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TIME LAG IN ICE CRYSTAL NUCLEATION IN THE ATMOSPHERE

PART. 2 — THEORETICAL

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PART II THEORETICAL

RÉSUMÉ

Effet de retard
dans l'ensemencement glaçogène atmosphérique

II. — Etude théorique

L'ensemencement d'un nuage surfondu par des noyaux atmosphériques présentant une suite continue de températures d'action est étudié théoriquement. L'expression générale obtenue, appliquée au cas de la distribution observée pour les noyaux atmosphériques, montre que 20 *à* 50% *des cristaux de glace produits se forment pendant les premières secondes, tandis que les autres se forment suivant un taux progressivement décroissant avec une constante de temps apparente d'environ* 6 *minutes. Il n'y a donc pas de distinction fondamentale entre les noyaux rapides et lents, et les chambres froides à temps de mesure rapides donnent une image correcte de la teneur en noyaux de l'atmosphère.*

SUMMARY

The nucleation of a supercooled cloud by atmospheric nuclei having a continuous range of nucleation temperatures is treated theoretically. A general expression is derived which, when applied to the observed distribution of atmospheric nuclei, shows that 20 — 50% *of the ice crystals produced form within the first few seconds, whilst the remainder form at a gradually decreasing rate with an apparent time constant of about* 6 *minutes. There is no fundamental distinction between prompt and delayed nuclei, and cold boxes with short measuring times give a correct picture of the nucleus content of the atmosphere.*

1. Introduction.

The production of ice crystals from a supercooled fog by the action of nuclei occurring naturally in the atmosphere differs from the nucleation process usually treated theoretically in that the atmosphere contains a large variety of nucleating particles with widely differing properties. In this paper we shall examine the nucleation by these particles of the cloud produced in a cold box, and show that their distribution of properties gives rise to an apparent time constant for the production of ice crystals. The calculated behaviour is in good agreement with the experimental results reported by Warner and Newnham in the first part of this paper.

2. Nucleation Theory.

The nucleation of a condensed phase from a supersaturated vapour has been discussed by many authors (Dunning, 1955) and is well established. In particular the rate of production of critical embryos which will develop, in our case, into macroscopic ice crystals, upon a foreign nucleating surface is given by

$$J = B \exp (- \Delta G^* / kT) \quad \text{cm}^{-2} \text{ sec}^{-1}. \qquad (1)$$

Here ΔG^* is the free energy required to form a critical embryo and B is a constant whose value depends upon the exact mechanism of the nucleation process, but which lies between 10^{24} and 10^{27}. We shall choose a value of 10^{26} here, and later show that any other choice in this range leads to almost identical results.

For a small nucleus the nucleation rate is simply proportional to the area, provided this is considerably greater than that covered by a critical embryo (diameter $\sim$ 200 Å). If the cold box initially contains N_0 identical nuclei each of area A, then the rate of production of ice crystals is

$$\frac{dN}{dt} = (N_0 - N) \; 10^{26} A \exp (- \Delta G^* / kT) \qquad (2)$$

giving

$$N = N_0 \; [1 - \exp (- \alpha t)] \qquad (3)$$

where

$$\alpha = 10^{26} A \exp (- \Delta G^* / kT). \qquad (4)$$

In the atmosphere, however, we have a distribution of nuclei, each type being characterized by a temperature T_0 at which its nucleation rate becomes appreciable. To make this more definite we shall define T_0 as the temperature at which $\alpha(T_0, T_0) = 1$ when the environment is saturated with respect to water. This implies that it takes, on the average, 1 second for a particle to nucleate an ice crystal at T_0. Any other reasonable definition of T_0 can be adopted without affecting the results. At any other temperature T, the value of α for nuclei with characteristic temperature T_0 will be denoted by $\alpha(T_0, T)$.

If we denote by $N_0(T_0)$ the initial population distribution of particles with characteristic temperatures T_0, then as an integrated form of (3) we have for the number N of particles nucleated after t seconds at a temperature T

$$N = \int_0^{273} N_0(T_0) \{ 1 - \exp[-\alpha(T_0, T)\, t] \} \, dT_0. \qquad (5)$$

Now at water saturation and temperature T, nucleation theory (Dunning, 1955) shows that

$$\Delta G^* / kT = \frac{16 \pi \sigma^3 v^2}{3k^3 \; T^3} f(\theta) [\log (P_L/P_S)]^{-2} \qquad (6)$$

where v is the volume occupied by an ice molecule, σ is the ice-vapour or ice-water surface free energy, depending upon whether the nucleation is by sublimation or freezing, and $f(\theta)$ depends on the properties of the ice-nucleus interface and hence varies from one nucleus to another. P_L is the saturation vapour pressure over water and P_S that over ice at temperature T. If we denote by ΔT the supercooling 273 — T, then to a very good approximation the logarithm is linear in ΔT, and treating T^3 as approximately constant, we can write

$$\Delta G^* / kT \simeq C (\Delta T)^{-2}. \qquad (7)$$

If we assume that all the nucleating particles have the same area — an assumption which we shall later show to be not as restrictive as it at first appears, then at the critical temperature T_0, since $\alpha(T_0, T_0) = 1$, $\Delta G^* / kT_0$ has a particular value independent of T_0. The more general form of (7) is thus

$$\Delta G^* / kT \simeq \gamma (\Delta T_0 / \Delta T)^2 \qquad (8)$$

where γ is a constant independent of T_0, and ΔT_0 denotes 273 — T_0. The equality is only approximate since we have assumed $kT_0 = kT$ which applies only over a limited range.

We now have the explicit expression

$$\alpha(T_0, T) = 10^{26} A \exp[-\gamma (\Delta T_0 / \Delta T)^2] \qquad (9)$$

and γ is determined from the condition

$$\alpha\,(T_0,\ T_0) = 1. \tag{10}$$

Equations (5), (9) and (10) give a complete solution to the problem when the area A and the distribution $N_0\,(T_0)$ have been specified.

3. Nuclei in the Atmosphere.

The integrated density of atmospheric nuclei active at a temperature greater than a particular value T_0 can be simply determined by a cold box counter method. The distribution $N_0\,(T_0)$ can then be obtained by differentiation. This cold box method leaves the exact definition of T_0 slightly ambiguous, but the change of nucleation rate with temperature is sufficiently rapid that uncertainties in definition are completely negligible.

Measurements carried out by various workers at this laboratory over a period of some years indicate that the distribution is exponential in temperature, of the form

$$N_0\,(T_0) = N_0 \exp\,(-\beta\,T_0) \tag{11}$$

where the constant β lies between 0.4 and 0.8 with a typical value of 0.6. This is generally true over a temperature range from — 15 to — 30° C, some anomalies have, however, occasionally been observed (Bigg, 1957).

For the purposes of the present calculation we shall assume the simple exponential distribution (11). Since the range involved in the integration is effectively only about 5° C, this will almost always be a very good approximation.

4. Numerical Results.

Equations (5), (9), (10) and (11) represent a complete solution to our problem under the assumptions we have made. It only remains to select an appropriate value for the area A and perform the integration. The most probable size for nucleating particles in the atmosphere is about 0.1 μ but one cannot "a priori" rule out particles in the range 0.01 — 1.0 μ. Happily, a numerical integration for each of these limiting sizes yields a curve almost identical with that for the preferred size 0.1 μ. This means that, for this sort of calculation, size effects can be completely ignored, and justifies our original assumption that all nuclei are of the same size. Again, changes in size are mathematically equivalent to uncertainties in the constant B of equation (1), so that these, too, are unimportant over at least the range indicated.

The reason for this insensitivity is that, as in all nucleation processes, the behaviour is almost completely dominated by the exponential term in α (equation 4). Changes in the cofactor are compensated for by very minor changes in the exponent and the integral is almost unchanged.

In Fig. 1 are shown the calculated curves of N as a function of time for a fog at T = —20° C and for three values of the parameter β.

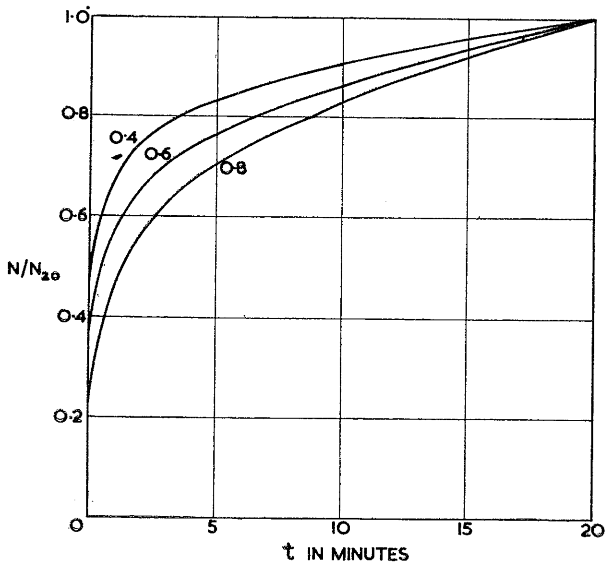

FIG. 1. — Number of ice crystals nucleated as a function of time, normalized to unity at 20 minutes. The parameter is β which defines the number of nuclei with characteristic temperature T_0 by

$$N_0 (T_0) = N_0 \exp(-\beta T_0).$$

These curves have all been normalized to unity at 20 minutes. It is seen that 20 — 50% of the crystals nucleate almost immediately, to be followed by the remainder at a much slower rate.

The nucleus count does not truly saturate under the assumptions we have made, but goes on increasing at an ever slower rate. Observation of this effect is limited by loss of nuclei to the cold-chamber walls, and even in the absence of this loss the count increases by less than 20% if the time is increased from 20 to 200 minutes.

Taking the curve for β = 0.6 as typical, we have plotted in Fig. 2 curves showing the number N_0 (T_0) of nuclei having a given characteristic temperature T_0, and the number N (T_0, t) of these which have become active after various times t. It can be seen that after only a few seconds (t = 0.1 min) all nuclei active at the fog temperature

(— 20° C) or above have produced ice crystals. It is these nuclei which contribute to the initial burst of crystals produced in the fog. After longer periods of time nuclei normally active below the fog temperature produce crystals, but after about 20 minutes little further increase in crystal count is observed. The total region of activity extends to about — 23° C after 40 minutes.

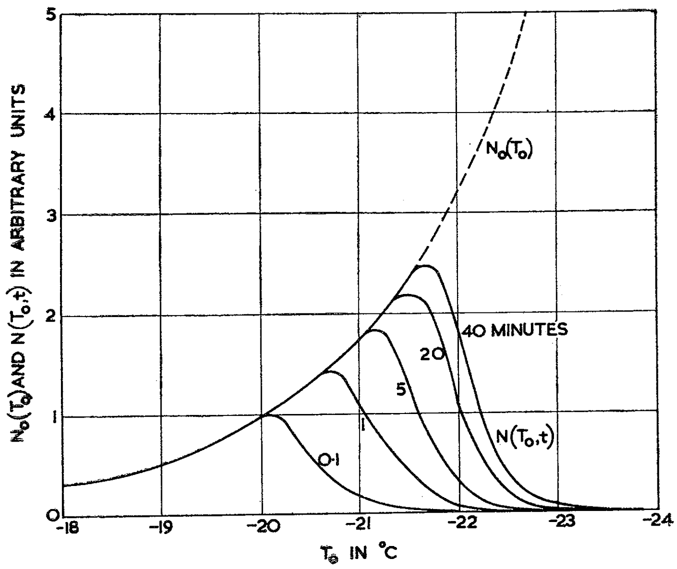

FIG. 2. — Number N_0 (T_0) of nuclei in the atmosphere having characteristic temperature T_0, and the number N (T_0, t) of these which have nucleated ice crystals after a time t in a fog at — 20° C.
t is shown as a parameter.

This makes it clear that there is no essential difference between the « prompt » nuclei and those that act after a longer time, but only a difference in activity. Indeed at a lower temperature the prompt nuclei will consist mainly of the delayed nuclei at the present temperature, whilst a new set of even lower activity will act as delayed nuclei.

From the nature of the integral (5) and its dependence on ΔT it is clear that the same state of affairs will persist over a fairly wide temperature range, say from — 10° C to — 30° C. For very small values of ΔT there may be an appreciable change in the time scale and in the numerical relation between prompt and delayed nuclei. However, this region is unimportant as there are virtually no atmospheric nuclei active above — 10° C.

5. Comparison with Experiment.

From our discussion above it is already evident that the theory explains many of the experimental effects observed by Warner and Newnham. In particular the appearance of prompt and delayed ice crystals, the fact that the crystals produced after 10 seconds number usually from 1/5 to 1/2 of the number produced after 20 minutes, and the virtual finality of the process after this time are all predicted by the theory.

For a more detailed comparison with experiment, account must be taken of the time constants associated with fall-out and growth in the cold box. This has been done, but results in only a slight modification of the curve of Fig. 1. To a reasonable approximation the number N (t) of ice crystals nucleated after a time t can be written

$$N(t) = N_1 + N_2 \left[1 - \exp(-t/\tau)\right] \qquad (13)$$

where N_1 represents the « prompt » and N_2 the « delayed » nuclei, and τ is a time constant of 6 — 7 minutes. This is however, merely a convenient empirical formula approximating the integral. It must be emphasized that « prompt » and « delayed » nuclei are not physically distinct and that the time constant τ is merely a matter of convenience and not an accurate or physically significant parameter.

The experimental scatter in values of the ratio of the count after 10 seconds to the count after 20 minutes is explained by the observed variation of nucleus activity distribution in the atmosphere, which we have denoted by the parameter β.

6. Conclusions.

The results of this theoretical study, taken along with experimental results confirming the theory, have important implications. The most significant conclusion is that the nuclei counted by cold boxes having counting times of the order of a minute are truly representative of the nuclei present. Extension of the counting time merely counts additional nuclei which are active at a slightly lower temperature.

The counts obtained after very long counting times are normally less than a factor of five greater than short time counts, and this effect is likely to be of less importance than the change of count with box temperature.

Finally, there is no physical distinction between « prompt » and « delayed » nuclei, and the apparent time constant of 6 — 7 minutes shown by the latter is merely characteristic of the nucleation process for ice on a distribution of nuclei and with a supercooling of about 20° C.

Applying these ideas to clouds, we see that no precise meaning is attached to the specification of the « number of nuclei active at temperature T » unless a time is also specified. The characteristic time is presumably the life time of the cloud in the supercooled state, say of the order of 100 minutes, but may be much less than this if there is much turbulence. A cold box count extending for 20 minutes will give the required nucleus count to within 10 — 20%, whilst a cold box count lasting only a few seconds will be within a factor 2 — 5. In view of the distribution of temperature within the cloud and the convection of air parcels, a count of this accuracy is sufficient for most purposes.

RÉFÉRENCES

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(2) Bigg, E.K. (1957) (personal communication).