Repeated Nucleation of a Supercooled Water Sample that Contains Silver Iodide Particles

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ABSTRACT

Experiments have been carried out on the kinetics of ice nucleation at constant temperature in a sample of supercooled water containing particles of silver iodide. An automatic apparatus was used to record the various times that elapse before nucleation occurs. The results show ice formation to be largely a stochastic process whose probability of occurrence during a given time interval increases by a factor of over 4 for each degree Celsius of supercooling. This finding may have implications for the behavior of ice nucleating particles in the atmosphere.

1. Introduction

Considerations of the effects that can result from seeding with silver iodide particles are often based on estimates of the numbers or concentrations of nuclei that are "active" at a given temperature. Such estimates are made by observing the numbers of ice crystals that are produced when the silver iodide particles are introduced into a supercooled cloud at some temperature, or otherwise exposed to conditions in which supercooled water or water vapor supersaturated with respect to ice is present.

The number of silver iodide particles that act as nuclei is found to increase rapidly with decreasing temperature. At temperatures lower than −20°C, the number of ice crystals that forms approaches the total number of particles that are present. In this case, nearly all of the particles act as nuclei (Vonnegut, 1949). At higher temperatures, the number of ice crystals initiated by a given number or concentration of silver iodide particles decreases dramatically. At −10°C only one in 10^3 silver iodide particles introduced into a supercooled cloud in a cold box may give rise to an ice crystal.

There are several possible explanations for the fact that at higher temperatures some particles serve as nuclei while most do not. Undoubtedly, as is often assumed, some particles may be more effective as nuclei than others because they are larger in size or because they have surface sites that are more active. Some particles may be less active because their surfaces are covered with contamination.

While recognizing that silver iodide particles can vary greatly in their effectiveness as nuclei, Vonnegut (1949) preferred another way of explaining the fact that only a small proportion of the particles initiate ice crystals at higher temperatures. In accordance with classical theory (Becker and Doring, 1935; Volmer, 1939), he suggested that nucleation might be a stochastic process that depends on the chance formation of a stable assembly of molecules in the ice lattice configuration on the crystal surface of the silver iodide. If such a chance process plays an important role in nucleation, the fact that silver iodide particle A initiates an ice crystal, while particle B does not, may have little to do with differences existing between them. It may only signify that the event happens on particle A before it happens on particle B entirely by chance. If such chance events are important in the nucleation process, it is to be expected that in the course of time the chance event that occurs on A will also occur on B.

Laboratory experiments (Vonnegut, 1949) showing that ice crystals continue to form in a supercooled cloud for as long as 30 min after it has been seeded with silver iodide particles suggest that a stochastic nucleation process may be taking place. However, there are other conceivable explanations. For example, some of the silver iodide particles may require exposure to supersaturation for an extended period of time before they become active. Another possibility is that they must collide with the supercooled water drops before they can initiate ice formation.

It is difficult to determine from cold-box experiments with silver iodide aerosols and supercooled clouds whether stochastic processes are important in the nucleation of ice on the silver iodide crystal surface. We have, therefore, carried out a series of somewhat dif-

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ferent laboratory investigations. Instead of observing a very large number of individual nucleation events, each caused by a different particle, we have examined the behavior of a single sample of water containing silver iodide particles that is repeatedly frozen and thawed at various fixed and accurately known temperatures. This technique is well suited to the study of stochastic effects because repeated use of the same sample eliminates some of the uncertainties that arise when different silver iodide particles are involved in successive nucleation events. The range of time intervals that can be studied with cold-box experiments is limited because the dispersed aerosols of nucleating particles can change as the result of coagulation and deposition on the walls of the chamber. There is no limitation, however, to the length of the time scale that can be investigated with the repeated freezing technique. Nucleation events that occur after the lapse of a week or longer have been observed.

2. Experimental apparatus

The automatic device used in these investigations has been described in detail by Baldwin and Vonnegut (1982). The samples consisted of approximately 0.01 g of distilled water into which large numbers of small silver iodide particles in the size range of 10 μm had been added. The water and silver iodide were contained in a U-shaped borosilicate glass capillary tube approximately 0.5 mm in diameter (Fig. 1).

The experimental procedure began with the immersion of the U-tube containing water and nucleating material to a depth of 10 mm into a bath maintained at some fixed temperature below 0°C. The well-stirred bath of water and ethylene glycol was maintained by a thermostat at any desired temperature to an accuracy of ±0.1°C. When placed in the bath, the water and nucleating material contained in the glass U-tube rapidly cooled, coming to within 0.1°C of the bath temperature in less than 10 s. The U-tube was arranged so that it could be immersed in, or withdrawn from, the bath by an electromagnetic solenoid.

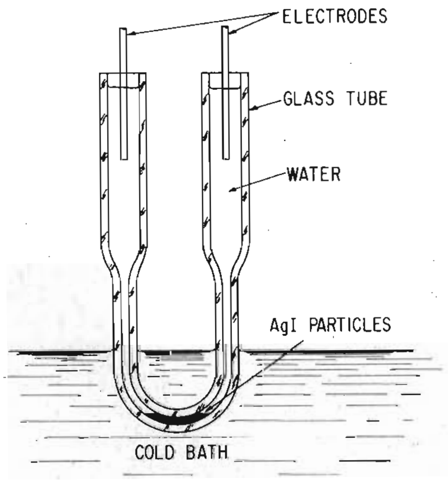

FIG. 1. Schematic diagram of glass capillary U-tube used for freezing experiments. The glass capillary tube is approximately 0.5 mm in diameter, and is submerged to a depth of 10 mm.

Studies of nucleation of a given sample could be carried out only over a limited temperature range of the bath. If the bath was too cold, the water froze very quickly, even before coming to the equilibrium temperature. If the bath was too warm, nucleation events became so unlikely that periods of weeks or longer might elapse before freezing took place. Accordingly, bath temperatures at which nucleation events occurred after intervals ranging from several seconds to several days after the capillary had been immersed in the bath, were chosen.

When nucleation occurred, ice crystals rapidly propagated through the supercooled water and the freezing was complete in a few seconds. The occurrence of freezing was readily detected by the large increase that it caused in the electrical resistance between two metallic electrodes immersed in the upper unfrozen portions of the water in the U-tube, which remained at room temperature. Upon freezing, the solidification of the water in the lower portion of the U-tube greatly impeded the movement of the ions and thus caused a sudden increase in electrical resistance. This abrupt change was detected by an electronic circuit that, by actuating the solenoid, withdrew the capillary from the bath. It then caused heated air from a hair drier to be blown over the lower portion of the tube and thus melted the ice. The operation of the hair drier was controlled by variations in the electrical resistance between the electrodes. The water in the U-tube was therefore warmed during each melting cycle to a fixed temperature estimated to be about 10–20°C. On melting of the ice, the solenoid was again deactivated, the sample reimmersed in the bath and the experiment repeated.

Data concerning the nucleation of the sample were recorded in two ways. A simple electromagnetic counter was actuated by each nucleation event. The average rate at which nucleation events occurred was determined by dividing the total number of events by the time period during which they occurred. Information on each freezing event was also provided by a clock which recorded the time interval that elapsed between the cooling of the sample in the bath and the sudden initiation of the ice phase.

In the publication describing the details of the apparatus, Baldwin and Vonnegut (1982) present the results of investigations on the nucleation of three samples of water inoculated with particles of silver iodide or silver–copper iodide. All of the samples showed similar behavior. At a constant temperature, the time required for nucleation was highly variable, and in all samples changes apparently took place in the behavior of the sample during the course of repeated freezings. Because Sample 1 changed the least and showed the most consistent behavior, it has been chosen to illustrate the stochastic nature of the freezing process, and the rapid increase in nucleation rate that takes place with decreasing temperature.

3. Experimental results

Figure 2 shows the time that elapsed before each of over 800 freezing events that occurred in Sample 1 at a bath temperature of −5.5°C. It can be seen that the time intervals before nucleation varied greatly. Sometimes the water froze only a few seconds after it had reached bath temperature, while at other times it remained unfrozen for periods of 5 min or more.

The distribution of the time intervals that elapsed before nucleation is illustrated in Fig. 3. It can be seen that the logarithm of the number of nucleation events that occur in each time interval decreases linearly with time.

Several months after the measurements shown in Fig. 3 were made, another series was carried out to determine how the rate of nucleation varies over a range of various fixed temperatures. For this series, the average time that elapsed before freezing is plotted as a function of temperature in Fig. 4.

4. Discussion and conclusions

It would be ideal in the studies carried out with this technique if the properties of the nucleating material in the sample remained entirely unchanged throughout the course of the experiments; however, this is evidently not the case. There are apparently long-term effects. A comparison shows that the average nucleation rate at −5.5°C shown in Fig. 4 is over an order of magnitude less than that indicated for the same sample at the same temperature in Fig. 3. This difference provides evidence that the sample decreased in its effectiveness as a nucleant during the several months that elapsed between the measurements. Apparently some change in the silver iodide particles occurred, perhaps as a result of slow rearrangements in the structure of their surfaces.

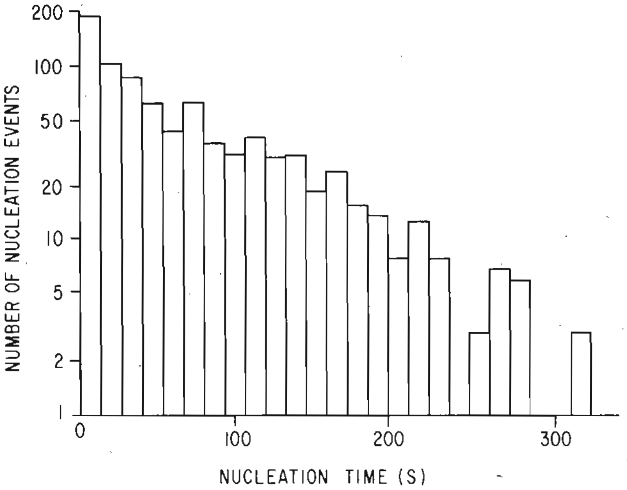

FIG. 3. Histogram on logarithmic scale showing how frequently the sample remained supercooled for various time intervals after being immersed in the bath at −5.5°C.

In addition to slow changes in the activity of the silver iodide surface, other more rapid changes were observed in the course of some experiments, such as those evident in Fig. 2. It will be noted that between trial numbers 210 and 260, rather abrupt changes occurred, and the sample froze almost immediately during nearly every trial. This anomalous period may be responsible for the slight excess of short times that can be seen in Fig. 3. Dorsey (1948) has noted similar behavior and suggested that nuclei can sometimes be changed as the result of the freezing process. This effect is not entirely unexpected, for the repeated propagation

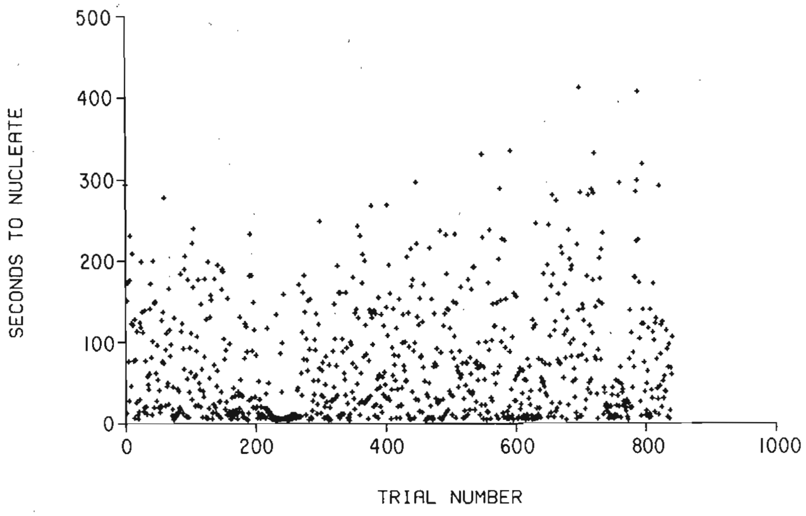

FIG. 2. Time intervals that elapsed before nucleation took place at −5.5°C.

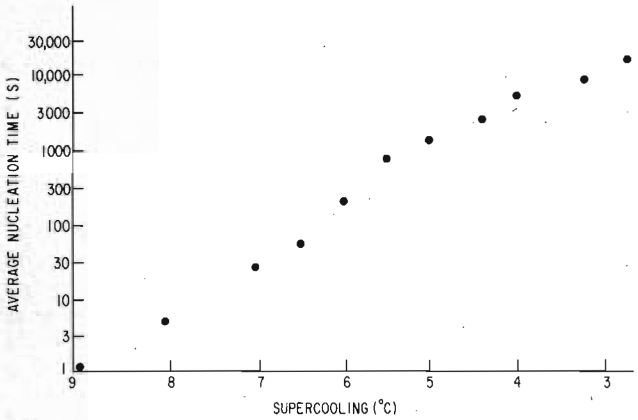

FIG. 4. Plot on a logarithmic scale illustrating the rapid increase in the average time elapsing before nucleation with increasing temperature. The average time lapses at the lower temperatures are based on hundreds of freezing events. Those at the higher temperatures, because they require much longer time lapses, are based on fewer points and are therefore more uncertain. The value for the highest temperature is based on only four freezing events.

of ice crystals through the mass of silver iodide particles will undoubtedly produce mechanical agitation that could affect their surface properties.

Even though the nucleating particles may be subject to some change during the course of the experiment, the behavior of the single sample as it is repeatedly immersed in the cold bath at different times can be approximated by the behavior of a large number of nearly identical samples immersed in the cold bath at the same time.

The nucleation of the sample appears to be quite similar to the decay of a radioactive atom, in that the probability that an atom will decay during a given time interval is invariant with time. If we consider the repeated nucleation of the same sample as nucleation occurring in a number of similar samples, the rate of nucleation is given by

$$dN/dt = -\lambda N, \qquad (1)$$

where N is the number of remaining unfrozen samples, t is the time, and λ is a constant of proportionality. In these experiments this constant is the average number of nucleation events occurring per unit time at a given supercooling. Integration of Eq. (1) gives

$$N = N_0 e^{-\lambda t}, \qquad (2)$$

in which N_0 is the initial number of unfrozen samples, and N is the number later at time t.

If the rate at which the samples nucleate is proportional to the number of samples, and that number is decreasing exponentially with respect to time, it is evident that the rate at which nuclei appear will also decrease exponentially with respect to time, as is indicated by Fig. 3. It is often convenient to think in terms of the half life of the supercooled sample, $T_{1/2}$, which is given by

$$T_{1/2} = 0.69/\lambda. \qquad (3)$$

Figure 4 shows that the average time required for the sample to freeze decreases rapidly with decreasing temperature. If the data in Figs. 2 and 3 are interpreted to indicate that silver iodide acts to increase the probability that the sample will freeze in a given time interval, this probability increases very rapidly with decreasing temperature. For each additional degree Celsius of supercooling, the probability that nucleation will take place during a given time interval increases by a factor of 4.6. This rate of increase is consistent with Vonnegut's (1949) measurements indicating that the half-life of 130–1400 Å diameter silver iodide particles in a supercooled cloud decreases by a factor of 4.8 per degree in the temperature interval −10 to −13°C.

As Pruppacher and Klett (1978) have noted, various other experiments on the heterogeneous nucleation of ice and supercooled water, based on the observation of numbers of independent supercooled droplets, have continued to give rise to divergent views concerning the nature of the process. For example, Bigg (1955) suggests that heterogeneous nucleation of a water drop is similar to homogeneous nucleation and is a stochastic process. On the other hand, Langham and Mason (1958) suggest that a drop has a definite freezing temperature which is determined by the characteristics of the most effective nucleating particle within it. The results of the experiments reported here, which are based on the repeated freezing of the same sample, appear to be more in accord with the predictions of the stochastic rather than the deterministic explanation.

In experiments with silver halide aerosols carried out in a large, carefully controlled, isothermal cloud chamber, Blumenstein *et al.* (1983) and DeMott *et al.* (1983) have shown that in the atmosphere nucleation can take place by at least four mechanisms, and have interpreted their findings by the use of chemical kinetic theory. It is evident from their analysis that the application of the results reported here to an understanding of the behavior of silver iodide particles in the atmosphere is complicated, and will depend on a variety of environmental factors.

If silver iodide particles in the atmosphere behave similarly to those in our experiments, ice crystal formation in supercooled clouds may depend not only on the characteristics of the individual particle, but also on the chance coming together of water molecules in the ice crystal lattice on the silver iodide surface. This process may take place only after the passage of a long period of time.

It is possible that other ice-forming nuclei present in the atmosphere may behave in a way similar to the silver iodide particles in our experiments. If this is true, the manner in which ice-forming nuclei will behave cannot be determined by subjecting a sample to brief and often unspecified periods of exposure to supersaturated conditions at various temperatures. Such tests will fail to differentiate between a population that contains a low concentration of particles that each has a high probability of causing nucleation, and a quite different population that contains a high concentration of particles that each has a much lower probability of causing nucleation during a given time interval.

In order to characterize a population of nuclei, it is necessary not only to measure the number of ice crystals that are produced at various temperatures, but also to measure the rate at which the ice crystals are produced and how that rate varies with time.

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