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34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
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CLOUD MICROPHYSICAL PROCESSES

J.A. LATHAM

University of Manchester
Institute of Science & Technology
Manchester, U.K.

Cloud physics

J. LATHAM

Physics Department, University of Manchester Institute of Science and Technology

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Abstract. A large number of complex and interrelated microphysical processes are involved in the formation of solid and liquid precipitation particles within clouds. These have received detailed attention in recent years and, with certain important exceptions, a moderately accurate quantitative description now exists of the growth and interactions of cloud particles, from their original formation on condensation or sublimation nuclei to their removal from the cloud as large precipitation elements. The objective of this article, which does not include a consideration of the macrophysical, dynamical approach to cloud physics, is to synthesize current knowledge of these microphysical processes and to establish which major problems have been effectively solved and which require appreciable further attention.

The basic physics of the three heterogeneous nucleation processes occurring inside clouds is now well established, although in the case of the formation of the ice phase some more specific information is required. Accurate quantitative predictions of the nucleating activity of artificially produced smokes are gradually emerging. The calculated growth rates of a population of cloud droplets growing by condensation within a rising parcel of air agree well with observation only if mixing between the parcel and its environment is considered. The efficacy of the collision and coalescence mechanism which supplants the condensation process is

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extremely sensitive to the values of the collision efficiencies for small cloud droplets. The most recent calculations suggest that the 18 μm threshold is incorrect and that droplets of smaller radii can collide. This point and the possible importance of electrical forces in triggering the coalescence process require further experimental study. The combination of the stochastic approach with recently determined collision efficiencies have produced realistic computations of the growth of populations of cloud droplets by means of coalescence. The extremely rapid growth rates observed in certain situations are probably a consequence of electrical forces. The majority of conditions under which raindrops become unstable while falling through a cloud have been established and are supported by a reasonable theory. Experimental studies of the movement of growth layers across an ice surface suggest strongly that the habit of ice crystals is controlled by variations in the surface migration distances of molecules, but further work on the prism faces of ice is required before a definitive conclusion can be drawn. Collection efficiencies of ice crystals have been measured and can be significantly increased by strong electric fields. A good quantitative understanding now exists of the heat and mass exchange of hailstones of simplified geometry, permitting accurate predictions to be made of the various growth regimes occurring in natural conditions. The dominant factors governing the density and structure of hailstones have also been established. However, the microphysics of the individual interactions occurring during the riming process is not well understood. None of the explanations that have been presented for the formation and multiplication of ice crystals within clouds at temperatures close to 0 °c have been rigorously explored, although electrofreezing is supported by appreciable evidence and may be responsible for the primary crystals in certain situations.

1. Introduction

In order to achieve a comprehensive understanding of the properties and behaviour of atmospheric clouds it is necessary to approach the problem from two quite separate viewpoints, which should ultimately converge. On the macroscopic scale attention is devoted to the dynamical properties of clouds, the movement of air within and around them, the exchange of energy between the clouds and their environment, the stability of the atmosphere, and the meteorological conditions under which particular cloud types develop, mature, and dissipate. The microphysics of clouds, on the other hand, is concerned with the constituent cloud particles, their interactions, and their growth to produce rain, snow, hail, and other forms of precipitation. It is this second line of approach that is adopted in the present article, the overall objective, as defined by Fletcher (1962 a), being to explain the behaviour of the cloud as a macroscopic entity in terms of the microscopic entities that compose it. Since it is difficult to obtain an overall perspective of the causal relationships and general continuity involved in the development of clouds from the discrete subdivisions utilized in the remainder of this article, a skeletal description of the essential microphysics falling within its scope is presented in the following paragraph.

Clouds are formed because the relative humidity of moist air increases as it is cooled by expansion. At a supersaturation ranging from a few hundredths to several tenths of 1% condensation occurs on microscopic neutral or charged dust particles, solution droplets, or soluble crystals. Above the condensation level the most active nuclei grow into droplets, and the supersaturation passes through a maximum. The number of droplets formed depends upon the number of nuclei activated, which is a function of the maximum degree of supersaturation attained. This depends upon the nucleus spectrum, the air temperature, and the updraught velocity. At temperatures below 0 °c cloud droplets become supercooled. These droplets will not freeze homogeneously unless the temperatures are extremely low, and freezing is generally a consequence of heterogeneous nucleation by foreign particles. Alternatively, ice may grow directly from the vapour on sublimation nuclei. The threshold temperature at which an ice-forming nucleus becomes effective depends upon its dimensions, surface and crystallographic structure, and physical properties. In view of their scarcity, ice crystals are not generally observed in clouds until their summits have penetrated to temperatures as low as about −20 °c, although evidence exists for the formation and multiplication of ice particles at much warmer temperatures in certain types of cloud. In the early stages of cloud development the particles are extremely small and grow only slowly. The cloud is therefore relatively stable. If growth continues the microstructure of the cloud eventually becomes unstable either by collision and coalescence or because of interactions between water droplets and ice crystals. The relative motion of small cloud particles involves complex aerodynamic analysis, and collision efficiencies are difficult to determine. The probability of coalescence or aggregation on collision depends upon a variety of factors including electrical effects and can range from zero to unity; the coexistence of ice crystals and supercooled droplets is immediately unstable in view of the difference in vapour pressure over ice and water. The growth of ice crystals from the vapour is most rapid when the crystals are small, because the diffusion gradients at the crystal surfaces are then very sharp. Once the crystals have become appreciably larger than the coexisting supercooled droplets the difference in their fall velocities produces an accelerating collision rate resulting in the formation of graupel or hail. Snowflakes are formed in glaciated regions of clouds by the aggregation of ice crystals. The development of precipitation particles may be significantly affected by electrical forces at many stages of their growth.

In view of the desire to provide a comprehensive discussion of the microphysical processes outlined in the preceding paragraph, limitations of space have precluded consideration of several topics of importance in cloud physics. These include cloud modification, cloud dynamics, radar studies, sources of atmospheric nuclei, the nucleating ability of specific materials, descriptive material obtained from studies of natural clouds, current techniques of measurement, and the physical properties of water and ice. A final subject to be excluded from consideration is the electrification of clouds. This topic is of great importance but is covered fully in the companion article by Stow (1969).

Despite these restrictions it has been necessary to devote less consideration than is desirable to many excellent microphysical studies. For a more detailed and comprehensive coverage of the various aspects of cloud physics the reader is referred to the excellent textbooks of Mason (1957) and Fletcher (1962 a). For a less advanced but broad coverage of the subject matter the reader is referred to the books of Mason (1962) and Byers (1965).

2. Nucleation processes within clouds

Three phase-changes may be associated with the formation and growth of clouds: the condensation of water vapour to form cloud droplets, the growth of ice from the vapour by means of sublimation, and the freezing of supercooled water droplets. A common characteristic of all three phase-changes is that they require nucleation. In any phase near the transition point there are microscopic variations in structure, discussed by Frenkel (1939, 1946) under the description 'heterophase' fluctuations, which correspond to the transient appearance of embryos of the neighbouring phase. An understanding of the nucleation process can be achieved from a study of these fluctuations.

Although nucleation is effected in the atmosphere by means of foreign particles, and is therefore heterogeneous, the essential physics of these phase-changes can most clearly be illuminated by consideration of the basically similar and simpler process of homogeneous nucleation and then extending this treatment to take account of the nucleating particles. This procedure is adopted in §§ 2.1 and 2.2, which are concerned respectively with the condensation of water vapour and the nucleation of the ice phase within clouds.

2.1. *Condensation of water vapour*

In the case of the homogeneous nucleation of water-vapour condensation the free-energy change ΔG associated with the formation of an embryo droplet of radius r in a supersaturated vapour of pressure p at a temperature T is given by

$$\Delta G = -\frac{4}{3}\pi r^3 n_L kT \ln\left(\frac{p}{p_\infty}\right) + 4\pi r^2 \sigma_{L,V}, \tag{2.1}$$

where n_L is the number of molecules per unit volume of liquid, k is Boltzmann's constant, p_∞ is the equilibrium vapour pressure at the temperature T over a plane liquid surface, and $\sigma_{L,V}$ is the interfacial free energy per unit area between liquid and vapour.

This free-energy change must be a minimum for a system in equilibrium, and the values of ΔG and r at this point are determined by setting $\partial \Delta G/\partial r = 0$ in equation (2.1), which yields

$$\Delta G^* = \frac{16\pi\sigma_{L,V}^3}{3\{n_L kT \ln(p/p_\infty)\}^2} \tag{2.2}$$

and

$$r^* = \frac{2\sigma_{L,V}}{n_L kT \ln(p/p_\infty)} \tag{2.3}$$

for the equilibrium values. Equation (2.3) is the classical formula derived originally by Kelvin (1870).

Droplet embryos with radii $r < r^*$ are unstable and tend to disappear under the buffetings of thermal agitation. However, embryos that have exceeded the critical radius r^* tend to grow without limit and become macroscopic droplets. It is therefore necessary to evaluate the rate at which embryos of this critical size are generated within the vapour. This calculation was first made by Volmer and Weber (1926), and their approach was subsequently improved by Becker and Döring (1935) and by more recent workers.

If we assume that the total number of embryo droplets is negligibly small in comparison with $n(1)$, the number of unassociated molecules per unit volume, then the number of embryos $n(r^*)$ having the critical radius r^* may be represented by

$$n(r^*) \approx n(1)\exp(-\Delta G^*/kT), \tag{2.4}$$

and the flux of embryos through the value r^* is then

$$J = Bn(1)\exp(-\Delta G^*/kT). \tag{2.5}$$

The constant B, representing the net rate at which an embryo of critical size gains one molecule through collisions with surrounding vapour molecules, can be determined from kinetic theory. Substitution of numerical values into equation (2.5) shows that the critical supersaturation for homogeneous nucleation of water-vapour condensation is extremely insensitive to the value of B, which explains why a dense fog suddenly appears as the saturation ratio is increased in expansion-chamber experiments, but is markedly dependent upon temperature. A comprehensive discussion of thermodynamic and kinetic aspects of the homogeneous nucleation of vapour condensation has been provided by McDonald (1962, 1963 a).

A similar procedure can be adopted in calculations of the nucleation rates governing the formation of droplets within atmospheric clouds by means of heterogeneous nucleation on condensation nuclei. In the case of the condensation of water vapour on a plane surface of an insoluble particle, which was first treated in detail by Volmer (1939), the critical supersaturation depends upon the angle of contact ϕ of the liquid on the substrate, which controls the curvature of the embryo droplet. The critical free energy is found to be

$$\Delta G^* = \frac{16\pi\sigma_{L,V}^3}{3\{n_L kT \ln(p/p_\infty)\}^2} f(M), \tag{2.6}$$

where $M = \cos\phi$ and

$$f(M) = \frac{(2+M)(1-M)^2}{4}. \tag{2.7}$$

The value of the critical free energy in equation (2.6) is different from that for the homogeneous case, presented in equation (2.2), only by the factor $f(M)$. Since $-1 \leqslant M \leqslant 1$ it follows from equation (2.7) that $0 \leqslant f(M) \leqslant 1$, so that foreign surfaces have the general property of reducing the free energy necessary to form a critical embryo. Calculation of the number of embryos of critical size and the nucleation rate per unit area follow the same lines as before and will not be presented. A detailed consideration of the kinetics of this process has been presented by Pound *et al.* (1954). Values of the critical saturation ratio required to produce a flux J of 1 cm^{-2}s^{-1} upon a plane substrate of given contact angle at 0 °C have been shown by Fletcher (1962 a) to vary from 1 at $\phi = 0$, through 2·9 at $\phi = 90°$, to 4·4, the homogeneous nucleation value, at $\phi = 180°$. Confirmation of these calculations was found by Twomey (1959 a) using glass surfaces covered with films of more or less hydrophobic substances in a continuous cloud chamber.

A further extension of the Volmer–Weber theory has been made by Fletcher (1958, 1959 a), who included the effects of particle size. If the nucleating particle is considered to be a sphere of radius r then the critical free energy can be evaluated as outlined previously except that the geometry is more complicated. The final result is

$$\Delta G^* = \frac{8\pi\sigma_{L,V}^3}{3\{n_L kT \ln(p/p_\infty)\}^2} f(M, X), \tag{2.8}$$

where

$$X = \frac{r}{r^*} = \frac{r n_L kT \ln(p/p_\infty)}{2\sigma_{L,V}} \tag{2.9}$$

and

$$f(M, X) = 1 + \left(\frac{1-MX}{g}\right)^3 + \left\{2 - 3\left(\frac{X-M}{g}\right) + \left(\frac{X-M}{g}\right)^3\right\} X^3 + 3MX^2\left(\frac{X-M}{g} - 1\right), \tag{2.10}$$

with

$$g = (1 + X^2 - 2MX)^{1/2}. \tag{2.11}$$

The nucleation rate per particle, based on the approximation that the kinetic coefficient is simply proportional to particle area, is given by

$$J \approx \frac{p}{(2\pi mkT)^{1/2}} 4\pi r^2 r^{*2} n'(1) \exp(-\Delta G^*/kT), \tag{2.12}$$

where m is the mass of a vapour molecule and $n'(1)$ is the number of single molecules adsorbed per unit area of surface. When $r > r^*$ the pre-exponential factor has the approximate value $10^{25} 4\pi r^2$.

These expressions were utilised by Fletcher to derive curves, illustrated in figure 1, showing the nucleation behaviour of insoluble particles as a function of radius and contact angle. It can be seen that in order to be an efficient condensation nucleus a particle must not only have a reasonably large diameter, but must also have a small contact angle for water. It is therefore incorrect to follow the procedure of many workers who have simply used the Kelvin equation to determine the nucleation efficiency of small particles; this assumption is correct only if $\cos\phi = 1$.

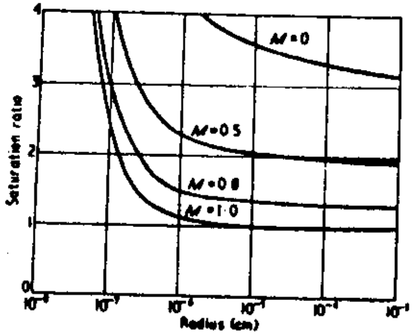


Figure 1. Critical saturation ratio for nucleation of a water droplet in 1 s upon a particle of given radius and with surface properties defined by $M = \cos\phi$. (From Fletcher 1958.)

Evidence in favour of the curves presented in figure 1 has been provided by the measurements of La Mer and Gruen (1952), Twomey (1959 a), and Fletcher (1959 b).

Fletcher (1962 a) pointed out that the existence of surface imperfections such as pits or steps, which will generally occur on nucleating particles, will always lower the supersaturation required for nucleation upon a plane or convex surface if the imperfections are large in comparison with the critical embryo. Indeed, if the contact angle is small enough and the angle of the step sufficiently acute for the embryo to possess a concave surface, then the embryo may be retained under unsaturated conditions, as it would also in a conical cavity, as demonstrated by Turnbull (1950). If the surface features are small-scale, such as the growth steps produced by the emergence of screw dislocations on crystal faces, the critical saturation ratio is not significantly altered. No quantitative studies have yet been made of the influence of surface features on the condensation criteria.

Condensation on ions is of little atmospheric interest, although nucleation theories would benefit from an explanation of the observation of Wilson (1899) that negative ions are active as condensation nuclei at much lower supersaturations than positive ions.

The nucleation of water droplets by small soluble particles is of great importance in the atmosphere. In particular, sodium chloride particles produced by the bursting of bubbles at the ocean surfaces are plentiful and highly efficient condensation nuclei, especially in maritime regions. The droplets involved are so large that it is a valid approximation to neglect the effects of statistical fluctuations and treat the droplets from a macroscopic equilibrium point of view, in which the behaviour of an individual particle becomes completely predictable. Since the water-vapour pressure over an aqueous solution is less than over pure water it is possible in many situations for droplet growth to occur in undersaturated conditions. This problem has been solved to a reasonably high degree of accuracy by the work of Kohler (1926), Wright (1936), Howell (1949), McDonald (1953 a), Dufour and Defay (1953), and many others, and the values of the critical radius and saturation ratio are given approximately by the equations

$$r^{*2} = \frac{3b}{a} \tag{2.13}$$

and

$$\left(\frac{p}{p_\infty}\right)^* = 1 + \left(\frac{4a^3}{27b}\right)^{1/2}, \tag{2.14}$$

where $a \approx 3{\cdot}3 \times 10^{-5}/T$ and $b \approx 4{\cdot}3im/W$; m is the mass of solute of gramme molecular weight W, and i is the van 't Hoff factor. These relations were utilized by Howell (1949) and other workers to derive Kohler curves giving the equilibrium radii of solution droplets as a function of the saturation ratio and to calculate the rates of growth of populations of cloud droplets by condensation. This latter topic is discussed in § 3.2.

Fletcher (1962 a) concluded from a brief discussion of mixed nuclei that condensation is particularly favoured upon particles consisting of a mixture of soluble and insoluble components. The presence of the insoluble components enhances the effectiveness of the soluble salts, since less water is required to make a droplet of given size, and the resulting solution is more concentrated. This important topic has received no detailed attention, however.

2.2. *Nucleation of the ice phase*

Although condensation occurs in the atmosphere at temperatures very close to the dew-point, marked supercooling of cloud droplets below 0 °c is generally observed. These observations are a consequence of the fact that foreign particles that are active in the nucleation of the ice phase are present inside clouds in concentrations much less than those of condensation nuclei. The nucleation of ice crystals within clouds may, in principle, be effected either by the freezing of supercooled water droplets or by direct sublimation of vapour upon foreign particles.

A theory of the homogeneous nucleation of ice crystals within a volume of supercooled water is formally almost identical with the theory of the nucleation of water droplets from a supersaturated vapour, which was considered in § 2.1. Based upon the original analysis of Becker and Döring (1935) it has been extended by several workers, notably Mason (1952), McDonald (1953 b, 1964), and Fletcher (1962 b, 1963 a). Within the supercooled liquid there is a population of water molecules which have combined to form embryonic groups of ice structure, the numbers of groups of a given size depending exponentially upon the free energy required for their formation.

Because ice is a crystalline structure it is no longer generally sufficient to consider the embryos to be spherical, and a more general polyhedral form must be considered. The exposed faces of the embryo will be those of lowest free energy, and the equilibrium habit can be determined by minimizing the total free energy of an embryo of given size with respect to its habit. Since no definite information is available concerning the free energies of different crystal faces it is necessary to use an average free energy σ_{SL} per unit area.

If we assume a particular crystal habit for the embryo then it is convenient to consider an inscribed sphere of radius r so that the volume of the embryo is $\frac{4}{3}\pi r^3 \alpha$ and its surface area $4\pi r^2 \beta$, where α and β are both greater than unity but approach unity as the polyhedron tends to a spherical shape.

Following the procedure adopted in §2.1 it can be shown that the nucleation rate is given by the equation

$$J \approx \frac{n_L kT}{h} \exp\left(\frac{-\Delta g}{kT}\right) \exp\left(\frac{-\Delta G^*}{kT}\right), \tag{2.15}$$

where h is Planck's constant, Δg is the activation energy for self-diffusion across the liquid–solid boundary, and the critical free energy is

$$\Delta G^* = \frac{16\pi \sigma_{SL}{}^3 \epsilon}{3(\Delta S_v \Delta T)^2}, \tag{2.16}$$

where $\epsilon = \beta^3/\alpha^2$, ΔT is the degree of supercooling, and ΔS_v is the entropy of fusion of ice per unit volume. Since the coefficient of $\exp(-\Delta G^*/kT)$ is of order 10^{33} cm^{-3}s^{-1} the nucleation rate may be expected to have a very sharp threshold. This prediction is qualitatively consistent with the observation of an extremely well-defined freezing threshold close to −40 °c.

Accurate computations of the rate of production of embryos as a function of the degree of supercooling cannot be made at present in view of uncertainty as to the geometry of the embryo, the value of Δg, and, particularly, the correct values of σ_{SL}. However, Mason (1952), utilizing the assumption that the embryo possesses the form of an isometric hexagonal prism and values of σ_{SL} calculated from the measured freezing temperatures of extremely pure droplets in the diameter range 1–50 μm, derived curve (ii) of figure 2, which is seen to be in excellent agreement with experimentally determined freezing temperatures of very pure drops over an extremely wide range of diameters. More recent measurements by Hoffer (1961) are also in good agreement with Mason's curve. Figure 2 also demonstrates that the median freezing temperature of impure water drops of diameter ranging from about 20 μm to 2 mm is related to the drop volume V by the equation

$$\log V = A - B(273 - T), \tag{2.17}$$

where A and B are constants for the particular sample of water under test.

The formal theory of the homogeneous nucleation of ice by sublimation has been covered essentially by the foregoing discussions of condensation and freezing, and will therefore not be presented. However, because of the rough similarity in the surface free energies of ice and water, the processes of homogeneous condensation and homogeneous sublimation proceed under similar conditions, and when the temperature is below 0 °c it is interesting to determine which process will occur more rapidly. Fletcher (1962 a) has shown that the rate of formation of crystals will exceed those of droplets if

$$\frac{\ln(p/p_S)}{\ln(p/p_L)} > \epsilon^{1/3} \frac{n_L}{n_S} \left(\frac{\sigma_{SV}}{\sigma_{LV}}\right)^{3/2}, \tag{2.18}$$

where p_S and p_L are the saturated vapour pressures over a plane surface of ice and water respectively, n_S and n_L are the corresponding numbers of molecules per unit volume, and σ_{SV} and σ_{LV} the corresponding interfacial free energies. From a consideration of equation (2.17) and the experiments of several workers Fletcher concluded that sublimation will not be important at temperatures above about −65 °c.

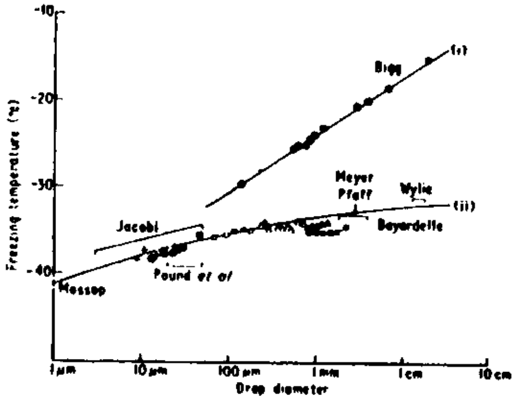


Figure 2. Freezing temperatures of supercooled water drops as a function of their diameters. (i) Experimental points of Bigg (1953 a) for drops containing foreign nuclei; curve based on equation (2.17); (ii) experimental points of Mossop (1955), Jacobi (1955), Pound *et al.* (1953), Bigg (1953 a), Meyer and Pfaff (1935), Bayardelle (1955), Wylie (1953), Carte (1956), and Langham and Mason (1958) for extremely pure drops, and curve for homogeneous nucleation from equation of Mason (1952): ● Bigg; + Carte; △ Mossop; □, ■ Langham and Mason.

Median freezing temperatures for diameters < 0·5 mm; otherwise lowest freezing temperatures. (From Mason 1962.)

The most satisfactory method of increasing the amount of precipitation from supercooled clouds is to initiate the ice phase by introducing seeding material, such as silver iodide, in the form of small particles. However, the degree of quantitative control over precipitation amounts is extremely small, since the physics and dynamics of cloud modification is imperfectly understood. The practical problem is to predict the nucleation behaviour of an aerosol of given size distribution when introduced into a cloud at a particular temperature. Before this problem can be solved it is necessary to understand the molecular kinetics and energetics of the heterogeneous nucleation of the ice phase. A detailed review of current thinking on this topic has been presented by Fletcher (1965).

In heterogeneous nucleation we consider the growth of an ice embryo upon a small foreign particle. The presence of the particle eliminates many of the statistical difficulties encountered in the theory of homogeneous nucleation, and since the experimental conditions are generally such that the embryo contains many thousands of molecules the validity of applying macroscopic concepts such as surface free energy is not really in question.

Following Fletcher (1960, 1963 b, 1965) we consider a small crystalline embryo 2 of prismatic habit growing upon a plane substrate 3, in an environment 1. The free energy ΔG required for the formation of this embryo depends upon the interfacial free energies σ_{ij} between the different phases and the free-energy difference ΔG_v per unit volume between phases 2 and 1. If the embryo has n prismatic faces, a thickness h, and a minimum width $2r$, then an explicit expression for ΔG can be written

$$\Delta G = \omega n r^2 h\,\Delta G_v + \omega n r^2(\sigma_{12} - \sigma_{13} + \sigma_{23}) + 2\omega n r h \sigma_{12}, \tag{2.19}$$

where

$$\omega = \frac{\pi}{n}\tan\left(\frac{\pi}{n}\right). \tag{2.20}$$

The expression for ΔG can be simplified by introducing the parameter

$$m = \frac{\sigma_{13} - \sigma_{23}}{\sigma_{12}}, \tag{2.21}$$

which measures the compatibility of the embryo with the substrate; m lies between -1 and $+1$ and approaches $+1$ for complete compatibility.

The critical free energy ΔG^* can be determined in the manner described previously, and it is then possible to estimate the distribution of embryos of various sizes upon the nucleating substrate. A similar procedure can be followed for shapes other than prismatic. In undersaturated conditions the distribution will be static, although individual molecular clusters will continually form and disperse. In supersaturated conditions the nucleation rate of free-growing crystals can be written

$$J \approx K \exp\left(-\frac{\Delta G^*}{kT}\right), \tag{2.22}$$

where the kinetic factor K involves both the number of adsorbed single molecules per unit area and a factor describing molecular capture. For the growth of ice crystals from the vapour K is extremely large ($\sim 10^{26}\ \mathrm{cm^{-2}\,s^{-1}}$), and the nucleation behaviour is therefore very sharp.

More general consideration of nucleation processes, together with a discussion of the nucleation behaviour of stepped surfaces, cavities, capillaries, and small particles, has been presented by Turnbull (1950), Fletcher (1958, 1959 a, 1960, 1962 a, 1963 c), Head (1961), and Higuchi and Fukuta (1966). In general, steps and re-entrant corners are favoured nucleation sites, and the nucleation efficiency of small particles decreases as their size decreases. This latter effect becomes serious for particles less than about 0·1 μm in diameter.

Fletcher has used the foregoing theory to calculate curves defining the temperature below which a particle of a given size and surface parameter m will nucleate an ice crystal within a particular time interval either by direct sublimation from the vapour or by freezing. The calculations in each case involve assumptions as to the free energy of an ice–vapour or ice–water interface, but the curves are not critically dependent on the values assumed and are also fairly insensitive to the shape of the particles involved. It is therefore possible to predict the nucleation behaviour of an aerosol from these curves provided it is known whether it acts by direct sublimation or by condensation followed by freezing, and that its particle-size distribution and the appropriate value of m can be found. In practice, however, it is difficult to establish these facts directly. For instance, in the case of silver iodide Fletcher (1959 b) has presented evidence suggesting that ice-crystal formation occurs by direct sublimation, and he derived on this assumption a theoretical curve of activity against temperature (Fletcher 1959 c) which was in excellent agreement with most experimentally determined activity curves. However, in the detailed studies of Bryant *et al.* (1959) and of Mason and van den Heuval (1959), who examined the nucleation behaviour of essentially plane and nearly monocrystalline substrates of silver iodide, it was found that at temperatures above − 12 °c ambient conditions slightly exceeding water saturation were required before ice crystals nucleated upon the substrate. This work suggests that between − 12 °c and the threshold temperature of − 4 °c ice-crystal formation is initiated by condensation followed by freezing. There exists a conflict, therefore, between the measured relationship between nucleating ability and particle size, which cannot be explained if silver iodide particles act as freezing nuclei, and the observed nucleation threshold of − 4 °c which is apparently inconsistent with the sublimation mechanism.

Further information which illuminates this problem is provided by the careful measurements of the nucleation behaviour of nearly monodisperse silver iodide aerosols performed by Edwards and Evans (1960, 1961, 1968) and Edwards *et al.* (1962). They established that silver iodide particles prepared at the isoelectric point are generally more efficient as freezing nuclei than as sublimation nuclei, and that even in carefully prepared monodisperse aerosols particles of the same size and habit may have different nucleation thresholds. This second finding is probably associated with the state of ionic adsorption or surface charge on the nucleating crystal, as predicted by Fletcher (1959 d). Fletcher (1965) considered it unlikely that the particles possessed surface features of dimensions sufficiently large to contribute significantly to this variability.

Fletcher concluded that freezing was probably the operative nucleating mechanism in the laboratory experiments described previously. In atmospheric clouds, however, the supersaturation rarely exceeds 0·1%, which is not sufficient to cause condensation upon a plane silver iodide surface, although some capillary condensation could occur in re-entrant cavities. The nucleation behaviour of a smoke under these circumstances will thus depend in detail upon its mode of preparation and injection into the cloud, and may well differ greatly from the predictions of laboratory measurements.

Clarification of the conflicting evidence concerning the mechanism responsible for the nucleation of the ice phase in atmospheric clouds and modification experiments is provided by the recent studies of Fletcher (1968). He made a revised calculation of the nucleation efficiency of silver iodide smokes as produced by real burners. In his original treatment Fletcher (1963 b) obtained theoretical activity curves on the assumption that the smoke particles acted as sublimation nuclei with a threshold temperature of − 4 °c. His revised calculations took account of the studies of Pruppacher and Neiburger (1963), Linke (1965), and De Pena and

Caimi (1967), together with the fact that the smokes contain a hygroscopic component which causes condensation on the particles in a cloudy environment. Nucleation then occurs by freezing with a threshold of −4 °c, as shown in figure 3, and sublimation is not of appreciable importance. The output curves predicted from this revised treatment are very similar to those derived from the sublimation mechanism but are about one order of magnitude higher, and in good agreement with experiment. This, however, is a much smaller output than would be predicted for simple freezing behaviour without the intervention of the soluble component.

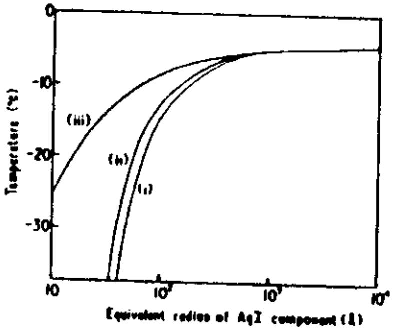


Figure 3. Calculated nucleation thresholds for smoke particles of (i) $(\mathrm{AgI})_4 \cdot \mathrm{KI}$ and (ii) $\mathrm{Ag} \cdot \mathrm{KI}$ in a cloud environment. Curve (iii) indicates the freezing threshold for AgI particles suspended in pure water. (From Fletcher 1968.)

Fletcher concluded that although the calculations were carried out for a silver-iodide–potassium-iodide complex the behaviour is not sensitive to the exact nature or mole fraction of the soluble component, so that the results may be regarded as having wide generality.

The consensus of evidence suggests that ice crystals are generally formed in situations of atmospheric importance by condensation followed by freezing, and not directly by means of sublimation. In this connection it should be noted that once a thin film of water has condensed upon a nucleating particle it may freeze owing to the nucleation of ice by the particle surface. A liquid film 100 Å in thickness may be sufficient for this purpose, so that no macroscopic droplet is developed, and current detection techniques would merely reveal the growth of an ice crystal. In addition, Fletcher (1962 a) has pointed out that a composite nucleus containing a soluble and an insoluble particle can act as a freezing nucleus at less than ice saturation.

From a discussion of the molecular aspects of nucleation and the studies of Fletcher (1959 c, 1962 b, 1963 a, 1964), Edwards and Evans (1962), Zettlemoyer *et al.* (1961, 1963), Mason *et al.* (1963 a), Van der Merwe (1963), and Miloshev and Krastanov (1963), Fletcher (1965) has proposed several criteria for efficient nucleating agents:

1. The habit faces of the nucleating material should expose at least one set of atomic sites that are close to the geometry of water molecules in some low-index plane of ice.

2. In order to reduce the entropy penalty the set of sites considered should contain approximately equal numbers of positively and negatively charged members.
3. The material should have a low shear modulus in order to minimize the elastic strain energy.
4. The nucleating surface should be hydrophobic and, in the case of sublimation, show finite but minimal water-vapour adsorption.

Fletcher concluded that a proper understanding of nucleation phenomena will be derived primarily from further fundamental studies of the structure and energetics of the interfaces involved, and of the adsorption and growth phenomena associated with them.

3. The growth of raindrops within clouds

Raindrops may be formed by the interaction of cloud droplets or by the melting of ice particles. In this section we are concerned with the former process, in which the growth does not involve the ice phase. The initial growth of cloud droplets occurs by condensation on active nuclei. This process becomes increasingly ineffective as the droplets grow, primarily because the concentration gradients of water-vapour molecules at the droplet surfaces diminish with increasing size, and is supplanted at a radius around 20 μm by collision and coalescence, a mechanism that becomes increasingly powerful as the droplet size increases. A knowledge of the collision and coalescence efficiencies of colliding droplets is of crucial importance for calculations of the rates of growth of droplets. These efficiencies are extremely sensitive to droplet sizes and the strength of electrical forces in the early stages of growth.

In calculations of the rates of growth of populations of cloud droplets by condensation or coalescence it is necessary to consider the combined influence of the growing particles upon their mutual environment.

3.1. *Growth of individual droplets from the vapour*

In §2 a discussion was presented of the nucleation of a liquid droplet on a foreign particle. Inside a cloud the concentration and distribution of droplets formed by this condensation process will depend upon those of the available active nuclei. The next stage of the growth process is continued growth by diffusion of water vapour to the droplets in a supersaturated environment.

We consider initially the growth of a solution droplet of radius r and density ρ_L at rest in a supersaturated environment in which the concentration of vapour molecules at a great distance from the droplet is n_0. This vapour diffuses towards the droplet and condenses upon it, and from the requirements of continuity of flow we can write the concentration of vapour molecules at any point R by the approximate equation

$$\nabla^2 n(R) = 0. \tag{3.1}$$

Solution of this equation with appropriate boundary conditions gives

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{D\rho_v}{r\rho_L}\left(\frac{p-p_r'}{p}\right), \tag{3.2}$$

where D is the diffusion coefficient of the vapour molecules, ρ_v the density of water vapour in the environment, p the partial pressure of vapour at a large distance from the droplet and p_r' that in equilibrium with the surface of the droplet.

The growth rates predicted by equation (3.2) are applicable, with a high degree of accuracy, to droplets at rest in their environment. In clouds, of course, droplets will be falling at their terminal velocities relative to the immediately surrounding air, and this ventilation effect increases the rate of supply of moisture. The corrected growth equation is given by

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{D\rho_v}{r\rho_L}\left(\frac{p - p_r'}{p}\right) f(Re, Pr'), \tag{3.3}$$

where the ventilation factor $f(Re, Pr')$, involving the Reynolds number Re and Pr', the analogue of the Prandtl number, has been calculated by Squires (1952 a) and ranges from 1·03 for droplets of 10 μm radius to 1·66 when $r = 100$ μm.

The next stage in the development of the growth equations is to evaluate the vapour pressure p_r' in equilibrium with the droplet during its growth. This involves the curvature of the droplet surface, the presence of solute, and the heating of the droplet by release of latent heat of condensation, a process that is governed by a continuity equation identical to (3.1) except that n is replaced by the temperature T. Incorporation of these factors along the lines already discussed results in a final growth equation, correct to a high degree of accuracy,

$$r\frac{\mathrm{d}r}{\mathrm{d}t} = G\left(S - \frac{a}{r} + \frac{b}{r^3}\right) f(Re, Pr'), \tag{3.4}$$

where S is the supersaturation of the environment relative to a plane surface of pure water, a and b involve respectively the effects of surface curvature and solute concentration upon p_r', and

$$G = \frac{D\rho_v}{\rho_L}\left\{1 + \frac{DL^2 \rho_v M_0 f(Re, Pr')}{RT^2 k f(Re, Pr)}\right\}, \tag{3.5}$$

where M_0 is the gramme molecular weight of water, R is the gas constant, L is the latent heat of vaporization of water, k is the thermal conductivity of air, and the dimensionless function $f(Re, Pr)$, involving the Prandtl number Pr, is a ventilation factor associated with the removal of heat from the droplet. Equation (3.4) is quite general and applies to the evaporation of large raindrops as well as to the growth or evaporation of cloud droplets. Equations governing the evaporation of raindrops in the presence of vertical gradients of temperature and relative humidity have been derived by Caplan (1966).

3.2. *Growth of a population of cloud droplets by condensation*

Equation (3.4) describes the growth of a single droplet in a supersaturated environment. However, in the atmosphere we are concerned with the growth of a large population of droplets in a rising air mass. Although it can be shown that in the early stages of growth, corresponding to drop radii of less than 10 or 20 μm, the large separations of individual droplets render their probability of mutual interaction negligible, the droplets nevertheless influence each other through their combined influence on their common environment.

A qualitative picture of the condensation process in a rising current of air can readily be presented. As the air ascends it expands approximately adiabatically, and the saturation ratio increases. As soon as the saturation point has been passed condensation occurs on the available suspended nuclei, the most efficient being activated first. For a period of time thereafter the supersaturation continues to increase, an increasing number of nuclei are activated, and the rate of production of liquid water continues to rise. Eventually, however, the increased rate of vapour removal associated with the growth of cloud droplets, which can be deduced by re-expressing equation (3.4) in terms of the rate of mass increase of droplets, produces a reduction in the degree of supersaturation which falls towards zero. Since, as can be seen from equation (3.4), $\mathrm{d}r/\mathrm{d}t \propto r^{-1}S$ the initially wide range of droplet sizes produced by the broad activity spectra of condensation nuclei will be narrowed as the smaller droplets grow more rapidly than the larger ones.

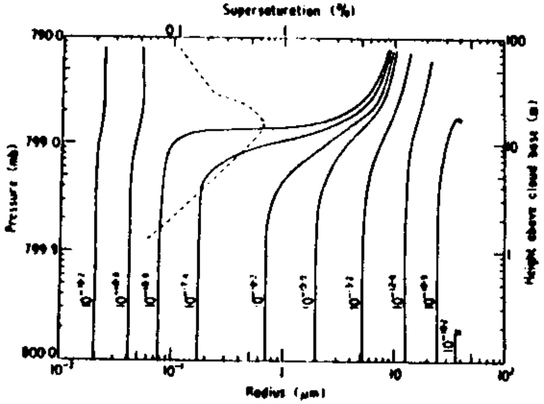


Figure 4. Growth of a population of droplets from a given distribution of NaCl nuclei as computed by Mordy for air ascending at 15 cm s⁻¹. The variation of the supersaturation is given by the broken curve in accordance with the scale at top. Each growth curve is labelled in terms of the number of moles of NaCl contained. (From Mordy 1959.)

The growth of populations of cloud droplets has been studied quantitatively by several workers using computational techniques, and the predictions of the preceding general argument have been confirmed. The general procedure adopted by Howell (1949), Mordy (1959), and Neiburger and Chien (1960) has been to assume an initial spectrum of nuclei and updraught speed U and to compute the rate of growth of droplets by condensation in an environment whose supersaturation can be calculated from the value of U by means of equations of the type formulated by Squires (1952 b), which assumes adiabatic ascent. Twomey (1959 b) has made similar calculations using observed nucleus spectra.

Typical growth curves of a population of droplets from a given distribution of sodium chloride nuclei computed by Mordy, which illustrate the narrowing of the droplet spectra and the increase and subsequent decrease of the supersaturation, are presented in figure 4. These curves also demonstrate that extremely small nuclei are ineffective in promoting growth at supersaturations of magnitude comparable with those occurring within clouds, and that giant sodium chloride nuclei grow extremely rapidly and fall out of the cloud. A further point evident from figure 4, which is also borne out by the calculations of the other workers, is that the supersaturation in a growing cloud is extremely small, typically about 0·1%, surpassing 1% only under extreme conditions.

The calculations of Howell, of Neiburger and Chien, and of Mordy were all based on the assumption that no mixing occurred between a parcel of air containing a specified population of condensation nuclei and its surroundings. However, the mixing parameter deduced by Mason and Emig (1961) permitted Mason and Chien (1962) to compute the growth of droplets by condensation upon a spectrum of salt nuclei as they are carried up in a small cumulus which mixes and exchanges heat, momentum, and water vapour with its surroundings. They showed that the fact that some droplets remain in the cloud longer than others is largely responsible for the evolution of a broad drop-size distribution which much more closely resembles observed spectra than those obtained from the previous calculations for a closed parcel. They conclude that it is difficult to explain the appearance of droplets larger than 30 μm radius in concentrations of order 1 cm^{-3} in terms of their growth on reported concentrations of giant hygroscopic nuclei.

The narrowing of the droplet spectra as condensation continues, predicted by Twomey, Mordy, and Neiburger and Chien and confirmed by East (1957), exposes a central problem of cloud physics. Since condensation produces a narrow spectrum of droplets of radii mainly of the order of 10 μm, how does a cloud produce rain? Although it has been demonstrated that mixing between different air parcels and variations in nuclei spectra and updraught velocity can produce some modifications of the predicted spectra, it is evident that condensation alone cannot produce precipitation within the available time. In the following sections the various mechanisms are discussed that may operate to produce the growth of precipitation within water, ice, and mixed clouds.

3.3. *Calculations of the collision efficiencies of cloud droplets*

Despite the narrowing of droplet spectra which has been shown to accompany continued growth of cloud droplets by condensation, the differences in radii and consequently in terminal fall velocities of droplets under gravity may cause droplets of different sizes to collide and coalesce. This mechanism will be particularly effective if giant salt nuclei are available to act as condensation centres, thereby producing larger droplets and correspondingly greater differential velocities and initiating an avalanche process in which the number of collisions and coalescences increases rapidly with time and results in the formation of raindrops. The efficacy of this growth process is crucially dependent upon two parameters: (i) the collision efficiency, which may be defined as the probability that a larger droplet will collide with a smaller one in its direct path, and (ii) the coalescence efficiency, defined as the fraction of colliding droplets that coalesce. The values of both parameters are expected to be sensitive functions of the radii of the interacting drop pairs and the strength of prevailing electrical forces. In view of the necessity for effecting a broadening of the narrow spectra of droplet radii produced by condensation, perhaps the most vital requirement is for accurate values of the collision efficiencies of cloud droplets in the radius range 10–30 μm.

In the case of the interactions of small droplets of similar size it is necessary to treat pairs of spheres in viscous flow. The Stokes approximation can be applied to the hydrodynamical equations describing the motion of two neighbouring spheres at low Reynolds numbers, taking account of the mutual interference of the flows. In an important paper Hocking (1959) found a solution for small droplets (of radius less than about 30 μm) by computing the drag force due to the flow field around both spheres. Since the accuracy decreases when the spheres are of very different sizes the method was not applied if the ratio r/R of the smaller to the larger droplet was less than 0·2. If, however, r/R is very close to unity the spheres repel each other.

Hocking's results for collecting droplets of radii 19, 20, 25, and 30 μm are reproduced in figure 5, where the collision efficiency E is plotted against the radius ratio r/R. E is defined as the fraction of those droplets, whose centres lie within the volume swept out by the falling drop, that are ultimately collected by it. The collision efficiencies are seen to be extremely sensitive to variations in R and r/R. Efficiencies exceeding 1·0 are seen to be possible in some cases, indicating a capture effect. However, the most important point that emerges from this calculation is that when the collecting drop has a radius of 18 μm or less its collision efficiency is essentially zero for all smaller droplets. The stability of most non-precipitating clouds is almost certainly a consequence of this sharp cutoff in collision efficiency, since droplets of radii greater than 20 μm are generally present inside such clouds only in extremely low concentrations. However, as pointed out by Fletcher (1962 a), the computed trajectories for small droplets just escaping collision shows that the droplets roll around each other with a spacing between their surfaces amounting to only a few per cent of the radius of the small droplet. This suggests that any mechanism that might cause distortion of the droplet surfaces at their closest approach might be effective in increasing the collision efficiency for such droplets from zero to some finite value.

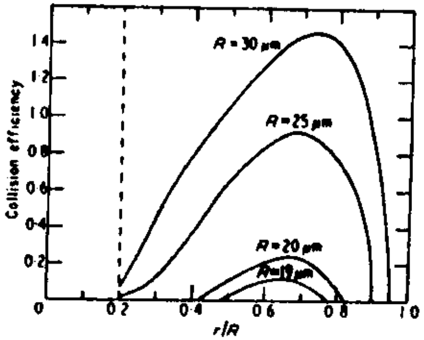


Figure 5. Collision efficiency according to Hocking for drops of radius R and droplets of radius r. (From Hocking 1959.)

For droplets larger than those considered by Hocking, collision efficiencies lie generally in the range 0·5 to slightly greater than unity. Accurate knowledge of collision efficiencies is therefore not so crucial a requirement since growth by collision and coalescence will assuredly occur, and variations of E will not influence growth rates profoundly. Nevertheless, the collision efficiencies at Reynolds numbers up to about 20, corresponding to water droplets of radius below 136 μm falling in air at 900 mb and 0 °c, which have been calculated by Shafrir and Neiburger (1963), are extremely useful for computations of the rates of growth of raindrops within clouds. In their study the drag force on each sphere was approximated using only the disturbance of the flow field due to the other sphere. The flow fields, including the nonlinear effects, were evaluated by a modification of a method followed by Jenson (1959). Using these flow fields for various spheres, trajectories for each pair were integrated and the collision efficiency determined. Their predicted collision efficiencies were close to 1 over an extremely wide range of r/R, falling fairly rapidly towards zero for values of r less than about 40 μm and more sharply towards zero for values of r/R greater than about 0·95. They conclude from this sudden reduction in E calculated for spheres of similar size that the wakes developed behind them are too weak to influence significantly the trajectories of the droplets. For drops of radius greater than 136 μm colliding with much smaller droplets the collision efficiencies deduced by Langmuir (1948), on the assumption that the droplet exerts a negligible influence on the airflow around the drop, appear to be adequate.

Despite the general acceptance of Hocking's calculated collision efficiencies and some experimental corroboration of his predictions provided by the experiments of Picknett (1960) and Woods and Mason (1964), recent calculations employing two independent methods of approach by Davis (1966), Sartor (1967 a), and Davis and Sartor (1967), using a much larger computer than was available to Hocking, suggest that his values are inaccurate and, in particular, that finite collision efficiencies do exist for larger droplets of radius less than 19 μm. Davis, following an approach used by Stimson and Jeffrey (1926) and Mande (1961), obtained a closed-form analytical solution to the two-sphere hydrodynamic problem. On the other hand, Sartor's method of determining the aerodynamic forces on the droplets consists of an extension of Hocking's solution, which is in the form of an infinite set of linear equations with an infinite number of unknowns, two of which are the drag coefficients. Hocking was forced to truncate the equation in a way that retains terms for his solution only as far as the seventh power in the reciprocal of the distance between the droplet separation expressed in units of R. This limitation was responsible for restricting Hocking's solution to radius ratios greater than 0·2. Sartor was able to retain many more equations and unknowns, obtaining the drag coefficients through matrix inversion techniques. In the methods of both Davis and Sartor the hydrodynamic forces were combined with gravitational forces to obtain relative droplet trajectories. Although the two approaches are quite distinct the results obtained by Davis and Sartor are identical within computational error.

Collision efficiencies computed by Sartor (1967 a) are illustrated in figure 6. It can be seen that over a wide range of r/R the values of E predicted by Hocking and Sartor are in close agreement for values of R close to 30 μm, but that significant deviations occur for smaller values of R and for values of r/R close to unity. In particular, Hocking's prediction that droplets of radius less than about 18 μm will not collide with droplets of smaller size is completely at variance with Sartor's calculated appreciable values of E occurring for $R = 8$ μm over a wide range of r/R. Another major discrepancy between the two studies illustrated in figure 6 is that Sartor predicts significant values of E for droplets of almost identical radii, whereas Hocking computed the probability of collision to be zero. The differences between the calculated collision efficiencies of Sartor and Hocking, although restricted to extremely small droplets, may be crucial to an explanation of the development of precipitation in water clouds. On the basis of his more extensive computational treatment, his excellent agreement with the independent calculations of Davis, and the observed development of rain within warm clouds, in which the effects of electrical forces or giant nuclei would not be expected to be important, it appears reasonable to conclude that Sartor's values of E are more accurate than those of Hocking and that the probability of collision of cloud droplets of radii less than 19 μm may be greater than zero. Support for this conclusion is provided by the model experiments of Telford and Cottis (1964).

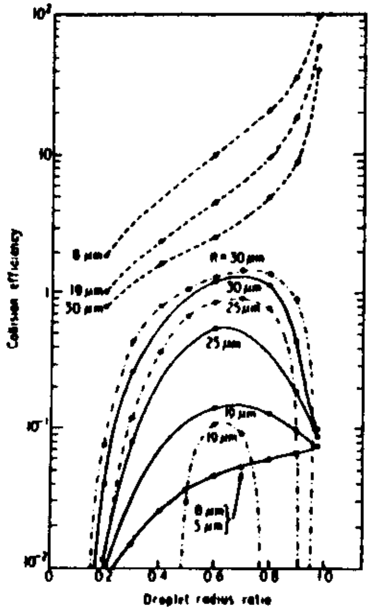


Figure 6. Collision efficiencies for uncharged drops of larger radius R in vertical electric fields of strength E. —— Sartor, $E = 0$; -·-·- Hocking, $E = 0$; - - - Sartor, $E = 6·9$ e.s.u.

Pearcey and Hill (1957) utilized Oseen's approximate solution of the hydrodynamic equations to compute the velocity field around a water droplet falling at terminal velocity. They predicted a parabolic wake for spheres of radius greater than about 35 μm, in which the velocities increase rapidly with increasing Reynolds number. A falling droplet of radius greater than this critical value may therefore capture a larger overtaking drop by sucking it into its wake. This effect may be observed even with droplets of the same size if they approach within a few drop diameters. Pearcey and Hill deduced that the collision cross section for drops of equal or nearly equal size will be many times the geometrical value, in view of the long interaction times resulting from their small relative velocities. On the other hand, the computations of Shafrir and Neiburger, supported by the analysis of Shafrir (1965), suggested that the collision efficiencies of drops of nearly equal size are zero. The large disagreement existing between these studies has been moderated by recent refined calculations by Neiburger (1967), who obtained values of collision efficiency that approach unity for radii of the bigger drop larger than 63 μm and decrease as though tending towards zero for smaller radii.

It is possible in principle that the number of collisions between cloud droplets of different size might be appreciably increased in a turbulent air stream, since velocity fluctuations of a particular frequency may increase the relative velocities between the large and small droplets owing to differences in their inertia. Mason (1957) concluded from a detailed discussion of this problem, based on the studies of East and Marshall (1954) and Saffman and Turner (1956), that the influence of small-scale turbulence in modifying the development of precipitation in all types of cloud is insignificant.

The strength of the electric fields within clouds ranges, in general, from several times the fair-weather value in non-precipitating clouds and clouds in the early stages of their development to breakdown magnitudes in thunderclouds. Median values of the charges carried on droplets in various types of cloud are approximately proportional to the radius of the droplets (Krasnogorskaya 1961, 1965, Petrov 1961) or the square of the radius (Twomey 1956, Krasnogorskaya 1968), and increase with increasing field strength. The collision efficiencies of cloud droplets will be influenced appreciably when the electrostatic forces between a pair of interacting droplets become comparable with the aerodynamic and gravitational forces. Computations of the effect of electric forces on droplet collision efficiencies have been made by Sartor (1960), Lindblad and Semonin (1963), Krasnogorskaya (1965), Plumlee and Semonin (1965), Davis (1965), Sartor and Miller (1965), Semonin and Plumlee (1966), and Sartor (1967 a). The electrostatic forces between charged cloud droplets situated in an electric field have been derived in the majority of these studies from the equations of Davis (1964) for conducting spheres, which have been verified experimentally by Saunders (1968 a).

Broad general agreement exists between the results of these various studies. The calculations predict that for highly charged droplets interacting in fields approaching breakdown magnitudes the collision efficiencies can be drastically different from those existing in the absence of electrical forces. The collision efficiencies are increased or decreased according to the balance between the sign and magnitude of the field and the individual droplet charges, although the majority of permutations favour an increase. For instance, Krasnogorskaya predicts that two uncharged droplets of radii 15 and 25 μm, which possess a collision efficiency of about 0·8 in the absence of a field, will possess values in vertical electric fields of strength 2, 6, and 10 kv cm^{-1} of 1·6, 5·2, and 8·4 respectively. If the radii of the uncharged interacting droplets are reduced to 8 and 10 μm, the predicted collision efficiencies are found to increase even more rapidly, from zero in the absence of a field to unity at a field strength of about 500 v cm^{-1} and approximately 4 at 1000 v cm^{-1}. Again, Krasnogorskaya computes that droplets of radii 6 and 10 μm, which do not collide in the absence of electrical forces, possess a collision efficiency of 0·31 if they carry charges of 10^{-7} and 10^{-6} e.s.u. respectively in zero field, and 1·20 if they interact, carrying the same charges, in the presence of a vertical positive field of strength 1200 v cm^{-1}. The effect of electric fields of thunderstorm magnitudes upon the collision efficiencies computed by Sartor (1967 a) for uncharged droplets of various sizes and radius-ratios is illustrated in figure 6.

Approximate equations of motion of two oppositely charged spheres moving in parallel electrical and gravitational fields through a motion-resisting medium were integrated numerically by Atkinson and Paluch (1968) to determine their effective cross section for collision. The 10 input parameters that determine the collision efficiency under the limitations imposed were assigned values appropriate for studying the motion of highly charged droplets in a thunderstorm. This study provides useful information concerning relative trajectories of droplets and the influence of electric forces on collision efficiencies. However, since the average separation of small droplets within clouds is about 100 radii, and the influence of surrounding droplets on the interaction of a droplet-pair becomes appreciable at separations below this value, the extremely high values of collision efficiency computed in certain situations by Atkinson and Paluch on the assumption of an isolated droplet-pair can have no atmospheric relevance.

An additional insight into the problem of the influence of electric forces on the growth of cloud particles has been provided by Colgate (1967). He considers the macroscopic process of the interaction between the intense pre-discharge fields within a thundercloud and the individual droplet charges. The stress due to an electric field in a cloud results in an unstable hydrostatic equilibrium, and so only a turbulent kinetic energy stress will lead to a steady state. The magnitude of the turbulence for a particular eddy size is related to the field energy density by the Kolmorgorov spectrum, and an eddy size of about 150 m is predicted for the initiation of lightning discharges. The charge separation required to give this breakdown electric field results in an average drop charge of 9×10^{-7} e.s.u. and a relative acceleration between positive and negative drops of 15 times gravity. This is sufficient to ensure rapid coalescence throughout the whole condensation drop spectrum. Although this mechanism will be ineffectual in weak fields, and therefore could not contribute significantly to the initial growth of drops by coalescence, its efficacy increases rapidly with increasing field strength, and it may be of paramount importance in fields of breakdown magnitudes. It is probable that this process contributed significantly to the observed rapid growth rates of precipitation discussed in § 3.4.

The calculations of these various workers demonstrate that, in general, the influence of electrical forces is most pronounced for smaller droplets, specifically for interacting pairs of droplets with low relative velocities. Perhaps the most important conclusion emanating from these computations is that electrostatic forces will promote collisions between droplets that would not come into contact in the absence of such forces. Hocking's cutoff radius is certainly inapplicable to interactions in the presence of strong electrical forces. The computations indicate that fields of magnitude below about 100 v cm^{-1} probably exert an insignificant influence upon the collision efficiencies of droplets, in which case the electrical forces operating within the great majority of clouds will be insufficient to modify the growth of raindrops. On the other hand, the influence of electric fields and charges will be greatest precisely in situations where the effect of an increase in the collision efficiency is most profound, namely where a cloud consists of extremely small droplets that possess zero or minimal efficiencies in the absence of a field. Under these conditions electrical forces may provide a trigger for the growth by coalescence of precipitation elements within a cloud. A more definitive assessment of this possibility must wait upon the measurement of experimental values of collision efficiencies and further information concerning the electrical properties of non-precipitating clouds.

3.4. *Experimental studies of the collision and coalescence of cloud droplets*

Presently available techniques do not permit direct laboratory measurements to be made of the collision efficiencies of water droplets. The parameter that has been measured is the collection efficiency, which is the product of the collision efficiency and the coalescence efficiency; although the coalescence efficiency will, in principle, be a function of the sizes of the interacting droplets and the strength of the prevailing electrical forces, considerable justification has been provided for considering its value to be unity for small cloud droplets.

Sartor (1954), Schotland (1957), Neiburger and Pruppacher (1965), and others have made some interesting model experiments in which the fall of cloud droplets in air was simulated by the fall of pairs of solid spheres or liquid drops through liquid viscous media. The requirements for dynamical similarity are that the Reynolds numbers, the radius ratio, and the ratio of the densities be matched, but the third condition is impossible to achieve in such experiments. The occurrence of a collision was determined from visual observation, changes in momentum, or charge transfer between the spheres. Over quite a considerable range of radii Sartor's values of collision efficiency agreed with those of Hocking, those of Schotland with those of Pearcey and Hill, and those of Neiburger and Pruppacher with those of Shafrir and Neiburger. However, in all three studies significant deviations occurred in certain situations, which were probably a consequence of the difficulty of determining whether the interacting simulated droplets actually came into contact. For this reason, together with the inability to attain complete dynamical similarity and the probability that the mechanisms of removal of barrier films of oil and air are quite different, these model experiments, although useful in illuminating many aspects of the relative motion of interacting cloud droplets, cannot be regarded as providing independently reliable values of collision efficiencies.

Several investigations designed to measure the collection efficiencies of cloud droplets have been conducted in recent years. The collection efficiencies measured by Gunn and Hitschfeld (1951) for drops of 1·5 mm radius falling through droplets of radius 6–100 μm were in good agreement with the collision efficiencies computed by Langmuir. Kinzer and Cobb (1958) traced the growth of single droplets as they fell through a dense and fairly uniform fog of droplets of radii 5·5–8 μm and thereby obtained collection efficiencies for a wide range of collector drop sizes. The measured variation of collection efficiency with the size of the collecting droplets was roughly consistent with that predicted by Langmuir for droplets larger than 20 μm radius, but the measured collection efficiencies for smaller collector droplets were much higher than the calculated values and, as suggested by Fletcher (1962 a), are probably a consequence of experimental difficulties and should be discarded.

Carefully controlled experiments which permitted the measurement of collection efficiencies in the size range covered by the calculations of Hocking have been performed using similar techniques by Picknett (1960) and by Woods and Mason (1964). In a particular experiment several thousand equally sized water drops produced by a spinning disk or, preferably, the vibrating needle device of Mason *et al.* (1963 b), were allowed to fall through a 1 m depth of cloud composed of saline droplets of radius between 1 and 12 μm maintained at their equilibrium radii in an ambient humidity of 84%, and then to fall onto a grease-coated slide. A drop landing on this slide quickly evaporated, leaving behind a small salt particle if it had previously collected one of the saline droplets. Recondensation upon the salt particle in a chamber which reproduced the temperature and humidity existing within the cloud produced a saline droplet of volume equal to that originally captured. Since the probability that the collector droplets had undergone more than one collision was negligible, it was possible to determine by microscopic examination of the slides the proportion of collector droplets that had undergone coalescence and the fraction of this that had coalesced with each size of salt droplet. Having determined the total number and size of collector droplets introduced into the cloud, and also the sizes and number concentrations of the saline droplets, the collection efficiency of drops of this one particular size for smaller droplets of different sizes could be evaluated.

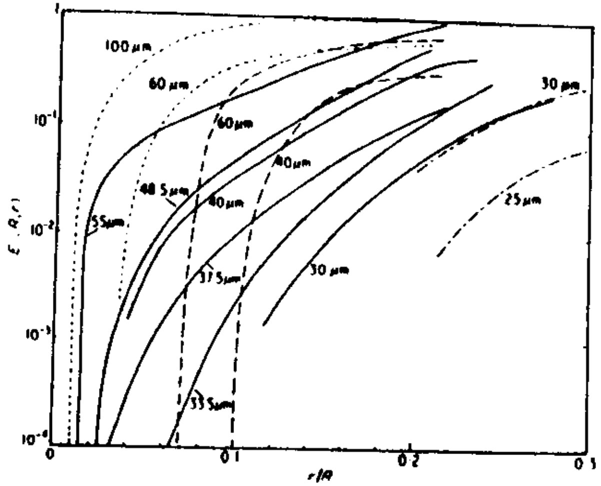


Figure 7. Comparison of experimental collection efficiencies and computed values of collision efficiency. Experimental: —— Picknett ($R = 30$ and 40 μm), Woods and Mason ($R = 33·5$, $37·5$, $48·5$, and 55 μm); —·—· Hocking ($R = 25$ and 30 μm), — — Shafrir and Neiburger ($R = 40$ and 60 μm), - - - - Mason ($R = 60$ and 100 μm). (From Woods and Mason 1964.)

These experiments confirmed Hocking's prediction that drops of radius less than 18 μm are unable to capture droplets of radius between 1 and 15 μm. Figure 7 shows that for drops of radius between 30 and 60 μm the experimental collection efficiencies agree, within the limits of experimental error, with the theoretical values of collision efficiency calculated by Hocking, Mason (unpublished data 1960), and Shafrir and Neiburger, except for values of $r/R < 0·1$, where the experimental values of collection efficiency are consistently higher than the calculated values and fail to show the sharp cutoff predicted by theory. As pointed out by Mason (1965 a) the theory is thought to be unreliable in this regime. Although these experiments apparently corroborate the threshold value predicted by Hocking it is possible, in view of the immense experimental difficulties in producing water droplets of radius less than 18 μm, which would evaporate to some extent during their passage through the undersaturated cloud, that the small but finite collision efficiencies predicted by Davis and Sartor may nevertheless be correct, although undetectable in these experiments.

The calculations of Pearcey and Hill appear to be confirmed by the experimental observations of Telford *et al.* (1955), who took streak photographs of groups of interacting, nearly equal-sized drops of radius about 75 μm rising slowly in a vertical wind tunnel and obtained enormous collection efficiencies of 12·6 ± 3·4. Further agreement with these calculations is provided by the experiments of Telford and Thorndike (1961) who studied collisions between freely falling drops of diameter ranging from 20 to 60 μm. Coalescence was occasionally observed of droplets of diameter about 45 μm but never in the case of smaller droplets. Collision efficiencies were not measured in these experiments.

Further quantitative information concerning the wake-capture of droplets of equal size is provided by the experiments of Woods and Mason (1965), who developed an ingenious technique for determining the collection efficiencies entirely from streak photographs. Many thousands of photographs of streams of droplets of radius r less than 35 μm failed to show a single coalescence event. With droplets of radius between 35 and 40 μm coalescence was occasionally observed, which may have been a result of small-scale eddying in the air stream. Droplets of radius between 40 and 100 μm had well-developed wakes, and coalescences between droplets of equal size were relatively frequent, with the corresponding collection efficiencies increasing from 0·5 to 0·9 with increasing radius within this range. The separation of consecutive droplets in the experiments of Woods and Mason was less than 10 radii. They conceded, therefore, that the differences between their measured collection efficiencies and those of Telford *et al.* may possibly be a consequence of weak interactions acting over large distances for long times. However, they concluded that a more probable reason for the discrepancies is that the relative motion of the interacting drops may be influenced at large separations by fortuitous eddies in the air stream. Although these various discrepancies are not fully resolved, the excellent quantitative agreement between the calculations of Neiburger and the measurements of Woods and Mason for $r > 63$ μm suggest that the collision efficiencies of drops of nearly equal size are close to unity for values of R in excess of a value between 40 and 63 μm and tend towards zero for lower values. The acquisition of a more accurate value for this threshold value of r, although interesting, is of little practical importance in cloud physics, since the concentration of droplets of radii greater than 40 μm in non-precipitating clouds is very small. It therefore appears unlikely that wake-capture contributes significantly to the development of precipitation within clouds. It is also probably of little consequence in precipitating clouds, in view of the observation of Nakamura (1964) that droplets of diameter ranging from 80 to 200 μm were never captured in the wake of drops of diameter 6·2 mm falling at their terminal velocities.

It is immensely difficult to study the final stage of the approach of two colliding droplets, culminating in their coalescence, in view of the minute and inaccessible volume and short time intervals in which the crucial processes occur. If the droplets come into close proximity the barrier to coalescence is presented by the air film between the droplet surfaces, which has to be expelled by the action of dynamical, gravitational, or electrical forces working against the viscous resistance of the air. Schotland (1960) studied the coalescence of electrically neutral water drops, of diameter ranging from 200 to 800 μm, falling on large hemispherical water surfaces. He found that the minimum height from which the drops had to fall in order to coalesce with the target was greater when the drops impinged at smaller angles of incidence and when the density of the surrounding gas was increased. A much more comprehensive investigation of this problem has been performed by Jayaratne and Mason (1964), who studied the impaction, bouncing, and coalescence of small water drops of radius ranging from 60 to 200 μm on plane and curved air-water interfaces.

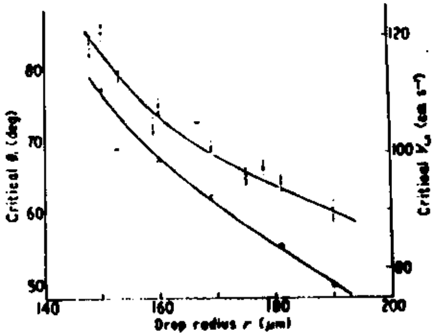


Figure 8. Variation with drop radius of the critical values of the normal component of incident velocity $V_{i,n}$ and of the impact angle θ_i at which an uncharged drop coalesces with a plane water surface. (From Jayaratne and Mason 1964.)

The influence of drop radius r, impact velocity V, angle of impact θ, drop charge q, and vertical field strength F upon the probability of coalescence was measured over a wide range of values. For instance, figure 8 presents the measured relationships between drop radius and the critical values of V and θ at which coalescence occurs between uncharged droplets and a plane water surface. Uncharged drops impacting at nearly normal incidence were found to remain in contact with the surface for about 1 ms, to lose about 95% of their kinetic energy during impact, and to rebound with an effective coefficient of restitution of about 0·2. Drops carrying a net charge and drops polarized in an applied electric field were found to coalesce more readily than uncharged drops of the same size and impact velocity. Accurate measurements were made of the magnitudes of the critical values of q and F required to cause coalescence as a function of V, θ, and r. Typically, droplets of radius 150 μm impacting at 100 cm s^{-1} coalesce if the charge exceeds about 10^{-4} e.s.u. or if the field exceeds about 100 v cm^{-1}.

If an impinging drop is to coalesce with a water surface it must first expel and rupture the intervening air film. By treating the undersurface of the drop as a flattened circular disk Jayaratne and Mason calculated that the minimum thickness, δ, achieved by the film during the period of contact is related to V, θ, and r by the equation

$$\delta = \left(\frac{3\eta}{8\gamma}\frac{\phi}{1+\epsilon}\right)^{1/3}(V\sin\theta)^{1/3}r, \tag{3.6}$$

where ϵ is the coefficient of restitution, $\phi =$ [illegible], γ is the surface tension, and η is the viscosity of air. This equation predicts values of $\delta \sim 0{\cdot}1$ μm, below which fusion may well take place under the influence of van der Waals forces. Several features of the observed relations between V, θ, and r are accounted for by this simplified theory, but the behaviour of drops impacting at nearly glancing incidence, and of relatively large energetic drops impacting normally, is not. Jayaratne and Mason showed that the electrical forces produced between the liquid surfaces by fields or charges at the moment of coalescence were much smaller than the dynamical forces produced by deceleration of the impinging drop. They concluded, therefore, that it is difficult to understand why charging or polarization should promote coalescence unless the electrical forces distort the liquid surfaces in such a way that drainage of the air film and the formation of a liquid bridge are facilitated. They pointed out that such a distortion has been observed by Allan and Mason (1962) with two water drops of radius 750 μm approaching each other in silicone oil under an external field of 1000 v cm^{-1}, and they suggested that distortion may not only cause more rapid thinning of the air film but may also induce its rupture by means of a micro-discharge.

Subsequent work has confirmed these suggestions concerning the role of electrical forces in inducing coalescence, and it has provided a more detailed physical explanation of this phenomenon. Photographic evidence for the deformation of the adjacent surfaces of colliding water drops carrying high charges of opposite sign obtained by Sartor (1967 b) is illustrated in plate 1. In addition, the calculations of Latham and Roxburgh (1966) of the localized fields in the near surfaces of closely separated drops situated in an external field demonstrate that distortion followed by disintegration will occur at close separations even if the external forces are extremely weak, owing to the mutual interaction of the polarization charges. As has been demonstrated by Miller *et al.* (1965), the onset of instability of the droplets in this situation is generally accompanied by the ejection of a fine jet of water, evident in plate 1, which travels along the field lines to strike the second droplet. The penetration of the air film by the water filament may therefore promote coalescence of the droplets. This argument is consistent with the observations of Allan and Mason (1961), Hendricks and Semonin (1962, 1963), Lindblad (1964), Plumlee (1964), and Jayaratne and Mason that the delay time between apparent collision and coalescence of two droplets decreases with increasing external field strength. A more detailed exposition of the calculations of Latham and Roxburgh is presented in § 3.6, in a discussion of the disintegration of raindrops.

Further information on the coalescence process has been provided by the experiments of Hendricks and Semonin and of Lindblad. A pair of hemispherical water drops were formed at the ends of two vertical tubes in a sealed chamber. The separation between the tubes was adjusted so that as the drops were formed their surfaces gradually came into contact. The velocity of approach of the two surfaces was governed by the rate of flow of water in the tubes and was arranged to provide values of 76 and 152 μm s^{-1}. The delay time before coalescence and the surface deformation of the two colliding drops were studied by photographing with a high speed camera the changing interference patterns from a monochromatic light source reflected from the approaching surfaces. The delay time was found to increase with increasing relative humidity and temperature. The photographs also showed, in agreement with the earlier studies of Derjaguin and Kussakov (1939) and of Prokhorov (1954), that the approaching surfaces became increasingly flattened as the separation decreased and that eventually a dimple formed in the middle of the deformation. All of these results are consistent with the idea that the barrier to coalescence is provided by the air film trapped between the adjacent surfaces. The influence of relative humidity and temperature on the delay time are consistent with Prokhorov's suggestion that the outflow of vapour from the liquid surfaces creates a hydrostatic pressure which prevents the surfaces from immediately merging together. It was also found that the delay time decreased rapidly with increasing potential difference between the approaching drops, and that small protuberances on the surfaces sometimes occurred in the presence of these electrical forces; similar results were obtained by Owe Berg *et al.* (1963). These observations are consistent with the suggestion of Latham and Roxburgh that coalescence may be triggered by the penetration of the air gap by a filament of liquid ejected from one of the surfaces, which has become unstable because the surface tension pressure has been overcome by the disruptive electrical pressure. A detailed theoretical and experimental study of the disintegration of pairs of water drops raised to equal and opposite potentials has been described by Azad and Latham (1968). Further evidence in favour of the suggestion that coalescence in the presence of electrical forces is initiated by electrohydrodynamical instability involving the ejection of liquid from one drop is provided by Plumlee's observation of a flow of current between two suspended drops across which a potential difference existed before visual coalescence was observed. In these experiments the potential differences did not exceed 10 v, so that dielectric breakdown of the air could not have been involved in the charge transfer.

Goyer *et al.* (1960) studied collisions between drops of diameter ranging from 600 to 790 μm and droplets of diameter 100 μm. They found that in the absence of an electric field 29·4% of the collisions resulted in coalescence. An increase in field strength was accompanied by an increase in coalescence efficiency, which possessed a value of 95·3% in a field of 38·4 v cm^{-1}. Unfortunately, however, the impact velocities and general experimental arrangement employed in these experiments were not representative of collisions occurring between drops of these dimensions inside clouds, and the quantitative values of coalescence efficiency are therefore inapplicable to atmospheric situations. Similar limitations apply to the results of Magono and Nakamura (1959), Freier (1960), and Cotton and Gokhale (1967).

Telford and Thorndike (1961) observed in wind-tunnel experiments that the collection efficiency of uncharged droplets of radius 45 μm for uncharged droplets of radii ranging from 30 to 35 μm was zero in the absence of an electric field and increased steadily with increasing strength of an applied vertical field. Woods (1965) showed that the coalescence rate of identically sized droplets of radius less than 40 μm increased linearly with applied charge above a threshold value of 5×10^{-6} e.s.u.; if the drops carried charges of the same size coalescence was found to be totally inhibited. In the experiments of Telford and Thorndike and of Woods the electrostatic forces between the interacting droplets were insufficient to exert a significant influence upon their relative trajectories, and the increased collection efficiencies were almost certainly a consequence of enhanced coalescence efficiencies. This conclusion is reinforced by the fact that the minimum charge observed by

Woods to produce coalescence agrees closely with the value predicted from the equations of Latham and Roxburgh if the thickness of the air film separating the surfaces of the droplets at the moment of local disintegration is equal to that calculated by Jayaratne and Mason.

Gunn (1965) performed photographic studies of the collisions in free fall of water drops of radius around 0·1 cm produced by means of a synchrodropper. He showed that as the energy of impact increases the type of collision changes progressively from recoil to coalescence or disruption (depending upon whether the collision was direct or glancing) to spatter, in which numerous tiny droplets are expelled radially at high velocities from the periphery of the interacting drops. Large numbers of droplets were also produced if drops made collisions with artificial hailstones at relative velocities comparable with those occurring inside natural clouds. Fields of about 400 v cm^{-1} were found to be sufficient to promote the coalescence of drops that would otherwise have recoiled. Gunn calculated that in typical heavy rain each drop in the millimetre size range undergoes about seven collisions with drops of comparable magnitude. He estimated that this collision frequency is sufficiently great to produce significant modifications of the drop-size distribution and, through inductive effects, the electrical properties of the entire rain cloud. Similar studies were made by Magarvey and Geldart (1962) using drops of equivalent diameter ranging from 0·5 mm to 1 cm.

Moore and Vonnegut (1960) observed intense rainfall from highly electrified clouds in New Mexico shortly after the initial detection of a radar echo. They estimated that the values of the droplet collection efficiencies consistent with the measured time intervals were 4 to 10 times greater than the accepted values pertaining to non-electrified clouds. These greatly enhanced rates of rainfall production were therefore probably a consequence of the combination of increased coalescence and, particularly, collision efficiencies in the intense fields. This explanation may also apply to the information provided by Muchnik (1965), who computed from rain shower data in the Soviet Union and the United States that the total condensed water in convective clouds is exchanged on the average every 7 minutes and in some individual cases every 3 minutes. As pointed out by Sartor (1967 a) these rates place a severe requirement on growth processes that cannot be met by the collision and coalescence of cloud particles when only gravitational and aerodynamic forces are acting. Vonnegut and Moore (1960) and Moore *et al.* (1962, 1964) observed gushes of rain or hail to follow lightning flashes in thunderclouds within even shorter periods of time. They proposed that in this situation drops in the vicinity of the lightning channel become highly charged by the capture of fast ions and then travel at high velocities in the intense local fields to collide and coalesce with numerous uncharged droplets in the surrounding regions of the cloud, thereby attaining precipitation dimensions with extreme rapidity. At present, no experiments have been performed to test this interesting and plausible hypothesis. It should be emphasized, however, that the fact that electrical forces can promote the growth of precipitation within clouds does not eliminate the possibility that the fields were produced by the gravitational segregation of charged cloud particles.

The discussion presented in the preceding paragraphs has demonstrated that the growth of liquid precipitation particles by the collision and coalescence of cloud droplets can be markedly influenced by electrical forces. However, it is apparent that an appreciable amount of further research is required in order to establish the exact conditions under which the role of electrical forces is dominant. The deficiencies are primarily experimental. Measurements are required over a wide range of droplet sizes of collision and coalescence efficiencies as a function of field strength and the sign and magnitude of the droplet charges. The microphysics of the coalescence process and the reality of the rain-gush hypothesis should be investigated in the laboratory. In all cases it will be necessary to ensure that the experiments accurately reproduce the essential characteristics of the natural interactions. The tentative conclusion to be drawn at this stage is that the role of electrical forces in the production of rain by the coalescence of cloud droplets is probably significant in certain circumstances.

3.5. *Growth of populations of cloud droplets by collision and coalescence*

In view of the computational difficulties of considering every possible coalescence of all existing cloud droplets, and the discrete manner in which new droplets are formed by coalescence, early studies of the growth of droplet populations utilized a 'continuous' model, in which larger droplets were assumed to grow as a group by continuous collection of water mass represented by a group of smaller droplets. This model was used by Bowen (1950) to calculate the rate of production of raindrops in clouds. Telford (1955) examined the discrete nature of droplet collection by allowing a portion of the droplets of the collecting group each to coalesce with one small droplet and thereby to form a small number of larger collecting droplets. Droplets of this new size themselves collect small droplets, and so on. As this process is repeated small numbers of successively larger droplets are formed. The number of new droplets formed by each group at each time step is governed by the probability of a large droplet collecting a smaller droplet in the given time interval. In this way Telford showed that the statistical nature of droplet collection would produce large drops at a much faster rate than predicted by the continuous model. An illustration by Berry (1967) of the difference between the continuous and stochastic models is presented in figure 9.

The discrete nature of droplet collection is embodied in the equation

$$\frac{\partial f(x)}{\partial t} = \int_{x_0}^{x_m} f(x_c)\, V(x_c, \epsilon) f(\epsilon)\, \mathrm{d}\epsilon - \int_{x_0}^{\infty} f(x)\, V(x, \epsilon) f(\epsilon)\, \mathrm{d}\epsilon, \tag{3.7}$$

which considers every possible coalescence of the droplets and describes the instantaneous change in the distribution function for each value of droplet size. In this equation $f(x)\,\mathrm{d}x$ is the number concentration of droplets having masses in the range x to $x + \mathrm{d}x$, x_c is the mass of a droplet which collects a smaller one of mass ϵ to form a droplet of mass $x = x_c + \epsilon$, x_0 is the smallest mass to undergo collection, and x_m $(= x/2)$ is the mass of the largest droplet collected. The factor $V(x, \epsilon)$ is the effective rate of volume sweep-out of the larger droplet with respect to the smaller and is defined by Berry (1965) as the 'collection kernel' of the integral equation. It is related to the linear collection efficiency Y_c by the equation

$$V(r, r_s) = \pi r^2 Y_c(r, \rho)^2 \Delta u(r, r_s), \tag{3.8}$$

where r and r_s are respectively the radii of the larger and smaller droplets, $\rho = r_s/r$, and Δu is the difference in terminal velocities. Melzak (1957) demonstrated the existence and uniqueness of solutions to equation (3.7) and added a term for particle breakup. In a comprehensive study Chandrasekhar (1963) discussed the formulation of the collection problem with application to colloidal particles.

Analytic solutions of equation (3.7) have been found by Golovin (1963) and Scott (1965) for special mathematical forms of V, while for more realistic forms it has been necessary to use numerical methods of solution. Numerical integration of equation (3.8) applied to the problem of aerosol growth has been presented by Zebel (1958), Hidy (unpublished data 1964), and for the case of 20 seconds of droplet growth by Twomey (1964), who demonstrated that the complete collection equation, a continuous droplet distribution, and Hocking's collection efficiencies combined to give an even greater growth rate of large droplets than calculated by Telford. Twomey suggested that the importance of the statistical effect is greatly dependent upon the probability of collection increasing with drop size. This suggestion was confirmed by Berry (1965), who conducted an extremely comprehensive numerical study of the effects of collection efficiencies on droplet growth.

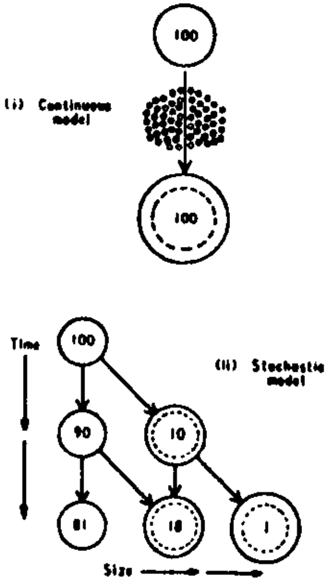


Figure 9. Continuous and stochastic models of droplet collection. The continuous model (i) assumes that small droplets are swept out as if their water were distributed uniformly in space; 100 large drops grow at the same rate and become 100 similar larger drops. The stochastic model (ii) assumes that, say, 1 in 10 of 100 large droplets will collect a small droplet during a given time, and then 1 in 10 of each large size will collect a smaller droplet; large droplets then grow at different rates; the distribution spreads. (From Berry 1967.)

Berry utilized the complete collection equation, a continuous droplet distribution, and a wide variety of collection efficiencies. He was able to perform calculations covering growth over a period of up to 30 minutes. His model assumed an infinitely high, isotropic, homogeneous column of air and cloud droplets, each droplet falling at its terminal velocity. He assumed an initial distribution of the form

$$f(s) = A\,e^{-s}, \qquad (3.9)$$

where A is a constant, $s = x/x_0$, and x is the mean droplet mass at time $t = 0$. The mean droplet radius was taken to be 10 μm, and the liquid water content was normalized to 1 g m^{-3}, giving an average droplet concentration of 227 cm^{-3}. Computations were carried out for 16 different forms of the collection efficiency. Berry found that when his results were displayed as a liquid-water content distribution over the logarithm of droplet radius four basic patterns of distribution change emerged. In the pattern produced by all realistic forms of the collection efficiency the peak of the initial distribution remains but is reduced, and a seconp maximum develops at higher values of droplet radius. The crucial parameters affected by the particular collection efficiencies selected are the height of the 'tunnel' connecting the two humps and the position and time of occurrence of the second maximum. Berry found that geometric sweep-out produces a high tunnel and a hump on droplets of 80 μm radius, whereas the collection efficiencies of Shafrir and Neiburger produce a very low tunnel and a hump at 150 μm. In general, the time required for the production of the second maximum increases with decreasing tunnel height. A low tunnel height is associated with a rapid increase of the collection kernel with drop size, while the hump is associated with a diminishing increase of the collection kernel at the larger drop sizes. Berry's calculations illuminate the sensitivity of the growth rates of drops to the assumed values of collection efficiencies and thereby underline the necessity for accurate measurements of this parameter over the entire size range of interest.

A similar conclusion can be drawn from the computations of Bartlett (1966), who concentrated on the development of drops with radii up to 40 μm by the coalescence mechanism. He did not use the stochastic collection equation but assembled new droplets by the addition of categories and an interpolation scheme designed to preserve liquid water. He utilized several different distributions considered to be characteristic of the early stages of various types of cumuli, and he assumed collection efficiencies identical with the collision efficiencies calculated by Hocking. He found that large drops develop rapidly in maritime clouds, and that for clouds characteristic of continental climates the coalescence mechanism is effective only if the maximum drop radius exceeds about 22 μm. A further condition for substantial growth is the existence of an adequate supply of droplets of radii between 14 and 20 μm. Bartlett also studied the effects upon the growth rates of small increases in collection efficiencies, which may be caused in the atmosphere by factors such as turbulence or electric fields. He found that the most important single parameter in determining the onset of the coalescence mechanism is the minimum drop size capable of capturing still smaller droplets. Generally, a significant effect was found if the change in the collection efficiency was equivalent to increasing the radii of the interacting drops by more than about 2 μm. Bartlett concluded that any future computations or experiments to determine changes in the collection efficiencies should look for effects of this magnitude.

Twomey (1966) extended his earlier model to include the radius range 1–1000 μm by using an irregular spacing of intervals. He concluded that varying the relative dispersion of the initial spectrum, while keeping the total liquid-water content constant, made no great difference to the evolution of larger droplets.

Berry (1967) refined and developed his previous work and has presented calculations of cloud droplet growth over the radius range from 4 to 200 μm for collection kernels representing hydrodynamic capture, electric field capture, and geometric sweep-out. His computed growth curves for the latter situation are presented in figure 10; the units of the droplet mass density function $g(\ln r)$ are mass of droplets per unit of $\ln r$, where r is the droplet radius. He finds in all cases that the rate of droplet growth is proportional to the magnitude of the kernel, and the pattern of growth depends upon the derivative of the kernel with respect to the droplet size. Below 60 μm a larger kernel derivative causes the distribution to spread. Above 60 μm the derivative of each kernel decreases to a common value that causes water to accumulate on large drops. This leads to a self-preserving distribution, similar to Golovin's asymptotic solution, in about 5 minutes when the liquid water content is 1 g m^{-3}. Berry finds that the stochastic model produces a growth rate nearly equal to the continuous model, contrary to the results of earlier studies, but transfers much more water to larger drops.

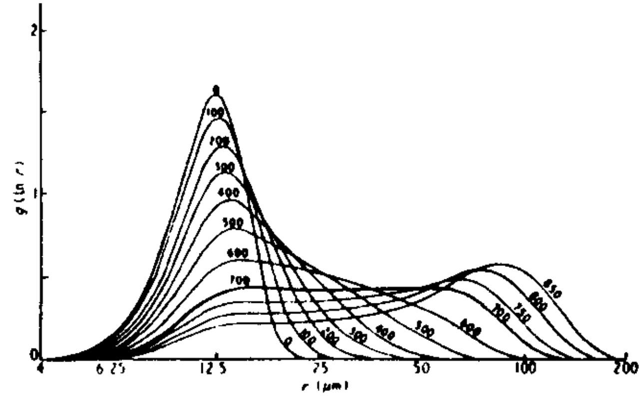


Figure 10. Computed droplet growth due to geometric sweep-out over a period of 850 s. The heavier line at 700 s indicates the appearance of the second maximum. (The units on the vertical axis are g m^{-3}/unit $\ln r$.) (From Berry 1967.)

3.6. *Disintegration of raindrops*

The disintegration of a raindrop within a cloud under the action of mechanical, electrical, or aerodynamic forces may significantly modify local droplet concentrations and space-charge densities. The disintegration process may also initiate the freezing of supercooled drops and, in highly electrified clouds, initiate lightning strokes. In addition, the interaction of pairs of droplets in the presence of electrical forces may promote their coalescence, separate appreciable quantities of charge or, in supercooled regions of the clouds, promote nucleation of the ice phase.

The physics of these processes has been extensively explored in recent years. Matthews and Mason (1964) studied the deformation and breakup of large freely falling water drops by means of high speed photography. They confirmed the observations of earlier workers that the drops become distorted and flattened, and, if their velocity relative to the air exceeds a critical value, eventually blow up to form a large bag supported on a toroidal ring of liquid. Finally, the bag bursts to produce a fine spray of droplets and the toroid breaks up into several large drops. O'Brien (1961) showed that this disintegration process is essentially the same vortex instability as is observed in miscible fluid vortex cascades. The critical conditions for breakup were calculated by Matthews and Mason with a reasonable degree of accuracy by assuming that at the instability point a drop possessed a hemispherical profile with its lower surface plane, and that equilibrium existed between the aerodynamic pressure and the total pressure difference set up across the vertical extremities of the drop by surface tension and hydrostatic forces. Extension of this simplified theory, however, to computations of the rate of expansion of the bag, did not provide good agreement with observation. Similar experiments in a supercooled wind tunnel by Koenig (1965 a) showed that the bursting of the bag was often accompanied by the initiation of freezing. It is unlikely, however, that this process is important in the glaciation of supercooled clouds, since ice crystals are generally produced by other mechanisms inside such clouds before liquid drops have grown to the enormous dimensions required for this mode of disintegration.

It has been established from the experiments of several workers, notably Nolan (1926) and Macky (1931), that a liquid drop situated in an electric field will become elongated along the direction of the field and will disintegrate if the field strength attains a well-defined critical value. These studies provided an approximate empirical relation $F(R_0/T)^{1/2} = 1{\cdot}6$ between the external field strength F, expressed in electrostatic units, the undistorted drop radius R_0, and the surface tension T. Taylor (1964) treated the problem theoretically for uncharged stationary drops by assuming that the drop retained a spheroidal shape until it reached the disruption point, and that the equations of equilibrium between the stresses due to surface tension and the electric field, and the difference p between the external and internal pressure, were satisfied at the poles and at the equator by the respective equations

$$2ab^{-2}T - p = (\widehat{nn})_a \tag{3.10}$$

and

$$T(ba^{-2}+b^{-1}) - p = (\widehat{nn})_e = 0, \tag{3.11}$$

where a and b are respectively the semi-major and semi-minor axes, and the electrical pressure terms $(\widehat{nn})_a$ and $(\widehat{nn})_e$ are related by known equations to R_0, the field strength, and the degree of deformation of the drop provided that the spheroidal approximation is retained. Elimination of p from equations (3.10) and (3.11) permits the deformation a/b to be calculated as a function of F. Taylor found a turning-point when $a/b = 1{\cdot}9$ and $F(R_0/T)^{1/2} = 1{\cdot}625$, which he assumed to be the criterion for instability; these predictions are in excellent agreement with measured values.

In clouds, of course, a raindrop falling at its terminal velocity will be subjected to aerodynamic pressures and the hydrostatic pressure difference between its vertical extremities; quantitative considerations of the importance of these additional factors have been presented by McDonald (1954, 1960). It is not surprising therefore that Ausman and Brook (1967) observed discrepancies of up to 15% from Taylor's criterion for instability in their studies of the disintegration of large drops falling through an electric field. The discrepancy increased with increasing

R_0 and was probably primarily a consequence of increasing values of the hydrostatic pressure-difference term. In addition, a raindrop falling in fields of strength close to breakdown values will almost certainly be highly charged, and contributions to the electrical pressure over its surface will be made by both the charge and the field. An attempt to treat the problem of the stability of charged drops in an electric field was made by Shih-ji and Jen-chung (1966), but an incorrect expression was utilized for the electrical pressure and their conclusions must therefore be disregarded.

A theoretical and experimental study of this problem was made by Abbas and Latham (1969 a). Taylor's spheroidal assumption was employed, and aerodynamic and hydrostatic pressure-difference terms were incorporated into the equilibrium equations from which the fields required to produce instability were determined.

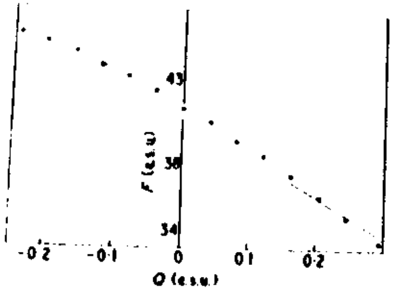


Figure 11. Experimentally determined relation between the critical values of F and Q. $R_0 = 0{\cdot}106$ cm; air temperature = 20 °c. ● experimental readings; —— theoretical curve. (From Abbas and Latham 1969 a.)

Values of $F(R_0/T)^{1/2}$ required for disintegration were computed as a function of the applied charge Q. The predicted values of $F(R_0/T)^{1/2}$ were tested experimentally for positively or negatively charged water drops with values of R_0 ranging from 0·10 to 0·17 cm falling through horizontal or vertical fields at temperatures varying from + 20 to − 18 °c. Agreement between theory, experiment, and the measurements of Ausman and Brook was good, with a maximum discrepancy of 3%. As predicted, the field required to disintegrate a falling drop was found to be markedly dependent upon the magnitude of the charge that it carries. The results obtained are illustrated in figure 11. On the basis of these studies it was proposed that the magnitude of the field required to produce the disintegration of charged raindrops falling through the intense electric fields of a thunderstorm – and thereby possibly to initiate a lightning stroke – can be expressed to within an accuracy of 2% by the equation

$$F(R_0)^{1/2} = 13{\cdot}6 - 8Q. \tag{3.12}$$

The mass loss accompanying the disintegration of falling drops was found to increase with F in a manner similar to that observed by Latham (1965) and Matthews (1967). Measurements on suspended drops of water showed that the values of charge and mass loss, q and ΔM respectively, accompanying the disintegration were close to the theoretical maxima. The close parallelism between the experimental curves of q against Q and ΔM against Q suggests that instability occurs over a large fraction of the surface area of the lower half of the drop. Further studies of the stability of individual drops subjected to electrical forces have been made by Ailam and Gallily (1962), Garton and Krasucki (1964), and Abbas *et al.* (1967).

The disintegration of highly charged evaporating droplets was studied in some elegant experiments by Doyle *et al.* (1964), who measured the strength of the electric field required to support evaporating charged droplets of initial radii ranging from 30 to 100 μm. Their observations indicated that as a charged droplet evaporates its surface density of charge increases until the electrical pressure attains a critical value, approximately consistent with the Rayleigh criterion, at which point the droplet disintegrates. The disintegration was accompanied by the ejection of one or more highly charged droplets, corresponding to a charge loss of about 30% of the original value. These studies were extended by Abbas and Latham (1967), who measured the radius R and charge Q continuously as the droplets underwent a series of disintegrations. They showed that the relationship between the charge loss ΔQ and the mass loss ΔM is such as to reduce the energy level of a droplet on disintegration by a minimal amount and to yield a residual drop of radius r on the verge of instability, and that it can be expressed by the equation

$$\frac{\Delta Q}{\Delta M} = \left(\frac{9T}{\pi\rho^2}\right)^{1/2} \frac{1}{R^{3/2}+r^{3/2}}, \tag{3.13}$$

where T and ρ are respectively the surface tension and the density of the drop. However, although this phenomenon will modify local droplet populations at the edges of the clouds it is unlikely to be of appreciable significance in cloud physics.

When two water drops are situated in an electric field whose direction is not perpendicular to the line of centres of the drops, the electric field strength is enhanced owing to the mutual interaction of the polarization charges. This enhancement will be particularly pronounced if the separation is small and the line of centres of the drops is approximately parallel to the direction of the field. Under these circumstances the drops will disintegrate in considerably lower external fields than are required for individual drops. A knowledge of the critical fields required to produce disintegration of one of a pair of closely separated drops as a function of their radii and initial separation may be of importance in determining whether two interacting droplets will coalesce, may provide a quantitative criterion for electrofreezing, and may be of importance in determining the efficiency of an inductive theory of cloud electrification which involves the transfer of charge between polarized drops approaching to within small separations in a cloud, and their subsequent separation under gravity to enhance the prevailing electric field.

A theoretical and experimental study of the deformation and disintegration of pairs of water drops situated in an electric field was performed by Latham and Roxburgh (1966). Their analysis utilized the assumptions adopted by Taylor in his treatment of individual drops and the theoretical values derived by Davis (1964), and confirmed experimentally by Latham *et al.* (1966), of the enhancement of the field in the region between the near surfaces of pairs of rigid spheres separated in an electric field. The equations of equilibrium at the poles and the equator were combined to give the equation, in the case of small drops,

$$F(R_0/T)^{1/2} = \frac{(72\pi)^{1/2} M(\alpha) I}{\epsilon}, \tag{3.14}$$

where $\alpha = b^2/a^2$, $M(\alpha) = \alpha^{4/3}(2 - \alpha^{1/3} - \alpha^{4/3})^{1/2}$, $I = 0{\cdot}5\,e^{-3}\ln\{(1+e)/(1-e)\} - e^2$, the eccentricity $e = (1 - b^2/a^2)^{1/2}$, and the enhancement factor ϵ is a known function of the separation of the drops. Solutions of equation (3.14) for various separations and deformations are presented in figure 12. It is seen that the critical field required to effect disintegration decreases rapidly as the separation of the drops is reduced.

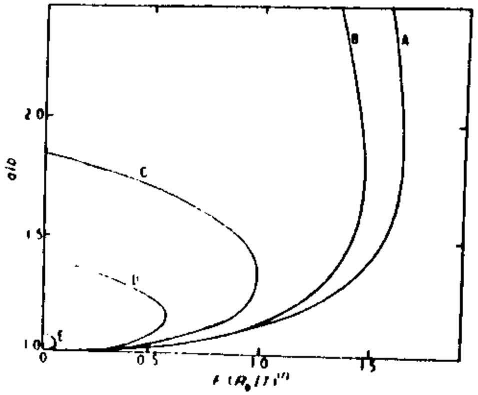


Figure 12. Elongation a/b of small water drops of initial separation x_0 as a function of $F(R_0/T)^{1/2}$. Curve A, $x_0/R_0 = 1000$; curve B, $x_0/R_0 = 3{\cdot}0$; curve C, $x_0/R_0 = 1{\cdot}0$; curve D, $x_0/R_0 = 0{\cdot}5$; curve E, $x_0/R_0 = 0{\cdot}1$. (From Latham and Roxburgh 1966.)

Table 1. Critical field F required for disintegration of a water drop of undistorted radius $R_0 = 0{\cdot}01$ cm separated from an identical drop by a distance x_0†

x_0/R_0	$F(R_0/T)^{1/2}$	F (v cm^{-1})	a/R_0‡
0·5	$5{\cdot}690 \times 10^{-1}$	18 340	1·098
0·3	$3{\cdot}287 \times 10^{-1}$	8416	1·054
0·1	$7{\cdot}887 \times 10^{-2}$	2019	1·019
0·08	$5{\cdot}911 \times 10^{-2}$	1514	1·015
0·05	$3{\cdot}211 \times 10^{-2}$	1035	1·009
0·03	$1{\cdot}647 \times 10^{-2}$	422	1·0053
0·01	$3{\cdot}910 \times 10^{-3}$	100	1·0019
0·005	$1{\cdot}574 \times 10^{-3}$	40	1·0009
0·002	$4{\cdot}716 \times 10^{-4}$	12	1·0004
0·001	$1{\cdot}898 \times 10^{-4}$	6	1·0002

† From Latham and Roxburgh (1966).

‡ Represents the elongation of the drop at the moment of disintegration.

This point is illustrated more accurately in table 1, which shows that the critical value of F required for disintegration of one of a pair of closely separated drops may be several orders of magnitude lower than that necessary to induce instability in an isolated drop. For larger drops a hydrostatic pressure-difference term incorporated into the equilibrium equations provided small but significant reductions in the predicted disintegration criteria. The calculated critical fields for drops of radius around 1 mm were found by Latham and Roxburgh to be in good agreement with experiment over a fairly wide range of separations.

Although pronounced local effects will accompany the disintegration of large isolated raindrops falling through the intense fields of a thundercloud, the most important role of the disintegration process may well be to promote coalescence or, by means of the interaction of droplet pairs, the glaciation or electrification of clouds in weak fields. The exact electrohydrodynamics and meteorological applicability of this difficult two-body problem remain to be determined.

4. The growth of ice particles within clouds

The growth of ice particles within clouds occurs both by direct vapour transfer from cloud droplets to ice crystals, because of the difference in vapour pressure over ice and water at the same temperature, and by the process of accretion of supercooled cloud droplets. Ice-crystal habit is important in both of these processes. In addition, snowflakes are formed by the aggregation of ice crystals.

In this section an assessment is given of present knowledge of the factors determining the habit of ice crystals growing from the vapour, together with a discussion of growth by sublimation, aggregation, and accretion.

4.1. *Growth of ice crystals from the vapour*

The growth of ice crystals from the vapour can be treated in essentially the same way as the growth of droplets from vapour, which was discussed in an earlier section. However, since ice crystals are not spherical a radius cannot be assigned to them. The diffusion of vapour to the crystal is treated in a manner derived from the analogous situation in electricity, namely that of a current flowing to an object in an electric field spherically symmetric at infinity. Such an approach can be shown to be justifiable and yields the equation of growth or evaporation for a stationary crystal

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{4\pi C\sigma}{L_s^2 M/KRT^2 + RT/DMp_s}, \tag{4.1}$$

where m is the mass of the crystal, T the air temperature, σ the super- or subsaturation, L_s the latent heat of crystallization, D the diffusion coefficient of water vapour in air, K the thermal conductivity of air, M the molecular weight of water, p_s the saturation vapour pressure of the environment at the temperature T, R the universal gas constant, and C a shape factor for the crystal equivalent to its electrostatic capacity. McDonald (1963 b) has calculated theoretical values of C for simple shapes most likely to be of interest in ice-crystal studies, and as illustrated in figure 13, has measured values of C for brass models possessing the shapes of typical snow crystals. The observed insensitivity of the values of C to reductions in the surface area of model crystals of similar maximum dimensions is probably primarily a consequence of the compensating increases of total edge-length.

If the ice crystal attains an appreciable fall speed it cannot be considered stationary with respect to the diffusion field, which will now be limited to a boundary layer around the crystal in which the vapour concentration and temperature gradients will be larger than those around a stationary crystal. For a spherical crystal of radius r Mason (1953) has shown that the concentration gradient at the crystal surface at a time t after being introduced into a new environment is given by

$$\frac{\partial\rho}{\partial r} = (\rho - \rho_0)\{r^{-1} + (\pi D t)^{-1/2}\}, \tag{4.2}$$

where ρ and ρ_0 are the vapour concentrations in the remote environment and at the surface of the crystal respectively. The second term in the curly brackets denotes the enhancement of the concentration gradient at the surface relative to the steady-state value, and this will be marked if $(\pi D t)^{1/2} \ll r$. It implies that dm/dt will be increased by a factor, determined experimentally for falling drops by Gunn and Kinzer (1949) and Kinzer and Gunn (1951)

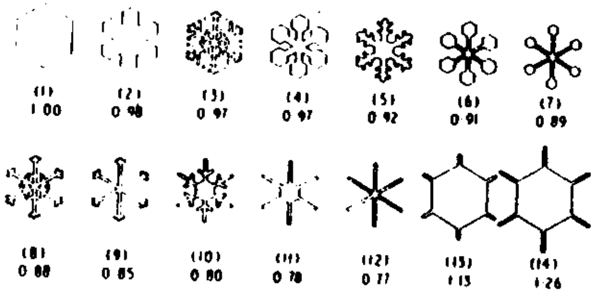


Figure 13. Forms and relative capacitances of 14 dendritic models of ice crystals. (From McDonald 1963 b.)

$$1 + \left(\frac{Vr}{2\pi D}\right)^{1/2} = 1 + 0{\cdot}28\,Sc^{1/3}\,Re^{1/2} = 1 + 0{\cdot}22\,Re^{1/2}, \tag{4.3}$$

where Re is the Reynolds number and $Sc = \nu/D$ is the Schmidt number, ν being the kinematic viscosity of the air.

The growth of evaporation of a ventilated ice sphere may therefore be represented by the equation

$$\frac{dm}{dt} = \frac{4\pi C\sigma}{A + B}(1 + 0{\cdot}22\,Re^{1/2}), \tag{4.4}$$

where $A = L_s^2 M/KRT^2$ and $B = RT/DM\rho_s$. Thorpe and Mason (1966) have shown this equation to be valid over the range of Reynolds numbers 20–250 for the evaporation of ice spheres suspended from a sensitive quartz microbalance in air streams of controlled humidity, temperature, and wind speed; excellent quantitative agreement between theory and experiment was found if the ventilation factor was increased slightly to a value of $1{\cdot}0 + 0{\cdot}26\,Re^{1/2}$. The accuracy of this amended factor was confirmed by Drake and Mason (1966), who measured the times of complete melting of small ice spheres in air streams of controlled temperature, humidity, and velocity. Their results agreed well with values predicted by a theoretical treatment, based on the considerations of Mason (1956), that involves heat transfer to the ice particle by condensation upon its surface, provided that allowance is made for the heat content of the water retained by the particle during the melting process.

For nonspherical ice crystals the ventilation factor must be determined experimentally in order to determine accurate values of growth rates. However, measurements of growth rates made under a variety of conditions by Reynolds (1952), Mason (1953), Okita and Kimura (1954), Isono *et al.* (1956), and others suggest strongly that the above equation yields growth rates of sufficient accuracy for most practical purposes when McDonald's values of C and a ventilation term based on an equivalent radius are utilized.

In a supercooled cloud ice crystals will grow much more rapidly from the vapour than droplets, primarily because the equilibrium vapour pressure is lower over ice than over water, but also because the nonspherical shapes of the crystals accentuate the flow of vapour to their surfaces. In fact, in clouds containing appreciable quantities of ice crystals the environmental vapour pressure may assume a value intermediate between the equilibrium values over water and ice, and droplets will evaporate to provide vapour for the growing crystals. The rates of growth of ice crystals from the vapour within supercooled clouds will therefore be expected to be greatest at a temperature at which the absolute vapour density difference between water and ice is a maximum. This prediction was confirmed by the calculations of Mason (1953), who found that the growth rate is a maximum at a temperature near −14 °c and decreases rather sharply at higher or lower temperatures. A more extended treatment of this problem by Byers (1965) has yielded essentially similar results.

In field and laboratory studies Hallett (1965 a) has shown that the temperature dependence of the habit of ice crystals growing in a water-vapour diffusion chamber is related to the growth of ice crystals in a supercooled cloud. The rates of growth occurring between −4 and −6 °c as needles or between −12 and −16 °c as dendrites may be in excess of those at intermediate temperatures by as much as a factor of 100. He points out that the effect of seeding a supercooled cloud or fog will therefore depend critically upon the temperature range within which it is confined.

4.2. *Habit of ice crystals grown from the vapour*

As pointed out by Fletcher (1962 a), if the growth of an ice crystal were a simple equilibrium process, then the resulting crystal habit could be determined by application of Wulff's theorem, which states that in equilibrium the distance of any crystal face from the centre of the crystal is proportional to the free energy per unit area of that face. Although no exact values of these free energies are known for ice, approximate values can be found by assuming that molecules interact only with their nearest neighbours, and counting the concentration of nearest-neighbour pairs linked across any crystal plane. As shown by Krastanow (1943), Wulff's theorem then predicts that the equilibrium form should be a hexagonal prism, the ratio of whose axial length to hexagonal diameter is 0·82.

However, although ice crystals formed in natural clouds or grown in the laboratory possess, in general, the shape of hexagonal prisms, the dimensional ratio may vary from less than 0·1 to more than 10. In addition, many complex forms such as stars, hollow prisms, scrolls, and dendritic plates commonly occur. Although it is difficult to imagine surface-energy changes adequate to explain the variations of simple prismatic habit, it becomes quite impossible to explain the more complicated forms on the basis of any equilibrium theory. Fletcher therefore concludes that the observed forms of ice crystals are not equilibrium structures but represent kinetic effects due to thermal or diffusion gradients, surface accommodation coefficients, and similar mechanisms, which have become 'frozen in' before attaining equilibrium.

Numerous attempts have been made to establish the dependence of ice-crystal shape upon the variables involved in crystal growth. Temperature and water-vapour pressure have been shown to be of great importance in this respect, and to a lesser extent the fall velocity of the growing crystal and the presence of fog droplets, organic vapours, or strong electric fields may also be important. In view of the existence of four basic forms, namely needles, prisms, plates, and dendrites, each of which is subject to a large number of variations, it has proved necessary to conduct rigidly controlled laboratory studies of ice-crystal growth. These can be divided into two general categories; in the first type, crystals have been grown under conditions close to water saturation in a droplet fog, while in the second the crystals have been grown in a droplet-free vapour whose temperature and supersaturation could be varied independently. The conditions created in the first type of experiment simulated more closely those occurring in natural clouds, but the second type has provided more detailed information concerning the growth process.

Table 2. Variation of ice-crystal habit with temperature†

0 to −3 °c	thin hexagonal plates
−3 to −5 °c	needles
−5 to −8 °c	hollow prisms
−8 to −12 °c	hexagonal plates
−12 to −16 °c	dendritic crystals
−16 to −25 °c	plates
−25 to −50 °c	hollow prisms

† From Hallett and Mason (1958 a).

Studies of the growth of ice crystals in supercooled water clouds produced in environments of controllable temperatures have been made by Nakaya (1951, 1954), aufm Kampe *et al.* (1951), and Mason (1953). Unfortunately, the presence of the droplets makes it very difficult to estimate the true supersaturation of the environment, and the results are therefore hard to interpret. Nakaya concluded from his experiments that the temperature rather than the supersaturation was the main factor controlling the droplet shape, except for dendritic growth which occurred only at relatively high supersaturations in the temperature range −14 to −17 °c. On the other hand, the conclusion emanating from a reanalysis of Nakaya's results and some electrical analogue experiments by Marshall and Langleben (1954) was that the dominant factor governing crystal growth is the supersaturation.

Clarification of this problem was provided by the studies of ice-crystal growth under controlled conditions of temperature and supersaturation in the absence of droplets by Shaw and Mason (1955) who grew ice crystals on a metal surface, Kobayashi (1957) who studied photomicrographically the habit of ice crystals growing upon a fine thread or rabbit hair in a diffusion chamber, and Hallett and Mason (1958 a) who utilized a more elaborate diffusion chamber incorporating movable ice plates to assist the study of growth at low supersaturations. These experiments agreed in confirming that the habit depends primarily upon the temperature, the predominant forms and transition temperatures agreeing closely with those presented in table 2.

The experiments of Hallett and Mason were particularly comprehensive. They were able to grow crystals over the temperature range 0 to −50 °c under supersaturations ranging from a few per cent to about 400%. Their technique of growing crystals simultaneously at all temperatures over the attainable range on a single nylon fibre, as illustrated in plate 2, revealed that the boundaries between one crystal form and another are extremely sharp. For instance, the transition between the plates and needles at −3 °c and that between hollow prisms and plates at −8 °c occurred within temperature intervals of less than 1 degc. Hallett and Mason grew crystals having an almost identical variation of habit with temperature from the vapour of heavy water, but with the transition temperatures all shifted upwards by almost 4 degc, in conformity with the difference between the melting points of H_2O and D_2O. Hallett and Mason studied the effect of supersaturation and temperature upon the growth form of a particular crystal simply by raising or lowering the fibre in the chamber. In all cases a crystal that had been transferred to a new environment assumed a habit characteristic of the new conditions.

The results of all of these studies are consistent with Nakaya's original contention that temperature rather than supersaturation is the dominant factor controlling the habit of crystals grown from the vapour. This conclusion is reinforced by experiments in which ice crystals were grown in air at reduced pressure or in other gases. If, as suggested by Marshall and Langleben, the basic habit is determined by the flux of vapour towards the growing crystal, which is proportional to the product of the diffusion coefficient of water vapour and the excess of the ambient vapour density over that in equilibrium at the crystal surface, the habit might be expected to change if grown at lower air pressures or in different gases. In fact, although reports of habit changes resulted from the experiments of Isono *et al.* (1957), Isono (1958), and Kobayashi (1958), some extremely comprehensive and well-controlled experiments by van den Heuval and Mason (1959) demonstrated that the variation of habit with temperature, involving plates, needles, hollow prisms, and dendrites, was unaffected by reducing the air pressure to 20 mmHg or by replacing the air by carbon dioxide, hydrogen, or helium. Only the growth rates of the crystals were affected, which is explicable in terms of the difference in the diffusion coefficients and thermal conductivities of the various gases.

The difficulty of growing ice crystals from the vapour at supersaturations of only a few per cent, comparable therefore with those occurring inside clouds, was resolved by Kobayashi (1961), who mixed two air streams saturated with respect to ice at different temperatures in order to produce a supersaturated mixture at an intermediate temperature. In contrast to earlier measurements (Kobayashi 1960) made under more variable conditions, he found that at supersaturations of only a few per cent the crystals tend to grow as nearly isometric prisms, but in the temperature range at which plates usually appear the crystals grow as very thick plates and approach a limiting c/a ratio of 0·8, whereas at temperatures normally associated with prisms they approach a limiting c/a ratio of 1·4. The results of Hallett and Mason and the later measurements of Kobayashi have been combined by Mason *et al.* (1963 a) to produce the curves illustrated in figure 14, which they consider to represent current knowledge of the variation of ice-crystal habit with temperature and supersaturation. It is clear from the diagram that the principal factor controlling the basic habit, as determined by the relative growth rates along the c and a axes, is the temperature. It is also apparent, however, that the secondary growth features are determined by the supersaturation or vapour flux. More recent experiments by Kobayashi (1965) have confirmed that the habit of ice is prismatic over the temperature range -22 to -90 °c.

Large deviations from the pattern of crystal habit with temperature illustrated in figure 14 have been observed when organic vapours were introduced into the diffusion chamber (Vonnegut 1948, Schaefer 1949, Nakaya 1955, Nakaya *et al.* 1958, Hallett and Mason 1958 b) or when the crystals were grown in the presence of strong electric fields (Bartlett *et al.* 1963). Fields of magnitude around 1000 v cm^{-1}, which certainly exist over a significant fraction of the volume of a mature thundercloud, were also found to accelerate the growth rates by a factor of up to about 100. Unfortunately, no physically complete explanation has yet been offered for the observed effect of organic vapours and electric fields upon the growth of ice crystals from the vapour.

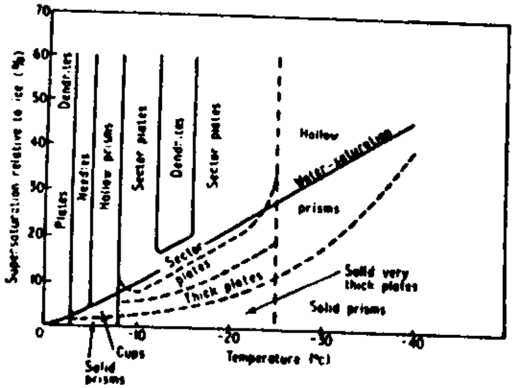


Figure 14. Experimentally determined variation of ice-crystal habit with temperature and supersaturation. (From a synthesis by Mason *et al.* (1963 a) of the work of Hallett and Mason (1958 a) and Kobayashi (1961).)

4.3. *Mechanism of habit change*

The habit changes undergone by ice crystals in the temperature range 0 to -25 °c, presented in table 2, are a consequence of changes in the relative growth rates of the basal and prism faces of the crystals. From a review of previous experiments on ice-crystal growth Mason (1965 b) concluded that the variations of habit are probably a consequence of variations in the rates of surface diffusion of molecules on the growing crystal faces.

The first direct experimental evidence that the water molecules arriving on the surface of a growing ice crystal may travel considerable distances before being incorporated into the crystal structure was provided by Bryant *et al.* (1959), who studied the epitaxial growth of ice crystals on the basal faces of natural cupric sulphide. The ice crystals exhibited interference colours when viewed in reflected white light. The colours gave a measure of the crystal thickness, changes of which could thereby be measured to within an accuracy of about 150 Å. At low supersaturations some crystals were observed to grow considerably in diameter with no discernible change in thickness, suggesting that molecules arriving on the upper basal surface were not being assimilated but were migrating over the surface and being built into the prism faces. This interpretation was reinforced by the observation that the lateral growth rate of two neighbouring plate-like crystals of constant, nearly equal thickness did not decrease as they approached each other, even when the intervening gap narrowed to about 1 μm. If the crystals had been growing mainly by direct deposition of vapour molecules on their edges they would have slowed down as they approached and shadowed each other, but a reduction in growth velocity would not be expected if growth occurred primarily by migration of molecules from the top surface. It was frequently observed that a small plate-like crystal did not thicken until it collided with a thicker crystal or a cleavage step on the substrate; on collision coloured growth layers, often originating from the point of contact, then spread across the crystal surface. This observation may be considered to be evidence of lateral growth of a new layer on the surface of the ice crystal. Hallett (1961) showed experimentally that at constant temperature and supersaturation the layers travel with uniform velocity inversely proportional to their thickness.

Hallett considered the case of a straight step of height h growing parallel to the basal plane by collecting material directly from the vapour phase and by surface diffusion. If X_s is the average distance which a molecule travels on the ice surface before re-evaporating, all molecules within a distance X_s on either side of the growing step will contribute to its growth. The velocity V of the step is then

$$V = \frac{(h+2X_s)A}{h\rho}, \tag{4.5}$$

where ρ is the crystal density and A is the net mass flux of vapour per unit surface area. If $X_s \gg h$ the step will grow largely by surface diffusion with $V \propto h^{-1}$. Hallett's measurements, therefore, suggest that the layers advance mainly by surface diffusion and not by direct deposition of water molecules from the air. Hallett also found that V increased steadily from -40 to -6 °c, decreased sharply with increasing temperature from -6 to -3 °c, and thereafter increased again as the melting point was approached. He assumed on the basis of the preceding argument that X_s will vary in temperature in a similar manner.

Mason *et al.* (1963 a) made more direct measurements of X_s by measuring the velocity of approach of two neighbouring growth layers. They assumed the critical separation at which the velocity slowed down to be equal to $2X_s$. In this way they obtained the curve of X_s against temperature illustrated in figure 15. The general form of their curve is similar to that obtained by Hallett, but whereas Hallett's maximum occurred at -6 °c that obtained by Mason *et al.* is seen from the figure to be located at -11 °c. In an attempt to resolve this difficulty Kobayashi (1967) employed Hallett's technique to measure the velocity of step-propagation, V, over the basal surface of ice grown on a covellite substrate. Photographs obtained in this investigation are presented in plate 3. The measured variation of V with temperature obtained in these extremely careful experiments was very similar in form to the curve of X_s against temperature obtained by Mason *et al.*, with a maximum occurring at a temperature of -11 °c. It appears reasonable to assume, therefore, that Hallett's results are incorrect and that an accurate description of the variation of X_s with temperature is provided by the experiments of Mason *et al.*

On the basis of their experimental curve illustrated in figure 15, Mason *et al.* have suggested an explanation for the variation of crystal habit with temperature. Since molecules arriving on the crystal surface have a surface migration length of several microns, they may reach an adjacent face before becoming incorporated into the lattice. The initial habit development from the embryo stage may therefore be determined by the relative values of X_s for the basal and prism faces. If X_s is greater for the basal face there will be a net transport of material by surface diffusion to the prism faces, and the crystal will start to develop a plate-like habit. The reverse will be true if X_s is greater for the prism faces. At present it has not proved possible to measure values of X_s for prism faces, but Mason *et al.* have suggested that the curve of X_s against temperature for the prism faces may be of the same general shape as that for the basal faces but displaced slightly along the temperature axis as indicated in the broken curve in figure 15. If this suggestion is correct the two curves will intersect at three places, thereby providing four temperature ranges in which the ratio of X_s for the basal and prism faces alternates between values greater than and less than unity. When this ratio exceeds 1 the early development will be plate-like, whereas prismatic columns will develop when the ratio is less than 1. If the actual curve of X_s for the prism faces against temperature provided similar intersection points to those assumed in figure 15 the sequence of habit changes predicted from this diagram would be consistent with that presented in table 2. In addition, analysis of figure 15 suggests that habit transitions will occur very sharply at -3 and -8 °c, but more gradually at -25 °c. These predictions are entirely in accord with observation.

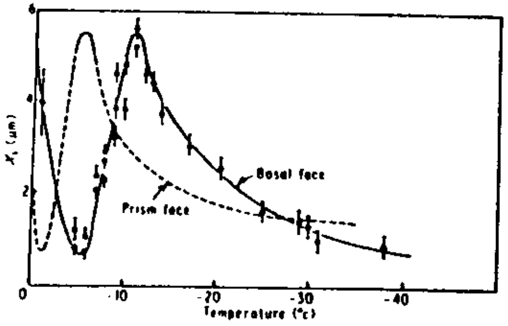


Figure 15. Mean surface migration distance X_s as a function of temperature. —— basal face; - - - - suggested curve for prism face. (From Mason *et al.* 1963 a.)

Developing this explanation of ice-crystal habit, Mason (1965 b) suggests that once the crystal dimensions become large compared with X_s surface diffusion will have little further effect on habit development, which will now be controlled primarily by the three-dimensional diffusion field. However, once a habit has been established in the early stages of growth, the diffusion field around the crystal will orient itself to conform to the crystal geometry and tend to maintain it. The observation that at moderate supersaturations crystals continue to develop as polyhedra suggests that the excess material arriving at the edges and corners is redistributed over the surface by surface diffusion. However, as the supersaturation is increased surface diffusion cannot redistribute material sufficiently rapidly to compensate for its nonuniform deposition, and growth occurs preferentially at the corners, resulting in the formation of sector plates, dendrites, hopper crystals, and other skeletal forms. Photographs by Mason *et al.* of steps and ridges on various types of ice crystal are illustrated in plate 4.

Mason considers, therefore, that the crystal habit is determined by the interaction between the surface migration of molecules and the nonuniform flow from the diffusion field. The relative rates of surface diffusion on the basal and prism faces are responsible for determining the habit in the early stages of growth, and this is later maintained and accentuated by diffusion of vapour to, and conduction of latent heat of crystallization away from, the crystal surface. This explanation is consistent with a substantial body of experimental evidence and must be preferred to that of Hobbs and Scott (1965), involving the nucleation of steps at the edges of crystals followed by the propagation across the faces of the crystal, which is based upon the incorrect results of Hallett and is inconsistent with the measurements of Kobayashi and of Mason *et al.* In order to resolve this question more conclusively, however, measurements of the velocities of step-propagation on the prism faces of ice crystals are urgently required.

4.4. *Aggregation of ice crystals to form snowflakes*

Although the primary mechanism of growth of ice hydrometeors to precipitation dimensions within the majority of clouds involves the accretion of supercooled water droplets, the aggregation of ice crystals may well be the dominant process in highly glaciated clouds. The growth of ice agglomerates is governed by the collision and aggregation efficiencies of ice crystals. The aerodynamic problems posed by the complexity and variability of the ice-crystal geometry have so far defied solution, and no theoretical computations have been made of the collision efficiencies of these particles; it is possible only to make semiquantitative estimates based upon collision cross sections for spheres. However, in recent years considerable knowledge has been gained of the adhesion process, and measurements have been made of the collection efficiencies of ice crystals, defined as the product of the collision and aggregation efficiencies.

Studies by Nakaya and Matsumoto (1953, 1954), Hosler *et al.* (1957), Hosler and Hallgren (1961), and others have demonstrated conclusively that adhesion of ice to ice occurs at temperatures below which pressure-melting is likely to be effective. These workers find that adhesion is a sensitive function of temperature, surface contamination, and relative humidity. Hosler and his coworkers concluded that their results were explicable in terms of the 'liquid-like layer' hypothesis propounded in elementary form by Faraday (1860) and developed by Weyl (1951). From considerations of minimum surface free energy Weyl proposed a reorientation of molecules in and near the surface of an ice specimen and that the thickness of this disordered layer will decrease with decreasing temperature and relative humidity. Circumstantial support for Weyl's hypothesis is provided by the experiments of Jellinek (1961) and the theoretical studies of Fletcher (1962 b) who calculated that the reorientation of water molecules in an ice surface near 0 °c extends in an exponentially decreasing manner for about 10 molecular layers below the surface before achieving the bulk-ice lattice arrangement, and that the theoretical relationship between the thickness of the distorted layer and temperature is similar to that between sticking force and temperature, measured by Hosler *et al.* However, although the 'liquid-film' hypothesis offers an explanation for several experimentally determined properties of ice, these phenomena can also be explained in terms of well-established physical efforts. Experiments by Kingery (1960) and Kuroiwa (1961) indicated that surface and volume diffusion of ice molecules were primarily responsible for the sintering of ice, but a comprehensive theoretical and experimental study by Hobbs and Mason (1964), supported by the low temperature investigations of Hobbs (1965 a), established that the dominant mechanism operative during the sintering of ice spheres in air at atmospheric pressure is evaporation of material from the surface of the spheres and condensation onto the concave region of the ice bridge growing between the two spheres. Hobbs (1965 b) showed that the observed time-dependence of the strength of snow firn is also explicable in terms of this mechanism. However, Hobbs and Radke (1967) found that in the absence of temperature gradients the densification of dry snow is controlled primarily by volume diffusion.

Table 3. Collection efficiencies and densities measured by Hosler and Hallgren†

Temperature (°C)	Mean collection efficiency‡ 127 μm diam.	Mean collection efficiency‡ 360 μm diam.	Mean density (g cm⁻³)‡ 127 μm diam.	Mean density (g cm⁻³)‡ 360 μm diam.
− 6 (prisms)	0·044	0·057	0·044	0·066
− 8 (prisms)	0·057	0·100	0·029	0·043
− 10 (prisms)	0·094	0·126		
− 11 (plates)	0·104	0·210	0·021	0·030
− 13 (plates)	0·099	0·185		
− 16 (plates)	0·068	0·104	0·013	0·022
− 18 (plates)	0·055	0·099		
− 20 (plates)	0·034	0·081	0·008	0·016
− 22 (plates)	0·041	0·076		
− 24 (plates)	0·028	0·058	0·009	0·014
− 26 (plates)	0·025			

† From Hosler and Hallgren (1961).
‡ Means are for 10 or more individual measurements.

Hosler and Hallgren (1961) measured the collection efficiencies of suspended ice spheres of original diameter 127 and 360 μm for ice crystals of typical dimensions ranging from 8 to 18 μm which were drawn past the spheres in a wind tunnel. The collection efficiency was estimated from the ratio of the number of crystals collected, determined from a comparison of the initial and final dimensions of the collector, to the number in the path of the collector, obtained by measuring the crystal flux using a sampling technique. Examples of the collection efficiencies and mean aggregate densities measured by Hosler and Hallgren at ice saturation are presented in table 3, which shows that appreciable aggregation occurred at a temperature of − 26 °c, the lowest utilized in these experiments. In the experiments of Hosler *et al.* some aggregation was found to occur at − 36 °c. The collection efficiencies are seen to increase with increasing temperature over the approximate range − 26 to − 11 °c and thereafter to decrease as the temperature rises to − 6 °c. The decrease of collection efficiency with increasing temperature between − 11 and − 6 °c was shown to be associated with an increasing proportion of prismatic crystals. Hosler and Hallgren concluded, therefore, that the basal faces of ice crystals possess greater adhesive properties than the prismatic faces. When their experiment was repeated in a dry atmosphere they found no evidence for adhesion at temperatures below − 4 °c.

In view of the strong experimental and theoretical evidence for increased collision efficiencies of water droplets in the presence of intense electric fields, discussed in a previous section, it appears logical to expect that the collision efficiencies for ice crystals will also be appreciably modified in the presence of strong electric forces. In fact, measurements by Latham *et al.* (1965) of the fields between model ice crystals suggest that, in general, an electric field within a cloud will produce a greater force between two ice crystals than between two droplets of the same mass as the crystals separated by the same distance. This contention was confirmed by the experiments of Saunders (1968 a), who made direct measurements of the forces between metallic models of ice crystals separated in an electric field. From the ratio of the measured forces between a model pair and conducting spheres of the same volume as the models Saunders obtained values of a force-enhancement factor, over a wide range of separations and crystal types, which may be utilized in computations of the effect of electric fields on the collision efficiencies of ice crystals. It appears probable, therefore, that fields in excess of about 100 v cm⁻¹ will modify significantly the collision efficiencies of small ice crystals, and that the effect of the electrical forces will be most pronounced when the relative velocities are low.

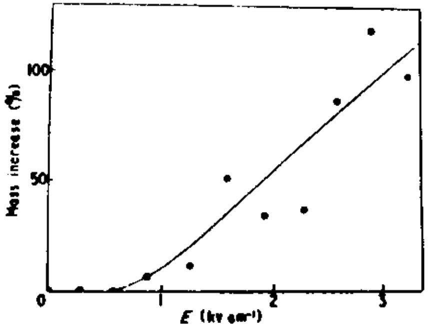


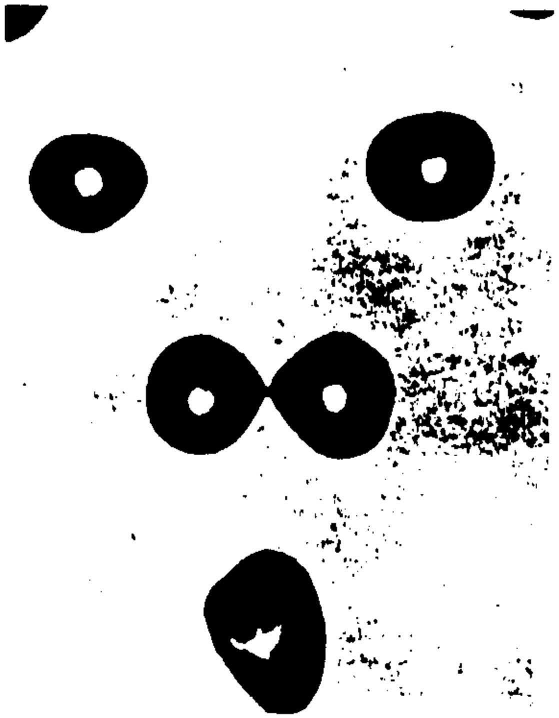
Figure 16. Increase of mass of an ice sphere exposed to a stream of ice crystals as a function of electric field strength *E*. Air temperature − 9 °c. (From Latham and Saunders 1964.)

Latham and Saunders (1964) performed experiments which demonstrated, as shown in figure 16, that the collection efficiencies of ice crystals colliding with an ice sphere increased rapidly with increasing electric fields above a threshold value of about 500 v cm⁻¹. These studies have been extended in some detailed but currently uncompleted experiments by Saunders (1968 b). Copious quantities of ice crystals of diameter ranging from 3 to 10 μm were grown at a selected temperature inside a cold room and were then drawn up two identical isothermal tubes in each of which was positioned an ice sphere maintained at the same temperature as the crystal stream to which it was exposed. A third tube contained a collector which permitted accurate values of the crystal concentrations and dimensions to be measured. The identical spheres, whose initial diameter was varied from about 200 to 2000 μm, were both straddled by toroidal electrodes, which enabled electric fields to be applied parallel to the lines of flow of the two crystal streams; in the experiments an electric field of selected strength was produced in one tube while no field was applied in the other. From the measured values of the growth rates of the two ice spheres, obtained both by means of a microbalance and by microphotography, together with the measured crystal concentrations and flow rates it was possible to determine absolute values of collection efficiencies as a function of field strength, ice-crystal and collector dimensions, temperature, air-stream velocity, and relative humidity. In the absence of a field the values of collection efficiency, after correction had been made for the fact that the crystal dimensions were increasing throughout the period of exposure, were comparable with those measured by Hosler *et al.* The rate of growth of the collector by means of aggregation was found to increase rapidly with increasing field strength above an ill-defined threshold value of around 300 v cm^{-1}. Typical photographs of aggregates grown in these studies are presented in plate 5. The physics of the enhanced growth was clarified in a separate experiment by Latham and Saunders (1967), who showed that the increased force required to separate two ice spheres situated in an electric field was not accompanied by an increase in the rate of growth of the ice bridge between the two spheres and is explicable entirely in terms of the calculations of Davis (1964) of the purely electrostatic forces between two conducting spheres situated in an electric field, which have been verified experimentally by Saunders (1968 a). Saunders (1968 b) found that in the presence of electric fields aggregation can occur at temperatures as low as − 50 °c, whereas in the absence of such forces aggregation was insignificant at temperatures below about − 30 °c. His measurements suggest that the primary role of electrostatic forces is to increase the aggregation efficiencies, although a significant increase in the collision efficiencies may occur in extremely strong fields. This conclusion was reinforced by the field measurements on the growth of ice particles by aggregation, made by Latham (1969) in Yellowstone Park. The evidence of agglomeration of ice crystals in the presence of electrical forces at temperatures at which aggregation does not occur in the absence of electrification is supported by the observations of MacCready (private communication 1967) that agglomerates of ice crystals were found in the anvils of strongly electrified thunderstorms at extremely low temperatures. Electrical effects may therefore also have been responsible for the aggregates of ice crystals in natural clouds observed by Douglas *et al.* (1956).

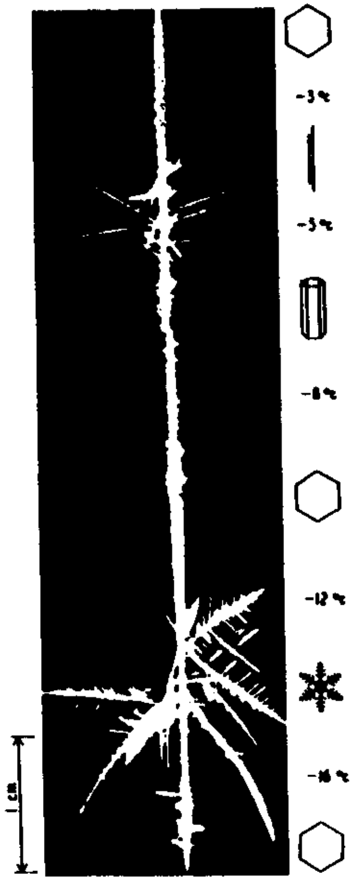
In order to calculate the rates of growth of snowflakes by the aggregation of ice crystals it is necessary to know the terminal velocities of the falling particles. Theoretical and experimental studies of this problem have been made by Braham (1963), Cornford (1965), Magono and Nakamura (1965), and several earlier workers. Magono and Nakamura found that their measured values of the fall velocity of snowflakes, U, could be expressed with a high degree of accuracy by means of the empirical equation

$$U = 330(\sigma - \rho)^{0.36}, \tag{4.6}$$

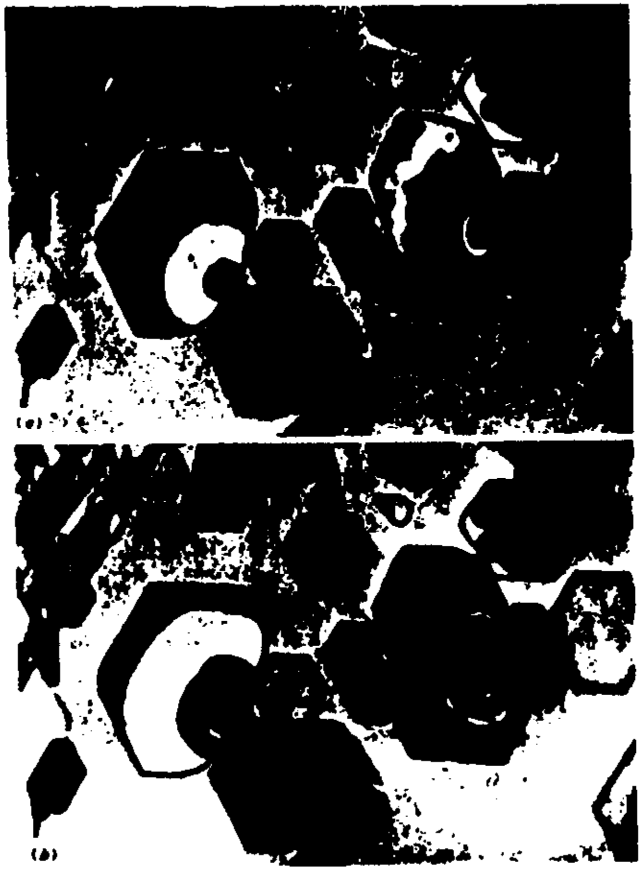
where σ and ρ are the densities of the snowflake and the air respectively. For individual ice crystals the velocities determined by Nakaya and Terada (1934) appear to be reliable.



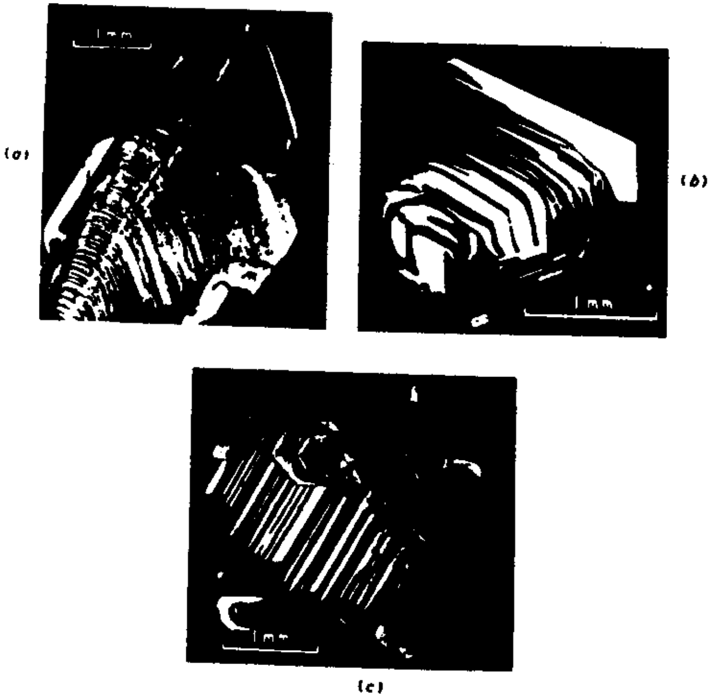
Oppositely charged drop-pairs of radius 80 μm in free fall. (From Sartor 1967 b.)



Variation of habit with temperature for ice crystals grown in a diffusion chamber. The sequence is: plates → needles → hollow prisms → plates → dendrites → plates. (From Hallett and Mason 1958 a.)

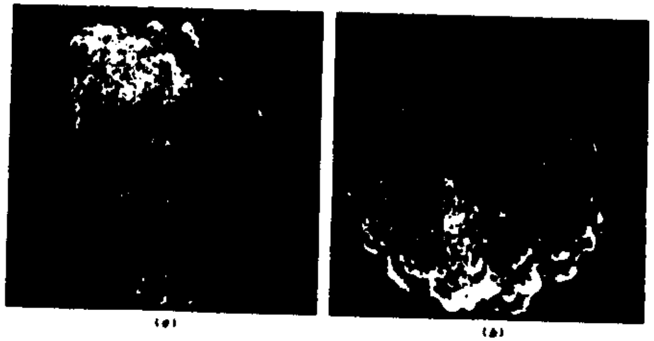


Epitaxial deposit of ice crystals on a cleavage surface of covellite showing successive stages ($a \rightarrow b$) of the spreading of growth layers across the basal face of the ice crystals. $T_s = -49.5$ °c, saturation ratio 1·4. Time interval = 180 s. (Magnification × 700.) (From Kobayashi 1967.)

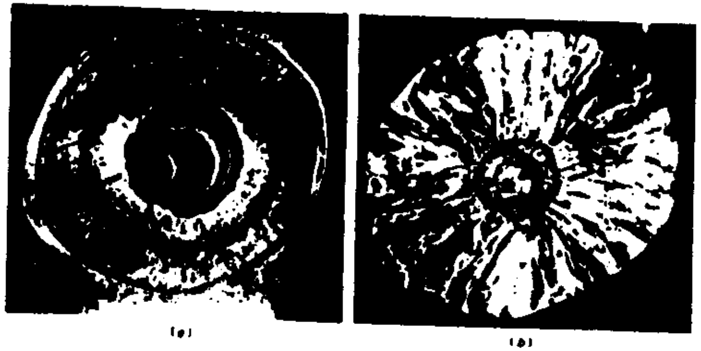


Steps and ridges on ice crystals. *(a)* The 'front' surface of part of a plate crystal showing narrow steps; *(b)* front surface of a shallow dish-shaped crystal showing a terrace of broad steps; *(c)* the 'back' (sheltered) side of a sector plate showing broad straight steps and radial ridges. (From Mason *et al.* 1963 a.)

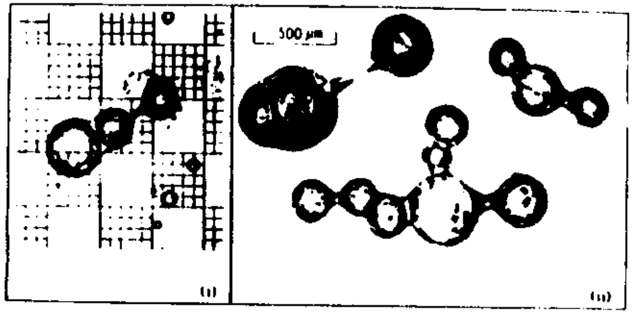
Photographs of ice crystals collected on an ice sphere of original diameter 1·5 mm in an electric field (E): *(a)* $E = 1{\cdot}65$ kv cm^{-1}; *(b)* $E = 0$. Air-stream velocity 20 cm s^{-1}, temperature −7 °c.



I. Photographs of artificial hailstones of diameter about 10 cm grown under various conditions of air temperature T_a, median droplet diameter d_m, and liquid-water content L. (a) $T_a \sim -21$ °c, $d_m = 29\ \mu m$, $L = 4{\cdot}3\ g\,m^{-3}$; (b) $T_a \sim -11$ °c, $d_m = 57\ \mu m$, $L = 3{\cdot}0\ g\,m^{-3}$. (From Bailey and Macklin 1968.)



II. Sections through a hailstone of diameter 4·0 cm. (a) Under translucent light; (b) same hailstone under polarized light. (From List 1960 b.)



Frozen drops (i) found in natural clouds over the Caribbean at temperatures above −5 °c by Mee (private communication), and (ii) produced in the laboratory during electrofreezing experiments by Smith (private communication). In (i), one small division = 20 μm.

4.5. *Growth of graupel and hail by the accretion of supercooled droplets*

The most rapid growth of precipitation elements inside clouds occurs when ice particles accrete supercooled water droplets which freeze wholly or partially on collision. The ice particle may have been formed by the freezing of a supercooled droplet, by growth from the vapour on a sublimation nucleus, or by a drop-splintering mechanism. Graupel is formed by a relatively slow accretion process in which each collected droplet freezes immediately upon impact, and the resulting structure is porous and of low density. The growth of hailstones, on the other hand, represents an extreme case of droplet accretion in which the latent heat released upon freezing of part of the accreted liquid may be sufficient to prevent freezing of the remainder. The pellet thus formed is covered with a liquid skin which freezes relatively slowly or retains liquid water within internal cavities (spongy ice) and is consequently dense and more transparent.

The equations for the heat balance of a growing hailstone were set up by Schumann (1938) and developed by Ludlam (1958). They failed to take account, however, of the existence of spongy ice, investigated by List (1959 a) and Macklin (1961), which is of crucial importance in the formation of hailstones. Experimental and theoretical studies by List (1960 a) provided quantitative information concerning the relation between the liquid-water content of spongy ice and the relevant growth conditions and provided a framework utilized by List (1961) for a comparison between the conditions required to produce various types of ice structure, such as spongy ice, compact ice, and porous ice.

List demonstrated that in the case of the growth of spongy ice the accretion of supercooled cloud droplets is accompanied by evaporation from the particle surface. On the other hand, Douglas (1960) has shown that there are areas of growth where condensation of water vapour occurs. A general treatment of the heat and mass exchange of hailstones, which delineates the conditions under which the various types of growth occur and establishes the boundary conditions which subdivide them, was provided by the comprehensive treatment of List (1963 a) for the case of spherical hailstones.

List assumes that the hailstone under observation is growing in a cloud containing supercooled water droplets possessing a temperature equal to that of the air, t_A, while the hailstone temperature t_D is determined from the conditions of thermodynamic equilibrium. In this situation the variation with temperature of saturation vapour pressure over the hailstone e_{sh} and over the cloud droplets e_{sv} will be as shown in figure 17. The problem is to find the point (e_{sh}, t_D) corresponding to the point (e_{sv}, t_A), which is assumed to be known. Since both the freezing of deposited water droplets and the sublimation of water molecules are always accompanied by the evolution of heat it follows that $t_D > t_A$ throughout the period of growth. If the accretion is zero ($M_{CP}{}^* = 0$) growth occurs only by sublimation and the hailstone temperature assumes its lowest value t_{DL} $(> t_A)$. Thus a branch of a curve is obtained which establishes for a particular value of t_A all possible growth conditions (e_{sh}, t_D) with $0\ °\mathrm{c} \leqslant t_D \leqslant t_{DL}$. This curve is divided by the point $(e_{sh} = e_{sv}, t_D)$ where no energy and mass exchange are allowed with the vapour phase ($M_{ES}{}^* = 0$). If, therefore, $e_{sh} < e_{sv}$ then the growth by accretion of cloud droplets is accompanied by an additional increase of mass by means of sublimation, while for $e_{sh} > e_{sv}$ accretion is followed by evaporation. Further intermediate points of interest occur where the mass increase through accretion equals that by sublimation or that lost by evaporation, although List showed that this latter equivalence can never be achieved. A final special case occurs when $t_H = 0$ °C, which corresponds to the growth of spongy ice.

Having established in qualitative terms by means of these thermodynamic arguments the existence of various regimes of growth and energy exchange associated with the growth of hailstones List proceeded to treat the problem quantitatively. He made several assumptions. Slowly rotating spherical hailstones were considered, even though Weickmann (1953), List (1958), and Sarrica (1959) had established that the majority of hailstones have ellipsoidal or even conical shapes, since basic equations of heat and mass exchange do not exist for these nonspherical particles.

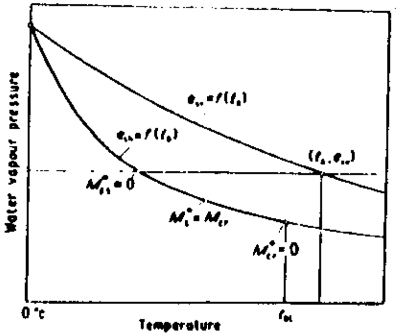


Figure 17. Saturation vapour pressure curves over water ($e_{sw} = f(t_A)$ for supercooled cloud droplets) and ice ($e_{sh} = f(t_H)$ for hailstones) as a function of temperature. (From List 1963 a.)

Further assumptions were that the effect of the collection of ice crystals upon the growth behaviour was negligible and that the density of the hailstones was equal to that of pure ice, which is justified by the studies of List (1958, 1959 b, 1961) and Macklin *et al.* (1960).

The total heat exchange of a growing hailstone is governed by the equation

$$Q_{KL}^* + Q_{ES}^* + Q_{CP}^* + Q_F^* = 0. \tag{4.7}$$

Q_{KL}^* denotes the heat component imparted to the hailstone per unit time by convection and conduction, Q_{ES}^* by evaporation and sublimation, Q_{CP}^* by accretion of water droplets, and Q_F^* by complete or partial freezing of the deposited water. List showed that the contributions of radiation and friction in the aerodynamic boundary layer to the total heat exchange are negligible. Expressions presented by List for the four heat components include, in the case of Q_{KL}^* and Q_{ES}^*, a factor θ which represents in the former case the ratio of the heat transfer through a natural (rough) surface to that through a smooth surface, and in the latter case the identical ratio corresponding to mass transfer. Values of θ have been determined experimentally by List (1960 a). The expression for Q_F^* involves a factor I which represents the fraction of deposited water which is frozen. I is equal to unity for all surface temperatures where $t_H < 0$ °C; when $t_H = 0$ °C I can be less than unity, in which case the deposit consists of a mixture of ice and water. The expressions for the heat components can be combined to give a general equation for thermodynamic equilibrium:

$$\frac{1{\cdot}68\,k(t_D - t_A) + C_{l,s} D_{wa} t_A^{-1}(e_{sh} - e_{sv})}{0{\cdot}785\,(L_f I - \bar{C}_w(t_D - t_A))} = \nu^{1/2} v^{1/2} D^{1/2} \theta^{-1} E \omega_f, \tag{4.8}$$

where k is the thermal conductivity of air, $C_{l,s}$ are the specific heats for transitions from liquid to gas and solid to gas respectively, D_{wa} is the diffusivity of water vapour in air, L_f is the latent heat of fusion at the temperature t_D, $\bar{C}_w$ is the specific heat of water averaged over the temperature range (t_D, t_A), ν is the kinematic viscosity of the air, D is the diameter of the hailstone and v its velocity relative to the air, E is the total efficiency of catch, and ω_f is the liquid-water content of the air.

The total increase of mass per unit time of a hailstone is compounded of that produced by accretion, M_{CP}^*, and that produced by exchange through the vapour phase by evaporation or sublimation, M_{ES}^*. Therefore

$$M_{tot}^* = M_{CP}^* + M_{ES}^*. \tag{4.9}$$

However, $M_{CP}^* = Q_{CP}^*/\bar{C}_w(t_D - t_A)$ and $M_{ES}^* = Q_{ES}^* L_{s,v}^{-1}$, where $L_{s,v}$ is the latent heat of sublimation or evaporation.

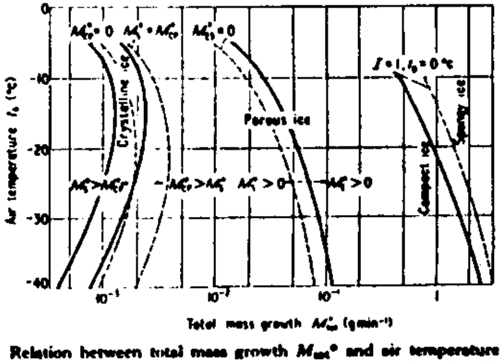


Figure 18. Relation between total mass growth M_{tot}^* and air temperature t_A with various growth zones and ice products. $D = 2$ cm; —— 800 mb, - - - - 200 mb. (From List 1963 a.)

From these general equations for the heat balance and material transfer between a spherical hailstone and its environment List was able to demonstrate the interdependences of the different variables such as air temperature, air pressure, liquid-water content, the diameter and fall velocity of the hailstone, its surface temperature, and its growth rate. As shown in figure 18 the equations also permit the delineation of various growth zones. It is seen that the curves for accretion divide the entire growth area into two zones, one with a mass increase predominantly from the gas phase ($M_g^* > M_{CP}^*$), the other with a mass increase predominantly from accretion ($M_{CP}^* > M_g^*$). As might be expected from latent heat considerations it is evident that the gas phase, even if it contributes substantially to the energy exchange, is unimportant for the deposition of mass upon larger hailstones. The growth regions in which accretion is predominant is seen from figure 18 to be subdivided by the curve $M_{ES}^* = 0$. On the left of this curve accretion is accompanied by sublimation, while on its right the mass increase is reduced by evaporation. A further dividing line is found in the curve $t_0 = 0$ °c, $I = 1$, on the right of which lies the growth zone of spongy ice.

List was able to interpret the information contained in figure 18 in order to classify observed ice deposits in terms of their growth conditions. To the right side of this curve $I = 1$, $t_0 = 0$ °c spongy ice occurs, and it is clear that this type of growth will be of importance in conditions favouring high growth rates. To the immediate left of this curve the freezing of the deposited water occurs relatively slowly, practically no air is taken in from the outside, and air originally dissolved in the deposited water will be released to the outside of the hailstone during freezing. The density of the resulting compact ice will therefore be only slightly below that of pure ice. Further towards the left in figure 18 lies the zone of porous ice in which

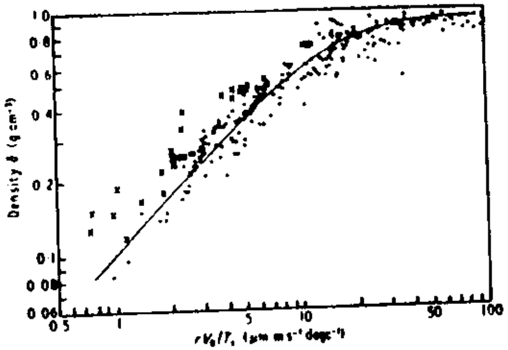


Figure 19. Density δ of rime ice as a function of the parameter (rV_0/T_s), where r is the median volume radius of the cloud droplets (in μm), V_0 their impact speed (m s⁻¹), and T_s the depression below 0 °c of the rime surface temperature. ×, $T_s < -20$ °c; ●, $T_s > -20$ °c. (From Macklin 1962.)

the freezing of individual droplets allows air from the environment to become encased, thereby producing ice of reduced density. As the equilibrium curve $M_a^* = M_{c,r}^*$ is approached the predominance of captured cloud droplets in determining the structure of the ice framework decreases, and to the left of this curve growth of crystalline ice occurs. Although sublimation is not significant on any large scale in the growth of hailstones it is clear that in nature all growth conditions between pure sublimation and the deposition of spongy ice are encountered.

A tremendous amount of research has been performed recently into the problem of hailstone growth. For instance, Macklin (1962) conducted a detailed experimental study of ice formed by accretion over a wide range of conditions, in order to ascertain the influence of the wind speed, ambient temperature, droplet diameter and liquid-water concentration in the supercooled cloud, and the size of the accreting object. The density of the deposits ranged from 0·1 to 0·9 g cm⁻³, the density increasing with increases in the first four of the above parameters, but decreasing with increasing object size. As illustrated in figure 19, it was found that the density could be expressed as a function of rV_0/T_s, r being the median volume

radius of the droplets comprising the cloud, V_0 the speed with which the droplets struck the object, and T_s the mean temperature of the accreting surface. Macklin explained the observed dependence of the density on the parameter rV_0/T_s in the following way, using the assumption that the droplets remain approximately spherical on freezing—this assumption is valid if the impact speed and the surface temperature are moderately low. When a supercooled droplet arrives at the surface of the deposit it begins to freeze, the initial freezing occurring over the area of contact between the droplet and the lower surface. If a bond can form quickly and with sufficient strength to overcome the impact momentum of the droplet, then the droplet is held in this position. If the bond is not formed quickly or strongly enough the droplet moves or slips over the surface of the frozen droplet on which it has impinged until it is brought to rest either by the strengthening of this first bond or by the formation of bonds with other frozen droplets. In both circumstances the structure is more compact and has a higher density. The density may, therefore, be expected to depend upon rV_0, which is proportional to the ratio of the impact momentum of the droplet and the area of contact between the droplet and the lower surface. In addition, the density will also be dependent upon the time of formation of the bond between the droplet and the underlying surface. The longer this time the more compact the structure will be. Since to a first approximation the time of formation of the bond is proportional to $1/T_s$, the density will then be a function of rV_0/T_s, as observed. Macklin also made a microscopic examination of the deposits. At low values of rV_0/T_s, corresponding to low densities, the droplets tended to freeze together as spheres, while at higher values they were distorted and spread considerably before freezing.

Hitschfeld and Stander (1967) performed a rigorous study of the temperature profiles in spherical and homogeneous hailstones falling through clear air. They calculated that a hailstone of about 1 cm in radius is liable to be about 12 degc colder than the ambient air. The cooling effect of hail on the air was shown to be small. Their calculations demonstrate that when a hailstone of radius about 1 cm falls through a cloud, its heat capacity delays the commencement of wet growth by up to 2 km. On the other hand, when hail grows in regions of high liquid-water content the heat capacity term for even the largest hail is unimportant in the heat balance equations. They conclude that such growth normally leads to mixtures of water and ice.

Experimental studies of heat transfer that take account of factors such as the nonsphericity of hailstones and their oscillation, rotation, and surface roughness have been made by Macklin (1963 a, 1964 a), List and Dussault (1967), and Bailey and Macklin (1968). The general heat and mass exchange of spherical hailstones has been discussed by Macklin (1964 b) and List (1964). The heat exchange ratios of hailstones have been studied in the laboratory and calculated for a model cloud by List *et al.* (1965). Experimental and theoretical studies of the melting times of small ice spheres and cones have been made by Drake and Mason (1966). A series of investigations of the growth criteria of spongy ice have been made by Knight (1968) and Knight and Knight (1968 a, b). The density, structure, surface configuration, and fall-speeds of hailstones have been studied by Macklin and Ludlam (1961), Macklin (1962, 1963 b), List (1963 b), Browning *et al.* (1963), and Bailey and Macklin (1968). The structure and growth of giant hailstones have been studied by Browning (1965, 1966). Critical liquid-water concentrations of large hailstones have been investigated by Macklin and Bailey (1966). More general discussions of the growth of hailstones have been presented by List (1960 b, 1961, 1965). Calculations and analyses of the growth of hail within natural clouds have been made by Browning and Ludlam (1962), Browning (1962, 1963), and others. The photographs in plate 6 illustrate two useful techniques that have been developed in studies of the structure, history, and physical properties of hailstones; artificial hailstones can be grown under controlled conditions in the laboratory and subsequently analysed, and thin sections of natural or artificial hailstones can be examined between crossed polaroids in order to reveal the constituent crystallites and by transmitted unpolarized light in order to expose the bubble structure. Despite this tremendous concentration of research effort into the problems of the growth, structure, and energy balance of hailstones, an accurate quantitative understanding is far from complete. However, it appears probable that the general approach of List, described above, will remain as a qualitatively correct framework into which subsequent, more specific, information can be incorporated.

Reinforcement for this conclusion is provided by Macklin and Payne (1967), who made a theoretical study of the assumptions underlying the simple heat-balance relations outlined previously, which have been used to predict the surface temperatures of ice deposits being formed by the accretion of supercooled water droplets. Calculations were made of the freezing and subsequent cooling times of a thin water film on the surface of a ventilated sphere initially at a uniform temperature. They demonstrated that this process effectively simulates hailstone growth. Their calculations show that both the freezing and the cooling processes are dominated by the sphere temperature and that except at temperatures very close to 0 °c the freezing time of the water film is short compared with the total time required to remove the latent heat of fusion by forced convection. This occurs because the heat of fusion is first conducted rapidly into the sphere, and then more slowly dissipated through the air boundary layer on the surface of the sphere to the environment. Their calculated liquid-water concentrations required to maintain a sphere at a steady temperature compare well with those obtained from the simple heat-balance relation for a spherical hailstone. They therefore conclude that although these original equations completely ignore the physical processes involved in the accretion of individual droplets, they are useful for predicting values for the mean temperatures of an accreting surface in a steady-state situation.

4.6. *Microphysics of the accretion process*

In order to obtain a more detailed understanding of the structure of hydrometeors growing by the accretion of supercooled water droplets it is necessary to establish the motion of the particles in free fall and, particularly, to study the microphysics of individual interactions between droplets and the growing particles. Brownscombe and Hallett (1967) have conducted an extremely comprehensive study of this problem. From a review of previous work on the fall motions of model ice crystals, notably by Willmarth *et al.* (1964), Podzimek (1965), and Starr and Mason (1966), they conclude that a falling dendritic or plate-like ice crystal upon which the growth of graupel or hail may originate will capture small cloud droplets in approximately equal proportions on both front and rear surfaces at Reynolds numbers in excess of about 100 because of oscillation of the crystals; at Reynolds numbers greater than about 500 the crystals will tumble over and over in fall.

Brownscombe and Hallett proceeded to study the impaction and freezing of individual droplets on an ice substrate. In the early stages of graupel formation the time interval between the arrival of successive droplets will be long in comparison with the time taken for the latent heat of solidification to be transferred to the environment, and the droplet and substrate will effectively be at the same temperature prior to nucleation. The final shape of a supercooled droplet colliding with and freezing onto an ice substrate will depend upon the crystallization velocity and the dynamics of the deformation process. Hallett (1964) showed that dendrites grew through supercooled water in bulk with a velocity component parallel to the basal plane given by $0{\cdot}08\,\Delta T^{1\cdot9}$, where ΔT is the degree of supercooling. Macklin and Ryan (1965) subsequently showed that the direction of maximum growth velocity occurs at an angle to the basal plane which increases with ΔT. Hallett's equation gives a maximum velocity of 4 cm s⁻¹ at −7 °c, 34 cm s⁻¹ at −20 °c, and an extrapolated value of 125 cm s⁻¹ at −40 °c. No accurate measurements have been made of the rate of deformation of supercooled cloud droplets impinging upon a solid surface. Brownscombe and Hallett assumed that a colliding drop assumed the shape of a spherical cap and calculated the extent of the deformation at various impact velocities by assuming that the kinetic energy is transformed entirely to surface energy as a result of the impact. They also showed that viscous dissipation, although insignificant at small deformations, will terminate the deformation before the ratio γ of the base radius r to the height h of the cap reaches 10. In order to obtain more detailed information on drop accretion Brownscombe and Hallett observed the profiles of supercooled droplets of radius 9 ± 1 μm, 19 ± 2 μm, and 40 ± 7 μm that were collected on the ice-coated edge of a microscope slide situated in a wind tunnel. The air temperature and the velocity of the air stream could be varied from 0 to −20 °c and up to 13·5 m s⁻¹ respectively. The results are summarized in table 4, which shows that the deformation of the resultant frozen droplet increases rapidly with increasing velocity and more slowly with increasing degree of supercooling. The observed deformation was found to be appreciably less than predicted from their simple calculations, except at small deformations. This may be explained in part by loss of energy by viscous dissipation, an effect which would be expected to increase at large supercoolings where the growing dendrites at the area of contact of the drop and the substrate would cause increased dissipation and reduce the propagation velocity of the drop periphery. The latter effect should

Table 4. Deformation of water droplets freezing on a smooth ice surface, as a function of radius R, free stream velocity U, and ambient temperature, measured by Brownscombe and Hallett†

U‡	$R = 10$ μm		$R = 18$ μm		$R = 40$ μm	
(m s⁻¹)	−10 °c	−20 °c	−10 °c	−20 °c	−10 °c	−20 °c
terminal	1·0	1·0	1·0	1·0	1·0	1·0
3·5		1·0		1·3	2·5	2·0
4·0			1·5			
5·0		1·5				
6·0			2·5	2·0	4·0	3·0
9·0		2·0		3·0	7·0	5·0
10·0	2·8					
10·5			5·5	4·5		
11·0		3·0				
13·5	5·0	4·0	8·0	7·0	11·0	9·0

† From Brownscombe and Hallett (1967).
‡ For impact velocity, reduce free stream velocity of 10 μm droplets by 0·9.

become very important as this velocity approaches the dendrite crystallization velocity, characterized by the amount of supercooling. Similar results were obtained by Macklin and Payne (1967), who measured the resultant spreading as a function of both ΔT and the temperature T_s of the ice surface, which could be varied independently. This additional degree of freedom is interesting since, in general, the surface temperature of a hailstone will be markedly different from that of the colliding droplets. They found that the ultimate degree of spreading decreased with decreasing ΔT and T_s but was more sensitive to the latter, because of the significantly greater rates at which heat can be transferred through the ice than through the air. This conclusion was confirmed by the calculations of Brownscombe and Hallett on the heat transfer from a supercooled droplet freezing onto a collecting particle of dimensions that are large compared with that of the droplet. In this case freezing takes place from the contact area outwards, freezing is asymmetrical, and an ice shell enclosing a liquid interior is not formed. However, Johnson and Hallett (1968) have established that a necessary but not sufficient condition for the shattering of freezing supercooled drops, which has been studied by Mason and Maybank (1960) and others, is that the freezing is symmetric. Brownscombe and Hallett concluded that shattering and possible accompanying electrification can occur only if the drop is accreted on a narrow spike, which restricts the heat flow to the substrate, or if the surface temperature is very close to 0 °c.

This conclusion suggests strongly that the experimental conditions under which copious splintering and electrification were measured over a wide range of temperature, impact velocity, and droplet diameter by Latham and Mason (1961) were not representative of those occurring in the atmosphere. In fact, Reynolds and Brook (1962) calculated that the rate of splinter production measured in these experiments would cause the glaciation of thunderclouds to proceed at an unrealistically rapid rate. Although the arguments of Latham and Mason (1962) and the calculations of Browning and Mason (1963) show that this conclusion is possibly over-generalized, and that compatibility between the experimental and the observed properties of natural clouds can be achieved if the bulk of the splintering and associated electrification is restricted to regions of strong updraught in thunderclouds, further research is required in order to establish definitively the conditions under which ice splinters are produced during the accretion of supercooled droplets.

Brownscombe and Hallett also discussed the structure of graupel and rime. An ice crystal that accretes supercooled droplets grows into a definite shape, such as a cone with base or apex pointing into the air stream, depending on the interaction of any oscillatory motion of the particle with the air flow and its influence on the manner in which individual droplets are added (Hallett 1965 b). In the early stages of growth the accreting surface may be unstable in the sense that a statistical fluctuation in the rate of drop accretion at any point may produce a protuberance whose collection efficiency is greater than that of the surface as a whole and therefore continues to grow. Evidence for such a suggestion is provided by Kidder and Carte (1964) and Macklin and Bailey (1966). If such an asymmetric mode of growth occurred the density of the accreted ice would be less than the value of 0·57 g cm^{-3} shown by Bernal (1960) to be produced if the growth occurred by the random packing of spheres. Low density rime could also be produced, according to Brownscombe and Hallett, by occasional accretion on crystals growing principally from the vapour phase or by growth from the vapour occurring in the neighbourhood of freezing droplets. On the other hand, densities higher than Bernal's value may be produced if drops deform on impact to achieve a value of y greater than about 5, in which case the drop could penetrate between the caps of neighbouring drops. Further information concerning the density of ice deposits formed by accretion has been provided by the studies of Macklin and Payne (1968).

Experiments by Brownscombe and Hallett suggested that drops accreting on particles growing spongily may interact first with a liquid layer whose thickness may be of the same order as the drop size and produce splash droplets even at large supercoolings for critical values of layer thickness. They have also presented a detailed discussion of the opacity and of the bubble and crystal structure of accreted ice, based in part upon the work of List (1959 a), Carte (1961), Macklin (1961, 1962), Browning (1966), and Carte and Kidder (1966). The opacity is related to the bubble-size distribution, which depends upon the details of the freezing process. Opaque ice forms when the particle is growing spongily or dry, with transparent ice forming when the growth is just wet. They show that marginally spongy growth at low temperatures is associated with small crystals and opaque ice. Figure 20 illustrates the relation between air temperature, surface temperature, and bubble structure of accreted ice, derived by Hallett and Brownscombe from their experiments and analyses of earlier laboratory work.

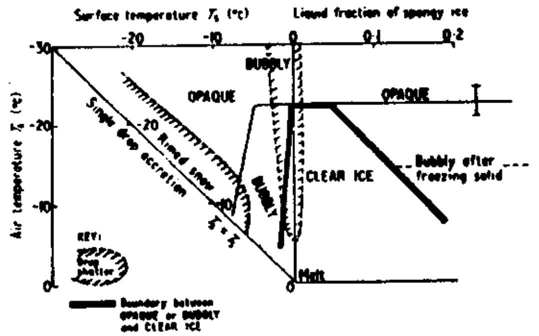


Figure 20. Relation between air temperature, surface temperature, and bubble structure obtained from the experiments of Brownscombe and Hallett. Surface temperature is 0 °c for spongy growth. Regions of possible drop shatter and charge separation are hatched. The position of the dividing line between opaque and bubbly ice for frozen spongy ice is uncertain because of the unknown effect of the drop impact velocity. *Clear ice*: no bubbles. *Bubbly ice*: bubble radius greater than 50 µm. *Opaque ice*: bubble radius less than 50 µm. The radius of 50 µm was arbitrarily selected as giving individual bubbles that could easily be seen. (From Brownscombe and Hallett 1967.)

4.7. *Formation and multiplication of ice crystals within clouds at temperatures close to* 0 °c

Airborne, field, and laboratory measurements by Hoffer and Braham (1962), Koenig (1963, 1968), Braham (1964), Mossop *et al.* (1967, 1968), and others have demonstrated the existence of large quantities of ice particles in clouds whose summit temperatures had never been below −10 °c, and of higher concentrations of ice particles in certain clouds at warm temperatures than can be accounted for by assuming a one-to-one relationship between ice crystals and natural freezing or sublimation nuclei. Two important problems, therefore, are to establish the origins of the primary ice particles and the mechanism responsible for the multiplication process.

In view of the fact that commonly occurring natural freezing nuclei are not effective at these warm temperatures Koenig (1965 b, 1968) and Braham (1968) have discussed various alternative ice-forming processes that may be operative at temperatures close to 0 °c. Koenig suggested tentatively that freezing may have been initiated in the clouds investigated by pre-activated nuclei, by evaporative cooling at the edges of the clouds, or by the disintegration of large supercooled drops; Koenig (1965 a) has previously shown in laboratory experiments that if supercooled drops suspended in an air stream went into the 'bag mode' described by Matthews and Mason (1964) freezing often accompanied fragmentation of the bag. However, no evidence was found for the existence of pre-activated nuclei in these clouds, the evaporative cooling process is difficult to reconcile with the observed occurrence of ice particles in the central regions of the clouds, and it was not demonstrated that the clouds contained drops of sufficiently large dimensions to break up in the manner described by Koenig.

Braham and Spyers-Duran (1967) and Braham (1967) have shown that certain types of cirrus clouds produce ice crystals that can survive up to about 6 km of clear air descent. Such crystals could fall into a shallow supercooled cloud and initiate the ice phase. Such a mechanism is unlikely to have been responsible for all observations of the presence of ice crystals within clouds at temperatures close to 0 °c, but it merits further study.

A further possible explanation discussed by Koenig and Byers is that of stochastic freezing in which the probability P that a drop will freeze is assumed to be related to its volume V, the degree of supercooling θ, and the cooling rate α by the equation

$$P = \frac{AV}{\alpha} e^{-B\theta}, \tag{4.10}$$

where A is a rate constant and B a constant.

This hypothesis is supported by the laboratory and field investigations of Gokhale (1965), Wexler and Donaldson (1966), Stewart (1967), and others, but it is inconsistent with Koenig's observation of symmetrical ice crystals in strato-cumulus and nimbo-stratus clouds that are smaller than many of the coexisting supercooled drops. The possibility considered by Vali and Stansbury (1966) that the freezing of drops is due to unspecified impurities each of which possesses a characteristic temperature at which it is certain to produce nucleation is supported by little direct evidence and is also inconsistent with Koenig's data.

A possible alternative explanation of these observations is provided by the experiments of Abbas and Latham (1969 b). Studies were made of the freezing of supercooled drops of radii R ranging from 0·106 to 0·134 cm suspended from insulating supports in an environment whose temperature could be varied from 0 to −45 °c. It was found that the probability of a drop freezing within a fixed interval of time τ was appreciably greater over the temperature range 0 to −22 °c if the surface of the drop was disrupted by either electrical or mechanical forces to produce a filament of liquid emanating from the localized area of rupture. For instance, for a 5 minute test-interval the fraction of drops studied that froze at temperatures −5, −10, −15, and −20 °c were 0·44, 0·62, 0·75, and 0·88 respectively if the drop was disrupted by means of an electric field, 0·25, 0·44, 0·50, and 0·58 if the surface was penetrated by an insulating fibre or conducting wire at the same temperature as the drop, but only 0, 0·02, 0·07, and 0·18 if the drop surface was not disrupted during this interval, but remained undisturbed, or was situated in a strong electric field just below the disintegration threshold, or was shaken violently on its support. These observations are illustrated in figure 21 and are totally inconsistent with the criterion for the occurrence of electrofreezing deduced by Pruppacher (1963 a, b), namely that the phenomenon is always associated with the movement of a triple-phase boundary. However, the observations are in agreement with the suggestion of Loeb (1963) that the most essential condition for the occurrence of electrofreezing is that a portion of the drop be drawn out into a thin filament; Loeb *et al.* (1938) had previously shown that such a filament may contain molecular aggregates which act as excellent freezing nuclei. These conclusions were reinforced by high speed photographs demonstrating that freezing originated from the area of disruption.

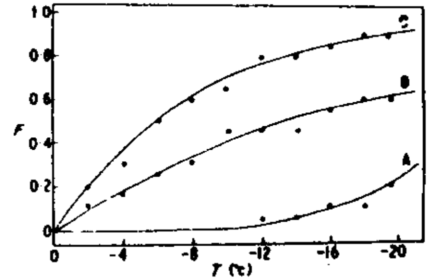


Figure 21. Relationships between the freezing probability F and the temperature T obtained from the experiments of Abbas and Latham. τ = 5 min., R = 0·106 cm.

A, drop surface not disrupted; B, drop surface punctured mechanically; C, drop surface disrupted electrically. (From Abbas and Latham 1969 b.)

It is improbable that the electrofreezing of individual isolated drops can be of any importance in the initial formation of ice crystals within clouds, since the magnitudes of the fields required to produce disintegration of large drops are around 10000 v cm^{-1}. Such fields are observed only in thunderstorms at a stage in the cloud development when precipitation is already well established. However, Latham and Roxburgh (1966) demonstrated that even in extremely weak external fields electrical pressures sufficient to produce disintegration can be created in the near surface of closely separated drops or droplets because of the mutual interaction of the polarization charges. In this situation the filament of water bridging the interacting droplets, which is produced by the immense localized electrical pressures and illustrated in plate 1, could provide a site for the initiation of electrofreezing. If this occurred inside clouds it would be expected that observations of frozen drop-pairs, linked by an ice bridge, would be made on penetrating supercooled clouds with aircraft carrying appropriate sampling equipment. Such particles have been found by Mee (private communication) to occur in moderately high concentrations within small nonprecipitating clouds over the Caribbean. These are illustrated in plate 7;

they are seen to bear a close resemblance to the particles produced in the laboratory by Smith (private communication) when supercooled droplets interacted in free fall in an electric field. In all the photographs of Mee and of Smith a pair of frozen drops are linked by a bridge of ice, as predicted from the foregoing argument. Additional droplets were then collected in the experiments of Smith when the frozen drop-pairs fell through the cloud at velocities greater than those of the individual drops. Further information concerning the physics of this phenomenon is required, but the electrofreezing hypothesis appears to offer a plausible explanation for the initiation of ice at warm temperatures within supercooled clouds.

The freezing of supercooled drops has been shown by many workers (e.g. Schaefer 1952, Bigg 1953 b, Langham and Mason 1958, Mason and Maybank 1960, Kachurin and Bekryaev 1960, Latham and Mason 1961, Evans and Hutchinson 1963, and Stott and Hutchinson 1965) to be accompanied by the ejection of numerous ice fragments. Koenig (1963, 1966) proposed that this mechanism was responsible for the avalanche process which must occur inside certain clouds in order to produce the observed concentrations of ice crystals. However, serious doubt has been cast on the atmospheric validity of these experiments by the studies of Pruppacher (1967) and of Dye and Hobbs (1966) who showed that significant shattering occurs only when the supercooled drops contain concentrations of carbon dioxide that are appreciably greater than those occurring in the atmosphere. In addition, Dye and Hobbs (1968) and Johnson and Hallett (1968) have presented additional arguments, concerned primarily with the heat transfer from freezing drops, which suggest that the conditions under which previous workers observed shattering were not representative of conditions in natural clouds, where drops are uniformly supercooled to the temperature of the environment prior to nucleation and are ventilated as they fall. In view of these objections to the previous work on drop shattering, Koenig (1968) concluded that a possible explanation for the formation of secondary ice particles is mechanical fracturing of ice crystals. He points out that if fracturing is the dominant process glaciation will occur most rapidly in the regions of clouds in which dendritic crystals grow. This suggestion can be tested experimentally. He suggests that the positive correlation believed to exist between rapidity of glaciation and drop size may be the result of the superior ability of large faster-falling ice particles incorporating these drops to break pieces off themselves or other particles during collision. Considerable further research is required in order to establish the origins of primary and secondary ice particles in supercooled clouds at temperatures close to 0 °c.

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