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ON THE PHYSICS OF MOTHER OF PEARL CLOUDS

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Summary. If 31.7 erg cm^{-2} is taken as the value of the specific free surface energy of an ice-water interface at 0°C, good agreement is obtained between theoretically determined critical temperatures for homogeneous nucleation in supercooled water and freezing experiments reported by several investigators. It is shown theoretically that pure water, formed below about $-$ 117°C, will remain supercooled (or vitreous) for a very long time. The temperatures in mother of pearl clouds are found to be $-$ 85°C to $-$ 100°C, and the concentration of condensation nuclei is about 0.5 cm^{-3}. The growth of the cloud particles is calculated for the three cases: supercooled water droplets, ice spheres formed by sublimation and supercooled solutions of nucleus matter which freeze when the necessary degree of dilution is reached. Particle radii of 1.2μ or less have been found. It is shown theoretically that the particle size spectrum is very narrow, in agreement with the brilliant iridescence very often observed. A marked asymmetry in the shape of the clouds is found, not only in the case of supercooled droplets transforming into ice particles within the cloud, but also in the case of pure water clouds.

1. Introduction. The nature of mother of pearl clouds has been discussed since the first observations of these clouds were made around 1870. By that time observations of temperature, wind and humidity from the upper air were not available, and the height of the clouds had not been measured with sufficient accuracy. The first reliable determination of the height of mother of pearl clouds was made by STØRMER (1930), who found that the clouds which occurred over Southern Norway on 26th December 1926 were situated at a height of 27 km. This, in addition to an improved general understanding of the conditions in the lower stratosphere, made it possible to start the study of the formation and nature of mother of pearl clouds anew on a more sound basis. For instance, the assumption that the clouds might possibly consist of other substances than water in any form has gradually lost its validity. It is now generally accepted that mother of pearl clouds consist of water substance, either in the liquid or in the solid phase.

The synoptic weather situations which lead to the formation of mother of pearl clouds have been studied by HESSTVEDT (1959). It has been found that the clouds can only be expected to form when certain criteria are fulfilled, especially regarding the vertical variation of temperature and wind. This, in combination with some recent theoretical investigations of the formation of mountain waves, made by PALM and FOLDVIK (1960), makes it probable that mother of pearl clouds are created as lenticular clouds on the crests of mountain waves.

The first part of the present paper (sections 2—9) contains a discussion of some physical properties of water and ice at temperatures ranging from the nominal freezing point to somewhat below — 100°C. In earlier works it has often been suggested that mother of pearl clouds consist of supercooled water droplets. This suggestion was mainly based upon the idea that the brilliant iridescence associated with the clouds is possible only in the presence of water droplets. However, iridescence may well occur if the clouds consist of ice spheres. Furthermore, the scattering of light is likely to be independent of the shape of the particles when their size is only a few wavelengths. This optical phenomenon, therefore, does not justify any conclusions as to the physical nature of the cloud particles: they may be ordinary ice crystals, possibly spherical aggregates of minute crystals, or supercooled water droplets, including the so-called "amorphous" or "vitreous ice" (MASON, 1952).

To the author's knowledge, no other observations have been made which make it possible to decide whether mother of pearl clouds are water clouds or ice clouds. The results obtained in sections 8 and 9 still leave this question unanswered. It is, however, shown that below about — 70°C the possibility of supercooling water increases rapidly with decreasing temperature. But since the temperatures in mother of pearl clouds are ranging from — 85°C to — 100°C, the accuracy of the results obtained is not sufficient to draw definite conclusions as to the nature of the clouds. Furthermore, the effect of the dissolved nucleus upon the freezing process is an unknown factor.

In the second part of the paper (sections 10—13) the growth of mother of pearl cloud particles has been calculated, assuming they are supercooled water droplets, ice particles or supercooled droplets which freeze after some time. Here, too, occur uncertainties in the results since so many of the quantities involved in the equations have never been measured. Reliable quantitative results can not be expected until extended observational data are available. It is, however, felt that the assumptions and extrapolations made are such that it is not likely that the conclusions which have been drawn are qualitatively misleading.

2. Supercooling of water. There is now general agreement among the cloud physicists concerning the existence of a temperature threshold, near — 40°C, below which supercooling of pure water is impossible or at least only possible under extraordinary circumstances. During the last fifteen years a series of experiments have been made, and with a few exceptions supercooling below about — 40°C has not been achieved. Furthermore, the experiments, which cover different parts of the droplet size spectrum, from radii below 1μ to above 1 mm, seem to bear each other out. Some of the results are plotted in Fig. 1. Bigg (1953), Mossop (1955), Jacobi (1955), Carte (1956) and Langham and Mason (1958) have made very careful measurements showing the relationship between the maximum supercooling and the droplet size. Other investigators, such as Meyer and Pfaff (1935), Lafargue (1950), Pound, Madonna and Peake (1953), Wylie (1953) and Bayardelle (1955) give only approximate values of temperature and water volume, but their data may be said to confirm the results mentioned above, since no serious disagreements exist. Some experiments which resulted in considerably smaller supercooling have been omitted, since it is felt that the deviating results, when compared with the above mentioned investigations, are caused by contaminations or by less-advanced technical facilities.

From the experimental plots in Fig. 1 we may define a curve representing the maximum supercooling of pure water droplets as a function of the droplet radius. One might for instance define such a curve by making use of the lowest critical temperature for each droplet size, claiming that these temperatures represent the most successful experiments. It is, however, felt that a more representative curve is obtained from the mean values of the results of Bigg, Mossop, Jacobi, and Langham and Mason. Such a curve would not deviate much from the theoretically predicted curve C in Fig. 1. It is worth noting that the difference between the critical temperatures obtained from the two definitions mentioned above would be about 1°C only.

In serious contradiction to the results plotted in Fig. 1 Rau (1944) claims to have supercooled water to — 72°C. Cwilong (1947) and Brewer and Palmer (1951) have repeated Rau's experiments, but were unable to reproduce his result unless the water droplets were contaminated with alcohol.

An interesting supercooling experiment should be mentioned here: Rosenqvist (1959), who used a very high rate of cooling, succeeded in supercooling a small volume of water to about — 80°C for a few seconds. Repeated tests showed freezing at quite different temperatures, and his result can only be appraised when systematic freezing experiments of a similar kind have been made. In any case, the conditions in Rosenqvist's experiment differ so widely from the nearly stationary conditions used by many other investigators that a direct comparison is probably not justified. Rosenqvist's result is, therefore, not necessarily in contradiction to the plots in Fig. 1, and a curve defining the maximum supercooling for droplets of various sizes may still have its validity.

The physical nature of the spontaneous freezing at the "— 40°C transition" has been discussed since its recognition at the end of the Second World War. Two possibilities exist: the crystallization may take place on solid foreign particles which can not be removed from the water by the techniques used (heterogeneous nucleation), or it may take place in entirely pure water without the aid of foreign nuclei (homogeneous nucleation). So far, this problem has not been completely solved. In spite of the advanced technical facilities for purification of water, one cannot, of course, completely exclude the possibility that the freezing has been initiated by a foreign particle.

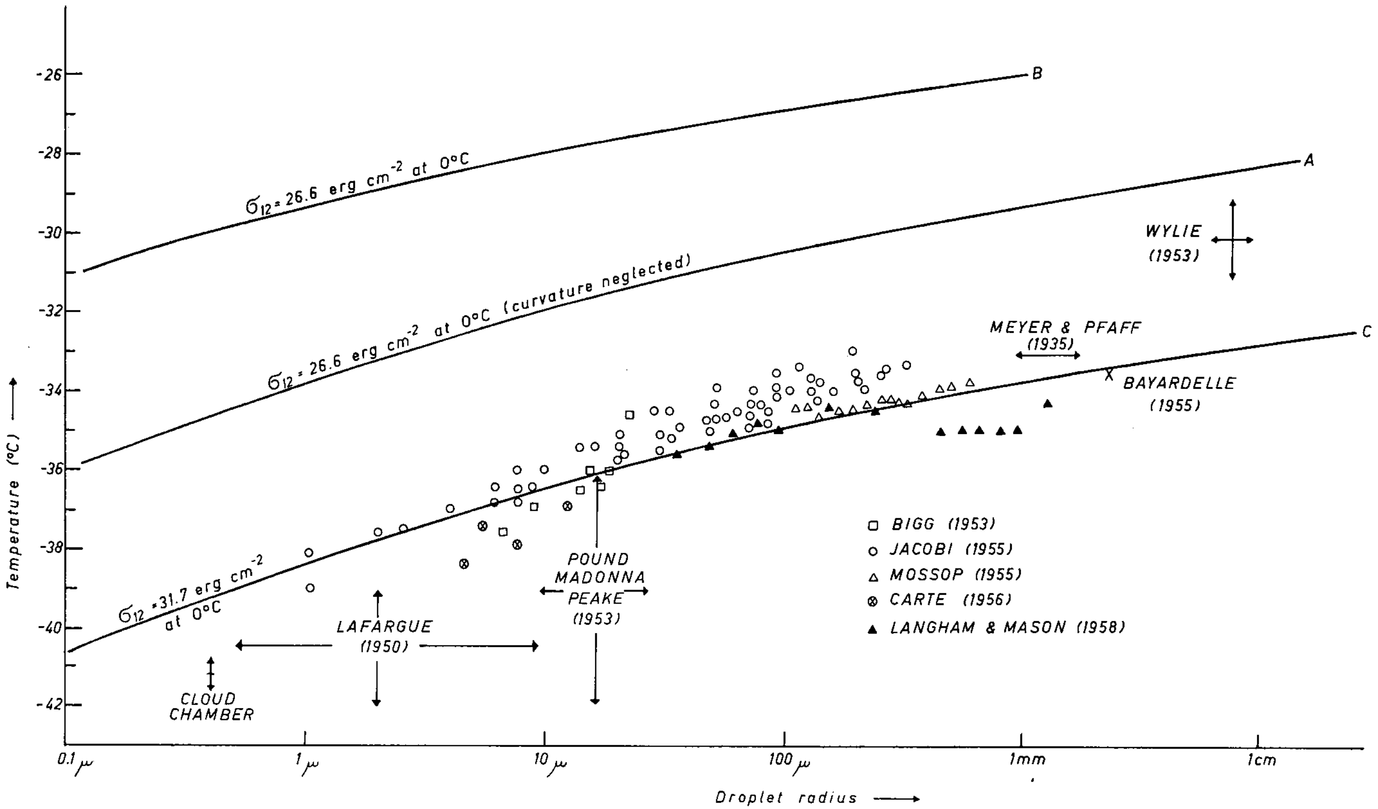

Fig. 1. Comparison between freezing temperatures obtained from experiments and critical temperatures determined from the theory of homogeneous nucleation. Curve *A* shows theoretically determined critical temperatures based upon a value of 26.6 erg cm^{-2} for the interfacial energy ice-water at 0°C, while curve *B* shows the same when account is taken for the curvature of the embryo. Curve *C* shows the critical freezing temperatures based upon a value of 31.7 erg cm^{-2} (29.3 erg cm^{-2} if the curvature is neglected) for the interfacial energy ice-water at 0°C.

On the other hand, VOLMER theory of homogeneous nucleation cannot readily be used because some of the quantities occurring in the formulae have not been determined with satisfactory accuracy. Nevertheless, at present, most cloud physicists regard it as a fact that the "— 40°C transition" is due to homogeneous nucleation.

In section 3 we shall make some refinements of the general expression for the rate of formation of ice embryo in a supercooled water droplet, and in section 7 we shall use the only existing experimental determination of the interfacial energy ice-water, and also a theoretical determination of the interfacial energy ice-water vapor, to predict theoretically the maximum supercooling for water droplets of various sizes. The discrepancy between theoretically and experimentally determined critical temperatures amounts to about 9°C. A change of about 5 erg cm^{-2} in the interfacial energies mentioned above would, however, be sufficient to give complete agreement between theory and experiments. It is therefore felt that the calculations below are favourable to the assumption that the spontaneous freezing of water droplets around — 40°C is due to homogeneous nucleation.

3. The theory of homogenous nucleation. Soon after the occurrence of VOLMER's textbook: "Kinetik der Phasenbildung" (1939), KRASTANOW (1940, 1941) introduced well-known viewpoints from the phase transition theory in meteorological problems. With the aid of expressions for the nucleation rates, given by VOLMER (crystallization of supercooled water) and BECKER and DÖRING (1935) (condensation and sublimation in supersaturated water vapor), KRASTANOW was able to make quantitative determinations which threw new light on the processes leading to the formation of water droplets and ice crystals in the atmosphere. VOLMER's expression has later been given a more complete formulation by TURNBULL and FISHER (1949). Their formulation is now generally accepted by cloud physicists and will also be used here:

$$J = \frac{nkT}{h} \exp\left(-\frac{A+W^*}{kT}\right) \tag{3.1}$$

where J is the rate of formation of ice nuclei with a radius or "characteristic length" $\geq r^*$ in 1 cm^3 of water, n is the number of molecules in 1 cm^3 of water, k is Boltzmann's constant, h is Planck's constant, T is the absolute temperature, A is the free activation energy for selfdiffusion of the water molecules and W^* is the free energy of formation of an ice nucleus of size r^*. For spherical embryo an expression for W^* has been developed by GIBBS:

$$W^* = \frac{4\pi}{3} r^{*2} \sigma_{12,\,r^*} \tag{3.2}$$

where $\sigma_{12,\,r^*}$ is the specific free interfacial energy ice-water, corrected for the curvature.

In earlier works r^* has been given by the expression

$$r^* = \frac{2\sigma_{12,\,r^*}}{\varrho_i L_{f,\,r^*}\, ln \dfrac{T_0}{T}} \approx \frac{2\sigma_{12}\, T_0}{\varrho_i\, L_f (T_0 \text{-} T)} \tag{3.3}$$

where ϱ_i is the density of ice, T_0 is the freezing point of water, $L_{f,\,r^*}$ is the curvature-corrected value of the latent heat of fusion L_f and σ_{12} is the interfacial energy of a plane ice-water surface. However, (3.3) is based upon the assumption that L_{f,r^*} is independent of the temperature. Since this is not the case, a revision is necessary. Let us consider a system consisting of an ice sphere of radius r surrounded by supercooled water. If the chemical potentials of water and ice are denoted by Φ_w and Φ_i, we have

$$d\,\Phi_w = v_w dp - \Psi_w dT \tag{3.4}$$

and

$$d\,\Phi_i = v_i\, dp' - \Psi_i dT = v_i\, dp + v_i\, d\left(\frac{2\sigma_{12}}{r}\right) - \Psi_i\, dT \tag{3.5}$$

where v_w and v_i are the specific volumes, p and $p' = p + \dfrac{2\sigma_{12}}{r}$ are the pressures and Ψ_w and Ψ_i are the entropies of water and ice, respectively. In the case of equilibrium we have

$$r = r^* \tag{3.6}$$

and

$$\Phi_w\,(p,T) = \Phi_i\,(p',T) \tag{3.7}$$

If the external pressure p is kept constant, combination of (3.4) and (3.5) gives, upon integration and substitution of (3.6) and (3.7)

$$r^* = \frac{2\sigma_{12,r^*}}{\varrho_i \displaystyle\int_T^{T_0} \frac{L_{f,\,r^*}}{T}\, dT} \tag{3.8}$$

At -40°C the use of (3.3) results in an error of about 20% in r^* and nearly 50% in W^*. In the evaluation of the probable value of the interfacial energy ice-water, made in section 7, the revised formula for r^* implies a raise of more than 2 erg cm^{-2} compared with results obtained from the formula previously used.

4. Dependence of the latent heat of fusion and the interfacial energy upon the curvature. Before we can calculate the critical radius r^* of the ice embryo from (3.8), account must be taken of the influence of the curvature upon the latent heat of fusion and the interfacial energy. An expression for the reduction of L_f, due to the curvature has been given by McDonald (1953):

$$L_{f,\,r^*} = L_f - \frac{2\sigma_{12,\,r^*}}{\varrho_i\, r^*} \tag{4.1}$$

which in combination with (3.8) gives

$$L_{f,\,r^*} = L_f - \int\limits_{T}^{T_0} \frac{L_{f,\,r^*}}{T}\, dT \tag{4.2}$$

This expression is very suitable for a step by step approximation of the values of $L_{f,\,r^*}$ and $\int\limits_{T}^{T_0} \frac{L_{f,\,r^*}}{T}\, dT$.

The effect of the curvature upon the surface tension vapor-water has been determined by Tolman (1949). If we assume that Tolman's results may be applied also for the interfacial energy ice-water, we may write:

$$\sigma_{12,\,r^*} = \frac{\sigma_{12}}{1 + \frac{2\delta}{r^*}} \tag{4.3}$$

Here δ denotes the distance from the surface of tension to the so-called dividing surface. In our calculations we shall assume $\delta = 10^{-8}$cm.

Substitution of r^* from (3.8) in (4.3) gives

$$\sigma_{12,\,r^*} = \sigma_{12} - \delta \varrho_i \int\limits_{T}^{T_0} \frac{L_{f,\,r^*}}{T}\, dT \tag{4.4}$$

The validity of (4.3) for ice crystals in water will not be appraised in this paper. In the calculations of the critical temperatures and interfacial energy (in section 7) we shall follow two different approaches: a) the influence of the curvature of the embryo upon the latent heat of fusion and the interfacial energy is given by (4.2) and (4.4), alternatively b) the influence of the curvature shall be neglected. The values of the interfacial energy obtained in these two ways differ by 2.4 erg cm^{-2} while the critical temperatures differ by 4°C.

It is interesting to note that, using the values of the interfacial energy obtained in section 7, the relation

$$\frac{\sigma_{12,r*}}{L_{f,r*}} = \frac{\sigma_{12}}{L_f} \tag{4.5}$$

proposed by McDonald (1953), is fulfilled with a very high degree of accuracy. It may further be shown that, in the temperature interval 0°C to — 50°C, the relation

$$\frac{\partial}{\partial T}\left(\frac{\sigma_{12}}{L_f}\right) = 0 \tag{4.6}$$

is also approximately valid. The maximum deviation in the temperature interval 0°C to — 50°C is smaller than 4%. Extrapolating below — 50°C, (4.6) therefore makes it possible to estimate the latent heat of fusion below — 50°C if the interfacial energy is known.

In the case of water droplets, the concepts of "interfacial energy" and "curvature" have a well-defined meaning which needs no further explanation here. In the case of ice crystals, however, the significance of these concepts is more difficult to interpret. For instance, it is not strictly correct to talk about "the" interfacial energy ice-water. In fact, the specific free surface energy is different for the different crystal faces. The concept of interfacial energy, as used in this paper, represents a weighted mean value for all crystal faces. We must therefore refer to a certain shape of the crystal. Mason (1952) assumed the embryo to take the form of isometric hexagonal prisms with height equal to the apical diameter. In this case the factor 4π in (3.2) has to be replaced by a factor $\omega = 22.93$, while $r*$ should be interpreted as the radius of a circle inscribed the hexagon. A revision of (3.8) is also necessary. The factor 2 should be replaced by 1.91 for this specific crystal form. The numerical factor in (3.2), upon substitution of (3.8), thereby changes from $16\pi/3$ to 27.9.

The concepts of "radius" and "curvature" of the critical embryo should be understood as $r*$, as defined above.

5. Activation energy for self-diffusion. In the expression for the rate of formation of ice embryo, (3.1), the activation energy for self-diffusion of water molecules, A, and the free energy increase associated with the formation of an ice embryo, $W*$, occur side by side. If we calculate $W*$, using values of the interfacial energy found in section 7, comparison may be made with extrapolated values of A. It then turns out that $W*$ is dominating at temperatures from the freezing point to about — 35°C, and an uncertainty in the determination of A will have only a slight influence on the nucleation rate. However, while $W*$ decreases with decreasing temperature, the opposite is the case with A. Below about — 50°C (se Fig. 2) we have $A > W*$, and in the vicinity of — 100°C, W^* is so small that J depends entirely on A. Physically, this means that at such low temperatures, the difficulty involved in the formation of an ice nucleus lies in the satisfaction of the energy requirements for maintenance of the self-diffusion, while the energy necessary for the proper formation of the nucleus is negligibly small. It should, however, be mentioned that the number of molecules in an embryo of critical size is so small at very low temperatures that it is no longer permissible to interpret such quantities as for instance the interfacial energy as statistical concepts. Below — 50°C the curve showing the variation of W^* with temperature must only be regarded as an extrapolation from the region where a statistical viewpoint may be used.

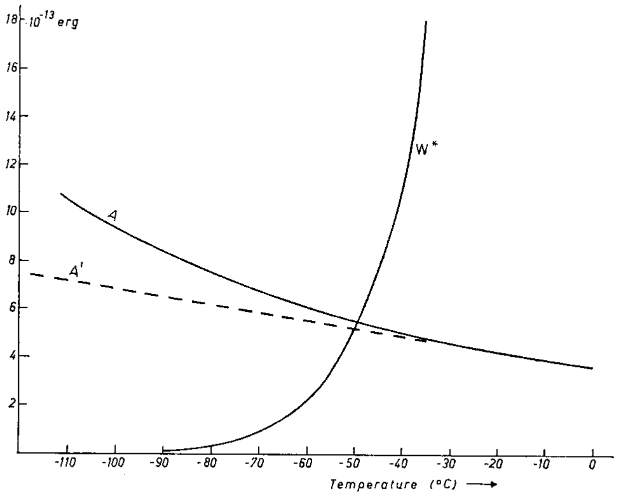

Fig. 2. Comparison between the free surface energy W^* of an ice embryo of size r^* and extrapolations of the activation energy for self-diffusion in water, A (curved extrapolation) and A' (linear extrapolation).

Consequently, at very low temperatures, reliable values of the nucleation rate J can only be obtained if A is known with relatively great accuracy. Unfortunately, this is not the case. McDonald (1953) computed A from viscosity data down to — 10°C, taking into account the order of the liquid structure of water. Below — 10°C he proposed a linear extrapolation (shown by the dashed curve A' in Fig. 2), a procedure which certainly represents a serious underestimation of A at very low temperatures. An attempt to compute the activation energy at low temperatures from extrapolated data of viscosity and of the increasing order of the liquid structure of water is shown by the solid curve A in Fig. 2. Though it is probable that this extrapolation represents an improvement compared with the linear extrapolation, the results are still unreliable and further improvement would be highly desirable.

6. **The interfacial energy ice-water.** The interfacial energy ice-water has been measured by Kubelka and Prokscha (1944). They used capillaries and observed the lowering of the melting point of ice due to the surface tension at the interface between the melting ice and the surrounding water. At — 4.8°C they found $\sigma_{12} = 25.4$ erg cm^{-2} with deviations of about 10% from the mean value. The validity of Kubelka and Prokscha's procedure will not be appraised here; we shall only point out that their value of σ_{12}, 25.4 erg cm^{-2} at — 4.8°C, is a reasonable one, compared with other determinations (Jacobi, 1955).

However, one single determination of the interfacial energy ice-water is not sufficient to make use of (3.1) in proving that the "$-40°$C transition" is due to homogeneous nucleation. In order to find the variation of σ_{12} with temperature, we shall make a useful evaluation of the interfacial energy ice-vapor, σ_{13}.

Applying Antonov's rule

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \tag{6.1}$$

and the expression for the surface tension water-vapor, σ_{23}, (Zemansky, 1957)

$$\sigma_{23} = 75.5\left(1 + \frac{T_0 - T}{368}\right)^{1.2} \text{erg cm}^{-2} \tag{6.2}$$

a value of 102.1 erg cm^{-2} is found for σ_{13} at $-4.8°$C. We shall now evaluate the dependence of σ_{13} upon the temperature and shall, in principle, use a viewpoint introduced by Mason (1952).

Mason tried to derive the value of σ_{13} at $-40°$C by considering the energy required to separate two crystal surfaces parallel to the (0001) face. Mason used a value of 4500 cal mol^{-1} for the *H*-bond strength and added 500 cal mol^{-1} for the dispersion forces. His "rough calculation" resulted in $\sigma_{13} = 102$ erg cm^{-2}, i.e. almost the same value as obtained above for $-4.8°$C. Mason's calculation has been criticized, but this seems to be a misunderstanding due to a misleading sentence in his paper. From a slightly different viewpoint, introduced by Briegleb (1949), Jacobi (1955) gives 98.5 erg cm^{-2} as the most probable value of σ_{13}.

Since the nature and the value of the forces between the molecular dipoles have not been established with sufficient accuracy, the precise value of σ_{13} can not be found by this method at present. On the other hand, it is possible to make a very useful statement as to the dependence of σ_{13} on the temperature. From the data given by Rowlinson (1951) it is possible to evaluate the variation of the forces which occur in his expression for the resultant force, for small variations in the intermolecular distance. Applying a coefficient of cubical expansion of $1.5 \cdot 10^{-4}$ deg^{-1}, a value which is likely to be in excess of the real mean value at low temperatures, we find that the variation of σ_{13} is less than 2% over a temperature range of 100°C. This means that, for our purposes, σ_{13} may be regarded as a constant. Since there is such good agreement between Kubelka and Prokscha's and Mason's values, we shall start the calculations in section 7 making use of the following expression for σ_{12}:

$$\sigma_{12} = 102.1 - 75.5\left(1 + \frac{T_0 - T}{368}\right)^{1.2} \text{erg cm}^{-2} \tag{6.3}$$

$$\approx 26.6\,(1 - 0.93 \cdot 10^{-2}(T_0 - T)) \text{ erg cm}^{-2}$$

It is interesting to note that, according to (6.3), the variation of the interfacial energy with temperature is

$$\frac{\partial \sigma_{12}}{\partial T} \approx 0.25 \text{ erg cm}^{-2} \text{ deg}^{-1} \tag{6.4}$$

which is in very good agreement with the value given by Jacobi (1955), who found $\frac{\partial \sigma_{12}}{\partial T} = 0.2$ erg cm^{-2} deg^{-1} from a combination of Volmer-theory and experiments.

7. Theoretical determination of the critical temperatures for homogeneous nucleation. Instead of the usual expression (3.1) for the rate of formation of ice nuclei in supercooled water, we shall introduce the droplet radius r_d in the formula and write

$$J_{r_d} = \frac{4\pi}{3} r_d^3 \frac{nkT}{h} \exp\left(-\frac{A+W^*}{kT}\right) \tag{7.1}$$

where J_{r_d} is the rate of formation of ice nuclei in a supercooled droplet of radius r_d. Let further "spontaneous nucleation" be represented by $J_{r_d} = 1$, i.e. by the formation of one nucleus pr. second. With the values of A and σ_{12} proposed in section 5 and 6, (7.1) becomes an equation in the droplet radius r_d and the critical temperature at which homogeneous nucleation should take place spontaneously according to the extended Volmer theory.

The relationship between r_d and the critical temperature thus calculated is shown by the curves A and B in Fig. 1. If we neglect the effect of the curvature of the ice embryo upon the latent heat of fusion and the interfacial energy, we get curve A. On the other side, if we use the expressions (4.2) and (4.4) for the curvature effect, the critical temperatures are increased by about 4°C (curve B).

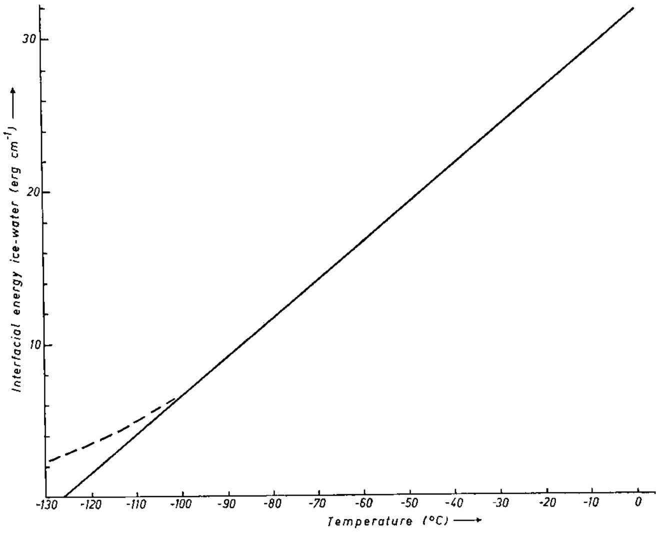

Fig. 3. Interfacial energy ice-water. The dashed curve indicates a revision (arbitrarily drawn) at low temperatures.

A comparison between the theoretically determined critical temperatures and the experiments show a discrepancy of about 5°C for curve *A* and about 9°C for curve *B*. It is, however, striking that the variation of the critical temperature with the radius of the supercooled droplet is correctly predicted by the theory.

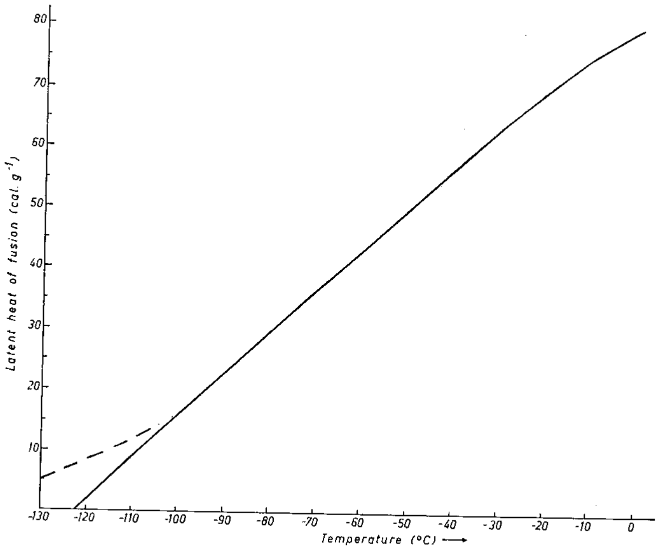

Fig. 4. Latent heat of fusion of ice. The dashed curve indicates a revision (arbitrarily drawn) at low temperatures.

In order to obtain complete agreement between theory and experiments we must select somewhat higher values of the interfacial energy ice-water. If we neglect the influence of the curvature upon σ_{12} and L_f, a value of 29.3 erg cm^{-2} for the interfacial energy at 0°C would result in critical temperatures given by curve *C* in Fig. 1. This value of σ_{12} is only slightly above the highest of the four values given by KUBELKA and PROKSCHA (1944). On the other side, if we take into account the variation of σ_{12} and L_f with the curvature of the embryo, we must use 31.7 erg cm^{-2} for the interfacial energy at 0°C in order to obtain complete agreement between theory and experiments (shown by curve *C* in Fig. 1).

It is felt that the trends of the curves *A*, *B* and *C* in Fig. 1 give very strong support to the assumption that the spontaneous freezing of supercooled pure water droplets observed in the − 30°C to − 40°C interval is due to homogeneous nucleation. And, if we consider this assumption as proved, it is justified to make use of the values of the interfacial energy determined above by VOLMER theory in combination with freezing experiments, rather than the values determined by KUBELKA and PROKSCHA and from MASON's value of σ_{13}. And since it is felt that the expressions for the curvature dependence of L_f and σ_{12} are, after all, more realistic than the rather rough assumption $\frac{\partial L_f}{\partial r} = \frac{\partial \sigma_{12}}{\partial r} = 0$, we shall use the expression

$$\sigma_{12} = 107.2 - 75.5\left(1 + \frac{T_0 - T}{368}\right)^{1.2} \text{erg cm}^{-2} \tag{7.2}$$

$$\approx 31.7(1 - 0.93 \,.\, 10^{-2}(T_0 - T)) \text{ erg cm}^{-2}$$

for the interfacial energy ice-water.

As already mentioned in section 4, the ratio between the interfacial energy and the latent heat of fusion is practically independent of the curvature of the embryo. It was further mentioned that this ratio varies very little with the temperature between 0°C and — 50°C. If we now assume that this is the case even below — 50°C, we may determine the latent heat of fusion below — 50°C from (4.6), (7.2) and known values of L_f above — 50°C. The variations of σ_{12} and L_f with temperature are shown in Fig. 3 and 4. According to (7.2) σ_{12}, and consequently also L_f, becomes zero at a temperature of — 125°C. Below this temperature, σ_{12} and L_f become negative. This result is based upon the validity of (6.2) even for such low temperatures. It is, however, more likely that σ_{12} and L_f should converge towards zero and not intersect the temperature axis. This is indicated by the dashed curves in Fig. 3 and 4.

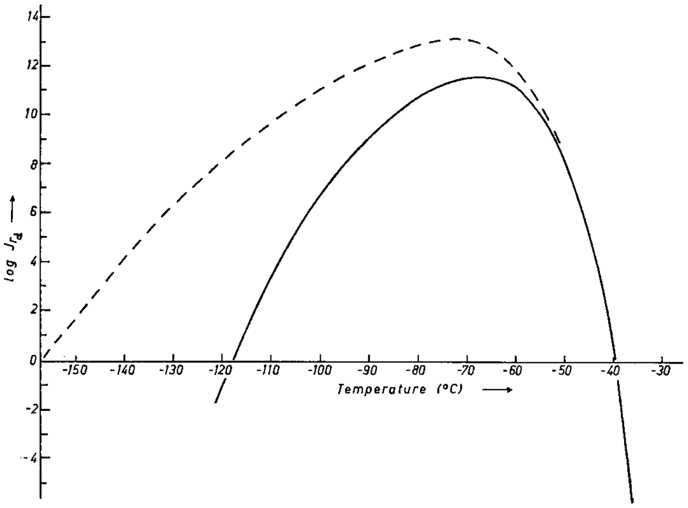

Fig. 5. Rate of nucleation in a supercooled water droplet of radius 1μ. The dashed curve corresponds to a linear extrapolation of the activation energy, while the solid curve corresponds to the extrapolation of the activation energy shown by curve A in Fig. 2.

8. The nucleation rate.

We shall next use equation (7.1) to compute the rate of formation of ice nuclei in droplets of radius 1μ, which is likely to be the right order of magnitude of the size of mother of pearl cloud particles. There has been made an attempt to determine the size of such particles from the distribution of the colours in mother of pearl clouds relative to the position of the sun. However, the method used is unsound, and the results therefore unreliable. Never-the-less, it is clear that the particles examined are smaller than those generally occurring in tropospheric clouds. It is felt that the selection of 1μ as a representative size of mother of pearl cloud particles is reasonable.

The variation of J_{r_d} with temperature is shown in Fig. 5. The dashed curve has been drawn in accordance with the linear extrapolation of the activation energy, while the solid curve corresponds to the curved extrapolation, shown in Fig. 2.

As might have been expected from the considerations in section 5, the two curves for J_{r_d} are almost identical for temperatures between the freezing point and about — 60°C. At still lower temperatures only a qualitative agreement exists. J_{r_d} is seen to increase from a very small value just below 0°C to a value of 1 ("spontaneous freezing") at about — 40°C. Below — 40°C $\mathcal{J}_{r_d}$ increases and attains a maximum value at about — 70°C. For still lower temperatures, $\mathcal{J}_{r_d}$ decreases but it is still positive, which means that supercooling is an improbable phenomenon. At very low temperatures, respectively — 117°C and — 157°C in the two cases, the curves again intersect the axis, which means that there exists a temperature below which crystallization of a supercooled droplet will not take place within a reasonable time.

It is interesting to compare RAU's observation of supercooled water droplets at — 72°C with Fig. 5. As we see, this temperature provides the minimum possibility of supercooling of water. This gives further support to the criticism against RAU's result, cited in section 2.

Since the linear extrapolation of the activation energy clearly represents an underestimation at very low temperatures, the corresponding values of $\mathcal{J}_{r_d}$, shown by the dashed curve in Fig. 5, are too high by several orders of magnitude. The correct value of the critical temperature of spontaneous crystallization must accordingly be higher, probably considerably higher, than — 157°C. A comparison between Fig. 2 and Fig. 5 shows how sensitive the theoretically determined value of the critical temperature is to the way of extrapolating A. In spite of the lack of reliable data of viscosity and of the order in the liquid structure of water at low temperatures, it is felt that the solid curve in Fig. 2 represents a more natural extrapolation of A from known values above — 10°C. The solid curve in Fig. 5 is therefore believed to be fairly representative, and most probably superior to the dashed curve.

Thinking again of mother of pearl clouds, the solid and the dashed curves in Fig. 5 show that the nucleation rate, though decreasing rapidly, is still above 1 in the temperature interval — 85°C to — 100°C. Supercooling of pure water should, accordingly, be improbable in this region. However, as will be shown in section 13, mother of pearl cloud particles are very small. The calculated maximum radius is 1.2μ, but for small values of the condensation coefficient radii of about 0.3μ have been found. This means that the dissolved nucleus mass may play an important role in the freezing process, at least during the first stage of the droplet growth.

The effect of the dissolved nucleus mass upon freezing near the — 40°C transition has been demonstrated by BIGG (reported by MASON, 1957). For saturated solutions of NaCl the maximum supercooling is increased by 15°C. For a nucleus mass of 10^{-15} grams the effect is considerable for droplet radii below 0.15μ. It is therefore not unlikely that mother of pearl cloud particles are formed as supercooled droplets of concentrated salt solutions. Whether these droplets will freeze or not depends upon the temperature, nucleus mass and the droplet size.

9. The structure of ice at low temperatures. In section 7 and 8 values of σ_{12}, L_f and $\mathcal{J}_{r_d}$ were obtained which may be used in the study of the structure of ice and water at very low temperatures. The determinations were based upon extrapolations, the validity of which may be questioned. In order to test the validity of the results, we shall compare them with some experimental data concerning the structure of water and ice at very low temperatures.

During the last years a series of experiments has been made. A summary of the results and a complete list of references has been given by LONSDALE (1958). It is generally agreed that the hexagonal form of ice is the stable form (at pressures occurring under atmospheric conditions) between 0°C and — 80°C. Below this temperature both hexagonal, cubic and amorphous ice have been observed, but the investigators give different transition temperatures. At temperatures below about — 140°C the condensate has always been found to be amorphous. Here the rate of crystallization is obviously so low that the amorphous (liquid) state will persist for a very long time. This observational fact may be compared with Fig. 5, which gives a critical temperature of — 117°C for transition from amorphous to hexagonal ice. If the interfacial energy cubic ice-water and the latent heat of fusion are known, a corresponding curve may be drawn for the rate of formation of cubic crystals in a supercooled droplet. This curve should, according to the condensation experiments, intersect the temperature axis near — 140°C. It is, however, not likely that a curve showing the rate of formation of cubic crystals in a supercooled water droplet should deviate much from the solid curve in Fig. 5, concerning the region — 100°C to — 150°C. It was shown in Fig. 3 that the interfacial energy hexagonal ice-water is so small in this temperature region that W^*, shown in Fig. 2, may be neglected compared with A. It is probable that this will also be the case with the interfacial energy cubic ice-water. The two rates of nucleus formation will therefore primarily be determined by the activation energy and will consequently be almost equal. This explains why it has been so difficult to derive the exact transition temperature from hexagonal to cubic ice, or vice versa, from condensation experiments. The difference in critical temperature is likely to be about 5°C, probably less. A quantitative discrepancy, therefore, exists between the theory and the experimental results of KÖNIG (1942) and HONJO (1956). On the other hand, fairly good agreement is found with the experiments of STARONKA (1939) and PRYDE and JONES (1952), while very good agreement exists with the results of BURTON and OLIVER (1935) and BLACKMAN and LISGARTEN (1957).

The very careful investigations of BLACKMAN and LISGARTEN were especially devoted to the determination of the transition temperatures. In condensation experiments they obtained amorphous ice between — 180°C and — 140°C. At higher temperatures, — 140°C to — 120°C, cubic crystals formed, and between — 120°C and — 100°C both cubic and hexagonal crystals occurred. Above — 100°C, only hexagonal crystals were present. In the opinion of the author, the results of a study of the crystallization of amorphous ice, heated from below — 140°C to — 110°C is more reliable than the direct study of the structure of the deposit formed in this temperature region. BLACKMAN and LISGARTEN observed a very distinct transition to cubic ice at temperatures between — 120°C and — 114°C, in very good agreement with the solid curve (for hexagonal ice) in Fig. 5.

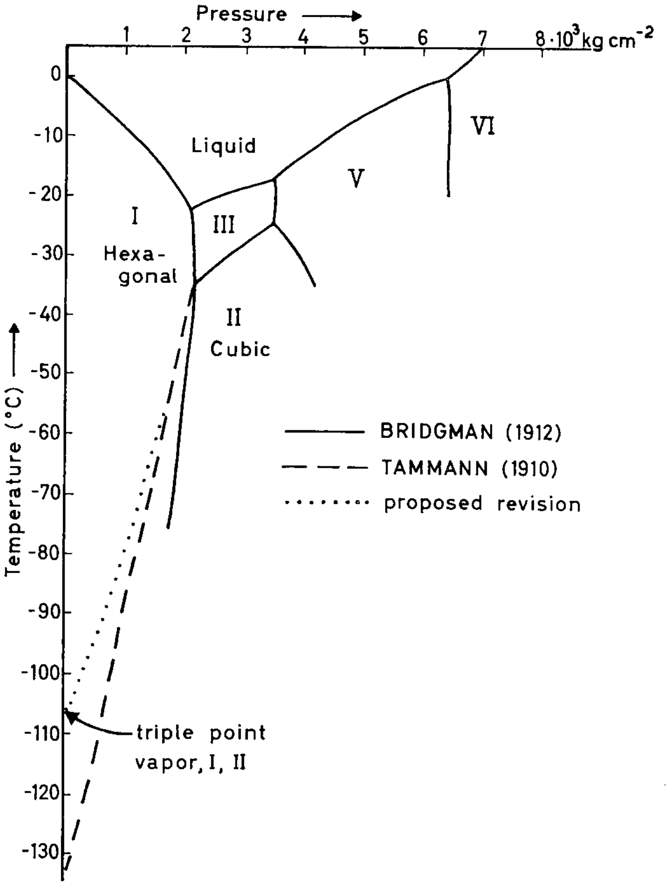

Fig. 6. Phase diagram for water.

It is interesting to compare the transition temperature between stable ice I (hexagonal) and stable ice II (cubic) with the phase diagram for water. This diagram is shown in Fig. 6. The equilibrium lines have been drawn according to Bridgman's data (1912). Three different curves separating the stable areas of ice I and ice II have been drawn. The solid line was drawn according to Bridgman's data, while the dashed curve corresponds to data given by Tammann (1910). The third dotted curve was drawn in agreement with the results of Blackman and Lisgarten, indicating a triple point near — 110°C and a pressure of about 10^{-6}mb. In accordance with Bridgman's data, hexagonal ice should be the stable form of ice at temperatures down to at least — 200°C, while Tammann predicts a transition temperature of about — 135°C. However, at the temperatures occurring in mother of pearl clouds, hexagonal ice is likely to be the stable form, though cubic or amorphous ice may occur, since the rate of crystallization is so small and the influence of dissolved matter is unknown.

10. Estimation of the temperature in mother of pearl clouds. Direct measurements of the temperature in mother of pearl clouds have never been made. However, on some occasions ascents have been made which indicate that the temperature must be exceptionally low. The mean temperature at 60 mb. (about 19 km) in mother of pearl cloud situations is — 72°C (Hesstvedt, 1959), and the trend of the temperature curves up to this level indicates a continued temperature decrease with height. On one occasion (Størmer, 1941), a temperature of — 83°C was observed at the level of mother of pearl clouds on a day when such clouds were observed; on another occasion, 29th February 1956, a temperature of — 82°C was recorded. These values probably represent the temperature in the undisturbed air. However, mother of pearl clouds are believed to form on the crests of waves set up by mountains, and due to adiabatic cooling the temperature on these crests may be somewhat lower (probably of the order 5°C) than in the undisturbed atmosphere. Temperatures about — 90°C or lower are, consequently, likely to exist in the clouds. This estimate of the temperature is supported by an estimate of the frostpoints in section 11 from an entirely different procedure.

11. Estimation of the frostpoints at mother of pearl cloud levels. Measurements of the humidity up to the levels of mother of pearl clouds have been made on three occasions in U.S. (Barret, Herndon and Carter, 1950). These measurements show great variations with height and time, also in the lowest part of the stratosphere (1—2 km above the tropopause). A series of humidity measurements up to 15 km, made over England (Murgatroyd, Goldsmith and Hollings, 1955, and Helliwell, Mackenzie and Kerley, 1957) shows a rapid decrease in humidity above the tropopause, but from a level generally a few thousand feet above the tropopause the frostpoints vary only slightly with height.

It is the author's opinion that the results obtained from the three ascents in U.S. cannot be taken as representative for the general distribution of water vapor in the stratosphere. Between 20 and 30 km dewpoints from — 54.4 to — 79.5°C have been found. However, during the winter the temperature at these heights are so often lower than the dewpoints mentioned that cloud formation should occur relatively commonly in the stratosphere. In this paper, therefore, only the observations taken over England will be used.

Table 1. *Frequency distribution for observed frostpoints at 48 000 ft over England.*

Temperature degrees *F*	Number of cases	Temperature degrees *F*	Number of cases
— 123	1	— 114	2
— 122	2	— 113	2
— 121	2	— 112	2
— 120	4	— 111	2
— 119	5	— 110	1
— 118	12	— 108	1
— 117	14	— 102	1
— 116	5	— 91	1
— 115	4	— 89	1

A frequency distribution for the observed frostpoints at 127 mb (about 48 000 feet or 14.5 km) is given in Table 1. It is seen that frostpoints of — 117 and — 118°F occur in 26 of 62 cases (42%) and that the deviations from these values are relatively small, apart from three cases with exceptionally high frostpoints. It has been suggested by MURGATROYD, GOLDSMITH and HOLLINGS (1955) that the instrument possibly has a constant error, reading 3°F too low. Accordingly, we will in this paper accept $-114.5°$F (or $-81.3°$C) as a mean frostpoint at 14.5 km and assume that only slight deviations from this value may occur. This frostpoint corresponds to a mixing ratio of $0.215 \,.\, 10^{-2}$ gr./kg. It is interesting to note that this frostpoint is almost equal to the frostpoints in the tropical tropopause. This gives strong support to the idea that tropospheric air enters the stratosphere mainly through the tropical jet.

We will now assume that no sources and sinks for water vapor exist between 15 and 30 km and that the turbulent mixing of the air will ensure a constant mixing ratio with height. It is then possible to calculate the vapor pressure and frostpoints at the different pressure levels. The frostpoints thus obtained are given in Table 2 for the appropriate levels.

Table 2. *Estimated frostpoints at the levels of mother of pearl clouds.*

Pressure (mb) .	60	50	40	30	25	20	15	10
Approximate height (km)..	19	20	21	22.5	24	25	26.5	29
Frospoint (degrees C) .	– 86	– 87	– 88	– 90	– 91	– 92	– 93	– 95

In this region of vapor pressure the difference between frostpoint and dewpoint is about 4.5°C. If we require supersaturation with respect to water in order to ensure cloud formation, air temperatures 4.5°C lower than the values given in Table 2 must occur. The temperatures thus obtained agree very well with the estimations in section 10.

12. Concentration of condensation nuclei in the stratosphere. The author is unaware of any published measurements of the concentration of condensation nuclei in the stratosphere. We therefore have to make estimates based upon extrapolations of known values of concentrations in the troposphere. The results thus obtained may, of course, deviate considerably from the concentrations really occurring in the stratosphere. If the nuclei, however, are of terrestrial origin, as will be assumed here, it is probable that we will arive at the right order of magnitude, at least concerning an upper limit of the concentrations. Two series of observations, reaching heights of 6–7 km, will be used (WIGAND, 1913 and WEICKMANN, 1957).

Concentrations of condensation nuclei are always given as the number of nuclei pr cm³. However, if the purpose is to study the variation of the concentration up to great heights, it is more convenient to use another expression for the concentration given by

$$N'_h = N_h \frac{25}{p_h} \cdot \frac{T_h}{178} \tag{12.1}$$

where N_h = observed concentration of nuclei (pr cm^3) at height h where the standard pressure is p_h mb and the standard temperature is T_h. N'_h represents the number of nuclei obtained if the air is expanded to 25 mb and cooled to 178°K. (These values will be used here to represent the pressure and temperature at 24 km, which is the mean height of mother of pearl clouds.) WIGAND's and WEICKMANN's values have been transformed by means of (12.1) and the results are shown in Fig. 7. For the purpose of estimating the concentration of nuclei of terrestrial origin at 24 km these curves have an advantage compared with the curves given by WEICKMANN as the effect of pressure and temperature of the air is eliminated. The decrease of N'_h with height is due to sedimentation only. WIGAND's observations indicate a concentration of the order 0.1 cm^{-3} at the mean level of mother of pearl clouds, while WEICKMANN's observations indicate a somewhat higher concentration.

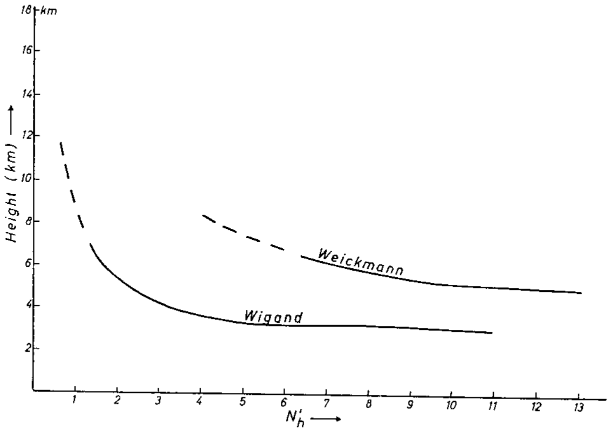

Fig. 7. Variation of N'_h with height. N'_h represents the concentration of condensation nuclei at the height h, adjusted to a pressure of 25 mb and a temperature of − 95°C.

Until observational data from the stratosphere are available, we can only make rough estimates as to the concentrations of condensation nuclei at the levels of mother of pearl clouds. From what is shown above, the concentrations are probably much smaller than 5 cm^{-3}. A value of 0.5 cm^{-3} seems to give a fairly good representation of the concentration of terrestrial nuclei at 24 km.

Due to the scarcity of condensation nuclei of terrestrial origin, exceptionally high saturation ratios (up to about 1.3) may, as will be shown in section 13, occur in mother of pearl clouds. At temperatures around − 10°C we know that a saturation ratio of about 4.1 is needed for condensation upon small negative ions, while saturation ratios higher than 5—7 will give homogeneous condensation, without the aid of condensation nuclei. These critical saturation ratios are dependent upon the temperature, and it might be of interest to clarify the possibilities of condensation without the aid of ordinary nuclei.

For homogeneous nucleation, BECKER and DÖRING (1935) give the following expression for the rate of formation of water droplets in supersaturated vapor

$$(12.2) \qquad J = \frac{\alpha e_s^{\,2}}{\varrho_w R^2 T^2}\left(\frac{2N^3 M\sigma_{23}}{\pi}\right)^{1/2}\left(\frac{e}{e_s}\right)^2 \exp\left(-\frac{16\pi M^2\sigma_{23}^{\,3}}{3\varrho_w^{\,2} k R^2 T^2\left(ln\frac{e}{e_s}\right)^2}\right)$$

where $\mathcal{N}$ is Avogadro's number, α is the condensation coefficient, e_s is the saturation vapor pressure and e is the ambient vapor pressure. In the case of homogeneous sublimation we have to replace ϱ_w and σ_{23} by ϱ_i and σ_{13}, respectively. Furthermore, the value of α will possibly be different in the two cases. Let us define spontaneous condensation by $\mathcal{J} = 1$, i.e. by the formation of one droplet pr. sec. per unit volume. This gives us an equation of third degree in $ln S = ln \frac{e}{e_s}$, the solutions of which are shown in Fig. 8 for temperatures between 0°C and $-$ 100°C. It is seen that homogeneous condensation is more probable than homogeneous sublimation for all temperatures considered. This result is in contradiction to the results of KRASTANOW (1940), who found that sublimation proceeds more easily at temperatures below $-$ 65°C. However, at about $-$ 100°C even homogeneous condensation requires saturation ratios which are far beyond what may occur under atmospheric conditions. Hence, the possibility of droplet formation by homogeneous condensation may be excluded.

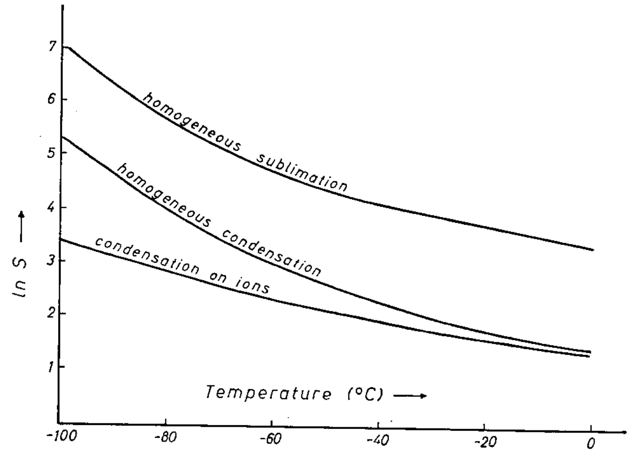

Fig. 8. Saturation ratio (with respect to water) required for homogeneous sublimation, homogeneous condensation and condensation on ions.

The possibility of condensation upon small ions may be evaluated by using the formula (MASON, 1957)

$$\frac{\varrho_w RT}{M} ln\, S = \frac{2\sigma_{23}}{r} - \frac{q^2}{8\pi\varepsilon r^4} \tag{12.3}$$

where q is the charge of the droplet and ε is the dielectric constant of air. The critical saturation ratio S^* is given by

$$\frac{d}{dr}(ln\, S) = 0 \tag{12.4}$$

or

$$ln\, S^* = \frac{3}{2}\sigma_{23}\sqrt[3]{\frac{4\pi\varepsilon\sigma_{23}}{q^2}} \tag{12.5}$$

The variation of S^* with temperature is shown in Fig. 8 for q = one electronic charge. It is seen that S^* increases with falling temperature, and small ions, consequently, may not be expected to act as condensation nuclei at the levels of mother of pearl clouds.

Bowen (1953) mentions 1 m^{-3} as a probable value of the concentration of condensation nuclei of cosmic origin at a height of 100 km. If these nuclei are brought down to 25 km by only the turbulent motion, a concentration of about 0.07 cm^{-3} should occur at this level. This concentration is probably generally small in comparison with the concentration of nuclei of terrestrial origin, but may, at times, be of the same order of magnitude. Although uncertainties exist in these estimations, it is not likely that the total concentration will be much higher than 1 cm^{-3}, and the rates of growth obtained in section 13 will still be valid.

13. The growth of mother of pearl cloud particles. The growth of cloud droplets may be computed from the formula

$$r\frac{dr}{dt}=\frac{DM}{\varrho_w RT}\left[e-e(r)\right] \tag{13.1}$$

where t is the time, D is the diffusivity of water vapor in air, e is the vapor pressure remote from the droplet and $e(r)$ is the vapor pressure at the surface of the droplet. Very often $e(r)$ has been replaced by the equilibrium vapor pressure at the surface, $e_w(r)$, but, as pointed out by several authors, (Langmuir, 1944, Howell, 1949, and Rooth, 1957), this simplification implies a considerable overestimation during the first stage of the droplet growth. Instead of (13.1) we shall use the formulation

$$(r+s)\frac{dr}{dt}=\frac{DM}{\varrho_w RT}\left[e-e_w(r)\right] \tag{13.2}$$

where $s=\frac{D}{\alpha}\sqrt{\frac{2\pi M}{RT}}$. The condensation coefficient, α, has been measured by Alty and Mackay (1935), who found the value to be as low as 0.036. Recent measurements by Rooth (private communication) show that α must be about 0.2, possibly higher. In our calculations we shall neglect the effect of the latent heats of condensation and sublimation. (It will be shown below that this effect is exceedingly small).

Let us assume that the cloud particles grow by condensation as the air mass rises uniformly and cools adiabatically. Then we have

$$\begin{aligned} T_d - T &= \gamma z \\ p &= p_d\left(\frac{T}{T_d}\right)^{3,5} \\ N &= N_d\cdot\frac{pT_d}{p_dT}=N_d\left(\frac{T}{T_d}\right)^{2.5} \end{aligned} \tag{13.3}$$

where $\gamma = 10^{-4}$ degrees cm^{-1} is the dry adiabatic lapse rate and z is the vertical displacement, reckoned from the cloud base. The index "d" is used to denote the appropriate values of the variable quantities at the cloud base, where the temperature is equal to the dewpoint temperature T_d. An expression for D is given in Smithsonian Meteorological Tables, 1951:

$$D = D'\frac{p'}{p}\left(\frac{T}{T'}\right)^{1.81} = D_d\left(\frac{T_d}{T}\right)^{1.69} \tag{13.4}$$

The primes are used to denote standard conditions: $D' = 0.226$ cm^{2}sec^{-1}, $p' = 1000$ mb and $T' = 273.16$°K. Substitution in the expression for s gives

$$s = \frac{D_d}{a}\left(\frac{T_d}{T}\right)^{2.19}\sqrt{\frac{2\pi M}{RT_d}} = s_d\left(\frac{T_d}{T}\right)^{2.19} \tag{13.5}$$

In order to find the ambient vapor pressure e we must account for the reduction of the vapor pressure due to condensation. If no condensation has taken place, we should have

$$e = e_d \cdot \frac{p}{p_d} = e_d\left(\frac{T}{T_d}\right)^{3.5} \tag{13.6}$$

However, by the formation of N droplets pr. unit volume, all of the same radius r, the vapor pressure is reduced by an amount e^*, given by

$$N\frac{4\pi}{3}\varrho_w r^3 = \frac{Me^*}{RT} \tag{13.7}$$

Consequently, we have for the vapor pressure

$$e = e_d\left(\frac{T}{T_d}\right)^{3.5}\left[1 - N_d\frac{4\pi}{3}\varrho_w r^3\frac{RT_d}{Me_d}\right] \tag{13.8}$$

For the effect of the curvature of the droplet and of the dissolved nucleus matter MASON (1957) gives the following expression

$$e_w(r) = e_w(T)\left(\exp\frac{2M\sigma_{23}}{\varrho'_w RT}\right)\left(1 + \frac{imM}{W\left(\frac{4\pi}{3}\varrho'_w r^3 - m\right)}\right)^{-\frac{\varrho_w}{\varrho'_w}} \tag{13.9}$$

where $e_w(T)$ is the saturation vapor pressure over a plane pure water surface of temperature T, m is the mass and W the molecular weight of the soluble nucleus, i is a factor which varies between 2.91 for saturated and 2.0 for infinitely dilute solutions and ϱ'_w

is the density of the droplet. An expression for $e_w(T)$ may be obtained from Goff-Gratch' formula (Smithsonian Meteorological Tables, 1951):

$$e_w(T) = e_w(T_d)[1 - 0.2046(T_d - T) + 0.01915(T_d - T)^2] \tag{13.10}$$

when $-$ 95.2°C is used as dewpoint temperature. Substitution of (13.4), (13.5), (13.8), (13.9) and (13.10) in the basic equation (12.2) gives, for $e_d = e_w(T_d)$:

$$\left[r\left(\frac{T}{T_d}\right)^{2.19} + s_d\right]\frac{dr}{dt} = \frac{D_d M e_d}{\varrho_w R T_d}\left(\frac{T}{T_d}\right)^3\left[1 - N_d\frac{4\pi}{3}\varrho_w r^3\frac{RT_d}{Me_d} - \left(\frac{T}{T_d}\right)^{-3.5}\right.$$
$$\left.(1 - 0.2046(T_d - T) + 0.01915(T_d - T)^2)\left(\exp\frac{2M\sigma_{23}}{\varrho'_w RTr}\right)\left(1 + \frac{imM}{W\left(\frac{4\pi}{3}\varrho'_w r^3 - \mathrm{m}\right)}\right)^{-\frac{\varrho_w}{\varrho'_w}}\right] \tag{13.11}$$

If we know T as a function of the time t, i.e. if the trajectory of the particles were known, (13.11) may be integrated and the droplet size could be determined in all parts of the cloud.

If the cloud elements are ice particles and not supercooled water droplets, an equation analogous to (13.11) may be obtained for the rate of growth. If we assume a spherical shape of the particles, we obtain

$$\left[r\left(\frac{T}{T_f}\right)^{2.19} + s_f\right]\frac{dr}{dt} = \frac{D_f M e_f}{\varrho_i R T_f}\left(\frac{T}{T_f}\right)^3\left[1 - N_f\frac{4\pi}{3}\varrho_i r^3\frac{RT_f}{Me_f}\right.$$
$$\left. - \left(\frac{T}{T_f}\right)^{-3.5}\left(1 - 0.1847(T_f - T) + 0.01605(T_f - T)^2\right)\exp\frac{2M\sigma_{13}}{\varrho_i RTr}\right] \tag{13.12}$$

in which the index "f" is used to denote the values of the variable quantities at the cloud base, where the temperature is equal to the frostpoint temperature T_f. Furthermore, we have to introduce a sublimation coefficient, α', in the expression for s_f.

Mother of pearl clouds are believed to form on the crests of mountain waves and we shall therefore define trajectories which are likely to describe the wave-motion as realistically as possible. Palm and Foldvik (1960) have studied mountain waves theoretically, using wind and temperature profiles similar to those generally observed in mother of pearl cloud situations (Hesstvedt, 1959). Vertical velocities have been calculated up to 25 km in the case of two-dimensional motion. If we assume a horizontal wind speed of 10 m sec^{-1}, which seems to be a reasonable value, we can plot the trajectory of the air particles (see Fig. 9). Here we shall study the growth of particles in a cloud formed on the second wave crest (marked by a square). A detailed study of

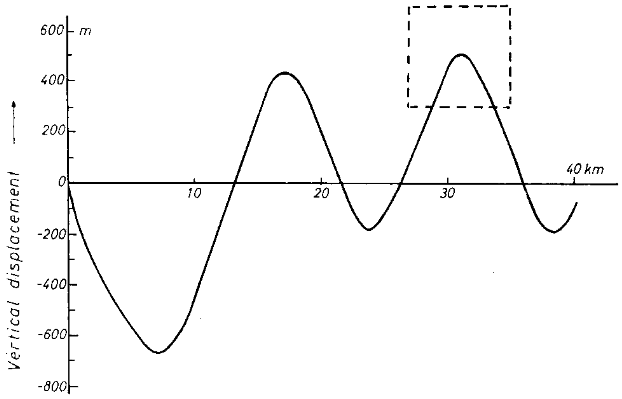

Fig. 9. Assumed trajectory at a height of 24 km in a mountain wave situation. 10 m sec^{-1} was used as horizontal wind speed; vertical velocities were taken from Palm and Foldvik's data (1960). The model clouds used in the calculations of the particle growth are situated on the second wave crest, marked by the square.

the motion in this region shows that the vertical velocity is very close to a linear function of time. Two different cases will be studied, with condensation levels 200 m (cloud "A"), respectively 100 m (cloud "B"), below the top of the wave. The trajectories are given by

$$z = 152\,t - 0.29\,t^2 \quad \text{(cloud ``}A\text{'')} \tag{13.13}$$

and

$$z = 108\,t - 0.29\,t^2 \quad \text{(cloud ``}B\text{'')}. \tag{13.14}$$

Since an integration of (13.11) and (13.12) in the complete form is so difficult, we shall make some simplifications which introduce only slight errors in the final result. For $T_d = -95.2°\text{C}$, $T_f = -90.6°\text{C}$ and an air pressure of 25 mb at the cloud base we have

$$s_d = \frac{3.64}{\alpha}\,\mu \text{ and } s_f = \frac{3.76}{\alpha'}\,\mu \tag{13.15}$$

Since we have $r \ll s_d$ and $r \ll s_f$ (except for the combination $\alpha = 1$ and cloud "A", where a slight revision is needed), and since $T_d - T \leq 2°\text{C}$ and $T_f - T \leq 2°\text{C}$, we may replace the terms $\left(\frac{T}{T_d}\right)^{2.19}$ and $\left(\frac{T}{T_f}\right)^{2.19}$ on the left side of (13.11) and (13.12) by the unit. Furthermore, we shall neglect the reduction of the supersaturation due to liquid and solid water content. Such a simplification would have been misleading in a study of tropospheric clouds. But in our case, with very slow particle growth and few condensation nuclei, the error is negligible unless we have $N \geq 1\ \text{cm}^{-3}$ and $r \geq 0.8\mu$. With these simplifications and the abbreviations

$$1 + \varphi = \left[\exp \frac{2M\sigma_{23}}{\varrho_w' RTr}\right]\left[1 + \frac{imM}{W\left(\frac{4\pi}{3}\varrho'_w r^3 - m\right)}\right]^{-\frac{\varrho_w}{\varrho'_w}} \tag{13.16}$$

$$1 + \varphi' = \exp \frac{2M\sigma_{13}}{\varrho_i RTr}$$

equations (13.11) and (13.12) become:

$$(r + s_d)\frac{dr}{dt} = 4.38 \cdot 10^{-10}\,[1 - 0.01685\gamma z - (1 + \varphi)\,(1 - 0.2018\gamma z + 0.01858(\gamma z)^2)] \tag{13.17}$$

and

$$(r + s_f)\frac{dr}{dt} = 4.88 \cdot 10^{-10}\,[1 - 0.01643\gamma z - (1 + \varphi')\,(1 - 0.1820\gamma z + 0.01555(\gamma z)^2)] \tag{13.18}$$

It is remarkable that (13.17) and (13.18) differ only very slightly as long as the difference $\varphi - \varphi'$ is small compared with the unit. As is easily seen, this will always be the case, except during the very first stage of the particle growth. Before we integrate (13.17) and (13.18) we shall consider the formation of the water or ice particles and the initial stage of the particle growth.

It has been shown by FLETCHER (1959) that insoluble nuclei, wet by water, of radii between 0.01μ and 0.1μ, will act as sublimation nuclei at moderate and high supercoolings before, and even a short time after, saturation with respect to water is reached. The reason is that the critical supersaturation with respect to water for droplet formation is not very different from the critical supersaturation with respect to ice for ice particle formation. The difference is important only a few degrees below 0°C. At lower temperatures the ratio between the saturation vapor pressures with respect to water and ice is increasing from 1 at 0°C to about 2 at -90°C, and very soon overcompensates the small difference in critical supersaturations. The critical saturation ratio for spontaneous droplet formation may be calculated from

$$ln\frac{e}{e_w} = \frac{2M\sigma_{23}}{\varrho_w R T r_n} \tag{13.19}$$

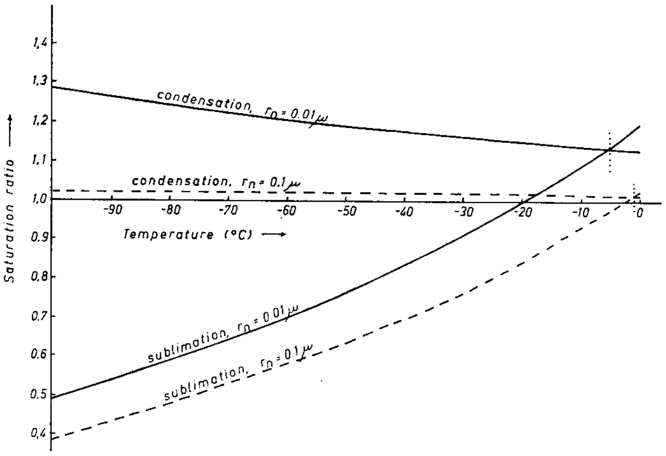

Fig. 10. Saturation ratio (with respect to water) required for condensation and sublimation upon insoluble nuclei of radii 0.1μ and 0.01μ.

where r_n is the radius of the nucleus. Correspondingly, we have for spontaneous formation of ice particles

$$ln \frac{e}{e_i} = \frac{2M\sigma_{13}}{\varrho_i R T r_n} \tag{13.20}$$

where e_i is the saturation vapor pressure with respect to a plane ice surface. The critical saturation ratios (with respect to water) thus calculated are shown in Fig. 10 for two sizes of nuclei, 0.01μ and 0.1μ. It may be concluded from Fig. 10 that insoluble nuclei will only act as sublimation nuclei at the temperatures prevailing in mother of pearl clouds. On the other hand, soluble nuclei will act as condensation nuclei. Due to the slow rate of growth, the concentration of nucleus matter will possibly be high enough to maintain the supercooling for a considerable time.

The results of the integrations of (13.17) and (13.18) are shown in Fig. 11 and Fig. 13—16 for different choices of the parameters: cloud type (ice or water cloud), amplitude, value of the condensation or sublimation coefficient, concentration of nuclei and nucleus mass. In the case of water and mixed clouds, the growth was started upon droplets of concentrated solution of NaCl, the nucleus being completely dissolved. This represents a slight overestimation of the droplet radius at the time $t = 0$, but the effect upon the continued growth is small for the nucleus sizes occurring at great heights. The maximum particle radius obtained was 1.2μ, but in most cases much smaller particles were found. It is seen that the particle growth is very sensitive to the condensation and sublimation coefficients; roughly, the maximum particle sizes calculated are proportional to a or a' (see Fig. 11, 14 and 16).

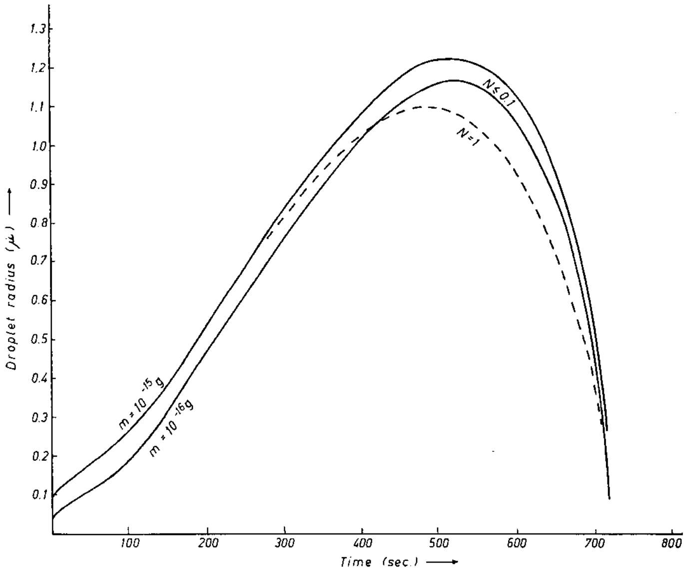

Fig. 11. Droplet growth in cloud "A" (condensation level 200 m below the top of the wave). The solid curves refer to nuclear masses of 10^{-15}g and 10^{-16}g NaCl and concentrations of condensation nuclei $N \leq 0.1$ cm^{-3}. The dashed curve shows the revision necessary if $N = 1$ cm^{-3}. $a = 1$ is used for the condensation coefficient. (See also Fig. 15).

The effect of the liquid water content upon the rate of growth is only slight. For $N < 1$ cm^{-3} the liquid water content is negligibly small, and even for $N = 1$ cm^{-3} it is so small that it may be neglected in the calculations, provided the particle radius is smaller

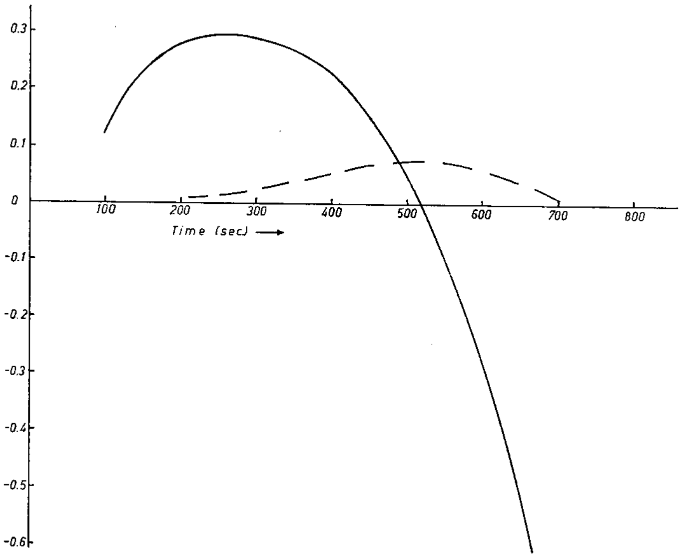

Fig. 12. The solid curve shows the supersaturation (with respect to water) in a water cloud "*A*". ($a = 1, m = 10^{-15}$g and $N \leq 0.1$ cm^{-3}). The dashed curve represents the reduction in supersaturation due to liquid water content for the case $a = 1$, $m = 10^{-15}$g and $N = 1$ cm^{-3}. (See also Fig. 11 and 15).

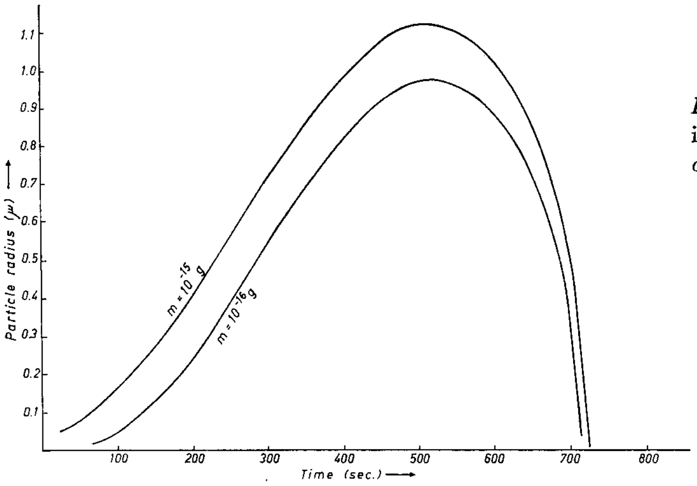

Fig. 13. Growth of ice particles in an ice cloud "*A*". ($N \leq 0.1$ cm^{-3}, $a' = 1$ and $m = 10^{-15}$g and 10^{-16}g).

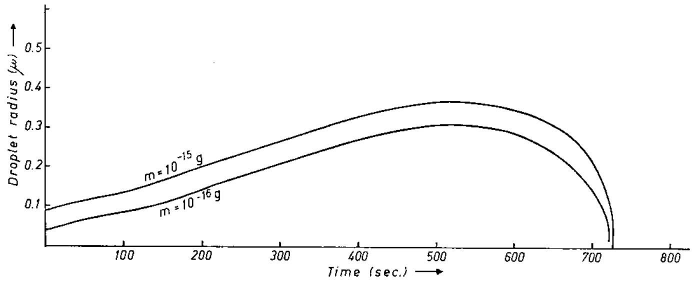

Fig. 14. Growth of droplets in cloud "*A*" ($N \leq 0.1$ cm^{-3}, $a =$ 0,2 and $m = 10^{-15}$g and 10^{-16}g). An impression of the effect of different selections of the value of a upon the droplet growth may be obtained from a comparison with Fig. 11.

than about 0.8μ (see Fig. 11). The relative importance of the liquid water content and the supersaturation due to the lifting of the air is shown in Fig. 12 for $a = 1$, $N = 1\ \text{cm}^{-3}$ and a water cloud of type "*A*".

It is seen from Fig. 11 and 13 that no important difference exists between the particle growth in a water cloud and an ice cloud, provided the latter is formed entirely by sublimation and not by the freezing of supercooled water droplets. (It is emphasized that Fig. 11 and 13 represent two different clouds and may not be used to compare the growth of liquid and solid particles in the same cloud.)

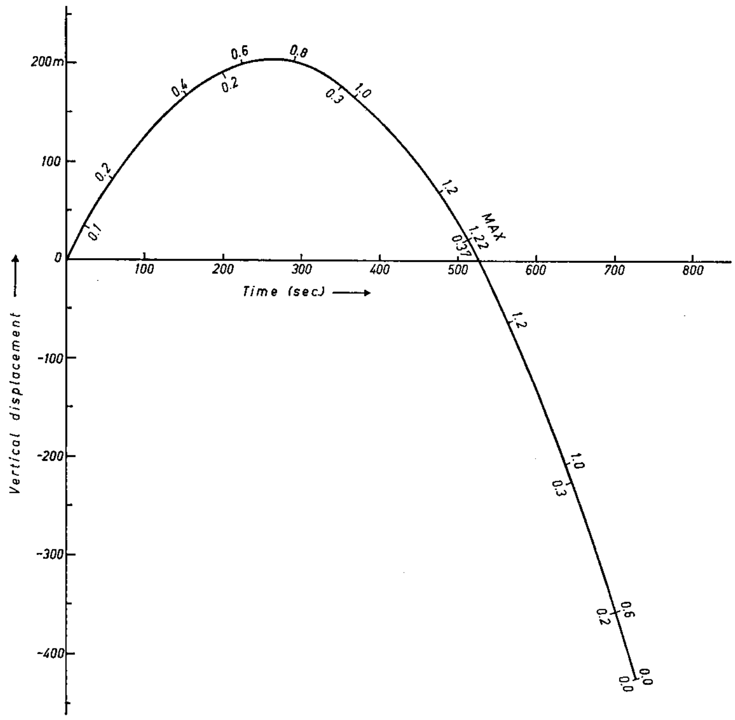

Fig. 15. Model of a mother of pearl cloud (water cloud, type "*A*"). The figures above the trajectory indicate the droplet radii in μ for the case $a = 1$, while the figures below the trajectory give the droplet radii for the case $a = 0.2$.

Fig. 17 shows the growth of particles in a cloud of type "*B*" for $a = a' = 0{,}2$. It is here assumed that the particles start their growth as droplets of supercooled, concentrated solutions of NaCl in water. When the solutions become so diluted that they contain 1 molecule of NaCl pr 100 molecules of water, freezing is thought to take place, and the particles continue their growth as ice spheres. They are then suddenly exposed to a very great supersaturation, due to the difference in vapor pressure over ice and water. The growth is therefore accellerated, and the evaporation starts at a level several hundred meters below the condensation level. For comparison, the growth of supercooled droplets in the same cloud is shown.

In Fig. 11, 13, 14 and 17 the growth of the particles is shown for two values of the nucleus mass: 10^{-15}g and 10^{-16}g. According to JUNGE (1952) nuclei of radii $> 0{,}25\mu$ (at water saturation), corresponding to more than 10^{-16}g nucleus mass, represent only 10% of the total number of nuclei in the troposphere. And since the larger nuclei are used in precipitation processes in the troposphere to a greater extent than the smaller ones, the mass of the most frequent nucleus size is probably smaller at 25 km than in

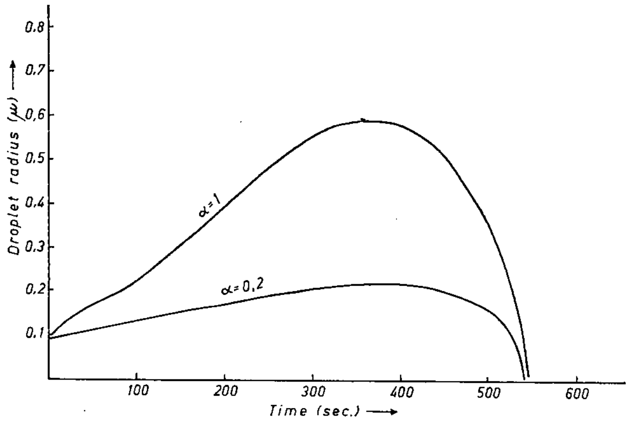

Fig. 16. Droplet growth in cloud "*B*" (condensation level 100 m below the top of the wave). ($N \leq 1$ cm^{-3}, $m = 10^{-15}$g and $\alpha = 1$ and 0.2).

the lower troposphere. Furthermore, it is important to note that the number of nuclei and the rate of growth are so small that great supersaturations occur soon after the condensation level is passed in the upwind part of the clouds. After less than 100 sec the supersaturation is of the order of magnitude 10% (see Fig. 12). Consequently, all the condensation nuclei, whatever their size and efficiency, will become active very soon after the condensation level is passed. Therefore, the lifetime will be approximately the same for all droplets. Based upon these considerations we may conclude that the particle size spectrum in a given part of the cloud will be very narrow. Deviations greater than $0{,}1\mu$ from the mean particle size would only rarely occur. Thus, good agreement exists between our theory and the iridescence associated with mother of pearl clouds. Such brilliant iridescence is only possible in clouds of almost equally sized particles.

A model of water cloud "*A*" is shown in Fig. 15. The droplet radius in different parts of the cloud is plotted along the trajectory. It is remarkable that the maximum droplet size is reached approximately when the droplet reaches the condensation level in the downwind part of the cloud. Complete evaporation of the droplets is reached considerably later, at a level about 425 m below the condensation level. Thus, a marked asymmetry results in the shape of the clouds. In a mixed cloud (see Fig. 17) the asymmetry is still greater, about 1000 m. Such asymmetry has at times been observed, but has generally been thought to be apparent and due to the observer's position in relation to the cloud and the wind direction, or due to solidification of some of the cloud drop-

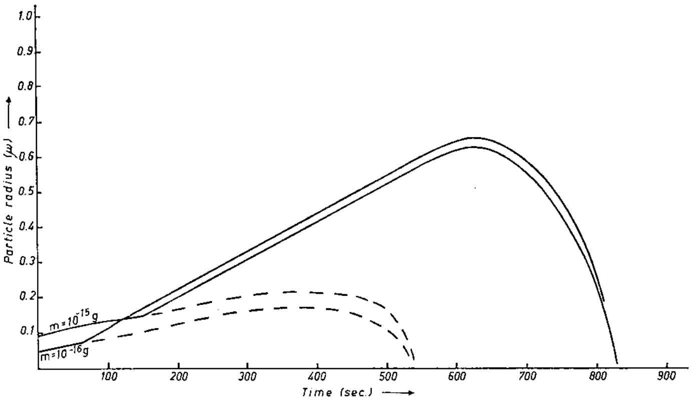

Fig. 17. Particle growth in a mixed cloud "*B*" ($\alpha = \alpha' = 0{,}2$, $N \leq 1$ cm^{-3}, $m = 10^{-15}$g and 10^{-16}g). The particles are assumed to form as supercooled water droplets which freeze when a dilution of 1 molecule of NaCl pr 100 molecules of water is reached.

lets. It results from our calculations that asymmetry will occur as well in pure water clouds. Since mother of pearl clouds are generally seen at a great distance, of the order 1—200 km, the skewness only amounts to a fraction of a degree and can only be determined by use of a theodolite or by photographic pictures. This was done 21th February, 1959, and differences in height of about 5—800 m were observed between the upwind and the downwind edge of the cloud.

We started our calculations by assuming that the released heats of condensation or sublimation are small and may be neglected. It is now possible to evaluate, approximately, the temperature rise due to condensation or sublimation. An upper limit for temperature rise $\triangle T$ may be calculated from

$$\triangle T \leqq \frac{L_s \varrho_w}{K}\left[(r+s)\frac{dr}{dt}\right]_{\max} \tag{13.21}$$

where L_s is the latent heat of sublimation and K is the thermal conductivity of air. Substitution of $L_s = 676$ cal g^{-1} deg^{-1} and K $\approx 4{,}15 \cdot 10^{-5}$cal cm^{-1}sec^{-1}deg^{-1} gives $\triangle T \leq 0{,}0024$°C. This temperature rise is equivalent to a reduction in relative humidity of only 0,05% and may therefore be neglected in our case.

As the growth of the particles in mother of pearl clouds is so slow, the liquid water content is very sensitive to the concentration of nuclei. It is therfore only possible to give the order of magnitude of the maximum liquid water content in a cloud; 10^{-7} and 10^{-5} g m^{-3} may be given as lower and upper limits.

14. Concluding remarks. The aim of this paper has been to study the physical properties of mother of pearl clouds, in particular to decide whether they are water, ice or mixed clouds and to describe the growth of the cloud particles. Unfortunately, it has not been possible to find satisfactory solutions to these problems. Especially the physical state of the cloud elements is still open for discussion since the freezing properties of more or less dilute solutions of salts in water can not be determined with a sufficient accuracy for the temperatures in question. Furthermore, the rate of growth of the cloud elements is very sensitive to the condensation, respectively sublimation coefficient. Until more experimental and observational data are at hand, we can hardly expect to make progress in the study of the physics of mother of pearl clouds.

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