Ice Nucleation Behavior of Silver Iodide Smokes Containing a Soluble Component

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ABSTRACT

The ice nucleation behavior of smokes consisting of silver iodide, together with a soluble component such as potassium iodide, is considered theoretically. It is proposed, when released into a natural cloud, that the smoke particles take up water to form solution droplets in each of which is suspended a small particle of silver iodide produced by hydrolysis of the mixed salt. If the temperature is low enough, this silver iodide particle may nucleate the freezing of the solution droplet. This process is treated thermodynamically, and the nucleation activity of the smoke particles is calculated as a function of size. It is found that the behavior is insensitive to the nature and exact concentration of the soluble component. Theoretical curves for the activity of such a mixed smoke are derived and show good agreement with experiment. This treatment supersedes the author's 1959 calculation based on the assumption of sublimation activity.

1. Introduction

Since silver iodide continues to be the material most commonly used in cloud seeding experiments and since the important operational parameter is the number of ice crystals which can be nucleated by the smoke of the burner under natural cloud conditions at a given temperature, it is important to know how this quantity depends upon the size distribution and chemical composition of the smoke.

A first approximation to the required information was calculated by the present author (Fletcher, 1959a) on the basis of treatment of size effect in heterogeneous nucleation (Fletcher, 1958) and the assumptions that the burner smoke behaves essentially like pure silver iodide and that pure silver iodide acts as a sublimation nucleus with a threshold at −4C. On these assumptions and the known condensation threshold for AgI (Fletcher, 1959b), ice crystal nucleation by condensation followed by freezing could be ruled out in the environment of a natural cloud. The activity curves calculated in this way were in quite good agreement with experiment for quite a wide variety of burners.

Despite this agreement, however, the treatment is not really satisfactory. Mason and Van den Heuvel (1959) have shown that silver iodide particles have a nucleation threshold of −12C for ice crystal production by sublimation and that it is the freezing threshold which occurs at −4C. Careful experiments by Edwards and Evans (1960) support this conclusion in more detail. Furthermore, the smoke produced by most generators is very far from being pure AgI and usually contains large quantities of the complexing agent, NaI or KI, in intimate mixture. It is therefore to be expected

that the smoke particles will be hygroscopic so that condensation can occur to form a solution droplet without the need of any appreciable supersaturation in the cloudy environment.

It is the purpose of the present paper to present a revised treatment which takes these effects into account. We must emphasize at the outset that the theory will be a macroscopic one in that many effects of importance at the molecular level will be neglected. This is, however, justified to some extent since we are ultimately concerned with the average behavior of a very large group of particles rather than with the behavior of individuals. A rigorous treatment should, of course, include all such molecular effects and then average over the possible surface configurations of all the particles but this does not seem possible at the present time.

2. Equilibrium of a solution droplet

Recent studies of a typical AgI smoke (de Pena and Caimi, 1967) show, as indeed was reported by Mason and Hallet (1956), that dry particles consist of some sort of complex mixed salt such as $(AgI)_2 \cdot KI$. When exposed to a moist environment the mixed salt takes up water to form a solution droplet and, unless the concentration is such that all the AgI can be dissolved as a complex, there will be a solid precipitate of AgI. If the temperature is sufficiently low, this solid particle may nucleate the freezing of the droplet.

To put this process on a quantitative basis, suppose the particle to contain a mass m' of the nucleating agent and a mass m of the soluble salt, its molecular weight being M and its Van't Hoff factor i. To simplify matters we will assume that the nucleating agent is com-

pletely insoluble in the salt solution, and that there is no limit to the solubility of the hygroscopic component. We shall return to check the validity of these assumptions later.

When the mixed particle is placed in an environment at water saturation, as in a cloud, it becomes a solution droplet whose equilibrium size is determined by the condition that the lowering of vapor pressure due to dissolved salt should exactly balance the increase in vapor pressure due to surface curvature. The supersaturation in a normal cloud is so small that only the very largest particles will be able to grow to macroscopic droplets and this will not affect our conclusions. This process is treated in detail in standard texts on cloud physics (e.g., Fletcher, 1962, pp. 58–62) where it is shown, provided the total volume of the solution droplet is large compared with the original particle volume, that

$$R \simeq \left(\frac{3im\rho_0 kT}{8\pi\rho\sigma M}\right)^{\frac{1}{3}} \simeq 3.6 \times 10^2 \left(\frac{imT}{M}\right)^{\frac{1}{3}}, \qquad (1)$$

where R [cm] is the equilibrium radius of the solution droplet, ρ its density, σ its surface tension, and ρ_0 the density of water.

From (1) we can now calculate the mole fraction of water in the droplet, the result being

$$\mathfrak{M} \simeq 1 - \left(\frac{32\pi\rho\sigma^3 M_0{}^2 M}{3\rho_0{}^3 k^3 T^3 im}\right)^{\frac{1}{2}} \simeq 1 - 9.2 \times 10^{-8} \left(\frac{M}{imT^3}\right)^{\frac{1}{2}}, \qquad (2)$$

where M_0 is the molecular weight of water. In the interests of simplicity we will assume the solution to be ideal and the segregation coefficient for the salt to be so small that ice which freezes from the solution is essentially pure. The driving free energy, per unit volume of ice, tending to cause freezing at temperature $-\Delta T[^\circ C]$ is then (Fletcher, 1962, p. 220) approximately

$$\Delta G_v \simeq \overline{\Delta S}_v \Delta T + nkT \ln \mathfrak{M}, \qquad (3)$$

where $\overline{\Delta S}_v$ is the average entropy of fusion over the range from $-\Delta T$ to 0C and n is the number of molecules per unit volume in ice. Using the numerical form of (2) and assuming that $\overline{\Delta S}_v$ is not greatly dependent on the presence of the dissolved salt, we have

$$\Delta G_v \simeq 1.13 \times 10^7 \Delta T - 2.4 \times 10^{-2} \left(\frac{M}{im}\right)^{\frac{1}{2}} \text{[ergs cm}^{-3}\text{]}. \qquad (4)$$

Eq. (3), of course, simply expresses the lowering of the equilibrium freezing point due to the solute, while (4) relates this to the concentration of solute in the droplet under consideration when it is in equilibrium with an environment at water saturation. It is known from experiment (Pruppacher and Neiburger, 1963) that any anomalous effects due to the influence of dissolved ions upon the structure of water are relatively small.

3. Nucleation behavior

It is now a straightforward matter, on the basis of generalized curves for the nucleation behavior of particles of various shapes (Fletcher, 1963) and the empirical knowledge that the contact parameter m for AgI yields a freezing threshold of $-4C$, to calculate the nucleation threshold for a particle containing a mass m' of AgI (assumed to be a compact crystal) and a mass m of soluble material. If, for simplicity, we take the AgI particle to be spherical, then the nucleation behavior for various amounts of accompanying soluble material is as shown in Fig. 1. Very similar curves will be found for other reasonable assumptions about the shape of the AgI particle.

From Fig. 1 it is immediately apparent that the nucleation activity of small silver iodide particles which accrete water from the vapor because of the presence of hygroscopic impurities is much less pronounced than that of similar pure particles in suspension in bulk liquid. In the case of mixed particles, the actual fraction of hygroscopic component present is not of great importance over the usual range of smoke compositions.

We have, so far, neglected any complications which might occur because of the limited solubility of the hygroscopic salt or because of the finite solubility of the AgI in the salt solution. A summary of the available data on these points is given by Linke (1965). A saturated solution of KI at 0C contains 127.5 gm of KI in 100 gm of water ($\mathfrak{M}=0.79$) while the eutectic composition at $-23.2C$ has 107.8 gm KI in 100 gm of water ($\mathfrak{M}=0.81$). None of the solution droplets in the calculation reaches this concentration, so that it is correct to assume that all the KI dissolves.

Though silver iodide is virtually insoluble in pure water, it is soluble in aqueous solutions of KI or other iodides, the solubility increasing with the concentration
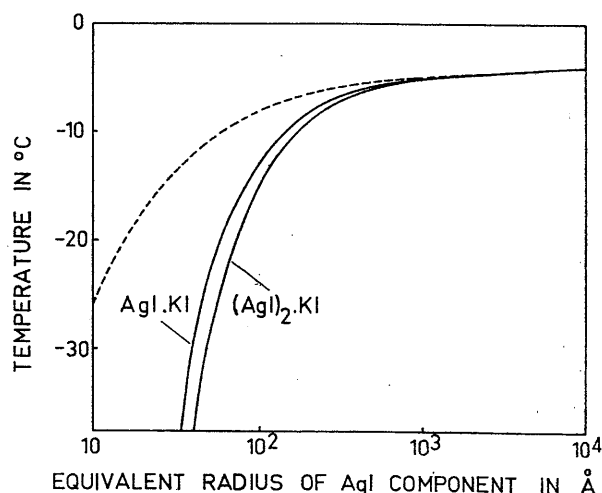

FIG. 1. Calculated nucleation thresholds for smoke particles of the composition shown in a cloud environment. The broken curve indicates the freezing threshold for AgI particles suspended in pure water.
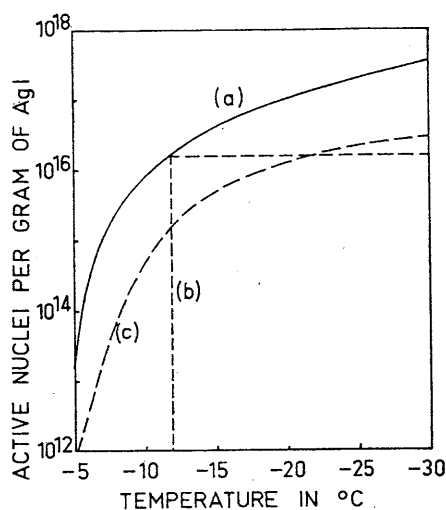
FIG. 2. Limiting activity curve (a) for a monodisperse smoke. The activity curve for such a smoke must be of the form (b), with a sharp threshold and touching curve (a) at only one point. A smoke with a broad spread of particle sizes must have an activity curve such as (c).

of the KI solution and with decreasing temperature. The most concentrated KI solution met in the calculations for Fig. 1 has $\mathfrak{M} \simeq 0.9$, which is equivalent to about 2 moles of KI per liter. Such a solution can dissolve about 0.2 moles of AgI per liter, so that only a very small fraction of the active nucleating material is dissolved and our neglect of this possibility is justified.

4. Nucleation activity of a smoke

With the fundamental nucleation curve of Fig. 1 established, we can now calculate the nucleation activity of any smoke of mixed $(AgI)_x \cdot KI$ particles for which the size distribution is known, the method being the same as that used previously (Fletcher, 1959a). In particular, we can calculate the limiting activity curve for a monodisperse aerosol as shown in curve (a) of Fig. 2. This curve gives the maximum number of nuclei active at a given temperature which can be produced from 1 gm of AgI in a KI-complexed solution. To reach a point on this curve the smoke must have a uniform particle size and will have an activity curve like (b) in Fig. 2, with no activity above the threshold temperature and a constant activity below. For a typical burner smoke, having a broad log-normal particle size distribution, the activity curve will always lie well below curve (a), and curve (c) is typical.

5. Conclusion

The limiting activity curve in Fig. 2, and hence any theoretical curve derived from it, is just about one order

of magnitude higher over its whole range than was the curve derived on the assumption of sublimation (Fletcher 1959a). This is very satisfactory since, though the earlier curve gave good agreement with measured activities for some generators, the apparent efficiency of others (notably the "Skyfire" burner) was much greater than 100%. With the present treatment the efficiency of the "Skyfire" burner approaches 30%, while other generators have efficiencies in the region of 10%. This is not an unreasonable situation, since any particles $\lesssim 100$ Å in diameter are effectively wasted, as are any particles much bigger than a micron since they produce only one ice crystal, no matter how large they may be.

The analysis we have carried out here makes no claim to rigor and many approximations have been made in the interests of simplicity. It does not seem likely that a much more careful treatment would modify the conclusions significantly and it would hardly be justified in view of some of the physical approximations made. The calculations were carried out for the case of a silver iodide/potassium iodide complex but the results make it plain that the behavior 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.

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