Freezing and shattering of supercooled water drops

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SUMMARY

Supercooled water drops of about 0·05 cm radius were frozen at temperatures between − 4°C and − 25°C under various conditions. Explosive shattering and ejected ice splinters were observed when supercooled drops were frozen under conditions of free convection in hydrogen and helium at 1·0 atm pressure, in air below 0·13 atm pressure and in carbon dioxide below 0·05 atm pressure. Drops did not fracture when ventilated at terminal velocity unless they were rotated about an axis normal to the airstream during freezing. Fracture was also observed when either the drops were not allowed sufficient time to attain thermal and solution equilibrium with the environment before nucleation, or when drops were frozen in carbon dioxide at a pressure above 0·3 atm.

A condition for drop fracture is the establishment of a strong shell of ice around the drop, which in turn depends on the distribution of heat transfer to the environment during freezing and on the effective thermal conductivity of the environment. The volume of gas dissolved in the drop is a secondary factor, except in the case of a very soluble gas such as carbon dioxide where splinters are produced by vigorous effervescence during freezing. In the atmosphere the shattering of an individual drop appears possible only if the drop rotates during freezing. This appears unlikely since any asymmetry in shape would tend to orient the drop as it fell.

LIST OF SYMBOLS

a	drop radius
c_w	specific heat of water
D	diffusion coefficient of water vapour in air – varies inversely as the gas pressure
D_w	diffusion coefficient of gas in water
F	ventilation factor
g	acceleration due to gravity
(Gr)	Grashof number $= 8a^3 g\,(\delta T)/\nu^2\,T$
K	effective thermal conductivity, $K = K_g + \beta D L_v$
K_g	thermal conductivity of gas
K_i	thermal conductivity of ice
L_f	latent heat of fusion
L_v	latent heat of vaporization
m	$= FK/K_i$
P	gas pressure
r	internal radius of ice shell
(Re)	Reynolds number $= 2a\nu/\nu$
S	solubility of gas in water, by volume
t	time
t_f	time of freezing
t_0	defined by Eq. (9)
T	temperature
T_e	temperature of environment
T_0	equilibrium melting temperature of ice
T_s	temperature of drop surface
δT	temperature difference in Grashof number
ΔT	supercooling of drop (usually $T_0 - T_e$)
ν	velocity of airflow past drop
y	$= r/a$
β	slope of linear approximation to vapour density – temperature curve
κ	thermal diffusivity of water
ν	kinematic viscosity of air
ρ_w	density of water
τ_1, τ_2, τ_3	relaxation times defined by Eqs. (2), (3) and (4).

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1. Introduction

Measurements of the concentration of ice crystal nuclei in the atmosphere at temperatures higher than $-15°C$ give maximum concentrations of about 10 per litre, with values several orders of magnitude smaller being quite common (Mossop 1963). Measurements of ice crystal concentrations in both cumulus and stratocumulus clouds (Murgatroyd and Garrod 1960; Koenig 1963) and estimates of the number of crystals produced during continuous snowfall (Mason 1956a) are in excess of the maximum observed nucleus concentration by as much as 100 times. There are three possible explanations for this discrepancy. (a) The technique of measurement of ice nuclei may not reveal all the active nuclei. This would particularly be the case for 'preactivated' nuclei whose activity is destroyed on warming above a critical temperature, in the neighbourhood of $-5°C$ (Mason and Maybank 1958; Roberts and Hallett 1968). (b) Delicate dendritic crystals may fracture as they fall. No experimental observations have been made of this effect although there is evidence that crystals fragment when growing on a surface fixed in a moving airstream (e.g. Kramer 1948). (c) Drops freezing individually or on accretion may fracture in the final stages of freezing to produce additional ice particles. The fracture of individual drops on freezing is the subject of the present study.

Drops fracture in two distinct ways. They *shatter* when an appreciable fraction of the drop is blown away – an effect which is easily observed. They *splinter* when the fragment is appreciably less than one tenth of the drop volume. Although ejected splinters can sometimes be seen, splintering can often only be inferred from the reaction of a suspended drop or from a change in its electric charge.

2. Previous work

Fragmentation of drops has been observed under many different laboratory conditions. Langham and Mason (1958) observed that when drops of radius 50 to 500 μ froze at the interface between two immiscible liquids they shattered by splitting in half. They also observed that drops of radius 50 μ shattered when they fell freely in an air column with a very steep gradient of temperature. Mason and Maybank (1960) carried out an extensive investigation of freezing drops, radius 30 μ to 0·1 cm, suspended on a fine fibre or thermocouple. Drops at positive temperatures were lowered into the cold cell and nucleated as they cooled at temperatures between $-5°C$ and $-25°C$, depending on the nature of the nuclei in suspension. Alternatively, drops were nucleated in a second cell filled with tiny ice crystals produced by a fragment of solid CO_2 and transferred to the main chamber. Of drops nucleated at $-1°C$ and subsequently frozen at $-10°C$, 46 per cent shattered and 90 per cent produced spikes; on average 54 splinters per drop were detected. Drops nucleated below $-9°C$ failed to shatter and did not produce spikes. Supercooled drops frozen in hydrogen shattered with about 20 splinters per drop. This effect was attributed to the lower solubility of hydrogen in water. Muchnik and Rudko (1961) observed shattering of 0·1 cm radius drops suspended on a thermocouple in a chamber cooled by solid CO_2. They found that 50 per cent of the drops formed spikes and between 20 and 50 per cent shattered when frozen at temperatures down to $-40°C$. Evans and Hutchinson (1963) and Stott and Hutchinson (1965) nucleated drops of radius 0·065 cm at about $-2°C$ by means of ice crystals produced in the wake of a piece of solid CO_2. The drops were subsequently frozen at $-15°C$ and between 10 and 15 per cent shattered. Dye and Hobbs (1966) froze 0·05 cm radius drops on a thermocouple in CO_2 – air mixtures. Drops were first suspended in the mixture at a temperature of $+2°C$ and then lowered into a cell at $-10°C$ where they were nucleated by ice crystals produced by a rod cooled in liquid nitrogen. In CO_2 concentrations of less than 1 per cent no shattering occurred and drops only formed small bulges. In greater concentrations of CO_2 shattering did occur; half the number of drops shattered in 80 per cent CO_2. Drops supercooled to $-12°C$ shattered when they were frozen in 25 per cent CO_2. Dye and Hobbs suggested that the shattering was caused by the pressure built up inside the drop by the large volume of CO_2 released as the drop solidified, and that shattering observed by previous workers might have been

caused by the presence of CO_2 gas in their apparatus. Kuhns (1966) observed that drops of radius 5 to 38 μ falling in a cold column with temperature gradient $0.5°C$ cm^{-1} did not shatter when freezing at $-36°C$ and one atmosphere (atm) pressure; neither did similar drops containing AgI in suspension when freezing at $-6°C$. It was estimated that drops up to at least 20 μ radius were in thermal (but not solution) equilibrium with their environment. Shattering was observed when the air in the column was replaced by CO_2, hydrogen or helium.

3. PRELIMINARY INVESTIGATION

Initial experiments were undertaken to study the electrification of shattering drops (as observed by Mason and Maybank 1960) in an environment free of CO_2. Drops of deionized water, radius 0.05 to 0.1 cm were frozen in a cylindrical cold cell (Fig. 1) which was cooled by circulating silicone fluid through a solid CO_2 heat exchanger. The CO_2 unit was sealed and the waste gas was piped well clear of the laboratory. The cell was closed with 'O' ring seals which completely isolated it from laboratory air. Drops were squirted from a hypodermic syringe inserted through a rubber seal on to the shellac tip of a 5 cm long, 15 μ diameter, polyester fibre in the upper part of the cell. When a drop formed on the base of the fibre, it was carefully lowered until it was level with the viewing window. The temperature was measured by a thermocouple placed 5 mm from the drop and at the same level. With the base of the chamber coated with ice, the drop temperature would be close to the wet bulb temperature at ice saturation, a depression of about $\frac{1}{2}°C$. The air in the chamber was stably stratified with a vertical temperature gradient of about $\frac{1}{2}°C$ cm^{-1}.

In the first series of experiments drops initially at a temperature of about $+1°C$ in the upper part of the cell were suddenly plunged into the cold chamber, where a cloud of ice crystals had been produced by means of a needle cooled in liquid nitrogen. For cell temperatures down to $-15°C$ less than 5 per cent of the drops shattered. At $-20°C$
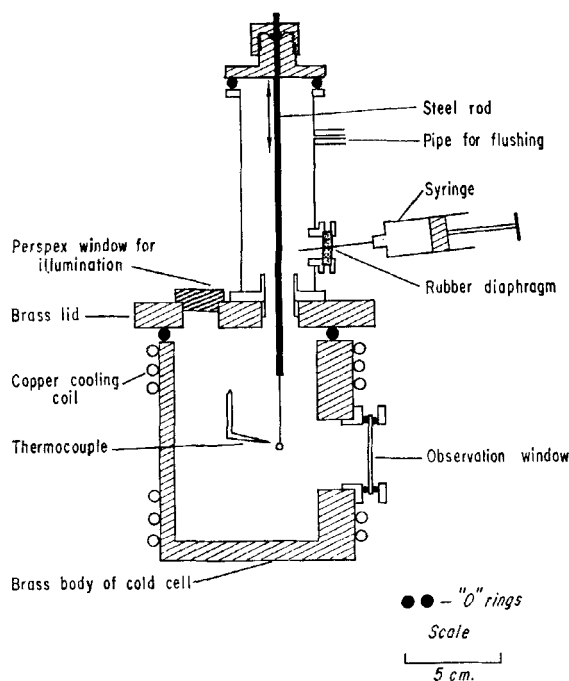

Figure 1. Experimental apparatus for freezing supercooled drops under free convection (not shown). Drops were nucleated by ice crystals from a needle cooled in liquid nitrogen inserted through a diaphragm in the top of the cell).

and $-25°C$, 10 per cent and 30 per cent shattered respectively. About 20 per cent of the drops also exhibited a slight reaction, showing that small splinters had been ejected. These frequencies are significantly less than those observed by Mason and Maybank (1960), 46 per cent at $-10°C$ and 26 per cent at $-30°C$. In the second series of experiments, at least 5 minutes elapsed before nucleation to permit the drops to come into thermal equilibrium with their environment. Only one drop in 200 shattered between $-4°C$ and $-20°C$. These experiments showed that enhanced shattering could be caused by thermal gradients in the drop prior to nucleation, even in the absence of CO_2. The effect of this gradient is shown in Fig. 2, a photograph taken shortly after the nucleation of a drop which was not in thermal equilibrium with its environment. The dendrites have grown in the form of a flat ring in the supercooled outer shell but have been unable to penetrate the drop centre which is still above $0°C$.

The freezing behaviour was also appreciably altered when the drop was suspended from a $30\,\mu$ radius copper wire. The drop froze downwards from the support in about half the time taken by a similar drop suspended on the polyester fibre.

4. DESIGN OF FURTHER EXPERIMENTS ON DROP SHATTER

In the experiments described above it was found that drops fractured more often when they :

(a) froze in a gas more soluble than air, such as CO_2,

(b) froze in a gas less soluble but a better thermal conductor than air, such as hydrogen,

(c) contained temperature gradients due to rapid cooling.

Shattering was prevented by a support of high thermal conductivity. None of these cases is relevant to the atmosphere, where even a large drop would not be subject to a temperature change much in excess of $0·01°C\ sec^{-1}$. While there is no metal support to cause asymmetrical freezing, there is a lack of symmetry in heat transfer by ventilation which may influence the freezing behaviour (Hallett 1965).

It follows that two types of experiments will be meaningful, those to demonstrate which physical parameters control the probability of shatter and those to simulate the freezing process as it occurs in the atmosphere. The process of drop freezing must be understood before any accompanying electrical effects can be interpreted. In the first category are studies of drops which attain both thermal and solution equilibrium with their surroundings and are frozen in free convection suspended on a thin fibre of low thermal conductivity. The second category includes observations of drops falling freely in air at a pressure and temperature appropriate to the atmosphere. The experiments to be described fall mainly into the first category, although some freezing drops suspended on a fibre were ventilated at their terminal velocity in air at 1 atm pressure.

In order to find out how long a drop should be left in a new environment before it is nucleated, its thermal and gas solution relaxation times were estimated as follows. It is assumed that the heat is removed by evaporation and conduction, that the drop has a uniform temperature T_s and that the environment is saturated over ice at the temperature T_e. From the heat transfer equation

$$\tfrac{4}{3}\pi a^3\, c_w\, \rho_w\, \frac{dT_s}{dt} = 4\pi K_g\, [T_s - T_e]\, aF + 4\pi\beta DL_v\, [T_s - T_e]\, aF \qquad . \qquad (1)$$

the time constant for thermal relaxation is obtained

$$\tau_1 = \frac{c_w\, \rho_w\, a^2}{3F\, (K_g + \beta DL_v)} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

The term $(K_g + \beta DL_v)$ can be considered as the effective thermal conductivity K of the environment, the second term being inversely proportional to the ambient pressure through the diffusion coefficient. Values for different gases are given in Table 1.

TABLE 1. EFFECTIVE THERMAL CONDUCTIVITY OF VARIOUS GASES
cal cm^{-2} sec^{-1} °C^{-1} ($\times 10^4$)

Gas	K_g	βDL_v		$K = K_g + \beta DL_v$	
		1·0 atm	0·1 atm	1·0 atm	0·1 atm
Air	0·53	0·22	2·2	0·75	2·73
H$_2$	3·8	0·75	7·5	4·55	11·3
He	3·32	0·6*		3·9*	
CO$_2$	0·33	0·14	1·4	0·47	1·73

* The diffusion coefficient of water vapour in helium is not known : these values are therefore approximate.

The following thermal conductivities are given for comparison (same units) :

ice	53
polyester fibre	$\simeq$ 5
copper	9×10^3

The factor F in Eq. (1) is a ventilation coefficient. For forced ventilation it is given for both heat and mass transfer by

$$F = 1·0 + 0·27 \, (\text{Re})^{\frac{1}{2}} \text{ provided (Re)} > 10.$$

For free convection, caused by the buoyancy of the heated air near the drop and the evaporation of water vapour into the air, it is given by

$$F = 1·0 + 0·27 \, (\text{Gr})^{\frac{1}{4}} \text{ provided (Gr)} > 10^{-3}$$

(Ranz and Marshall 1952; Kyte, Madden and Piret 1953).

The time constant for thermal diffusion inside the drop can be estimated from Jakob's (1949) equation for the temperature distribution in a conducting sphere following a sudden change of the surface temperature. The expression is an exponential power series, the time constant τ_2 of the fundamental term being

$$\tau_2 = a^2/\pi^2 \, \kappa. \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

Internal circulation within the drop will reduce this time constant. Similarly, the relaxation time for solution equilibrium τ_3 is given by

$$\tau_3 = a^2/\pi^2 \, D_w. \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

Calculated values of these relaxation times are shown in Table 2.

TABLE 2. ESTIMATED THERMAL AND SOLUTION RELAXATION TIMES (in seconds)
OF 0·05 cm RADIUS WATER DROPS IN AIR

External thermal relaxation time (τ_1)				Internal thermal relaxation time (τ_2)	Solution of air relaxation time (τ_3)
Free convection		Forced convection at terminal velocity			
1·0 atm	0·1 atm	1·0 atm	0·1 atm		
13	3·5	2·5	1	0·2	13

In the present experiments a drop was left in its cold environment for a period of at least 5 minutes before nucleation, which was long enough to ensure thermal and solution equilibrium.
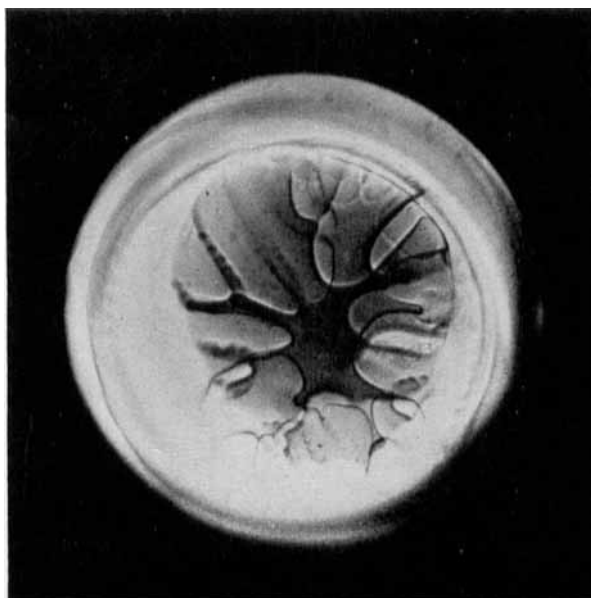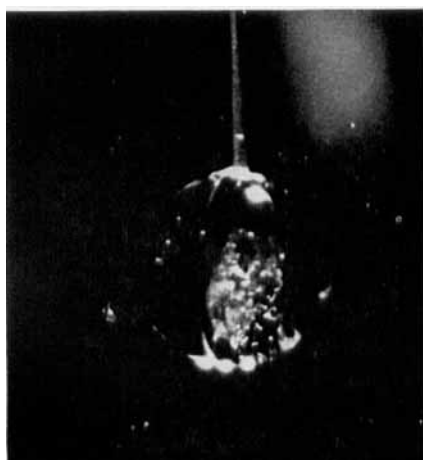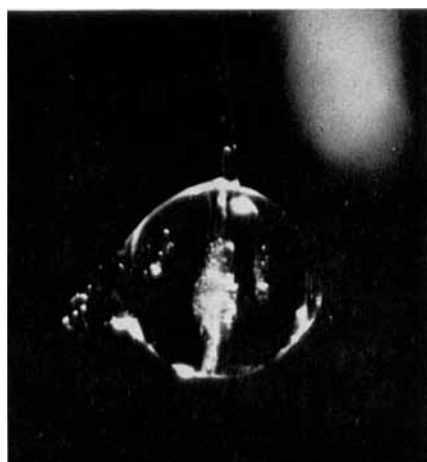
Figure 2. Freezing of a drop 1 mm diameter with a centre above 0°C. Dendrites have grown from the periphery but have failed to penetrate the centre. The outer shell is just beginning to form. Photograph taken 10 seconds after nucleation; complete freezing took a further 40 seconds.
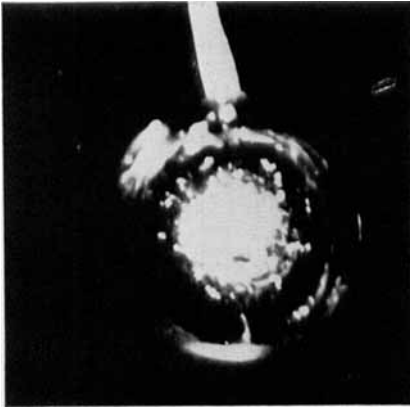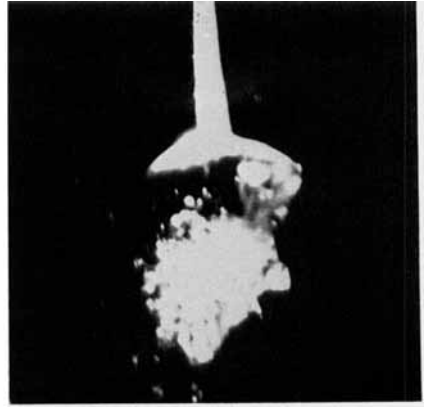

A

B

Figure 3 (a), (b). A pair of photographs taken at slightly different angles of a drop frozen at − 4°C in air at 1 atm pressure, showing a bubble plane, small central bubble cluster and a short spike.
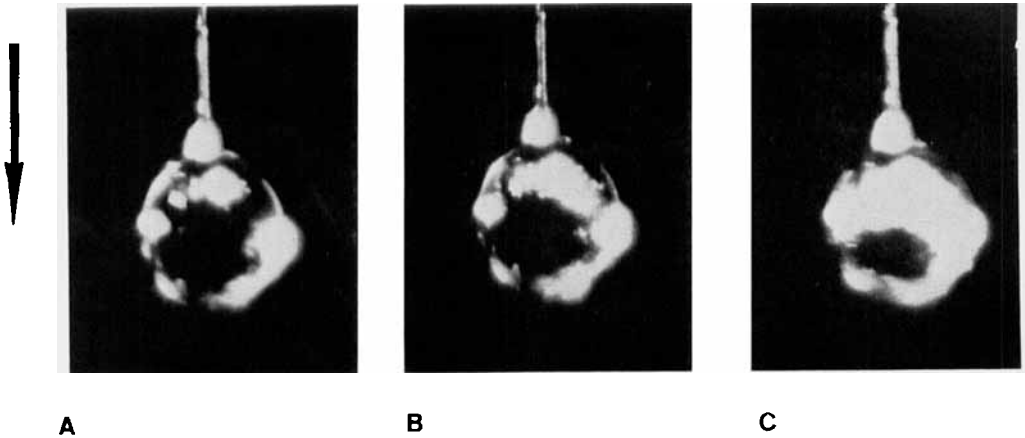
Figure 5 (a), (b).   Two views at 90° of the residue of a drop which froze and shattered in hydrogen at − 18°C. The clear symmetrical shell and bubble core can be easily seen.

Figure 6 (a), (b), (c).   Drops freezing asymmetrically in a vertical wind tunnel.   The wind comes from the top. The time interval between each photograph was about 2 seconds.

The thermal conductivity of the polyester fibre is about 7 times the effective thermal conductivity of air (Table 1). The latent heat released during the freezing of a 0·05 cm radius drop initially supercooled by 10°C is 0·04 calories over a period of about 50 seconds. The maximum amount of heat conducted along a 7 μ radius polyester fibre during this time, assuming that the temperature gradient in the fibre is the same as the steady state temperature gradient in the air, $(T_0 - T_e)/a$ is 2×10^{-4} calories which is small compared with the total heat released. On the other hand, a copper thermocouple wire of the same radius conducts more heat than is available and would clearly dominate the freezing process.

Suitable design of an experiment can therefore minimize the effect of non-equilibrium conditions and the mode of suspension on drop fracture. The effect of the ambient temperature, the amount of gas in solution and the rate and manner of the freezing can then be studied by freezing drops in different gas environments at different pressures. The experiments to be described were designed to show which parameters were important and relevant to a drop falling freely in the atmosphere.

5. EXPERIMENTAL

The process of drop freezing under free convection was investigated in the chamber described in Section 3. The chamber was flushed with the desired gas for several minutes before sealing it and adjusting the pressure, which was measured by a mercury manometer. Most drops were of deionized distilled water, although when distilled water was used the freezing behaviour was not noticeably different. The supercooled drops were nucleated by several techniques. At 1 atm it was convenient to use a cold needle to produce a cloud of ice crystals, as already described, but this method could not be used at lower pressures without breaking the seal. It was found that drops of deionized water nucleated heterogeneously at about -22°C to -25°C. In order to ensure thermal and solution equilibrium the drop was left for several minutes at -20°C. The temperature was then reduced at about 1°C min^{-1} until nucleation occurred. Drops were also nucleated by lowering them to touch a small ice crystal which had been grown on a fine fibre below the drop. When the three methods of nucleation could be compared there were no obvious differences in the freezing behaviour.

Changes in the electric charge of the drop were detected by an induction electrode in the form of a 5 mm diameter wire ring situated directly below the drop. The potential of the ring was measured by a 'Vibron' Model 62A electrometer with a 1 pF input capacity and recorded on a galvanometer recorder. The calibrated sensitivity was $1·1 \times 10^{-5}$ e.s.u. per millivolt and the noise level on the most sensitive range was about 0·5 mV.

In order to study the effect of ventilation on the freezing behaviour a 2·5 cm diameter horizontal wind tunnel was constructed. The drop was suspended at the centre of the tunnel on a fibre hanging from the roof, and was nucleated by inserting a cold needle upwind of the drop. The tunnel was also operated from a hydrogen cylinder at a maximum velocity of 25 cm sec^{-1}.

6. OBSERVATIONS

(a) Air, 1·0 atm pressure

The initial ice growth on nucleation at temperatures above -6°C was in the form of dendrites growing as a flat sheet or pair of sheets inclined at a small angle. This form of growth was also observed in bulk supercooled water by Hallett (1964) and Macklin and Ryan (1965). At lower temperatures the ice structure became more complex and on nucleation at about -8°C the drop became opaque due to many tiny gas bubbles coming out of solution. Patterns on the surface of the drop suggested that the internal structure consisted of sets of parallel planes. The boundaries between the sets of planes were often preserved in the completely frozen drop as a clear plane passing through the central core of bubbles. Due to the rapid growth of dendrites in supercooled water (e.g. 8 cm sec^{-1}

at $-10°C$), the nucleation growth was completed in a time very much less than the total freezing time (e.g. 50 sec at $-10°C$). Once the dendritic growth had ceased, the subsequent rate of freezing was governed by the heat transfer between the drop and its colder environment. This led to the inward growth of an ice shell whose exact shape depended on the degree of symmetry of the heat transfer.

At temperatures above about $-8°C$ the frozen drop consisted mainly of clear ice with one or two clusters of bubbles, usually in the form of twisted surfaces. Most drops were distorted from the spherical by a smooth bulge and, occasionally, a spike about as long as the drop diameter. Less than 1 per cent of the drops which froze at $-6°C$ shattered.

When the environment was colder than about $-8°C$ the freezing behaviour was quite different. Almost immediately after nucleation a bulge began to form in the upper hemisphere, followed by a gradual clearing of the initial opacity. The skin of the bulge would suddenly burst, and liquid water could be seen spreading over the drop surface. This phenomenon was called a ' collapsing bulge ' and usually occurred several times in succession. About half way through the freezing process a shell of clear ice could be seen at the base of the drop. At this stage bubbles of gas started to grow in size, only to be compressed again as the internal pressure increased. The bubbles would then suddenly grow again, presumably due to some relief of internal stress. This bubble relaxation often occurred several times during the latter half of the freezing process, although occasionally it did not happen at all. The completely frozen drop generally consisted of a clear shell of ice surrounding an approximately spherical core of bubbles. On some drops a plane of bubbles passed through the central core, intersecting the surface in a crack. No preferred orientation of cracks relative to a bulge or the supporting fibre was noticed. In the upper hemisphere of the drop several collapsing bulges in the same region combined to give a somewhat knobbly bulge, never distorting the drop more than about $\frac{1}{3}$ of a radius from the spherical. This is to be contrasted with the spikes about two radii long which were observed on drops not in equilibrium with the environment. Supercooled drops freezing
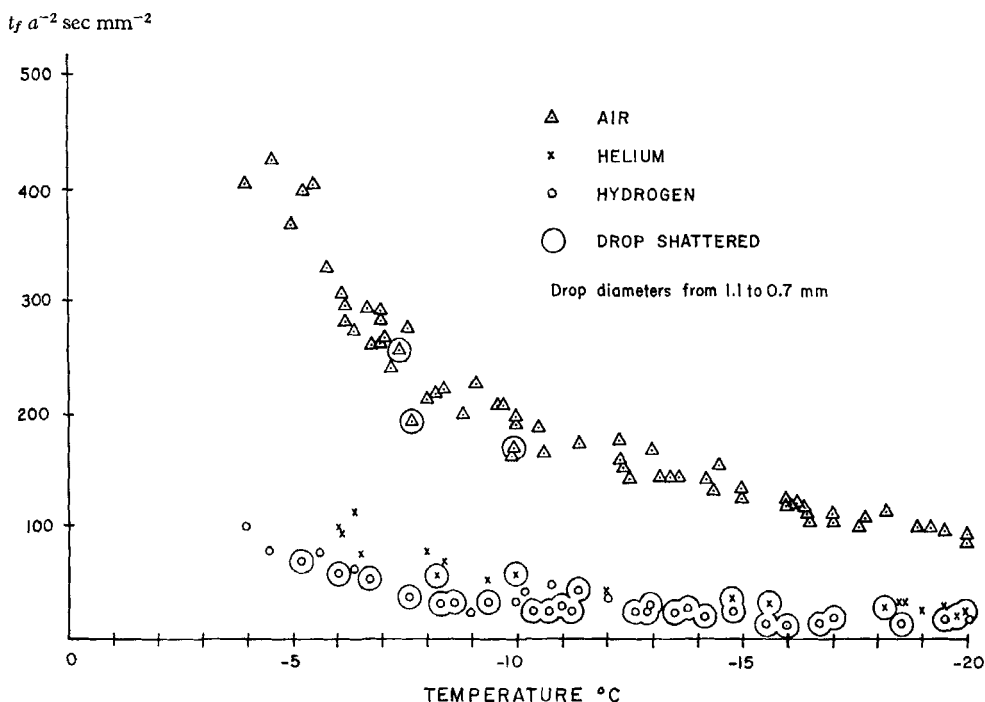

Figure 4. Freezing times of millimetre drops in various gases. Drops shattered much more frequently in hydrogen and helium than in air.

in air rarely shattered, the overall frequency of such events being less than 1 per cent over the temperature range − 4°C to − 20°C. In contrast, Mason and Maybank (1960) reported a shattering frequency of 6 per cent at − 15°C. The total time of freezing (reduced to that appropriate for a 1 mm diameter drop by dividing by the square of the drop radius) (a) is plotted against the temperature in Fig. 4.

By far the most convincing demonstration of the ejection of ice splinters from freezing drops is the measurement of charging of the drop. Slight reactions occurring during freezing were associated with a discontinuous change of drop charge, showing that charged particles had been ejected. Some charging events were correlated with a bubble relaxation during freezing but collapsing bulge events gave no detectable change in charge. Although slight reactions were frequent in drops not in equilibrium with their environment, less than 1 per cent of uniformly supercooled drops had any significant charging events due to the possible ejection of small particles. The possibility that some charging events were due to liquid particles being ejected must also be borne in mind.

As a check on the estimate of the time taken to reach thermal equilibrium (see Section 4) the time between taking the drops from room temperature and nucleating them in an environment at − 17°C was varied from 0·04 to 10 times the calculated relaxation time. There was a tendency for shattering to occur at the shorter times, for splintering and slight reactions to occur at intermediate times, and for no effects at all to occur at the longest times.

The cloud of ice crystals produced when a cold needle was inserted in the cold cell rendered the convective airflow past the drop visible. From the length of the streaks produced by the crystals on a photographic film exposed for a known time, the velocity of the airflow near the drop was estimated to be about 3 cm sec^{-1}. Under similar conditions in hydrogen and helium the velocity was not measurable, less than 0·1 cm sec^{-1}.

(b)   Gases other than air

The behaviour of drops freezing in hydrogen or helium was quite different from that in air. Drops still became opaque on nucleation below about − 8°C, but soon cleared to reveal an almost symmetrical and rapidly thickening shell of ice (Fig. 5). About 80 per cent of drops in hydrogen and 30 per cent in helium shattered and drops froze much faster than they did in air. The frequency of shattering in hydrogen was 4 times that observed by Mason and Maybank. The difference is probably due to their hydrogen atmosphere being less pure than that used in the present experiments.

Results for the very soluble gases nitrous oxide (N$_2$O) and carbon dioxide were different from both air and hydrogen. Drops became opaque on nucleation at all temperatures between − 4°C and − 22°C and remained opaque during the whole freezing process. Bubbles of gas formed just below the surface, often moving rapidly to form long winding tubes of gas. Spikes, sometimes several per drop, were longer and thinner than spikes from drops frozen in hydrogen. Bubbles burst at the drop surface to produce copious splinters but drops rarely shattered into large fragments. The frozen drop was opaque with a dense network of surface cracks, and was often distorted by large hollow protuberances.

Carbon dioxide was diluted with a less soluble gas by reducing the pressure of a pure carbon dioxide atmosphere and filling the cell with air or nitrogen until the pressure was again ambient. In 50 per cent carbon dioxide no drops shattered, although several splinters were ejected. Effervescence did occur, but the large protuberances characteristic of drops freezing in pure carbon dioxide were absent. In 25 per cent carbon dioxide freezing was more gentle, little effervescence occurred and only a few small spicules formed. The frozen drops were somewhat clearer but the bubble distribution was still noticeably denser than that in drops freezing in air. It was only when the carbon dioxide concentration was reduced below about 10 per cent that the freezing behaviour was indistinguishable from that of drops in air. This frequency of shatter is lower than that found by Dye and Hobbs

(1966) and can be attributed to a closer approach to thermal equilibrium in the present experiments.

In argon at 1 atm drops froze in the same way they did in air. However, in argon at 5 atm pressure drops froze at $-20°C$ in a way similar to that in diluted CO_2, with a denser bubble structure. At this pressure, the solubility of argon is about 15 per cent of that of pure CO_2.

(c) Reduced pressure

Drops were frozen in air over a range of pressures from 0·05 to 1 atm, after nucleation at $-20°C$ to $-25°C$ by the slow cooling method (Section 5). The drops always went opaque on nucleation. Above about 0·5 atm the freezing behaviour was similar to that of drops in air at 1 atm. Collapsing bulges ceased to form below about 0·3 atm, and below 0·13 atm every drop shattered violently.

The behaviour of drops freezing in CO_2 at reduced pressure began to change only below 0·4 atm. Between 0·25 and 0·05 atm drops did not effervesce at all and small bubbles appeared throughout the entire drop towards the end of freezing. Bubbles grew irregularly at the lower pressure. Between 0·05 and 0·01 atm every drop shattered. The freezing behaviour of drops in air below 0·13 atm and in CO_2 below 0·05 atm was similar to that of drops in H_2 and He at 1 atm pressure.

Dye and Hobbs (1968) have repeated some of the experiments described here and obtained essentially similar results except in air at reduced pressure. They did not observe shattering at pressures as low as 0·03 atm. Their experimental techniques differed in a number of respects from those used in the present work, but there is one major difference which could account for the disagreement. Their drop was suspended only 5 mm below the supporting rod, and it is possible that heat conducted down the rod may have induced convection currents in the vicinity of the drop. As shown in Section 7, even quite weak convection currents can inhibit shattering. The fibre used in the present work was 5 cm long and therefore the drop was less likely to be influenced by the supporting rod.

(d) Ventilation

Drops ventilated at their terminal velocity in the wind tunnel froze in a distinctive way. At temperatures below $-8°C$ the drop went opaque as before and then cleared within about 2 seconds as the ice interface spread from the upstream side through the drop, nucleating bubbles as it passed (Fig. 6). As this front traversed the drop, a bulge grew continuously in the rear. The freezing time was about $\frac{1}{5}$ that of drops freezing under free convection. No drops shattered and no cracks were observed. Drops suspended on a more rigid fibre froze in a similar manner. When these drops were rotated about an axis normal to the airstream several times during their period of freezing, shattering and cracking invariably occurred. Drops suspended on crossed fibres and rotated several times about a horizontal axis during freezing under free convection at $-10°C$ cracked but failed to shatter. Bulges formed at each end of the axis of rotation. Drops were also frozen in a stream of hydrogen, at 25 cm sec^{-1}. The freezing was more asymmetrical than for drops freezing under free convection in hydrogen but shattering still occurred, mainly by blowing off the downwind end of the drop.

(e) Accretion

A drop, radius 0·05 cm, was suspended on a fibre in front of an ice target 0·5 × 2 cm in the wind tunnel at a temperature of about $-12°C$. After equilibrium had been reached the wind speed was increased until the drop blew off and accreted and froze on the ice. This was repeated for several drops, each landing on top of the previous one. The wind speed was increased to about 10 m sec^{-1} as the final drop was accreted; this froze almost equally from front and back and split in half during the final part of the freezing.
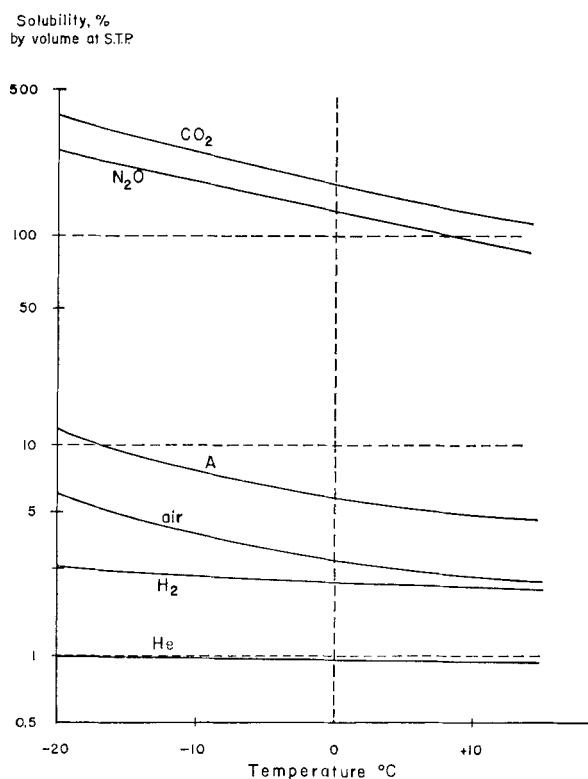
Figure 7. The solubility (by volume, per cent) of gases in water as a function of temperature, extrapolated from data given in the International Critical Tables.

7. DISCUSSION

In these experiments it was found that whether or not a drop fractured during freezing depended on both the heat transfer from the drop to its environment and on the amount of gas dissolved in the water. The effect of the crystal structure of the drop was secondary since no significant change in freezing behaviour was observed when different methods of nucleation were used. Fragmentation was related to heat transfer in that a complete, relatively strong ice shell had to form before pressure could build up inside the drop. Given a strong ice shell, the pressure which was attained during freezing (and hence the likelihood of fracture) depended on the volume of gas in the drop in the form of bubbles, since these increased the compressibility of the liquid interior.

The solubility of various gases in water at 1 atm pressure, extrapolated to $-20°C$, is plotted in Fig. 7. The solubility is expressed as the volume of gas at S.T.P. per unit volume of water (per cent) and is proportional to the ambient pressure.

Heat is removed from a freezing drop by conduction to the environment and by evaporation of the relatively warm surface into the colder environment. The freezing time t_f of the drop (defined as the time from the instant of nucleation until the drop is completely solidified) is derived from a simple model in the Appendix. It is shown that

$$t_f = \frac{\rho_w L_f a^2}{3FK\Delta T} [1 - \Delta T c_w / L_f]. \qquad . \qquad . \qquad . \qquad (5)$$

In Fig. 8 t_f/a^2 is plotted against $1/\Delta T$. The relation is linear as predicted by Eq. (5), and from the slopes of the lines through the experimental points the values of the ventilation
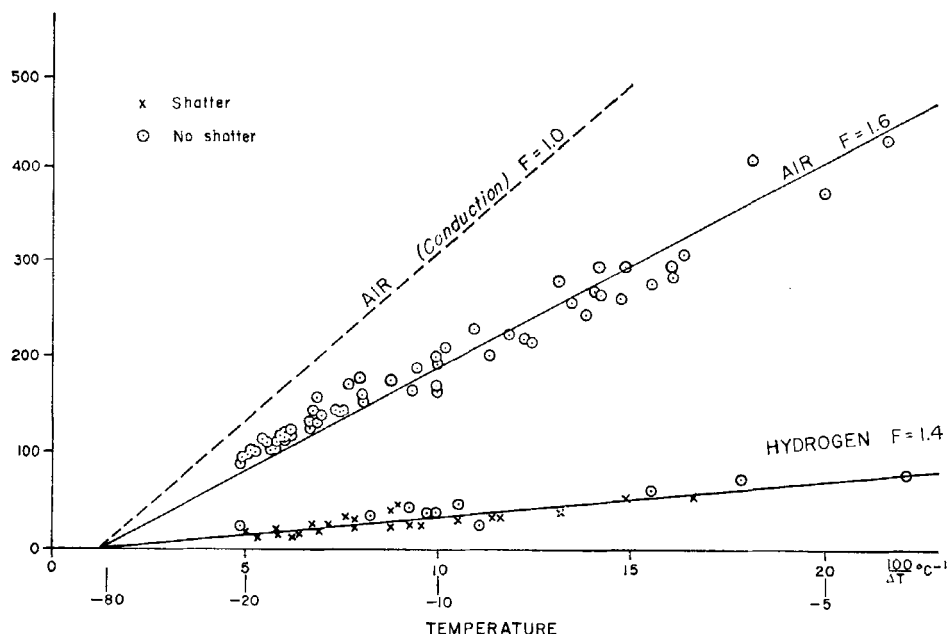
$t_f \, a^{-2}$ sec mm^{-2}

Figure 8. The freezing time of millimetre drops in air and hydrogen against $1/\Delta T$, showing shatter events. Correlation lines are drawn for the indicated values of the ventilation factor F.

factor F for drops freezing in air and hydrogen at 1 atm were found to be 1.6 ± 0.1 and 1.4 ± 0.1 respectively. The factor F represents the enhancement of heat transfer by convection (free or forced) over molecular transport processes.

In addition to increasing the rate of freezing, convection causes heat to be transferred asymmetrically. This was strikingly displayed when drops were ventilated in a wind tunnel. Only when a drop was rotated, restoring some symmetry to the heat transfer, were cracking and shattering observed. The collapsing bulge seen on the upper half of drops freezing in air at 1.0 atm is evidence that some asymmetry of freezing was present even in the relatively weak air flow (about 5 cm sec^{-1}) associated with free convection. The experiments showed that a rotated drop was more likely to fracture the greater the ventilation velocity. This suggests that both the symmetry of heat transfer and the rate of freezing were important.

Whether or not supercooled drops fracture when freezing under free convection may therefore depend on the *symmetry* of heat transfer, on the *overall rate* of heat transfer and on the amount of gas in solution. The effective thermal conductivity K is plotted against the gas solubility S in Fig. 9, which shows that the onset of shattering occurs when K exceeds about 2.5×10^{-4} cal cm^{-1} sec^{-1} °C^{-1}. This value is almost independent of gas solubility, although gases with high solubility cause splintering due to bubbles bursting at the drop surface. The freezing behaviour of drops in hydrogen, helium, air below 0.13 atm pressure and carbon dioxide below 0.05 atm pressure was remarkably similar. Drops froze symmetrically and rapidly and most shattered violently. The low velocity of small ice crystals in hydrogen and helium compared with that in air shows a lack of appreciable convection currents (buoyancy caused by heating is offset by the higher density of diffusing water vapour) and implies a uniform distribution of heat transfer, which is consistent with the observed symmetrical freezing. It is also consistent with the measured value of the ventilation factor F being less in hydrogen than in air.
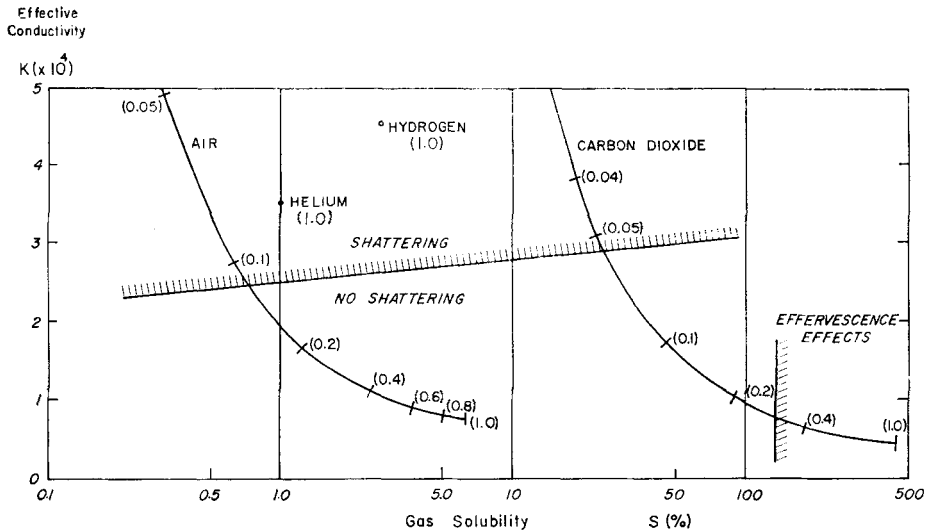
Effective
Conductivity

K (x 10^4)

Figure 9. Relation between the effective conductivity K of the drop environment, gas solubility and drop shatter. The figures indicate the gas pressure in atm.

Free convective flow in a gas is characterized by the Grashof number

$$(Gr) = 8ga^3 \, \delta T / \nu^2 \, T \qquad . \qquad . \qquad . \qquad . \qquad (6)$$

where δT is the difference between the temperature of the drop and the virtual temperature of the environment and T is the absolute temperature of the environment. Weak free convective flow, when the buoyancy force is small and/or the gas has a high kinematic viscosity, is characterized by a low Grashof number. Values of (Gr) when shattering occurred were all less than 0·1. When shattering did not occur, the value was greater than 1·0. Since the Grashof number varies as a^3, it would be of interest to see whether drops smaller than 0·05 cm radius shatter when freezing by free convection.

While symmetry of heat transfer has been shown to be a dominant factor in causing drop shatter, symmetry has also been linked with high conductivity in the present experiments. It is therefore possible that a high freezing rate may also increase the probability of drop shatter. This view is consistent with the results of Kuhns (1966) who found that 20 μ radius drops under free fall shattered in hydrogen but not in air. The enhanced heat transfer caused by free or forced convection at these low velocities is small (1 per cent) which is unlikely to change the symmetry of freezing significantly in either case. Kuhns' result may therefore be attributed to the higher effective conductivity of hydrogen, leading to a more rapid freezing rate.

Although it appears likely that both symmetry of heat transfer and effective conductivity are most important in controlling the fragmentation of freezing drops, it is possible that other factors such as the gas content of the water and the structure formed on nucleation may play subsidiary roles. For example, under certain conditions the symmetry of heat transfer could vary during freezing in such a way that an initially weak, deformable ice shell forms over part of the drop surface and later in the freezing time becomes rigid enough to withstand distortion. The resulting increase of pressure and hence the possibility of fragmentation depends on the volume of water still unfrozen when the shell becomes rigid and on the volume of gas bubbles in the water, since these provide space into which the freezing water can expand. Clearly, in the absence of any bubbles, an enormous pressure would be generated due to the low compressibility of water, quite sufficient to keep any dissolved gas in solution and to ensure shattering.

8. METEOROLOGICAL IMPLICATIONS

Supercooled drops exist in the atmosphere at temperatures down to $-40°C$, where the pressure is about 0·3 atm. Drop shatter induced by low air pressure will not therefore occur under atmospheric conditions. It was found that drops ventilated under terminal velocity in air failed to shatter unless they were rotated. In the atmosphere drops in free fall could rotate, most likely in the size range where eddy shedding begins (Re about 200). However, tank experiments with spheres and spheres with protrusions showed that rotation about an axis perpendicular to the fall direction did not occur although spheres did fall along a helical path. Shattering caused by drop rotation therefore appears unlikely to occur in the atmosphere.

Whilst drops of radius 0·05 cm and 5 to 38 μ have not been observed to shatter under free fall at a pressure of 1 atm there remains a possibility that drops of intermediate size freezing at temperatures above $-36°C$ may do so. The heat transfer rate is increased by ventilation and becomes equal to the critical value for shatter shown in Fig. 9 for a drop which has a Reynolds number of about 230 (radius 470 μ at 1 atm; 300 μ at 0·3 atm). Eddy shedding takes place for flow at this Reynolds number so that the flow does not appear to be sufficiently symmetrical to permit shattering. In other words, atmospheric conditions are such that the rate of heat flow from an individual freezing drop is neither fast enough nor sufficiently symmetrical to cause shattering. It would be most desirable to observe drops of this size range freezing under conditions which adequately simulate those occurring in the atmosphere.

9. CONCLUSION

Drops of about 0·05 cm radius have been found to shatter only if a strong enough shell of ice has been established by symmetrical heat transfer to the environment. Heat transfer is asymmetrical when drops freeze under free or forced convection in air in fixed orientation. It is symmetrical when drops freeze by free convection in an environment of high effective thermal conductivity (hydrogen, helium, air below 0·13 atm pressure, carbon dioxide below 0·05 atm pressure) and when drops are rotated in forced convective airflow. In addition, drops freezing in very soluble gases such as carbon dioxide and nitrous oxide splinter copiously due to the release of large volumes of gas. Taken together with the work of Kuhns (1966) it is concluded that drops larger than 5 μ radius are unlikely to fracture on freezing in free fall in the atmosphere. However, drop freezing on accretion provides a more likely physical situation for splinter production under certain conditions. This possibility has been examined in detail elsewhere (Brownscombe and Hallett 1967).

REFERENCES

Brownscombe, J. L. and Hallett, J.   1967   'Experimental and field studies of precipitation particles formed by the freezing of supercooled water,' *Quart. J. R. Met. Soc.*, **93**, pp. 455-473.

Dye, J. E. and Hobbs, P. V.   1966   'Effect of carbon dioxide on the shattering of freezing water drops,' *Nature*, **209**, pp. 464-466.

1968   'The influence of environmental parameters on the freezing and fragmentation of suspended water drops,' *J. Atmos. Sci.*, **25**, pp. 82-96.

Evans, D. G. and Hutchinson, W. C. A.   1963   'The electrification of freezing water droplets and of colliding ice particles,' *Quart. J. R. Met. Soc.*, **89**, pp. 370-375.

Hallett, J.   1964   'Experimental studies of the crystallization of supercooled water,' *J. Atmos. Sci.*, **21**, pp. 671-682.

                                     1965   'On the structure of precipitation elements formed by the freezing of supercooled water,' *Proc. International Conference on Cloud Physics, Tokyo and Sapporo*, pp. 201-204.

Jakob, M.   1949   *Heat Transfer*, John Wiley and Sons Vol. I, p. 263.

Koenig, L. R.   1963   'Glaciating behaviour of small cumulonimbus clouds,' *J. Atmos. Sci.*, **20**, pp. 29-47.

Kramer, C.   1948   'Electrische ladingen aan berijpte oppervlakken,' *Ned. Met. Inst. Med. en Verh.*, Series A, pp. 54.

Kuhns, I. E.   1966   'The supercooling and nucleation of water,' Ph.D. Thesis University of London.

Kyte, J. R., Madden, A. J.   1953   'Natural convection heat transfer at reduced pressure,' *Chem. Eng. Prog.*, **49**, pp. 653-662.
   and Piret, E. L.

Langham, E. J. and Mason, B. J.   1958   'The heterogeneous nucleation of supercooled water,' *Proc. Roy. Soc.*, **247**, pp. 493-504.

Macklin, W. C. and Ryan, B. F.   1965   'The structure of ice grown in bulk supercooled water,' *J. Atmos. Sci.*, **22**, pp. 452-459.

Mason, B. J.   1956a   'The nucleation of supercooled water clouds,' *Sci. Progress*, **44**, pp. 479-499.

                                     1956b   'On the melting of hailstones,' *Quart. J. R. Met. Soc.*, **82**, pp. 209-216.

Mason, B. J. and Maybank, J.   1958   'Ice nucleating properties of some natural mineral dusts,' *Ibid.*, **84**, pp. 235-241.

                                     1960   'The fragmentation and electrification of freezing water drops,' *Ibid.*, **86**, pp. 176-186.

Mossop, S. C.   1963   'Atmospheric ice nuclei,' *Z. Angew. Math. Physik.*, **16**, pp. 456-486.

Muchnik, V. M. and Rudko, J. S.   1961   'Osobennosti zamerzaniia pereokhlazhdennykh kapel vody' (Peculiarities of freezing supercooled water drops), *Trudy Ukrainsk Hydro Meteorological Institute*, **26**, pp. 64-73.

Murgatroyd, R. J. and Garrod, M. P. 1960   'Observations of precipitation elements in cumulus clouds,' *Quart. J. R. Met. Soc.*, **86**, pp. 167-175.

Ranz, W. E. and Marshall, W. R.   1952   'Evaporation from droplets,' Part 2, *Chem. Eng. Prog.*, **48**, pp. 173-176.

Roberts, P. and Hallett, J.   1968   'A laboratory study of the ice nucleating properties of some mineral particulates,' *Quart. J. R. Met. Soc.*, **94**, pp. 25-34.

Stott, D. and Hutchinson, W. C. A. 1965   'Electrification of freezing water drops,' *Ibid.*, **91**, pp. 80-86.

APPENDIX

THE FREEZING TIME OF A SUPERCOOLED DROP

Consider a drop supercooled to the temperature of the environment, T_e. When the drop is nucleated at time $t = 0$ dendrites grow rapidly through the drop until stored specific heat at T_e has been converted into latent heat at T_0, the equilibrium melting temperature of ice. Due to the high velocity of growth of ice in supercooled water (e.g. 8 cm sec^{-1} at $-10°$C) the nucleation growth is completed in a small fraction of a second. The drop then consists of a mixture of ice and water with a fraction $[1 - \Delta T c_w / L_f]$ of its volume yet to freeze. Subsequent freezing occurs by the transfer of heat by conduction and evaporation to the environment. Assuming that the heat transfer is spherically symmetric, a spherical ice shell will form with internal radius r at time t. Since the shell thickens with a finite velocity $\simeq 10^{-2}$ cm sec^{-1} the local supercooling at the interface must be $\simeq 0.2°$C (Hallett 1964). Therefore to sufficient accuracy we can neglect the interface supercooling.

Then :

   Rate of release of = Rate of heat conduction = Rate of heat loss by evaporation and
   heat by freezing   through the ice shell   conduction to the environment.

Following Mason (1956b) we obtain

$$4\pi r^2 \frac{dr}{dt} \rho_w L_f \left[1 - \Delta T c_w / L_f\right]$$

$$= - 4\pi K_i \, ar \, (T_s - T_0)/(a - r)$$

$$= 4\pi a FK \, (T_s - T_e) \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

Where $K = K_g + \beta D L_v$ the 'effective thermal conductivity' of the environment. β is the slope of a linear approximation to the vapour density-temperature curve, and a value of $1 \cdot 7 \times 10^{-7}$ g cm^{-3} °C^{-1} was adopted in the present work, giving a maximum error of 10 per cent between 0°C and -20°C. Eliminating T_s from these equations gives

$$3t_0 \frac{dy}{dt} = \frac{-1}{(1 - m) \, y^2 + my} \qquad . \qquad . \qquad . \qquad . \qquad (8)$$

Where

$$t_0 = \frac{\rho_w L_f a^2}{3FK\Delta T} \left[1 - \Delta T c_w / L_f\right] \qquad . \qquad . \qquad . \qquad (9)$$

$$m = FK/K_i \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (10)$$

$$y = r/a \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

Integrating Eq. (8) from $t = 0$, $y = 1$ to $t = t_s$, $y = 0$

$$t_f = t_0 \, (1 + m/2) \qquad . \qquad . \qquad . \qquad . \qquad (12)$$

The largest value of m encountered in the present work is $0 \cdot 1$ in the case of hydrogen. For drops in air, $m = 1/70$. Hence, to sufficient accuracy, the time of freezing is given by

$$t_f = t_0 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (13)$$

It can be shown from Eq. (7) by eliminating r that the surface temperature T_s of the drop remains close to 0°C except near the completion of freezing, when it falls to the environment temperature. This can also be deduced from a consideration of the relative thermal conductivities of ice and air.