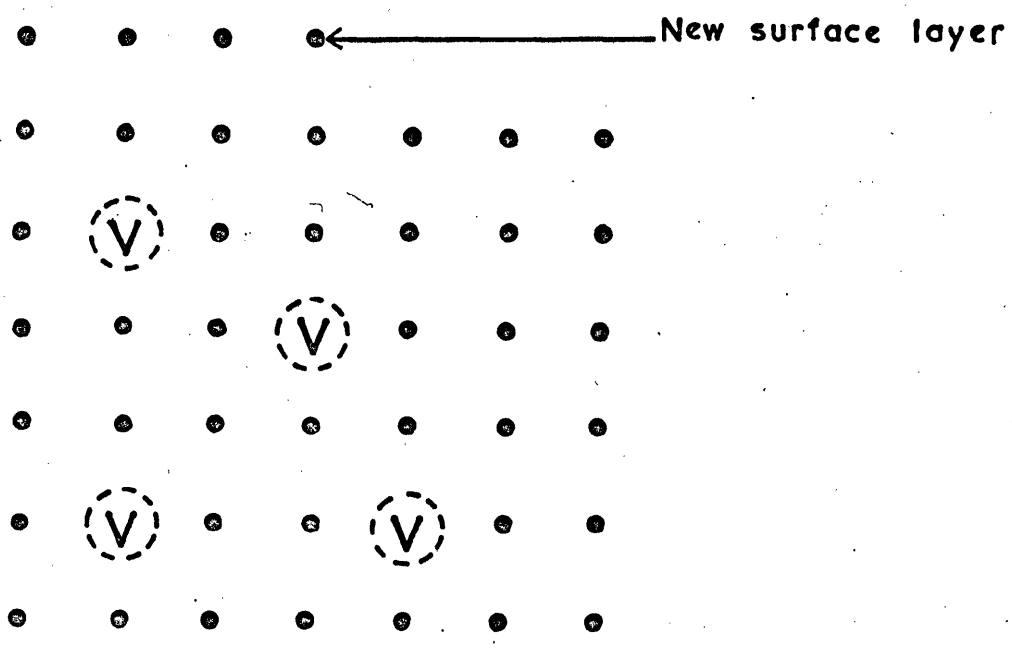
In this section the mechanism of sintering by volume diffusion will be considered in greater detail and Kuczynski's equation for the rate of growth of the neck by volume diffusion will be derived.

The diffusion of molecules through a solid crystal is rendered possible by the existence of a definite number of vacant lattice sites within the crystal at any temperature above absolute zero. These vacancies can arise in two ways, constituting what are known as Frenkel defects and Schottky defects (Fig. 8). In the case of Frenkel defects a certain proportion of the molecules are displaced from their normal positions in the lattice into interstitial positions, leaving vacant positions in the normal lattice. With Schottky defects, on the other hand, molecules leave lattice positions in the interior of the crystal and take up normal positions on the surface.

The work necessary to form a Frenkel defect depends on the interstitial volume available for the molecule, If the crystal is subjected to pressure this work will be increased and there will be a decrease in the number of lattice defects. A tension force, however, will enhance



a) Frenkel defects



b) Schottky defects

FIG.8 Two possible mechanisms for the formation of vacant lattice sites

the formation of defects within the crystal. The same is true for Schottky defects. Under the conditions existing for sintering, the portions of the crystal in the neighbourhood of the neck are under tension forces, hence the concentration of vacancies in this region will be greater than elsewhere in the system. This vacancy gradient gives rise to the diffusion of molecules into the neck, thereby causing the neck to grow in size.

In the case of Frenkel defects, there exists two possible mechanisms for diffusion.

(a) By the migration of interstitial molecules from one interstitial position to another.

(b) By molecules jumping from normal lattice sites into neighbouring lattice vacancies. In this process the molecules and the vacancies change place. This is termed "vacancy diffusion".

It can be shown from energy considerations that vacancies are more likely to migrate than are interstitials. For Schottky defects only vacancy diffusion can, of course, operate. Fig. 9 illustrates a sequence of jumps by which a vacancy first formed at B, on a concave surface WXYZ,

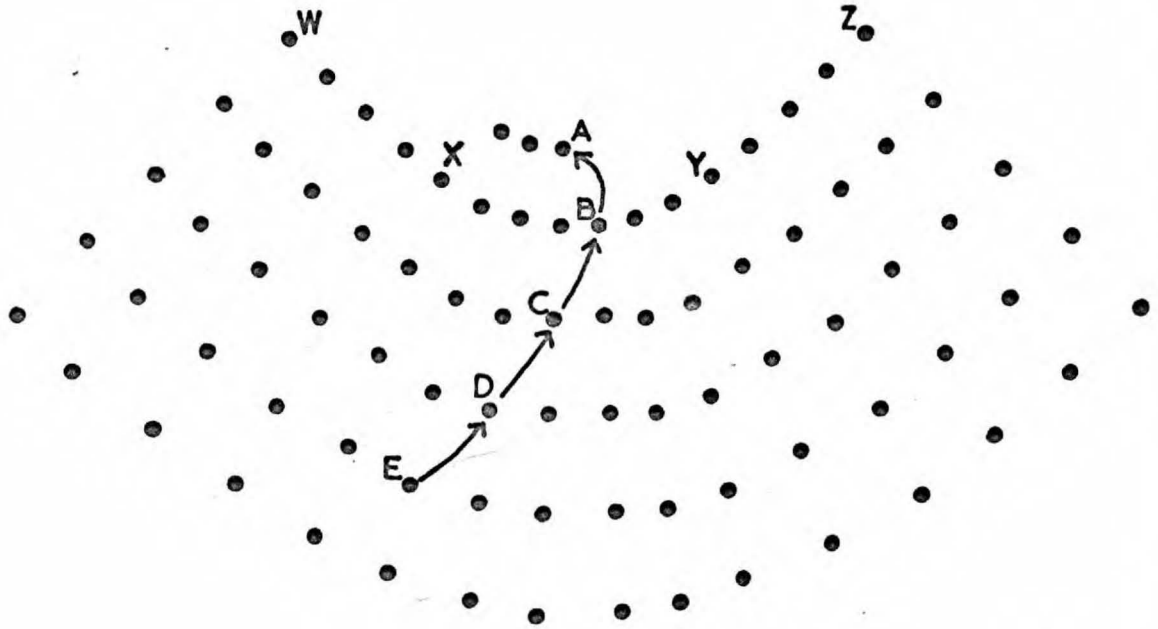


FIG. 9 Sequence of jumps in which a vacancy first formed beneath a concave surface migrates into the interior of the crystal

migrates by vacancy diffusion to a point E in the interior of the crystal.

It has been shown above that the difference in vapour pressure existing between the neck and the surface of the spheres is related to the gradient in the chemical potential, $\mu - \mu_h$. Similarly, the difference in vacancy concentration, $C_\rho - C_o$, between the neck and regions well removed from the neck is determined by the gradient of $\mu - \mu_h$ within the crystal. In this case, the corresponding expression to equation (9) is

$$C_\rho - C_o = \frac{C_o \delta^3 \gamma}{\rho kT} \qquad (26)$$

where, C_ρ and C_o are the concentrations of vacancies beneath a concave cylinder of radius ρ and beneath a plane surface respectively. In order to calculate the contribution to the rate of sintering by volume diffusion it is necessary to estimate over what distance the concentration of vacancies falls from C_ρ to C_o. Kuczynski (1949) considers this concentration drop to occur over a distance of the order ρ, so that the gradient in vacancy concentration may then be written as

$$\frac{C_\rho - C_o}{\rho} = \frac{C_o \delta^3 \gamma}{\rho^2 kT} \qquad (27)$$

The flow of vacancies I (per cm^2 per sec) produced by the gradient given in equation (27) will be

$$I = D' \frac{C_\rho - C_o}{\rho} \qquad (28)$$

where, D' is the coefficient of vacancy diffusion. The rate of increase of the volume, V, of the neck is therefore

$$\frac{dV}{dt} = A\delta^3 \frac{C_\rho - C_o}{\rho} D' \qquad (29)$$

where, A is the area from which the vacancies are diffusing and is given by equation (14), V is given by equation (15), and δ^3 is the volume occupied by a vacancy which is equal to the volume occupied by a molecule. Substituting values in equation (29) and integrating leads to the expression

$$x^5 = \frac{20r^2\delta^3\gamma}{kT} \delta^3 C_o D' t \qquad (30)$$

If a vacancy exists in a lattice it may migrate by exchanging positions with any one of the near neighbour molecules. A particular molecule, however, can only migrate by vacancy diffusion if one of its near neighbour lattice sites happens to be vacant. For this reason the

coefficient of vacancy diffusion, D', is much greater than the coefficient of volume diffusion, D_V. The relation is

$$D_V = \frac{\text{concentration of vacancies}}{\text{concentration of lattice sites}} D'$$

that is, $D_V = C_o \delta^3 D'$ (31)

Equation (30) may therefore be written as

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3 D_V}{kTr^3} t \quad (32)$$

which gives the rate of sintering of two spheres due to volume diffusion.

The equilibrium concentration of vacancies, C_o, may be written in the form $C_o = Xe^{-U/RT}$, where X is a constant and U is the energy required to form a vacancy. Also, the coefficient of vacancy diffusion, D', is of the form $D' = Ye^{-E/RT}$, where Y is a constant and E is the energy barrier that a molecule has to overcome in order to move into an adjacent vacant lattice site. Equation (31) may therefore be written as

$$D = XY\delta^3 e^{-(U + E)/RT} \quad (33)$$

or, $$D = D_o e^{-W/RT} \quad (34)$$

where $W = U + E$ is the total activation energy for volume diffusion and D_o is a constant referred to as the frequency factor.

It is to be noted that the diffusion coefficient D_V in equation (32) is not strictly identical with the self-diffusion coefficient as measured by radioactive techniques. This difference arises from two sources. If an appreciable contribution to the radioactive diffusion coefficient arises from a process of direct interchange of molecules, there will be no corresponding contribution to D_V in equation (32). Also, if diffusion is predominently due to the migration of vacancies, it has been shown by Bardeen and Herring (1951) that the D_V defined by equation (31) is greater than that measured by a radioactive tracer by about 10%. This arises because a tracer atom has a preponderant chance of making two successive jumps in opposite directions. However, these effects are probably no greater than the experimental error involved in measuring the diffusion coefficient, hence for all practical purposes D_V is the same as that measured by a radioactive tracer.

2.5 Sintering by surface diffusion

In addition to the transfer of material into the neck by bulk diffusion, there will be a migration of molecules in the neighbourhood of the surface of the two spheres, wherethe diffusion coefficient may differ from that in the interior of the crystals. An expression for the contribution to the rate of sintering due to diffusion of this type has been derived by Kuczynski (1949) and his treatment, with slight modifications, will now be given.

The radius, ρ, of the neck, the volume, V, of the bridge and the concentration gradient, $(C_\rho - C_o)/\rho$, are the same as for volume diffusion and are given by equations (13), (15) and (27), respectively. However, the region in which diffusion now takes place is confined to a surface layer of approximately one molecular layer, δ, in depth. The limiting area, A_s, to be substituted into Fick's equation is therefore given by

$$A_s = 2(2\pi x\delta) = 4\pi x\delta \qquad (35)$$

and the corresponding rate of increase in the volume of the neck is

$$\frac{dV}{dt} = A_s \delta^3 \frac{C_\rho - C_o}{\rho} D_B' \qquad (36)$$

where D_B' is the coefficient of vacancy diffusion in the boundary layer near to the surface of the crystal. By substituting into the equation (36) and integrating the following expression is obtained for the rate of sintering

$$\left(\frac{x}{r}\right)^7 = \frac{112\gamma\delta^4 D_B}{\pi k T r^4} t \qquad (37)$$

where D_B is the coefficient of diffusion in the boundary layers and is given by

$$D_B = C_o \delta^3 D_B' \qquad (38)$$

Kuczynski equates the diffusion coefficient D_B with the surface diffusion coefficient, D_s, of the solid. However, the concept of diffusion considered above is not that which is normally termed surface diffusion. It might better be called "boundary diffusion", for it takes place by the usual mechanisms responsible for volume diffusion (migration of vacancies and interstitials) but it is confined to a layer just beneath the surface of the crystal. In this boundary region it might be expected that the diffusion coefficient will be greater than the bulk

diffusion coefficient, D_v, but less than the true surface coefficient, D_s.

Surface diffusion proper consists of the migration of adsorbed atoms on the surface of the crystal. The a adsorbed atoms are formed either by condensation from the vapour or by evaporation into the surface from kinks existing on the surface (Burton et al.,1949). The rate of sintering between a plane and a sphere due to surface diffusion of this type has been considered by Cabrera (1950). If this treatment is extended to the sintering of two spheres, it may be shown that

$$\left(\frac{x}{r}\right)^5 = \frac{80\gamma\delta^3}{kTr^3}\,\frac{n_o\delta^3 D_s}{y_s}\,t \qquad (39)$$

where, n_o is the number of adsorbed molecules per cm^2 on a flat surface and y_s is the mean migration distance of molecules on the surface. Equation (39) shows the same dependence on time, t, and the radius, r, of the spheres as the equations previosly derived for evaporation-condensation by diffusion through the environmental gas and for volume diffusion through the spheres themselves.

2.6 Sintering by viscous or plastic flow

Frenkel (1945) has supposed that under the action of surface tension forces a solid might flow as a viscous liquid. This flow was assumed to arise from the diffusion of vacant lattice sites. Assuming that the material flowed as a Newtonian viscous liquid, of viscosity η, Frenkel derived the following expression for the rate of sintering

$$\left(\frac{x}{r}\right)^2 = \frac{3\gamma}{2\eta r} t \qquad (40)$$

where η is related to the diffusion coefficient D_V by

$$\frac{1}{\eta} = \frac{D_V \delta}{kT} \qquad (41)$$

Frenkel's treatment has been criticised by Nabarro (1948) who shows that the movement of lattice vacancies cannot, in a single crystal, result in viscous flow.

A similar expression to equation (40) may be derived for the case of plastic flow, apart from a different temperature dependent coefficient multiplying the time t. However, it is thought (Herring, 1953) that surface stresses will not normally cause appreciable plastic flow even at high temperatures.

2.7 Summary of equations

The equations for sintering that have been derived in the preceding pages may be summarized as follows.

1. Sintering by viscous or plastic flow

$$\left(\frac{x}{r}\right)^2 = \frac{3\gamma}{2\eta r} t \qquad \text{(eqn. 40)}$$

2. Sintering by evaporation-condensation

Case (i) Direct Transfer, $\lambda > \rho$

$$\left(\frac{x}{r}\right)^3 = \frac{12M\gamma p_o}{\rho^2 RTr^2} \left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} t \qquad \text{(eqn. 16)}$$

Case (ii) Diffusion Transfer, $\lambda < \rho$

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3}{kTr^3} \frac{\alpha}{\beta\left(\frac{kT}{p_o m D_E} + \frac{L_s^2 m}{\kappa kT^2}\right)} t \qquad \text{(eqn. 25)}$$

3. Sintering by volume diffusion

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3}{kTr^3} D_V t \qquad \text{(eqn. 32)}$$

4. Sintering by boundary diffusion

$$\left(\frac{x}{r}\right)^7 = \frac{112\gamma\delta^4}{\pi kTr^4} D_B t \qquad \text{(eqn. 37)}$$

5. Sintering by surface diffusion

$$\left(\frac{x}{r}\right)^5 = \frac{80\gamma\delta^3}{kTr^3}\ \frac{n_o\delta^3 D_s}{y_s}\ t \qquad \text{(eqn. 39)}$$

All of the above equations are of the form

$$\left(\frac{x}{r}\right)^n = \frac{B(T)}{r^m}\ t \qquad (42)$$

where, B(T) is a temperature dependent term and n and m are positive integers. The actual values of B(T), n and m depend on which of the mechanisms of sintering is considered.

In attempting to conclude which of the above mechanisms is responsible for sintering, the theoretical equation for the proposed mechanism should agree with the experimental results on the growth of the neck on all of the following points.

(a) Time dependence

(b) Particle size dependence

(c) Temperature dependence

(d) Absolute rate of growth

(e) Effect of environment

and, (f) Effect of added impurities.

Only when such general agreement is found can the mechanism of sintering be deduced with confidence.

2.8 Application of theory to the sintering of ice

Before describing the experimental results on the sintering of ice, the above theory will be applied to ice in order to deduce theoretically the mechanism of sintering that is to be expected.

The mean free path, λ, of a molecule in the vapour phase may be calculated from the kinetic theory expression

$$\lambda = \frac{kT}{\sqrt{2}\pi s^2 p} \qquad (43)$$

where, s is the diameter of a molecule and p the total pressure. For a water molecule in air at atmospheric pressure and a temperature of $-10^{\circ}C$ this gives a mean free path of approximately 10^{-5}cm. Now, for spheres 100μ in radius, ρ is of the order 10^{-4}cm., that is about 10λ. Sintering by evaporation-condensation will therefore take place by diffusion through the environment (Case ii) rather than by direct transfer (Case i). Under these conditions sintering by evaporation-condensation, volume diffusion and surface diffusion of the type considered by Cabrera,

will all show the same time dependence and particle size dependence. To decide which of these three mechanisms is likely to predominate in the sintering of ice, the absolute rates of sintering must be calculated for each of the three cases.

From equations (25), (32) and (39) it can be seen that the relative magnitudes of sintering by evaporation-condensation, volume diffusion and surface diffusion are respectively, $\frac{\alpha}{\beta\left(\frac{kT}{p_o m D_E} + \frac{L_s^2 m}{\mathcal{K} k T^2}\right)}$, D_V, and $\frac{4\delta^3 D_s n_o}{y_s}$. These terms may be called the "effective diffusion coefficients" for the three cases. Assuming for the moment that the condensation coefficient, α, is unity, at $-10^{\circ}C$ the effective diffusion coefficient for evaporation-condensation is approximately 3×10^{-7} $cm^2 sec^{-1}$. For volume diffusion the effective diffusion coefficient is simply D_V which, from radioactive measurements on the diffusion of tritons in ice (Riehl and Dengel, 1962), is 1.5×10^{-11} $cm^2 sec^{-1}$ at $-10^{\circ}C$.

In order to estimate a value for the contribution from surface diffusion it is to be noted that $D_s n_o$ may be written as $\nu e^{-(U_s + W_s)/kT}$ where, ν is the vibration frequency of

surface molecules which for ice is about $5 \times 10^{12} sec^{-1}$, U_s is the activation energy for surface diffusion and W_s is the energy required to take an isolated adsorbed molecule from the surface into the vapour phase. Although the actual value of $(U_s + W_s)$ is not known it is possible to state its minimum value. In order to take an adsorbed molecule off the surface at least one hydrogen-bond must be broken, the minimum value of W_s is therefore one-half of the latent heat of sublimation of ice. This also gives the minimum value of $(U_s + W_s)$ since U_s is a positive quantity. The mean migration distance, y_s, has been measured on the basal plane of ice by Hallett (1961) and also by Mason et al.(1963), y_s is approximately 4×10^{-4} cm at $-10^{\circ}C$. The maximum possible value of the effective diffusion coefficient for surface diffusion is therefore

$$\frac{4\delta^3\nu}{y_s} e^{-(U_s + W_s)} = \frac{4 \times 18 \times 5 \times 10^{12}}{6 \times 10^{23} \times 4 \times 10^{-4}} e^{-\frac{8.3 \times 10^{-13}}{2 \times 1.38 \times 10^{-16} \times 263}}$$

$$= 1.7 \times 10^{-11} \text{ cm}^2 \text{sec}^{-1}$$

The values of the effective diffusion coefficients for sintering by evaporation-condensation, volume diffusion and surface diffusion are therefore 3×10^{-7}, 1.5×10^{-11}, and $1.7 \times 10^{-11} cm^2 sec^{-1}$, respectively.

To summarize: on the basis of the above calculations it appears that the sintering of ice in air at atmospheric pressure will take place by the mechanism of evaporation from the surface of the spheres followed by diffusion through the environment and condensation in the concave region of the neck. If this is the case the size of the neck, x, between two spheres of radius r should vary with time, t, according to the relationship

$$\left(\frac{x}{r}\right)^5 \propto \frac{t}{r^3}$$

and should also show a variation with temperature given by the temperature dependent terms in equation (25). Variations in the nature of the environment might also be expected to effect the course of sintering. The experimental results that were obtained are discussed in Chapter 4.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Preliminary investigations

In the initial stages of the present investigation into ice sintering, the spheres of ice were obtained by freezing drops of water onto fine glass fibres. It is difficult to produce spheres much less than $\frac{1}{2}$ mm in diameter by this method, and the surfaces of the spheres are generally rather irregular in shape. If two such ice spheres are viewed under a microscope and then pushed gently into contact, the boundary of the contact region cannot be clearly seen, therefore, direct measurements of the radius of contact and its variation with time are not possible. As a result of this, attempts were made to develop a method for measuring the area of contact by means other than visual observation, but a sufficiently sensitive test of this type was not found. Eventually the problem was overcome by devising a method for producing ice spheres in the size range 20 to 300μ diameter to an accuracy of a few microns. The sphericity of these spheres was such that the neck between two particles in contact could be

clearly seen under a microscope and rates of sintering accurately measured. Before describing this method a short account will be given of two techniques for measuring the area of contact that were investigated but which were not subsequently used.

(i) Electrical conductivity method

Bowden and Tabor (1939) have shown that the junction conductance, c_j, between two metallic spheres of radius r, joined at contact by a circle of radius x ($x \ll r$) is

$$c_j = 2\lambda_s x \qquad (44)$$

where λ_s is the specific conductivity of the bulk material. By measuring the junction conductance between two sintering spheres it should be possible to determine the variation in the radius of contact, x, with time. Such a method is relatively simple for metal spheres because of the high value of the conductivity. Pure ice, on the other hand, has a specific conductivity of the order 10^{-9} $(\text{ohm-cm})^{-1}$ which, together with the small areas of contact involved in sintering, gives rise to a considerable constrictive resistance. This means that fairly high voltages must be applied across the ice spheres in order to produce measurable currents. The current, however, must not be sufficient to

cause the ice to melt. Kohlrausch (1900) has derived the following relationship between the potential difference, U, across the constriction and the maximum difference in temperature, Θ, between the interface and the bulk material

$$U^2 = 8 \int_0^{\Theta} \frac{\sigma}{\lambda_s} d\Theta \qquad (45)$$

where σ is the thermal conductivity of the material. With a steady potential, U, of 10 volts across the spheres, a current of 4×10^{-9} amperes was obtained, and the value of Θ calculated from equation (41) is approximately 10^{-6} °C, hence, the heating produced under these conditions is negligible.

Provided the specific conductivity, λ_s, in equation (44) remains constant with time, the junction conductance will increase linearly with the radius of the neck. Under these conditions the current should show a steady increase in value as sintering progresses. In the case of the sintering of ice, however, no such increase in current was observed experimentally. With a constant applied voltage across the ice spheres the current showed a steady decrease in value with time. This effect was subsequently found to be the result of a time variation in the conductivity of

ice. In experiments designed to measure the direct current conductivity of ice, Bradley (1956) has observed that the conductivity decreases slowly with time. He attributes this to the gradual decay with time of the proton migration in ice. Measurements of junction conductance were also attempted using alternating voltages but the current still showed a steady decrease with time. As a result of this effect no direct measurements on the rates of sintering between ice spheres could be obtained by methods involving electrical conductivity.

(ii) Thermal conductivity method

When two objects at different temperatures are brought into contact over a small area, the area of contact very quickly attains an intermediate temperature. Heat then flows into the colder material under relatively steady-state conditions at a rate which only depends on the initial temperature difference, the radius of the contact area, and the conductivity of the material.

Powell (1957) has recently described a simple instrument, known as a thermal comparator, which utilises the rate of heat flow across a constriction to measure either thermal conductivities or the cross-sectional area of the constriction.

The thermal comparator consists of two similar metal balls embedded into a block of thermally insulating material, one of the balls is flush with the under-surface of the block whilst the other is slightly proud of the surface. When the block is placed onto a flat surface the protruding ball makes contact with the surface over a small area, whereas, the other ball does not come into contact with the surface. If both balls are now quickly raised to a high temperature, the subsequent rate of loss of heat of the ball in contact with the flat surface will exceed that of the other ball due to the additional rate of cooling through the contact region. The difference in the rates of fall of temperature of the two balls may be determined by fixing a thermocouple to each ball and connecting these in opposition so that the differential voltage can be recorded.

If the test surface and the ball in contact with it are made from the same material of thermal conductivity σ and specific heat c, it may be shown that the initial rate of fall in temperature of the ball due to conduction across an interface of radius x is

$$\frac{dT}{dt} = \frac{2\sigma x}{cW} T_o \qquad (46)$$

where W is the mass of the ball and T_o the original temperature difference between the ball and the test surface. By measuring dT/dt experimentally it should be possible to find the radius of contact, x, by means of equation (46).

Two phosphor-bronze balls, 2 mm in diameter, were embedded into a block of balsa wood in the manner described above. The upper surfaces of both balls could be touched simultaneously with the tips of the two prongs of a copper fork which passed through holes in the top of the balsa wood. By heating the handle of the fork, equal quantities of heat could be quickly conducted along the prongs and transferred to the two balls. The fork could then be withdrawn and the rates of fall in temperature of the two balls recorded by means of thermocouples. Test runs showed that when both balls cooled under similar conditions in air, the initial rates of fall in temperature were equal. When one of the balls was in contact with the test surface, however, the two rates of fall in temperature were markedly different.

To extend the use of the thermal comparator to measurements of rates of sintering between ice surfaces, the lower halves of both metal balls were coated with a layer of ice.

The comparator was then placed onto a block of ice at $-10^{\circ}C$ when sintering took place between the ice sphere and the ice block with which it was in contact. At given intervals of time equal quantities of heat were quickly transferred to both balls by means of the copper fork. On withdrawing the fork the difference in the rates of fall in temperature of the two balls was measured with the differential thermocouple.

In the case of the ice coated surfaces the differential temperature effect observed was much smaller than that obtained with metals. This difference arises for two reasons. Firstly, the thermal conductivity, σ, of ice is about two orders of magnitude smaller than that of metals. Secondly, the temperature difference, T_o, used with ice cannot be made too large or the ice will melt. For example, with metal spheres T_o is usually about $50^{\circ}C$, whereas with ice it cannot be made much more than $5^{\circ}C$. It can be seen from equation (46) that both of these effects will cause a reduction in the magnitude of dT/dt. As a result of this it was not possible to make the thermal comparator sensitive enough to detect the small changes in area produced by the sintering of ice. It is possible that the method could be

made sufficiently sensitive to measure sintering rates in metals where dT/dt can be made as much as three orders of magnitude greater than for ice.

A full description will now be given of the experimental method that was finally adopted for measuring the rates of sintering between two ice spheres.

3.2 Production and freezing of uniform drops of water

Uniform drops of water over a considerable size range were obtained by using a resonating hypodermic needle of the type first described by Mason et al. (1963). This consisted of a hypodermic needle, through which water was forced under pressure, rigidly fixed to the diaphragm of a vibrating headphone. By adjusting the frequency of the vibrations the needle could be made to resonate. In this condition the water was thrown off in a number of stable streams. Each stream consisted of numerous individual drops, uniform in size to $\pm 2\mu$. By varying the resonating frequency and the pressure head of water, a $1\frac{1}{2}$ inch long needle of 30 gauge could be made to produce drops from 20μ to 300μ in diameter.

Drops greater than 300μ diameter were obtained by passing

a fine fibre of glass wool through one of the streams from the vibrating needle. The number of drops collected on the fibre depended on the speed with which it was passed through the stream; by varying this speed, drops of diameters from 300μ to 1 mm were obtained.

The apparatus used for freezing water drops of 20μ to 300μ diameter into polycrystalline ice spheres is shown in Fig. 10. Water drops thrown from the vibrating hypodermic needle fell through a hollow metal tube two feet long which was 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 ice spheres, uniform in size to within a few microns. The larger drops collected on glass wool were frozen by direct cooling in a refrigerator. Ice produced in this way was quite often free of air bubbles, or contained just one large air inclusion. The polycrystalline structure of these ice spheres was clearly revealed by viewing them with transmitted white light through crossed polaroids. Under these conditions the randomly oriented crystals comprising the sphere produce a patchwork of colour (Fig. 11)

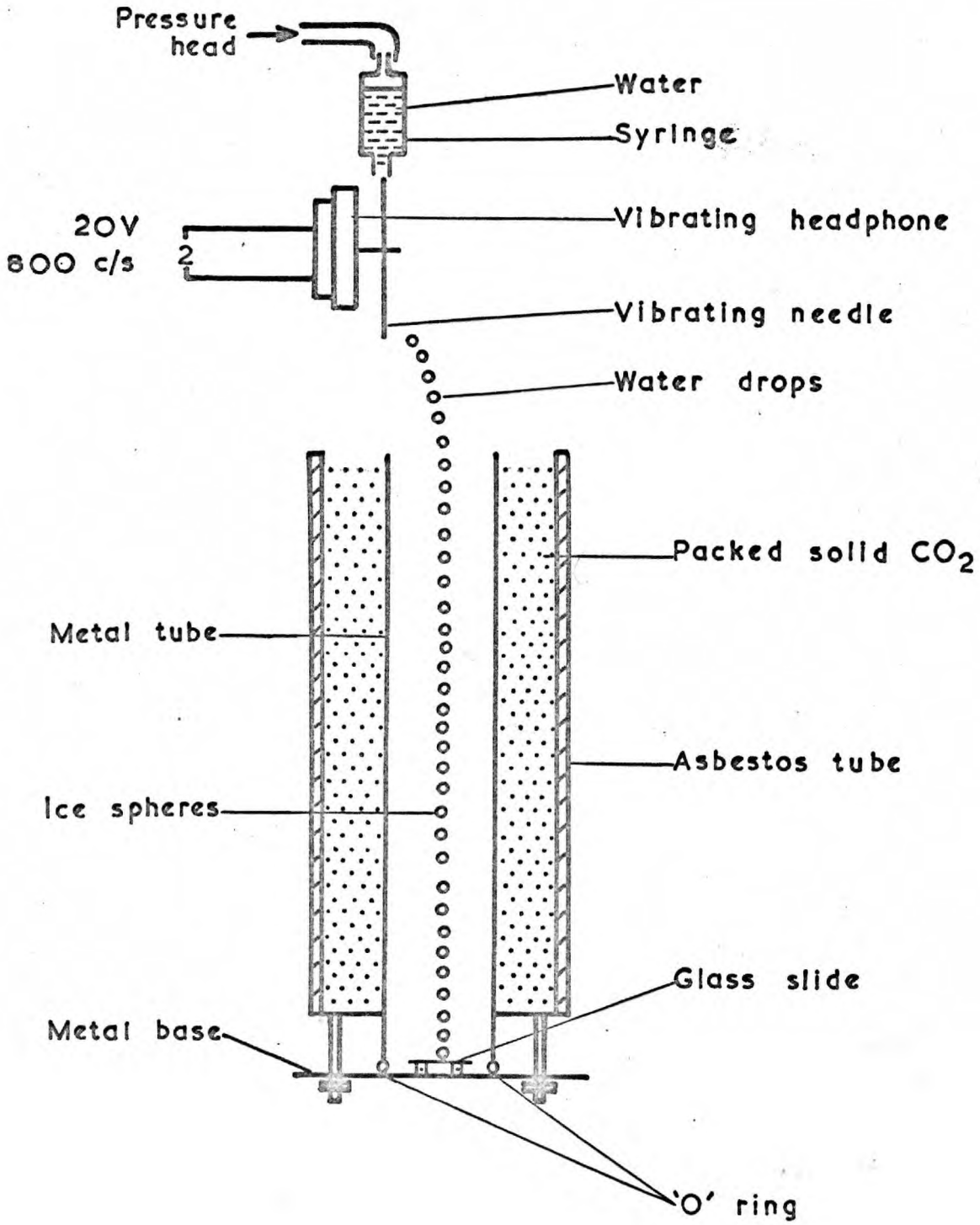


FIG.10 Method for producing ice spheres 100μ – 500μ diameter

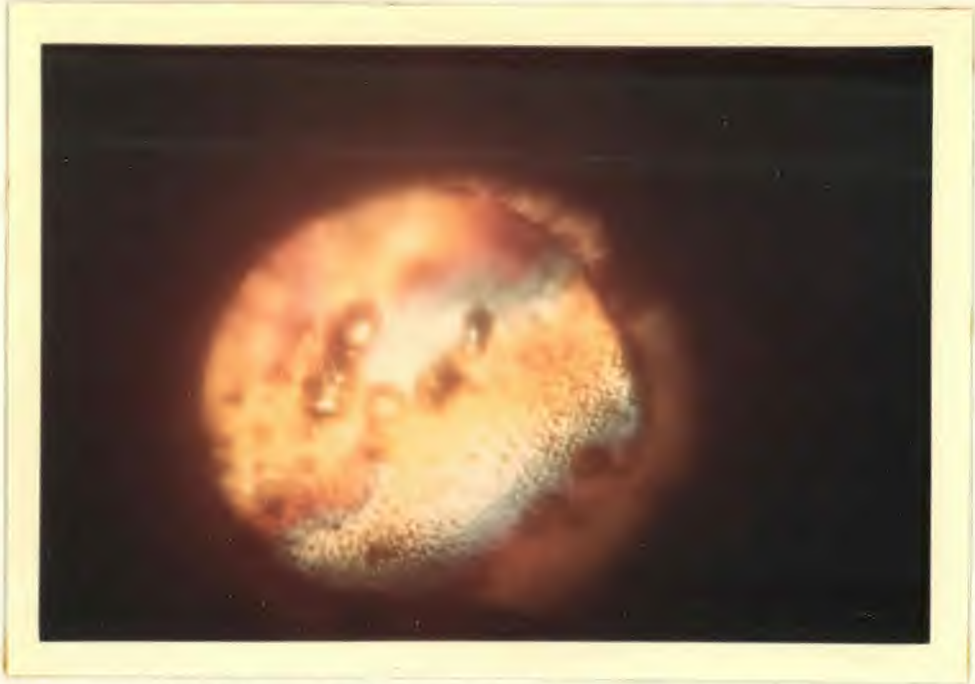
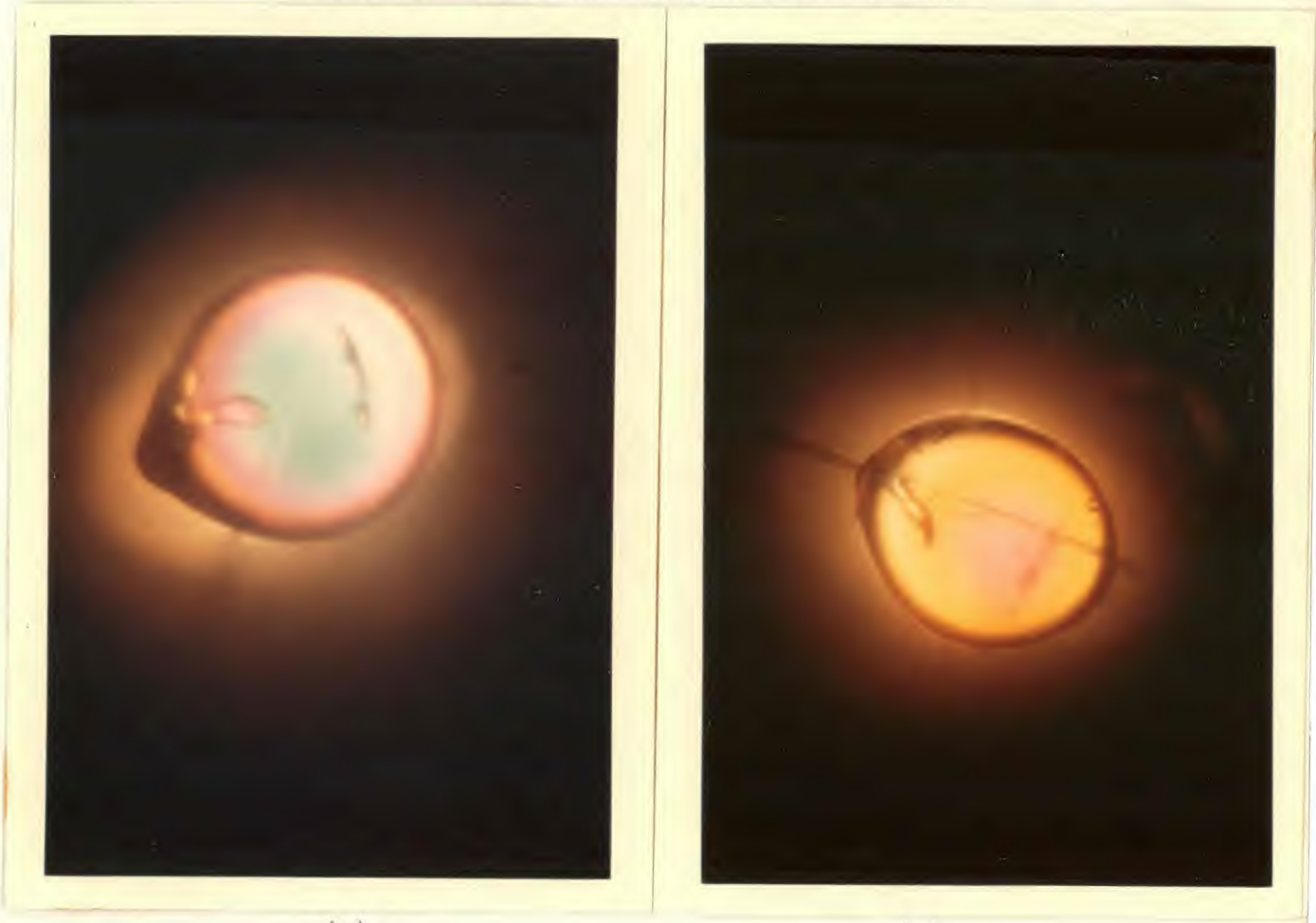


FIG. 11 A POLYCRYSTALLINE SPHERE OF ICE



(a) (b)

FIG. 12 SINGLE CRYSTALLINE SPHERES OF ICE

Particular care was taken at all times to keep the ice spheres as clean as possible. After freezing the drops the only solid surface with which the ice spheres came in contact was the clean glass slide. In the majority of cases distilled water was used, but some measurements were also taken on ice spheres frozen from water which had been distilled and then passed through an ion-exchange column.

A few experiments were carried out using drops frozen in liquid nitrogen but this method was thought to be unsatisfactory for the following reasons:

(a) The ice contained numerous small air bubbles.

(b) Many of the spheres shattered on freezing.

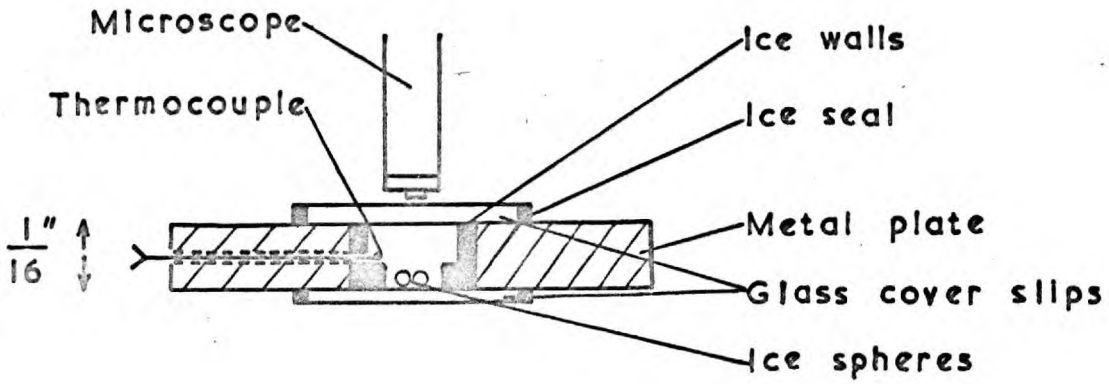
(c) Impurities in the liquid nitrogen were likely to have been deposited onto the ice surfaces.

Rates of sintering were also measured for single crystal ice spheres. It is possible to freeze a water drop into a single crystal provided that nucleation can be made to occur at a temperature above about $-10^{\circ}C$. This was achieved by placing a few fine particles of silver iodide onto a fibre of glass wool, upon which a small water drop was collected

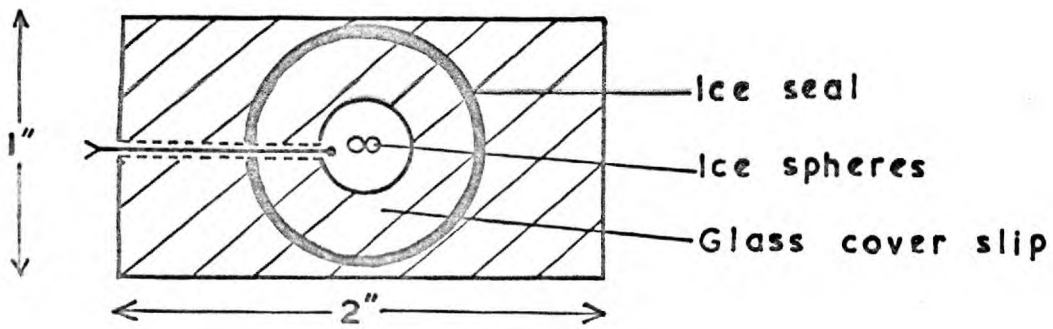
and then cooled slowly to a few degrees below $0^{\circ}C$. The presence of the silver iodide caused nucleation to occur at about $-4^{\circ}C$, producing a single crystal of ice. When viewed with transmitted white light through crossed polaroids, the single crystals gave rise to a series of brightly coloured concentric rings (Fig. 12 and Frontispiece) that were easily distinguishable from the random colouring produced by polycrystalline ice spheres.

3.3 Measurement of rates of sintering

For measurements of rates of sintering in air at atmospheric pressure the ice spheres were contained inside a small sealed chamber (Fig. 13) which consisted of a thin glass base and top and metal walls. The metal plate containing the chamber was attached to the stage of a microscope and the whole assembly was placed in a refrigerator controlled to $\pm\frac{1}{2}^{\circ}C$. Temperatures were measured by means of a thermocouple which lay inside the chamber close to the spheres. The walls of the chamber were covered with ice to ensure an ice-saturated environment. Spheres as small as 50μ in diameter could be kept in this chamber for several days without showing any signs of evaporating.



Side view



Plan

FIG.13 Ice saturated chamber in which growth of "ice-bridge" is observed

The hundreds of ice spheres collected from the freezing tube were shaken into the chamber before freezing the glass top into position. The contents were then scanned under a microscope to find two spheres connected by a small neck; in a few cases, however, an initial contact was made by gently pushing two ice spheres together prior to sealing the lid of the chamber. Measurements on the growth of the neck between two ice spheres were made directly through a microscope using a $\frac{1}{2}$ inch objective and a x 10 micrometer eyepiece. With this arrangement the size of the neck could be measured to an accuracy of a few microns. The light source used for illuminating the spheres was filtered by several inches of heat absorbing glass, and was only switched on during the brief periods when measurements were being made.

Rates of sintering were also measured in air below atmospheric pressure; the apparatus that was used for this is illustrated in Fig. 14. After placing the ice spheres in the chamber and pushing two suitable spheres gently into contact, the glass cover slip was sealed down by freezing it onto the perspex chamber. Air was then evacuated from the chamber until the required pressure was reached. The

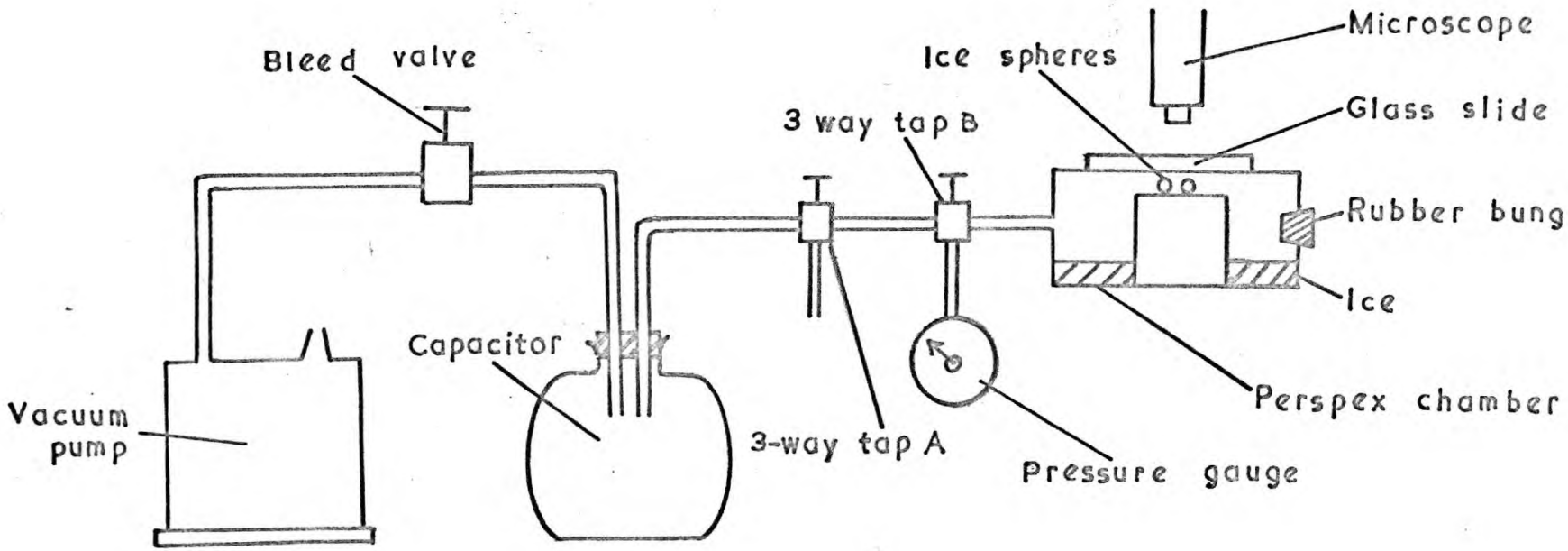


FIG. 14 Apparatus for measuring sintering in air at reduced pressure and in an atmosphere of hydrogen

3-way tap B was then turned so as to form a closed system consisting of the chamber and the pressure gauge. With this arrangement it was possible to have a continuous measure of the pressure in the chamber and therefore to ensure that no leaks occurred during an experiment. The same apparatus was used for measuring rates of sintering in an atmosphere of hydrogen. In this case, after placing the spheres in the chamber and sealing the lid, the chamber was first evacuated and then filled with hydrogen gas.

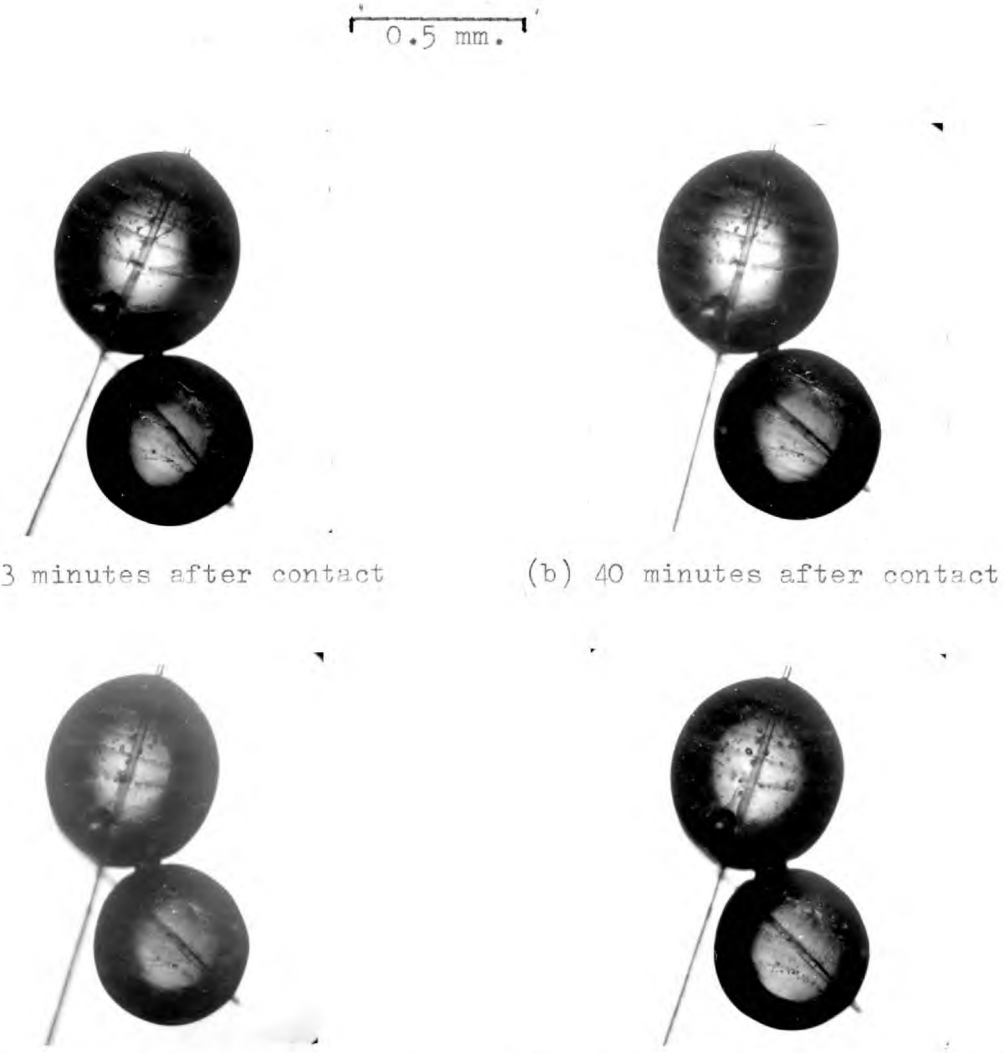
CHAPTER 4.

RESULTS AND DISCUSSION

4.1 Sintering of ice in air

The rate of growth of the neck between two ice spheres was measured for spheres in the size range 50 to 700μ diameter, at temperatures between $-3^{\circ}C$ and $-20^{\circ}C$. The photomicrographs shown in Fig. 15 illustrate four stages in the growth of the neck between two ice spheres at $-5^{\circ}C$. These show quite clearly the extent of the neck growth which occurred over a period of about five hours following the initial contact between the spheres.

The results of measurements on the rates of sintering between polycrystalline ice spheres are shown in Figs. 16 to 20 where $\log\left(\frac{x}{r}\right)$ is plotted against $\log t$. It can be seen from these graphs that, after an initial period of about ten minutes, the experimental points lie on straight lines. It has been shown in Chapter 2 (eqn. 42) that the graph of $\log\left(\frac{x}{r}\right)$ against $\log t$ should be a straight line of slope n, where n can take the values of 2, 3, 5 or 7 depending on which mechanism of material transport predominates. The departure from linearity exhibited by the



(a) 3 minutes after contact

(b) 40 minutes after contact

(c) 153 minutes after contact

(d) 320 minutes after contact

FIG. 15 FOUR STAGES IN THE GROWTH OF THE NECK BETWEEN TWO ICE SPHERES AT $-5^{\circ}C$

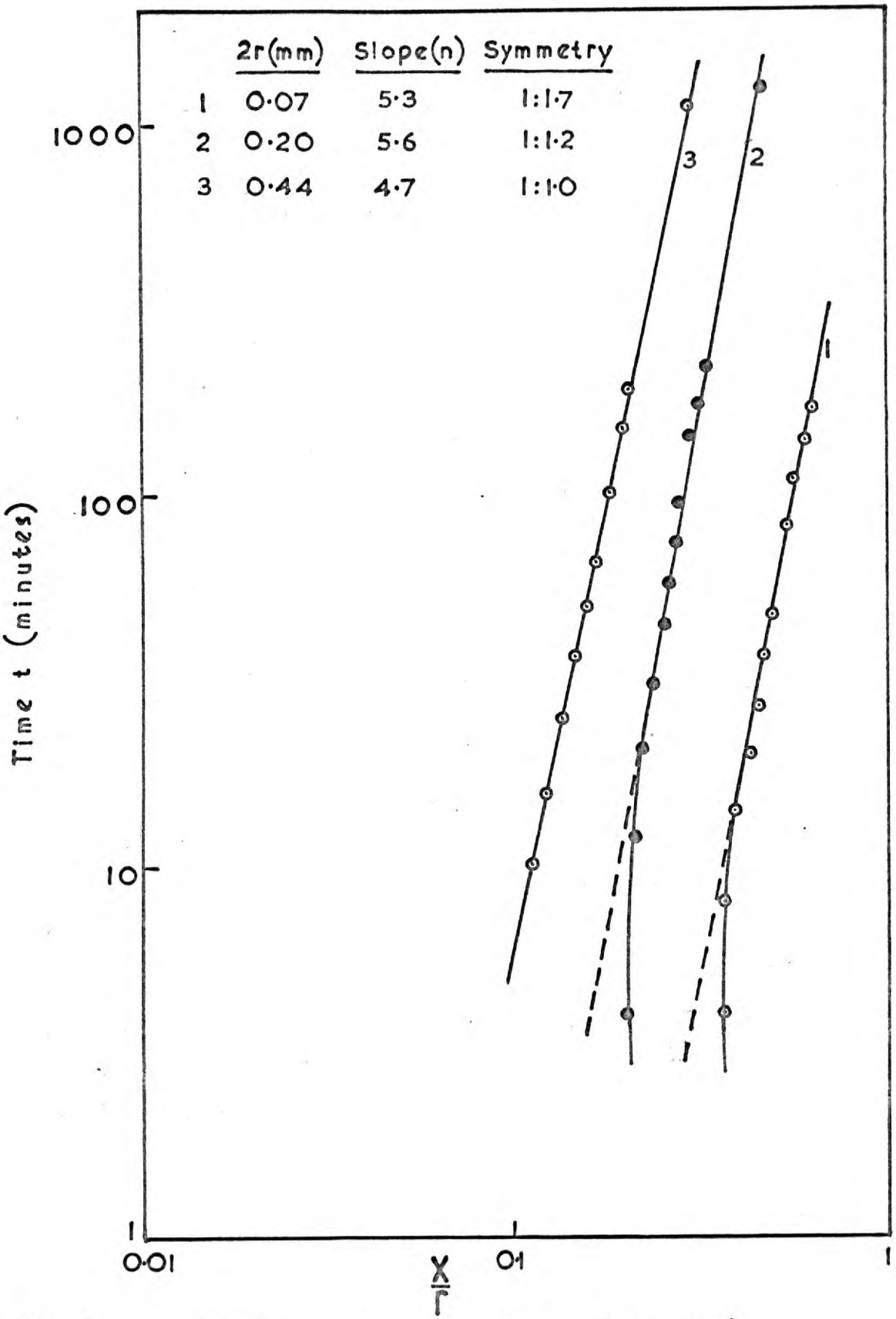


FIG. 16 Rates of sintering for polycrystalline ice spheres at $-3^{\circ}C$

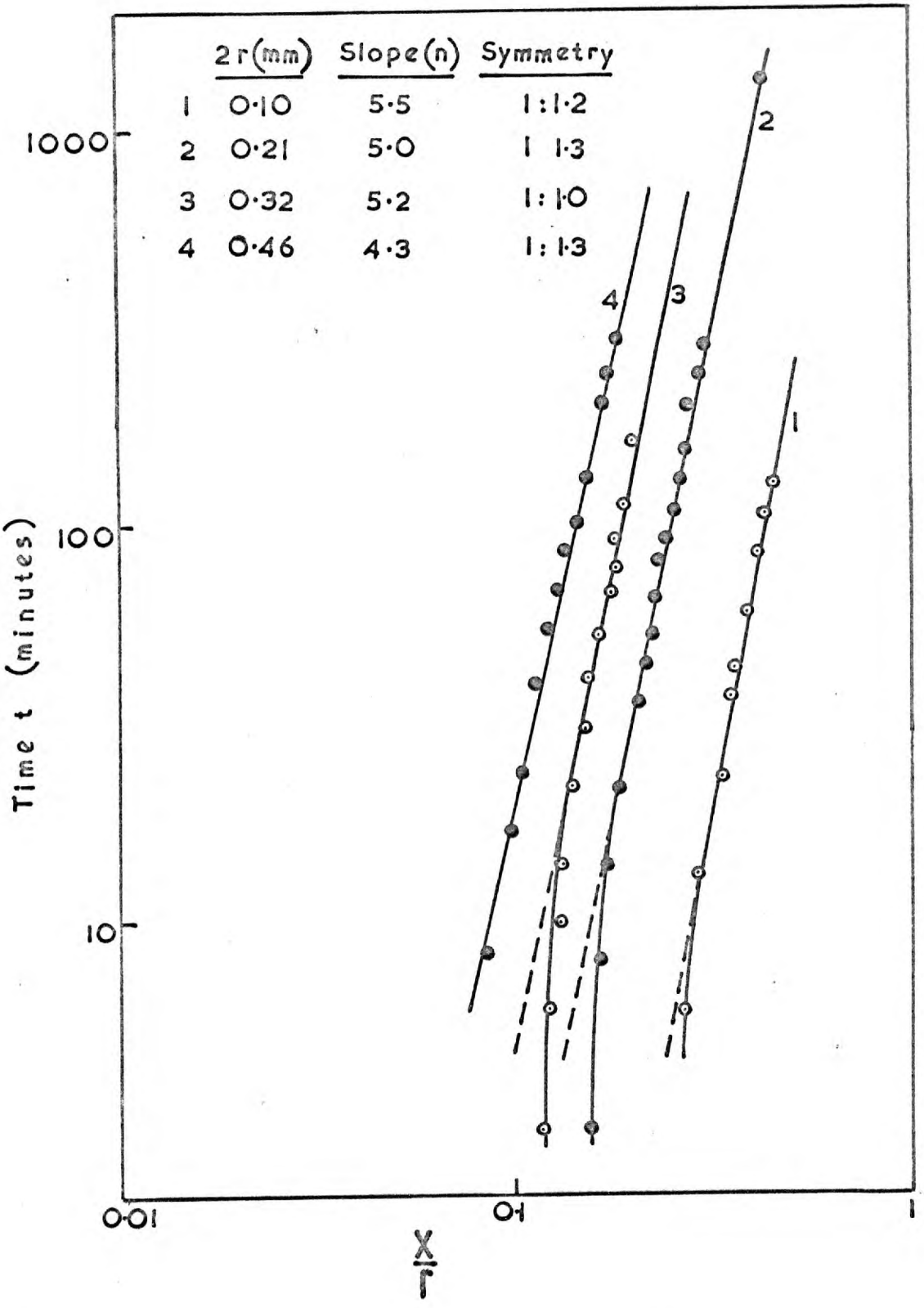


FIG. 17 Rates of sintering for poly-crystalline ice spheres at $-5^{0}C$

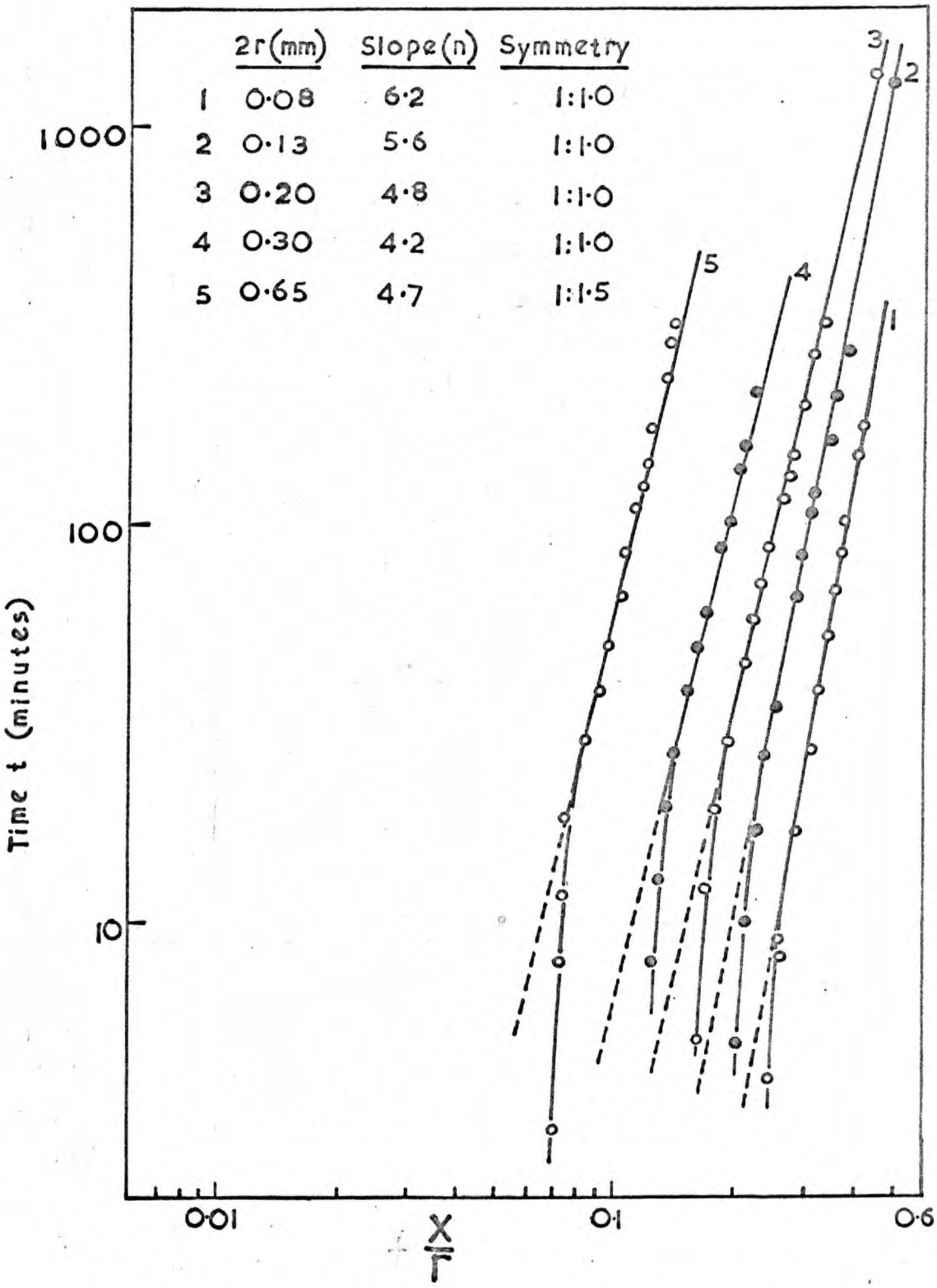


FIG. 18 Rates of sintering for poly-crystalline ice spheres at -10°C

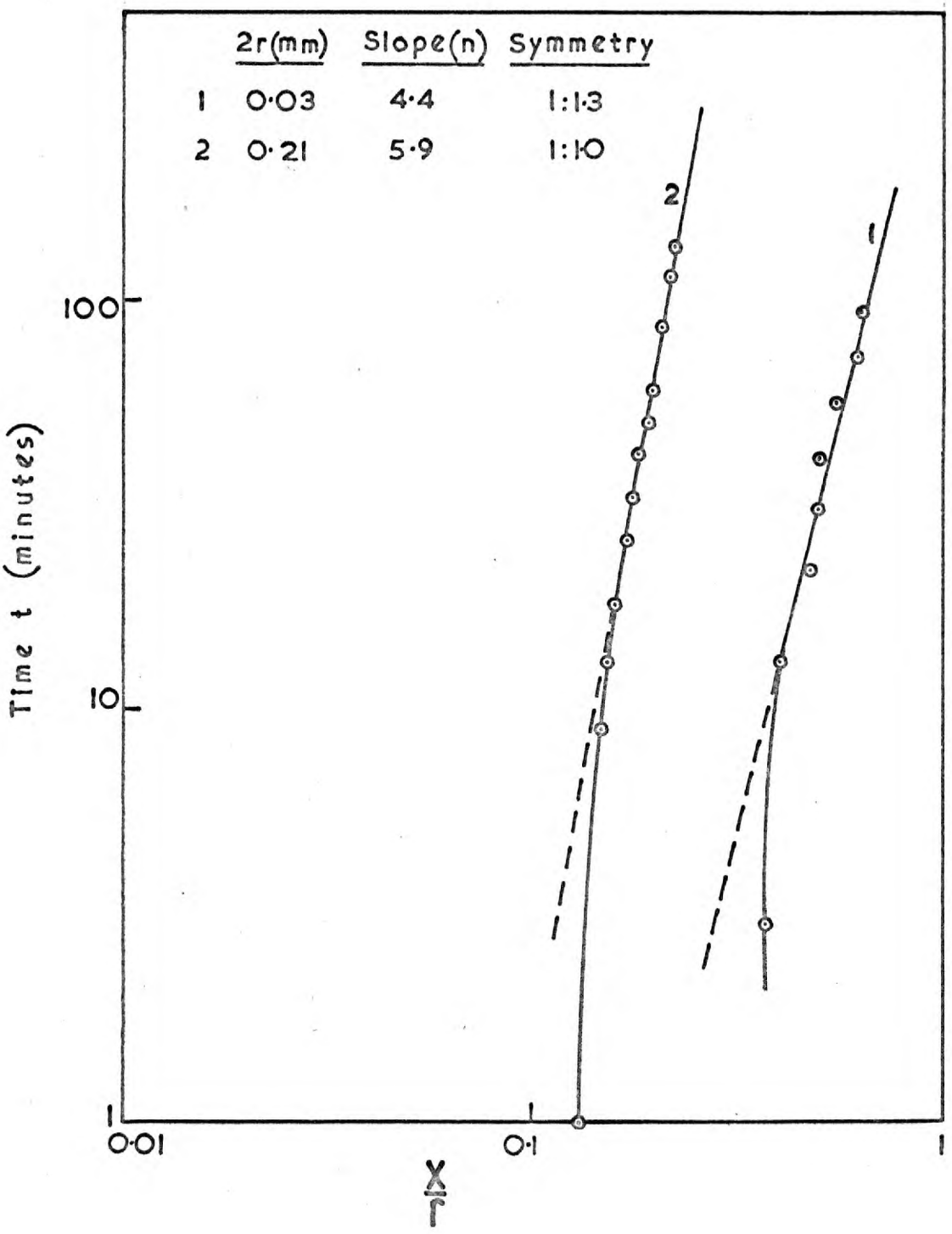


FIG. 19 Rates of sintering for poly-crystalline ice spheres at $-15^{0}C$

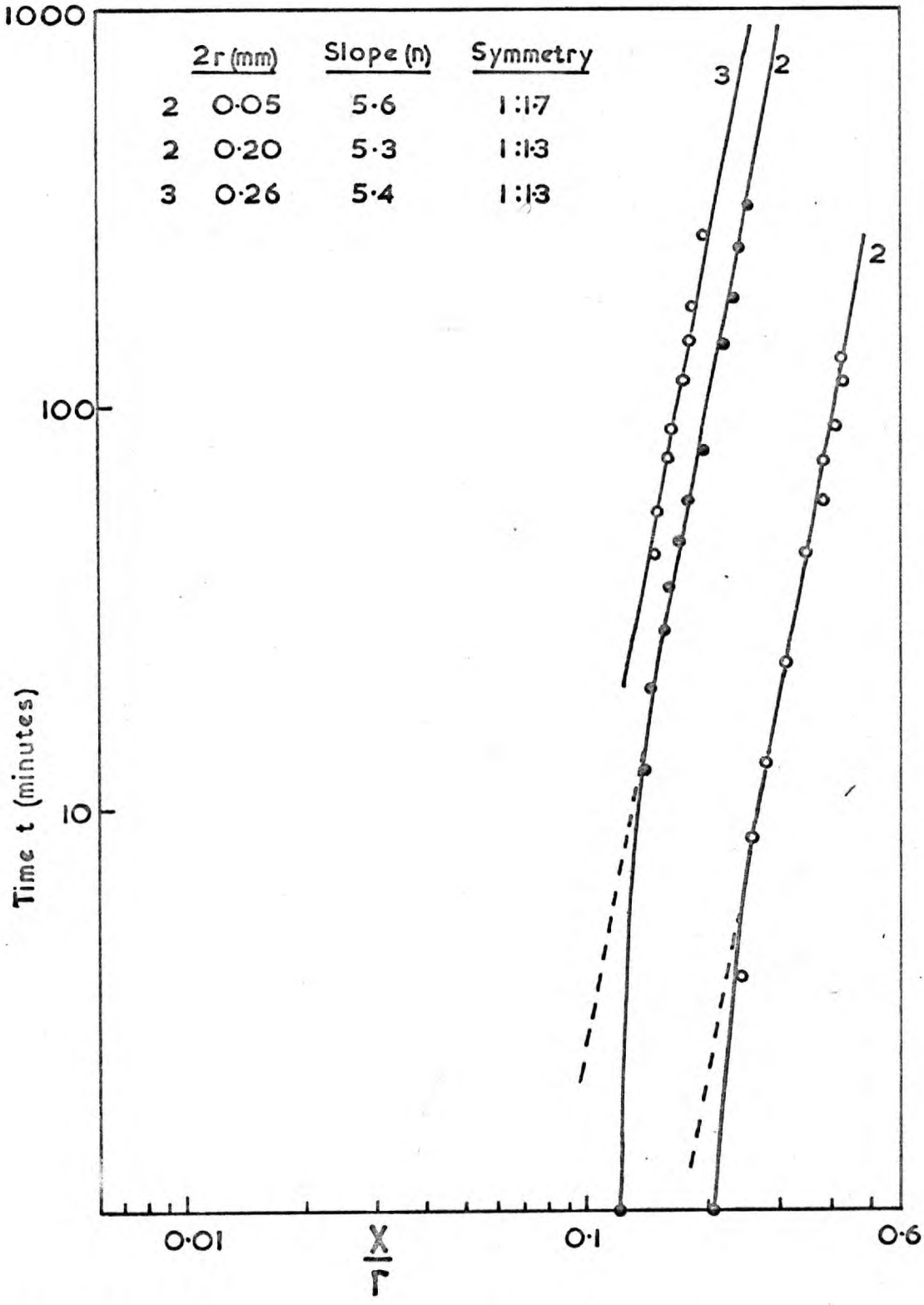


FIG. 20 Rates of sintering for polycrystalline ice spheres at -20°C

majority of the experimental results during the first ten minutes or so of sintering can be explained by a slight modification in equation (42) to take account of the experimental method that was used.

Equation (42) has been derived on the assumption that time t is measured from the moment of contact between the spheres, that is, t = 0 when x = 0. In the majority of cases, however, the spheres were in contact for some unknown time before the first measurement was taken. In these cases, time t was measured from the moment at which the first measurement was taken, therefore equation (42) becomes

$$(\frac{x}{r})^n = \frac{B(T)}{r^m} (t + t_o) \qquad (47)$$

where t_o is defined by

$$(\frac{x}{r})^n = \frac{B(T)}{r^m} t_o \qquad (48)$$

x_o being the radius of the neck at the first measurement. Now, whilst t is small compared with t_o, x/r will not increase greatly with t, but when t becomes much greater than t_o equation (47) approximates closely to equation (42). Under these circumstances log (x/r) increases

linearly with log t, the slope being given by n. Taking the mean value of all the slopes shown in Figs. 16 to 20 the value of n is found to be (5.2 ± 0.5).

In addition to measuring the overall size of the neck as a function of time, measurements were taken of the relative growth of the neck on either side of the original point of contact. In this way the symmetry of the growth could be found. In Figs. 16 to 20 the ratio of the growths on either side of the original point of contact are given under the heading "symmetry"; these figures show that, in the majority of cases, reasonably symmetrical growth took place. A number of cases were observed, however, in which one side of the neck grew at the normal rate whilst the other side showed little or no growth. A possible cause for this behaviour is discussed later.

The value of m in equation (42) can be found from the effect of the size of the spheres on the time required for x/r to reach a given value. In Fig. 21 the time required for the neck to grow to one-quarter the diameter of the spheres is plotted against the radius of the spheres. The possible theoretical values of m are 1, 2, 3 and 4, and from Fig 21 the slopes of the lines at -3°, -10° and

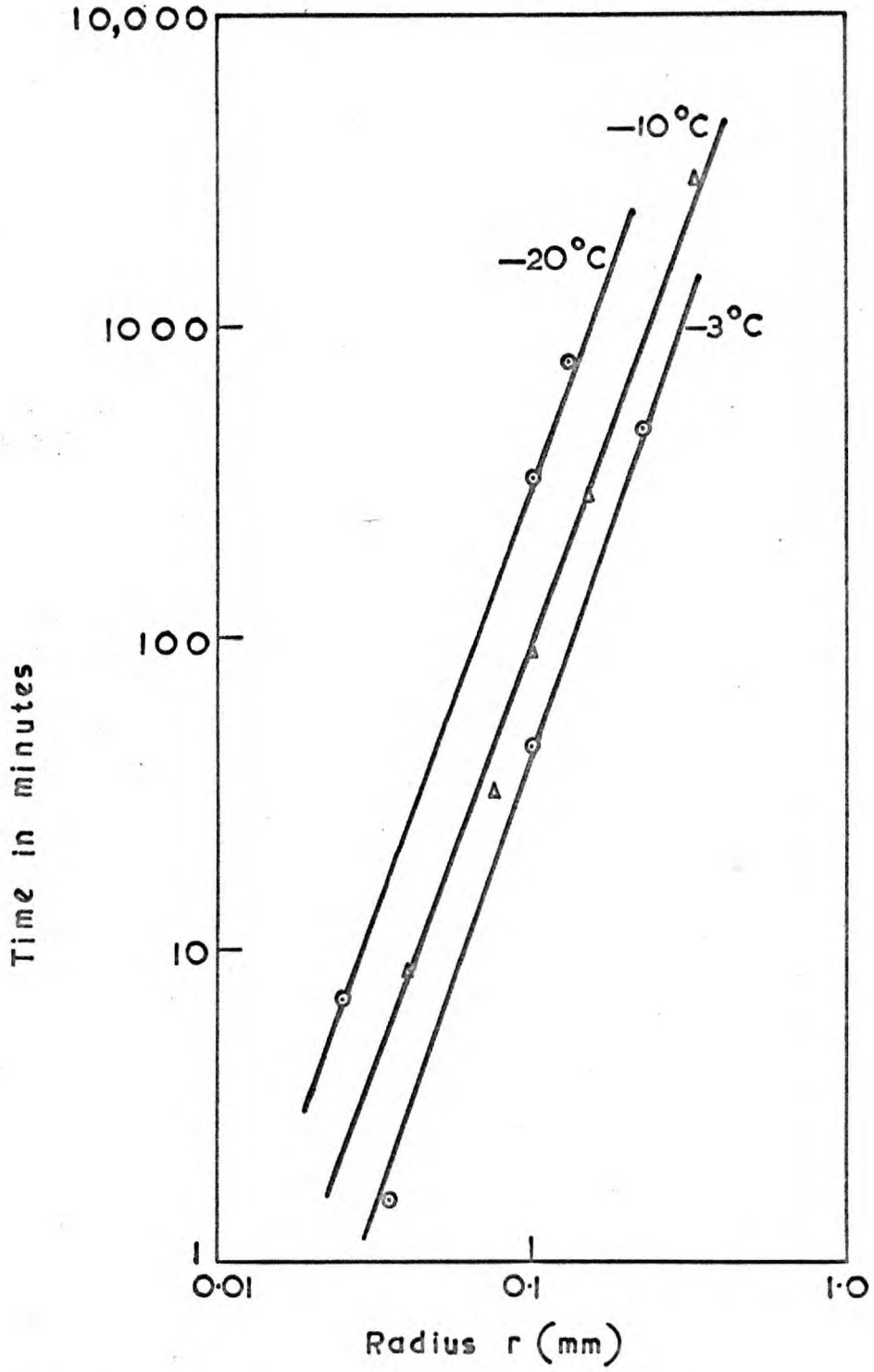


FIG. 21 Time required to reach a specific geometry $\frac{x}{r} = 0{\cdot}25$

$-20^{\circ}C$ are 2.9, 2.8 and 2.8 respectively. These values agree closely with the theoretical value of 3 for m.

A comparison of the above results with the theory shows that there are three possible mechanisms for the sintering of ice, namely, evaporation-condensation by diffusion through the environment, volume diffusion, or surface diffusion; in each of these cases the theoretical values of n and m are 5 and 3 respectively. To decide which of these three mechanisms is responsible for the sintering, the absolute rates of material transfer must be compared with the experimental results. The effective diffusion coefficient for evaporation-condensation (Case ii) is $\frac{\alpha}{\beta\left(\frac{kT}{D_E m p_o} + \frac{L_s^2 m}{\mathcal{K} kT^2}\right)}$, for volume diffusion D_V, and for surface diffusion $\frac{4\delta^3 D_s n_o}{y_s}$; from equations (25), (32) and (39) these are all equal to $\left(\frac{x}{r}\right)^5 \frac{k}{20\gamma\delta^3} \frac{r^3 T}{t}$. If t is taken as the time required for $x/r = 0.25$, this last expression becomes $\frac{2r^3 T}{t}$

The time taken for $x/r = 0.25$ can be found from the experimental results shown in Figs. 16 to 20. Fairly large

experimental errors are involved in this determination, for slight changes in the slope of the best line through the experimental points in Figs. 16 to 20 will give rise to large variations in the time taken for x/r to reach a given value. This experimental error is inevitable in view of the fact that the size of the neck increases as $t^{1/5}$.

The experimental values of $\frac{2r^3T}{t}$ as a function of temperature are shown in Fig. 22; the scatter in the results is seen to be about a factor of 2. Two of the possible theoretical values of $\frac{2r^3T}{t}$, as given by the effective diffusion coefficients, are also shown in Fig. 22. Those for evaporation-condensation by diffusion through the environment have been calculated on the assumption of a condensation coefficient, α, equal to unity, and values of D_E, p_o, L_s and $\mathcal{K}$ have been taken from Mason (1957). The corresponding curve for volume diffusion in Fig. 22 has been plotted from values of D_V given by Riehl and Dengel (1962). The effective diffusion coefficient for sintering by surface diffusion is not shown in Fig. 22 since exact values are not known, but

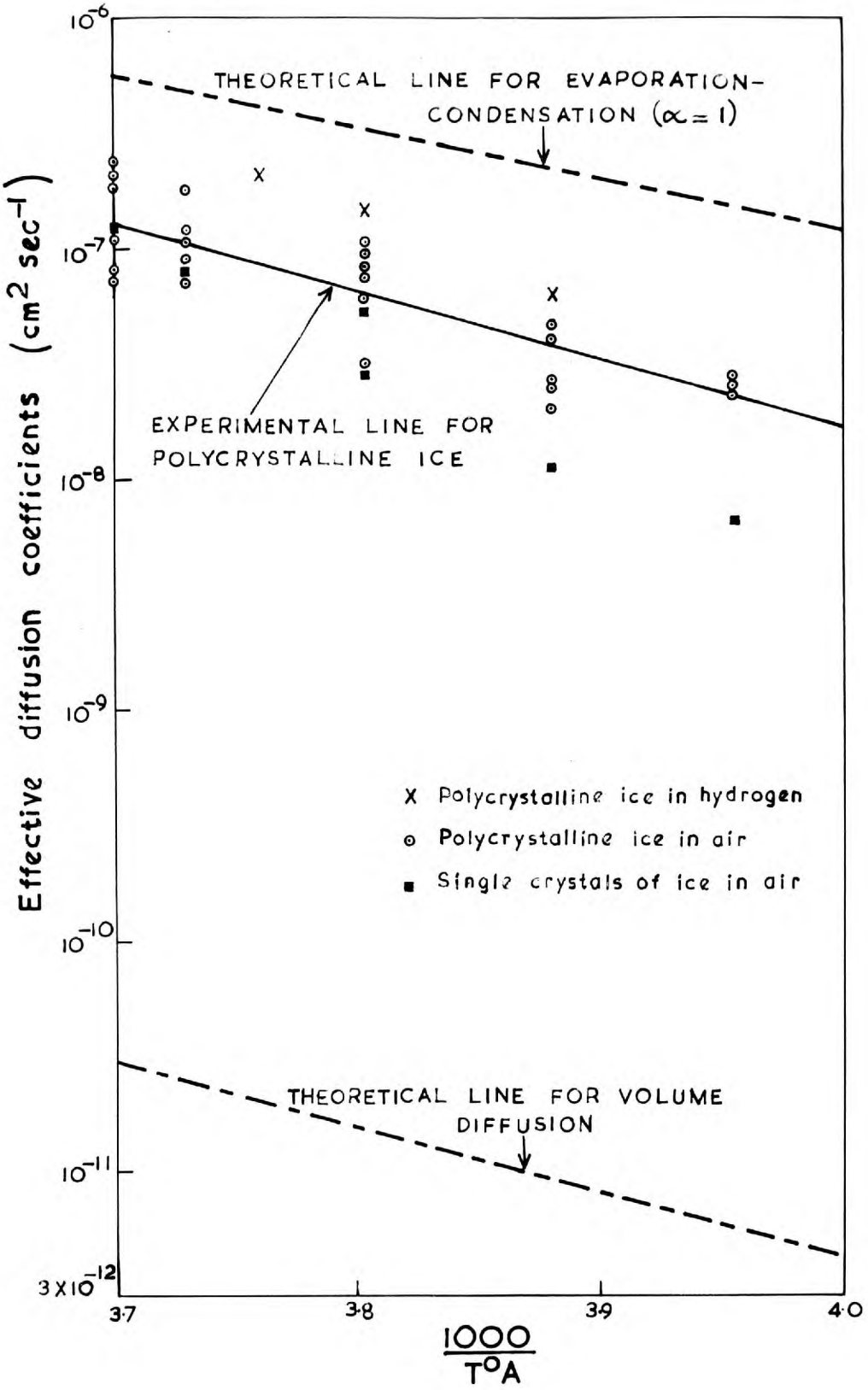


FIG. 22 Comparison of effective diffusion coefficients

it has already been shown (page 70) that the contribution from surface diffusion is of the same order as volume diffusion.

A comparison of the experimental results with the theoretical curve for volume diffusion shows that sintering by this mechanism is three orders of magnitude less than that observed experimentally; hence, volume diffusion cannot be the predominant mechanism in the sintering of ice. The theoretical values for evaporation-condensation, on the other hand, are in fairly close agreement with the experimental results, being about five times greater at $-10^{\circ}C$. A factor of five is not much greater than the total error to be expected from the approximations made in the theory and the experimental errors. It is also to be remembered that the theoretical curve for evaporation-condensation represents the maximum possible values since the condensation coefficient, α, has been taken as unity. Finally, the temperature dependence of the experimental results is similar to that predicted by the evaporation-condensation theory which has an activation energy of 11kcal/mole, compared with the experimental value of (14 ± 3)kcal/mole. It is concluded on the basis of these observations that the

sintering of ice takes place by a process involving evaporation from the convex surface of the spheres, followed by diffusion through the environment, and condensation to the concave neck.

Very few measurements have been made on the condensation coefficient, α, of ice. Davis (1961) has obtained a few isolated values of α for polycrystalline ice at -80°C which vary from 0.4 at an excess pressure of 1×10^{-5} mm Hg to 0.7 at 5×10^{-5} mm Hg. The present results indicate that between -3° and -20°C, and at atmospheric pressure, the average value of the condensation coefficient for polycrystalline ice cannot be much less than 0.2.

It is to be expected that the condensation coefficient will depend on the crystallographic orientation of the substrate crystal and also on the smoothness of the surface on the molecular scale. It has been observed by Hallett (1961), for example, that in some cases the basal plane of ice may have a condensation coefficient approaching zero. This was deduced from the fact that even in an environment of 50% supersaturation, thin plates of oriented ice crystals showed no increase in thickness. During the growth of the neck in sintering, the surface of the crystal is continually

changing, hence α in equation (25) will represent some average value which is typical of a polycrystalline ice surface. It has already been mentioned that on a few occasions portions of the neck exhibited no growth at all, this was probably due to the substrate crystal having a particularly low value of α.

Some experiments were also performed on the sintering between two spheres of ice in the form of single crystals. The results obtained were similar to those for polycrystalline ice spheres with n and m equal to 5 and 3 respectively. Below about $-10^{\circ}C$, however, the experimental values of $\frac{2r^3T}{t}$ for the single crystals fall below those for polycrystals (Fig. 22). This means that transfer by evaporation-condensation is less for single crystals than for polycrystals below about $-10^{\circ}C$. The reason is probably that a polycrystalline surface has many high index faces which give rise to greater rates of evaporation than do the surfaces of single crystals. This effect will be smaller at higher temperatures where the rates of evaporation for both single crystals and polycrystals is fast. The condensation coefficient might also be higher on a polycrystalline surface than on a single crystal.

The results described above were obtained with ice frozen from distilled water. Measurements were also made on spheres frozen from tap water and conductivity water; in both cases the results obtained were practically identical with those previously described.

4.2 Effect of environment

All of the results that have been described so far were obtained with the ice spheres situated in the chamber shown in Fig. 13. This provides an environment of air at atmospheric pressure which is saturated with respect to a plane surface of ice. The effect of varying the environmental conditions was investigated and the results obtained will now be described.

The first condition to be changed was the degree of saturation of the surrounding air. The ice spheres were situated in an open environment of air which was sub-saturated with respect to ice. The spheres could be kept under these conditions for about an hour before showing signs of evaporation. Sintering was observed to take place during the first twenty minutes or so but after this time very little growth of the neck took place. This

observation shows that in the initial stages of sintering the environmental conditions far removed from the neck have little effect on sintering. The supply of vapour to the neck must therefore come from portions of the spheres very close to the neck region which are able to maintain the air in the immediate vicinity of the neck near ice saturation. This fact supports an assumption previously made in deriving equation (25) that the change in pressure from p_ρ to p_o occurs over a distance of the order of the radius of the neck ρ (see page 51). Eventually a stage is reached in the growth of the neck when the environmental conditions will predominate: in a sub-saturated environment no further growth of the neck will then be possible.

If sintering takes place by a process involving diffusion through the environment, changes in the coefficient of diffusion of water vapour through the environment, D_E, should have an affect on the rate of sintering. It must be remembered, however, that the rate at which the neck can grow is determined not only by D_E but by the rate at which the latent heat of sublimation can be removed from the neck. This effect has already been discussed and is

included in equation (25) through the term $\frac{L_s^2 m}{\mathcal{K}kT^2}$.

$$\left(\frac{x}{r}\right)^5 = \frac{20\gamma\delta^3}{kTr^3} \frac{\alpha}{\beta\left(\frac{kT}{D_E m p_o} + \frac{L_s^2 m}{\mathcal{K}kT^2}\right)} t \qquad \text{(eqn. 25)}$$

In air at atmospheric pressure the numerical values of $\frac{kT}{D_E m p_o}$ and $\frac{L_s^2 m}{\mathcal{K}kT^2}$ at $-10^\circ C$ are 2.2×10^6 and 1.1×10^6 cm. sec. gm^{-1}. Hence both terms are of the same order of magnitude, which indicates that under normal conditions in air the growth of the neck is already limited to some extent by the rate at which the latent heat can be dissipated.

If the pressure is reduced to 1/10 of an atmosphere, D_E will be increased by a factor of 10, but the thermal conductivity $\mathcal{K}$ will remain unchanged. The net result is that the rate of sintering is only increased by a factor of 2.5. This effect is not much greater than the experimental error involved in measuring the rate of sintering. Measurements were taken in air at 1/10 atmospheric pressure but no increase in the growth rate was observed.

In an atmosphere of hydrogen gas both D_E and $\mathcal{K}$ are increased, the former by a factor of 3.4 and the latter by

a factor of 7. Substituting these values into equation (25) it is found that the rates of sintering in hydrogen should be greater than in air by a factor of 4. The experimental results obtained in hydrogen are included in Fig. 22 where it can be seen that the rates of sintering were about $2\frac{1}{2}$ times faster than those in air. In view of the experimental error involved this result is in fair agreement with that predicted by the theory.

If the diffusion term $\frac{kT}{D_E m p_o}$ in equation (25) is increased due to a reduction in either D_E or p_o, the effect on the rate of sintering may be considerable. For example, if the product $p_o D_E$ is decreased by a factor of 10, the rate of sintering will be decreased to 1/7 of its value in air at atmospheric pressure. It is well known that if a small piece of ice is immersed in silicone oil, very little evaporation takes place even over a period of weeks; this is a result of the saturation vapour pressure, p_o, of water vapour in silicone being extremely small. The rate of sintering of ice in an environment of silicone should therefore be considerably less than that in air.

Two ice spheres were immersed in silicone oil and then

brought gently into contact. With the silicone maintained at a constant temperature of $-3^{\circ}C$, the point of contact between the spheres was observed periodically for several days: no growth of the neck could be detected throughout this period. A reduction in the rate of growth also took place when the spheres were immersed in kerosene, the rate being about 1/10 of that in air. In terms of the evaporation-condensation mechanism these results are readily explained by the very small value of equilibrium vapour pressure p_o in equation (25). The small amount of growth observed in kerosene is explained by the slightly higher value of p_o in kerosene compared with that in silicone.

If volume diffusion were responsible for the sintering of ice, the only effect an environment of silicone could have would be to reduce the value of the interfacial surface energy, γ, in equation (32). A maximum reduction in γ would occur if the silicone oil completely wetted the ice, in this case the interfacial energy wouldsimply be the difference between the surface tensions of ice-air and silicone-air. The surface tension of the silicone was 21 dynes/cm , hence the maximum effect the silicone could have

would be to reduce γ from 100 to 79 dynes/cm . This would produce a mere 20% reduction in the rate of sintering. The drastic reduction in the rate of sintering produced by silicone is therefore strong evidence that volume diffusion is not responsible for the sintering of ice.

If the sintering of ice took place by surface diffusion, immersion in silicone oil might change the rate of sintering for two reasons. Firstly, the surface energy, which provides the driving force for sintering, would be reduced in the manner discussed above. Secondly, the surface diffusion coefficient, D_s, in equation (39) would be changed due to the presence of the silicone oil. The magnitude of the change in D_s cannot be predicted, therefore, it is not possible to conclude a priori that the effect of silicone oil described above eliminates the possibility of sintering by surface diffusion. However, additional experimental evidence was obtained which suggests that the contribution from surface diffusion to the sintering of ice is negligible.

It has been demonstrated experimentally by Hallett and Mason (1958) that the presence of small traces of silicone vapour or iso-butyl alcohol vapour profoundly influences the growth habits of ice crystals grown from the vapour.

They attribute this effect to changes in the relative rates of diffusion on the basal and prism faces of ice. If surface diffusion were predominant in the sintering of ice, it is likely that the presence of these vapours would change the rate of sintering due to changes produced in D_s. Rates of sintering were measured in the presence of silicone vapour and iso-butyl alcohol vapour, these were found to have no measurable effect on the rate of growth of the neck. It may be concluded, therefore, that surface diffusion plays a minor role in the sintering of ice.

4.3 Effect of added impurities

The first group of impurities that was investigated comprised ammonium fluoride (NH_4F), hydrofluoric acid (HF) and ammonia (NH_3). Solutions of these substances were prepared in concentrations of 10^{-2} molar. Drops of the solutions were then frozen into solid spheres and rates of sintering measured in the usual manner. The results obtained with these mixed crystals showed somewhat greater experimental scatter than was found with pure ice spheres; but, in general, the rates of sintering were slightly reduced by the presence of these impurities (Fig. 23).

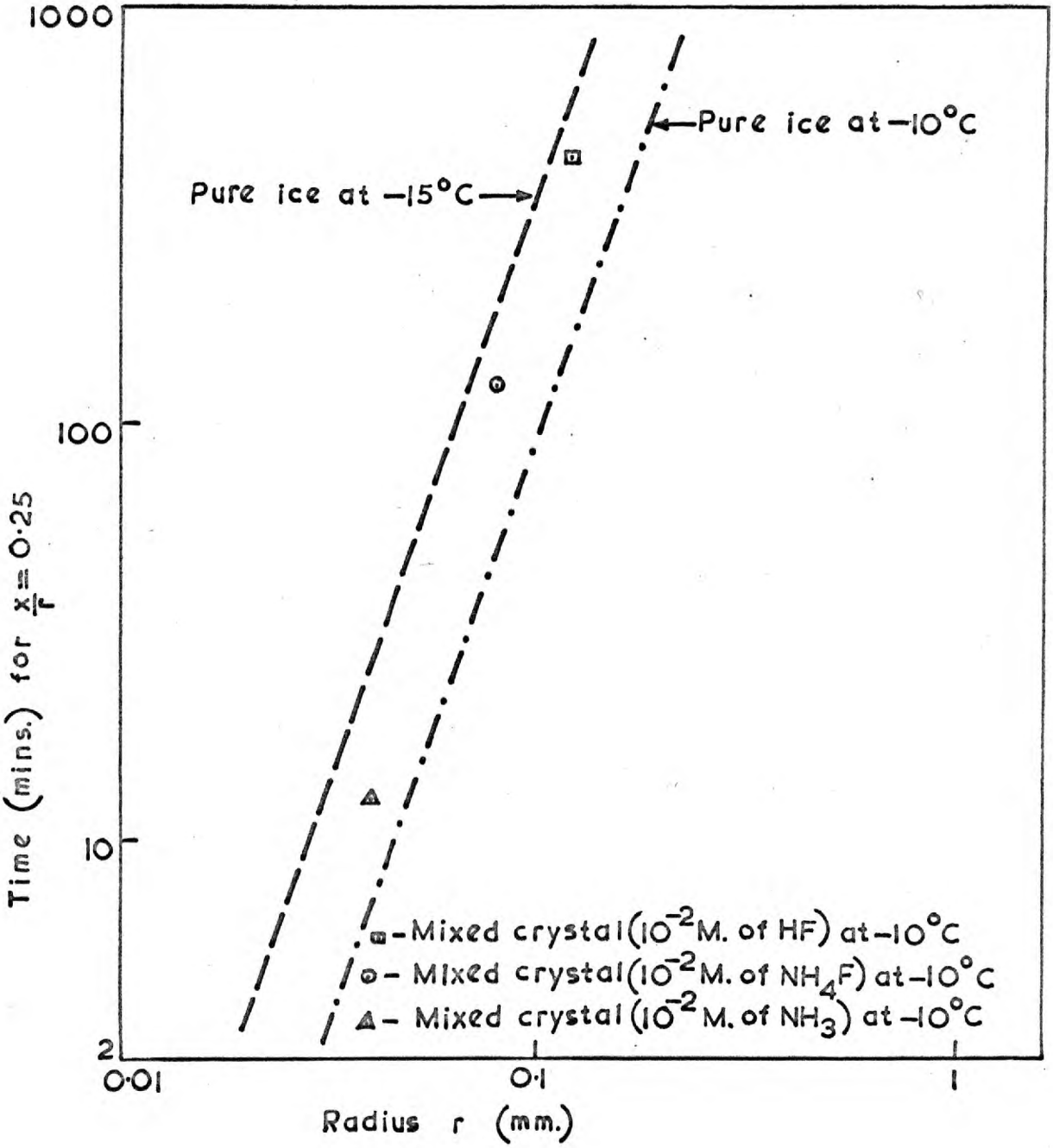


FIG. 23 Comparison of rates of sintering for mixed crystals with pure ice

The magnitude of the effect that dissolved impurities should have on sintering may be estimated as follows. The lowering of the vapour pressure produced by a dissolved salt is given by

$$p_o - p_o' = P \frac{id}{s} \qquad (49)$$

where, p_o and p_o' are the equilibrium vapour pressures of the pure solvent and the solution, d and s are the densities of the vapour and the solution, i is van't Hoff's factor, and P the osmotic pressure. P may be written as

$$P = cRT \qquad (50)$$

c being the concentration of the solution in moles/litre and R the gas constant. Now, the impurities being considered dissociate into two ions in water hence i = 2, and putting $c = 10^{-5}$, equations (49) and (50) give a depression in the vapour pressure of $(p_o - p_o') = 6 \times 10^{-4}$ mb. This will not produce a vapour pressure at -10°C over a mixed crystal equal to that at -13°C over pure ice, (Fig. 23).

The variable results obtained with mixed crystals were probably due to the differing amounts of impurity actually incorporated on the surface of the spheres compared with that in the volume. Results obtained with higher

concentrations of salts, to be described below, show quite clearly that when a solution droplet is frozen the solute can become highly concentrated on the surface of the crystal. Hence, ice spheres frozen from solutions of 10^{-2} molar may have much higher concentrations than this at the surface. Therefore a value of 6×10^{-4} mb represents the minimum depression in the vapour pressure that can be produced by a 10^{-2} molar solution.

The second class of impurities investigated were surface active agents such as cetyl trimethyl ammonium bromide (CTMAB) and sodium hexadecyl sulphate (NaCS). These substances should effect the coefficient of surface diffusion, D_s. The method employed was to place small pieces of the surface agents in contact with pure ice spheres and then observe if any alteration occurred in the rate of sintering. Both CTMAB and NaCS were used in this way but neither was found to influence the sintering process. It must be concluded that these surface active agents do not increase the surface diffusion to such an extent that it becomes the predominant mechanism of sintering. Any decrease that may have been produced in the surface diffusion coefficient would not, of course, be detected by these experiments.

An interesting phenomenon was observed in the case of ice crystals produced from a solution of 1% NaCl. The spheres were maintained at a temperature of $-10^{\circ}C$ and appeared on first sight to be quite solid. But, on bringing two of the spheres into contact a very rapid growth of the neck took place. Within a minute or so this produced a neck of the size that would have taken several hours with pure ice spheres. A similar effect was observed with ice spheres froma 1% NH_4F solution. Fig. 24 shows the rate of growth of the neck at $-10^{\circ}C$ between ice spheres frozen from a 1% NH_4F solution. The measurements were taken from a series of time-lapse photographs (N.B. in Fig. 24 time is given in seconds). The actual rate of material transfer in this case is nearly 300 times greater than that for pure ice ! This effect is obviously due to the presence of a thin layer of liquid on the surface of the spheres. This is produced by the preferential freezing of the pure water which leaves behind a highly concentrated salt solution on the surface of the sphere which has a melting point of well below $0^{\circ}C$.

The series of photographs shown in Fig. 25 illustrate a sequence of events that was observed on a number of

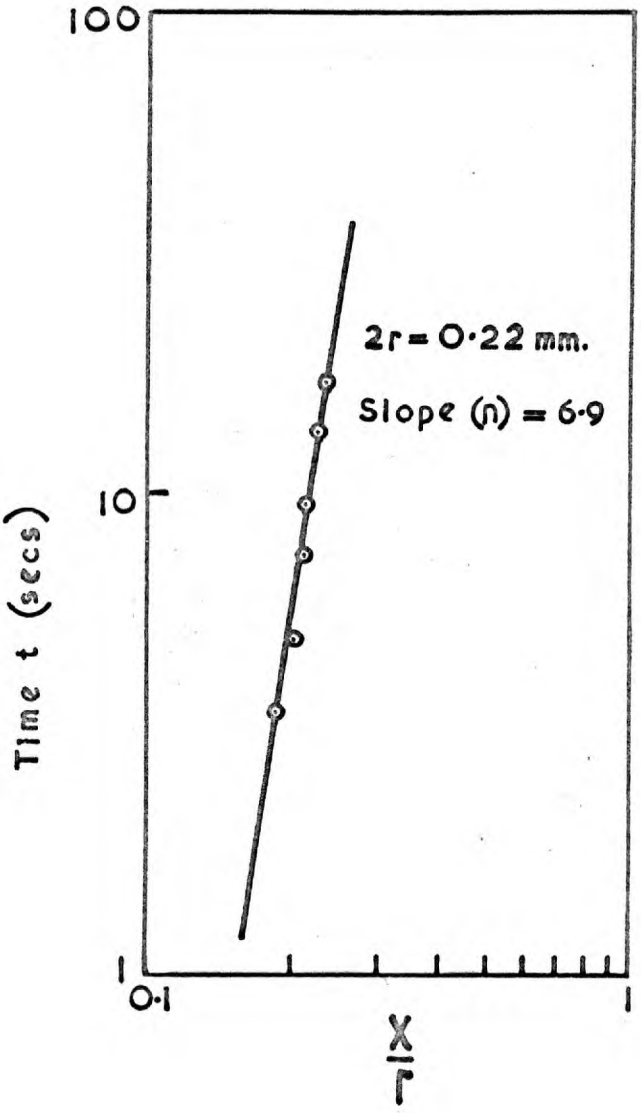
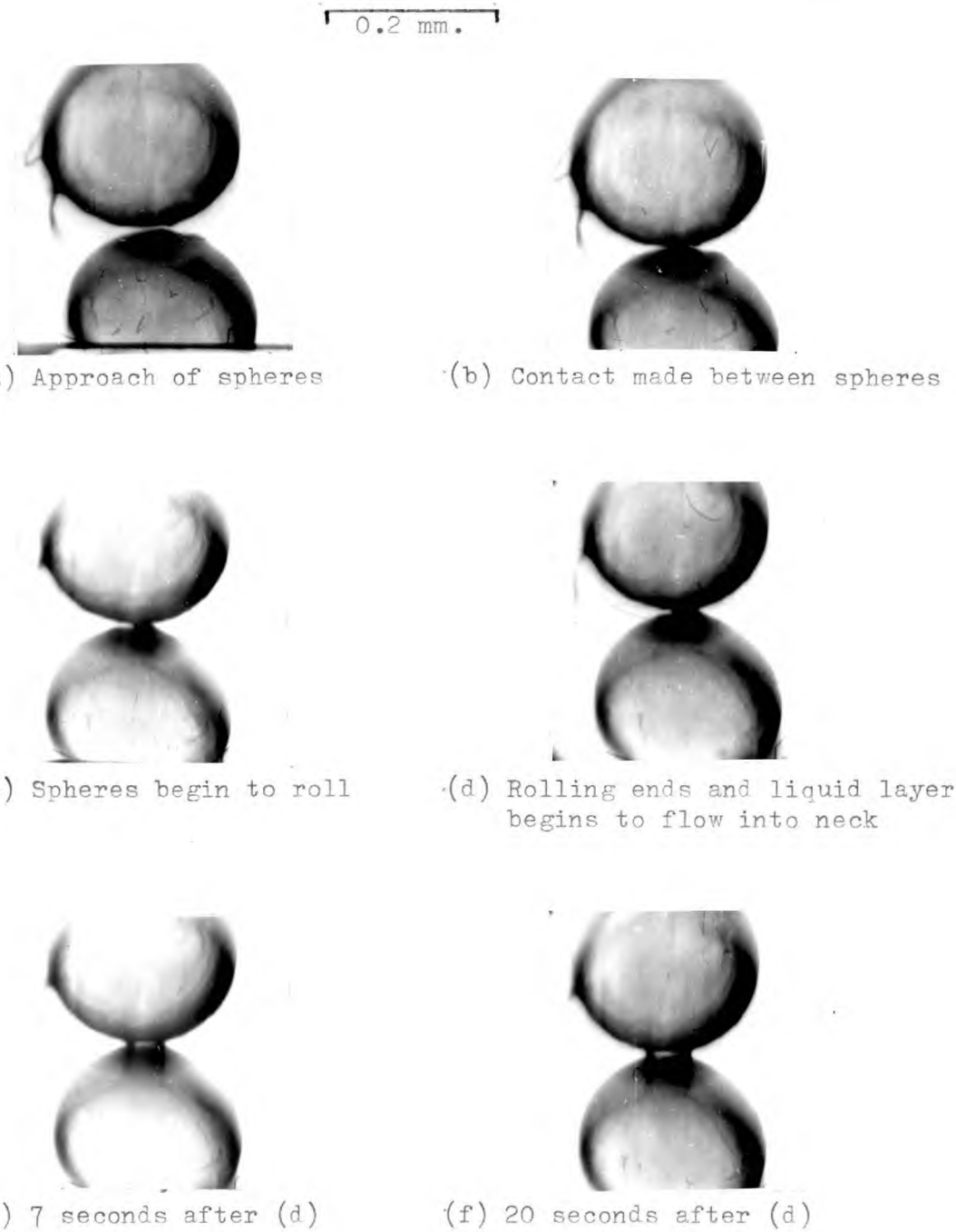


FIG. 24 Rate of sintering for ice spheres frozen from 1% NH_4F solution and exhibiting a surface liquid layer at $-10^{\circ}C$



(a) Approach of spheres

(b) Contact made between spheres

(c) Spheres begin to roll

(d) Rolling ends and liquid layer begins to flow into neck

(e) 7 seconds after (d)

(f) 20 seconds after (d)

FIG. 25 FLEXIBLE ADHESION AND FLOW OF LIQUID LAYER AT $-10^{\circ}C$ BETWEEN ICE SPHERES FROZEN FROM 1% NH_4F SOLUTION

occasions when using spheres frozen from 1% salt solutions. This consisted of a rotation of the two spheres on being brought into contact, followed by the rapid flow of liquid into the contact region. This phenomenon is obviously similar to that observed by Nakaya and Matsumoto (1954) and has been discussed in Chapter 1. The present experiment demonstrates quite clearly that the rotation is due to an actual liquid layer on the surface resulting from the lowering of the melting point by the highly concentrated salt solution.

4.4 Sintering of D_2O ice

Several measurements were taken on the rates of sintering of ice spheres frozen from "heavy" (D_2O) water of 99.7% purity. The results obtained were similar to those of pure ice, but the actual rates of sintering were lower than those measured for H_2O ice at the same temperature. The results are shown in Fig. 26 where it can be seen that the rates of sintering of D_2O ice at $-10^{\circ}C$ corresponds to those for H_2O ice at $-14^{\circ}C$. This result is predicted by equation (25) for sintering by evaporation-condensation, for the equilibrium vapour pressure, p_o, of D_2O ice at $-10^{\circ}C$

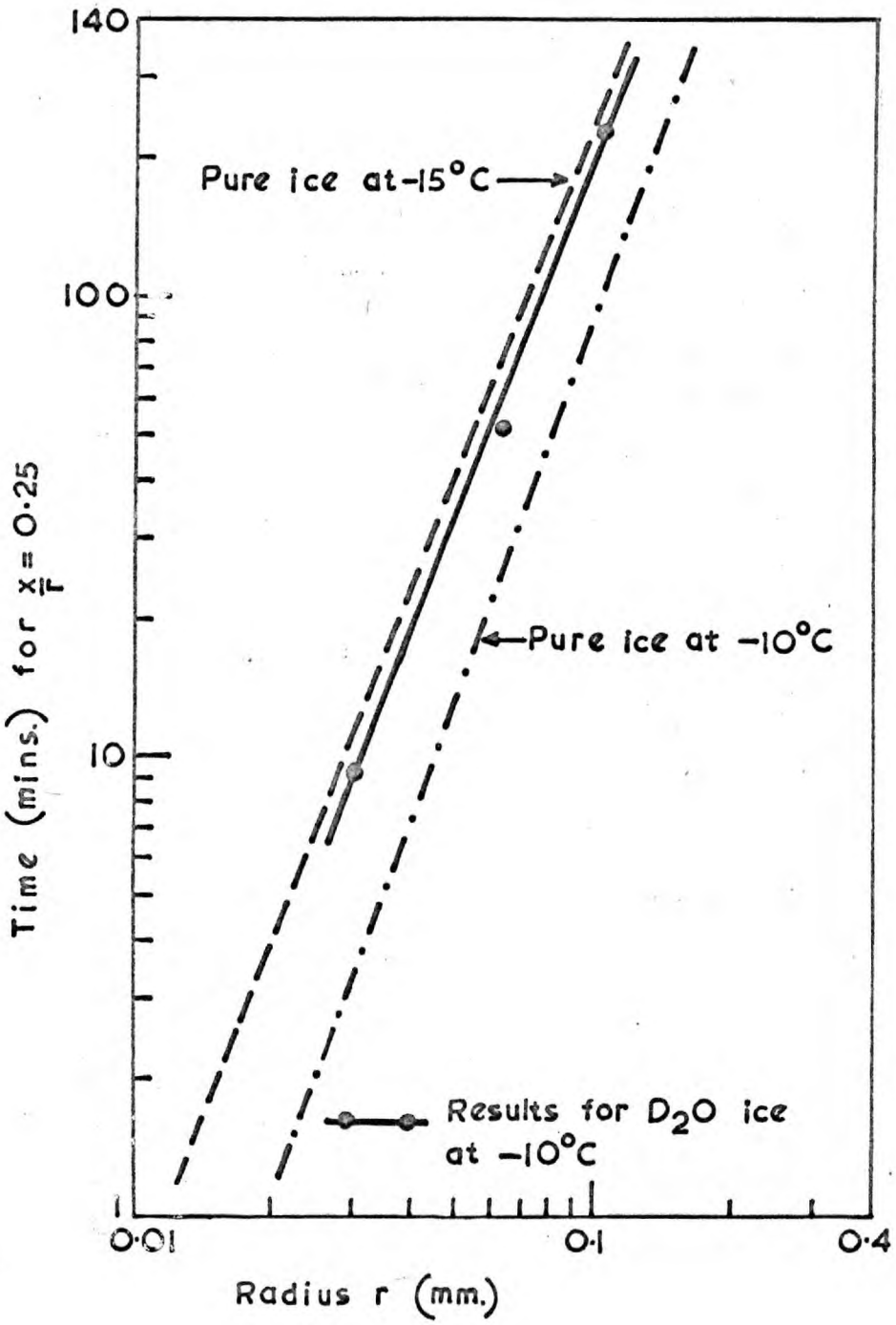


FIG. 26 Comparison of rates of sintering for D_2O ice with ordinary ice

is equal to that for pure ice at about $-14^{\circ}C$.

4.5 Comparison with previous work

Two papers have been published on the sintering of ice, that of Kingery (1960) and Kuroiwa (1961); the conclusions reached by both of these workers differ from those presented in this thesis. An account now follows of the results obtained by Kingery and Kuroiwa and these will be discussed in the light of the present work.

In Kingery's experiments measurements were made on the rate of growth of the neck between two polycrystalline ice spheres over the size range 0.2 to 6 mm diameter. The experimentally observed measurements were found to follow a relationship of the form

$$(\frac{x}{r})^7 \propto \frac{t}{r^4}$$

Using Kuczynski's analysis as a basis for interpreting this result, Kingery concluded that the sintering of ice took place by boundary diffusion as given by equation (37). The temperature dependence of the diffusion coefficient obtained by Kingery was given by

$$D_B = D_o e^{-W/kT}$$

where, D_o was found to be 10^{22} $cm^2 sec^{-1}$ and the activation energy W was 27.5 kcal/mole. No other supporting evidence for sintering by boundary diffusion was provided by Kingery.

The reason for the discrepancy between Kingery's experimental results and those that have been described in § 4.1 appears to be as follows. In Kingery's experiments the ice spheres were not contained in an ice saturated enclosure but were situated in a sub-saturated cold room. These conditions were such as to cause a net evaporation from the spheres, and after thirty minutes or so, as can be seen from Kingery's graphs, no further growth of the neck took place. All of Kingery's measurements were therefore confined to the first ten minutes or so of sintering. Now, it has been shown on page 96 that in the initial stages of sintering the observed rates of growth will be less than the growth rates predicted by equation (42), and this effect is clearly shown in Figs. 16 to 20. For this reason Kingery's experimental results cannot be used to determine n and m in equation (42). Therefore, Kingery's conclusion that surface diffusion was predominant cannot be justified.

Furthermore, a value of D_o equal to 10^{22} $cm^2 sec^{-1}$ is excessively large even for ice. Values of D_o for metals,

for example, are in the range 10^{-3} to 10^{5} cm^2/sec. Also, Kingery's value of 27.5 kcal/mole for the surface activation energy is more than twice the latent heat of sublimation!

Kuroiwa has measured rates of sintering of polycrystalline ice spheres less than 100μ in diameter. In these experiments the spheres were contained in an ice saturated enclosure and measuremnts were taken over several hours; the results obtained agree, within the experimental scatter, with those obtained in the present work (Fig. 27). Kuroiwa found that the rate of sintering followed a relationship of the form

$$(\frac{x}{r})^5 \propto \frac{t}{r^3}$$

Comparing this with Kuczynski's equation for volume diffusion, equation (32), Kuroiwa concluded that volume diffusion was responsible for the sintering of ice. He did not, however, use his experimental results to calculate the volume diffusion coefficient, D_v. It has already been shown in § 4.1 that if this is done the result obtained is three orders of magnitude greater than the value of D_v measured by radioactive tracers. If Kuroiwa's results are interpreted on the basis of the new theory developed in § 2.3 they agree with the evaporation-condensation theory (Case ii).

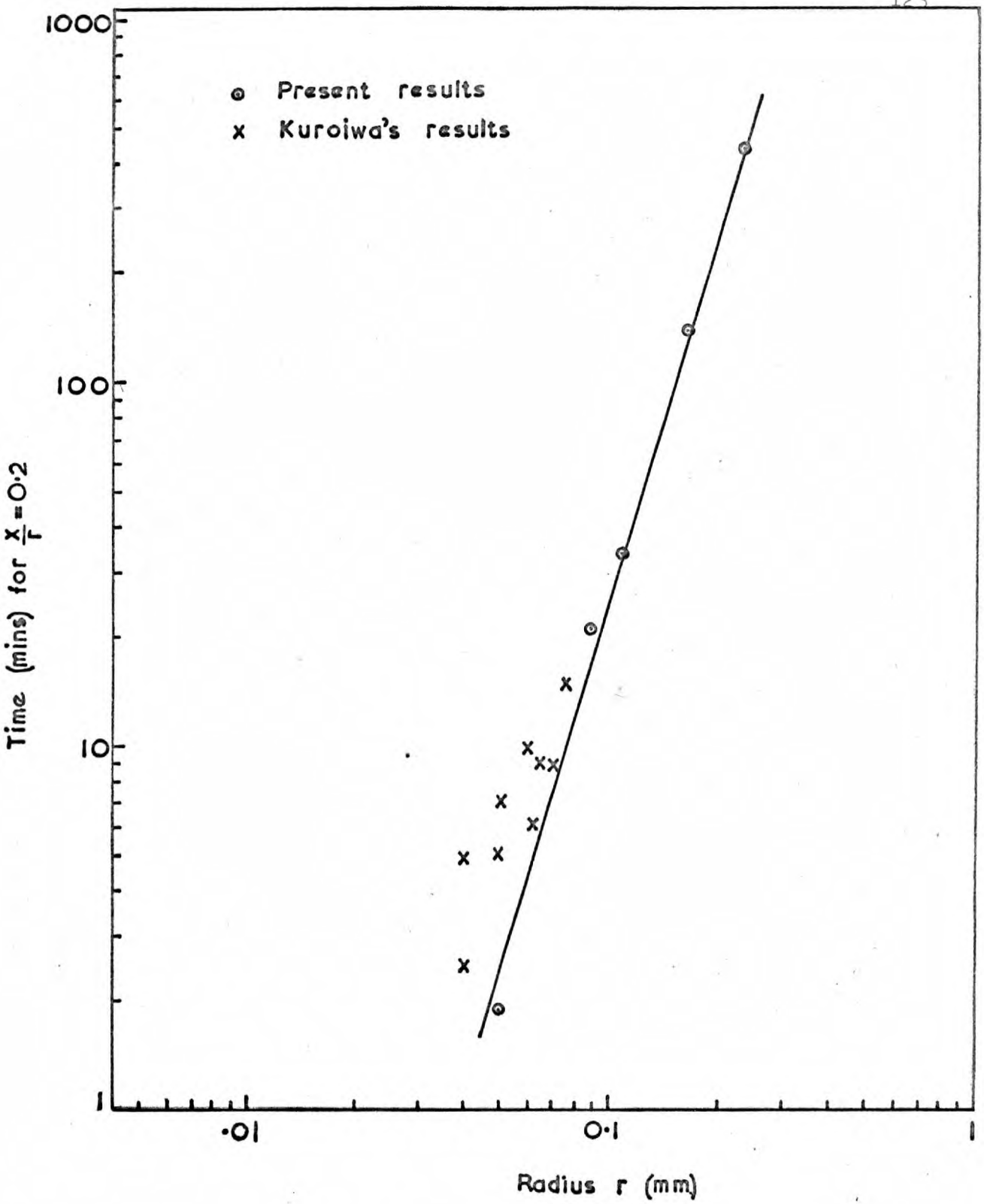


FIG. 27 Effect of sphere radius on time taken for $\frac{x}{r} = 0{\cdot}2$ at $-3^{0}C$

4.6 Concluding remarks

In the first chapter of this theis two theories were discussed which have been put forward to explain the phenomenon of ice adhesion. The first of these, the pressure-meltingtheory, was shown to be ineffective at temperatures lower than about $-1^{o}C$, therefore, it offere no explanation of the adhesion of ice at low temperatures.

The second theory postulated the existence of "liquid-layers" on the surface of ice down to $-30^{o}C$. No supporting evidence for "liquid-layers" on the surface of pure ice has been obtained in the present work. If such layers did exist they would give rise to a continuous and rapid supply of liquid to the neck between two ice spheres, this would produce much larger growth rates than those observed experimentally. Indeed, it might be expected that if a "liquid-layer" existed on the surface of pure ice it would produce rates of sintering similar to the results obtained with spheres frozen from a 1% salt solution, for these are known to have an actual liquid-layer present on the surface.

The work described in this thesis demonstrates that the adhesion between particles of ice can take place by what may be described as a "cold-welding" process. This

is produced by a transfer of material to the point of contact between two spheres, thereby producing a solid ice-bond. It has been shown that the most probable mechanism by which the transfer of material takes place, consists of evaporation from the surface of the spheres, followed by diffusion through the environment, and condensation in the highly concave region at the point of contact between the spheres.

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