Time Lag in Ice Crystal Nucleation by Silver Iodide

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ABSTRACT

Measurements have been made of the time lag which silver iodide particles exhibit in the nucleation of ice crystals at temperatures between −8C and −16C. The time lag is approximately exponential, the decay constants being 3.6 minutes and 1.4 minutes at −8.5C and −15.5C, respectively. The decay constant at −15.5C is less by a factor of 4.5 than that for natural ice nuclei. The observed time lag is in qualitative agreement with Fletcher's theory.

1. Introduction

The apparent time lag in the nucleation of ice crystals by silver iodide was first noted by Vonnegut (1948). It was observed that when a sample of silver iodide smoke was injected into a supersaturated supercooled atmosphere, ice crystals formed on these smoke particles and that measurable numbers of new crystals were still forming 30 minutes after the smoke had been injected. Several possible causes for such time lag were discussed by that author.

More recently, the nucleation of ice on natural freezing nuclei in the atmosphere at temperatures between −19C and −24C has been investigated empirically by Warner and Newnham (1958). It was found that some of the particles nucleated more rapidly than others and a time constant for the lag in nucleation by these nuclei was determined. The time constant of 6.3 minutes was about the same as the theoretical value predicted by Fletcher (1958). Fletcher attributed this apparent time lag to characteristics of the nucleation process for ice on a distribution of particles having various physical and chemical properties, and indicated further that the time constant should vary with the degree of supercooling.

The present report describes an investigation of time lag in ice nucleation by a silver iodide aerosol in the temperature range −8C to −16C.

2. Experimental Equipment and Procedures

Two types of silver iodide cloud seeding generator were used, both burning a solution prepared in the following way: one part by weight of sodium iodide was dissolved in five parts of acetone; then four parts of silver iodide were dissolved in this solution and finally diluted with 50 parts of acetone.

The first generator was that used in Commonwealth Scientific and Industrial Research Organization (CSIRO) cloud seeding experiments on aircraft (Smith *et al.*, 1958). It was fitted to a suitable air blower for ground operation. The consumption of solution was 9 liters per hour corresponding to 9.2 grams of silver iodide per minute.

In the second burner, the silver iodide solution was atomized with a paint spray gun using compressed air at 2.5 atmosphere pressure. The atomized solution was sprayed at a rate of 1 liter of silver iodide solution per hour (1 gram of silver iodide per minute) from a range of 10 cm into the flame of a large kerosene blow lamp which burnt 2 liters of kerosene per hour. This was the generator used by Smith and Heffernan (1954) for measurements of decay rates of AgI nuclei.

Dilution of the AgI smoke to a level where measurements could be easily carried out was made by feeding the smoke from the burners directly into a large mixing tunnel where the airflow was 10^6 liters per minute. Further dilution was obtained by sampling 1 liter of air from the end of the mixing tunnel and combining it with 100 liters of clean air in a sealed container. The concentration of silver iodide in this 100 liter box was approximately 10^{-10} gm cm^{-3} of air.

The apparatus used for measuring the time lag in the ice nucleation was a modified cold box of the Bigg-Warner (1957) type used as a mixing chamber. For these measurements, a mixing chamber had to be used in preference to an expansion chamber so that the lifetime of the cloud in which the crystals grew could be controlled. The cold chamber consisted of a 10-liter cylindrical copper tank with a perspex viewing lid. A persepex ring containing six 2-inch diameter brass trays covered by a rotatable disk was placed in the bottom of the tank. The disk mechanism enabled one tray to be exposed at a time (see Fig. 1). The six trays and rotating mechanism were placed in the tank and cooled to the

required temperature. This took approximately 10 minutes. All six trays contained an aqueous sugar solution, the specific gravity of which was controlled (Table 1), so that at the operating temperature the sugar solution did not nucleate spontaneously and the crystals which formed in it grew in diameter at approximately 1.5 mm per minute. A supercooled cloud of water vapor was maintained in the chamber by inserting, and changing at 5-min intervals, a semipermeable membrane (Schaefer, private communication 1960), containing 35 cc of distilled water at a temperature of 20C. Air temperature in the cold chamber was measured with a mercury-in-glass thermometer resting on the bottom of the chamber. The change in air temperature with depth in the cold box is given by Warner (1957).

When the operating temperature had been reached and maintained for 1 minute, a sample of the nuclei under test was injected into the fog by means of a syringe. These samples which varied in size from 2 cc to 30 cc were taken by syringe from the 100 liter light-sealed box which had been filled with a sample of smoke produced from the generator. The first of the trays in the cold box was then uncovered. Ice crystals produced in the fog by the injected sample grew, and some, assumed to be a representative sample, fell on the collecting surface. The time of fall of a 15μ ice crystal from the top of the tank to the collecting surface is about 20 seconds.

After a given time, usually 2 minutes, the crystals in the first tray were counted and the covering disk rotated to expose a second tray. This procedure was repeated for successive trays in each sequence of six. The dilution of the silver iodide smoke was controlled so that when the sample was injected into the chamber, about 100 crystals were observed in the first tray. By using graded time intervals, depending on the number of crystals in each tray, observation times of up to 20 minutes could be obtained, trays with few crystals being used twice. During this time 6 to 10 readings were obtained. Each of these readings is represented by one point of Figs. 2 and 3 derived in the manner described in the next section. In all observations care was taken to prevent ice formation on the cylinder walls, trays and exposing mechanism, by coating them with a film of glycerine before each experiment.

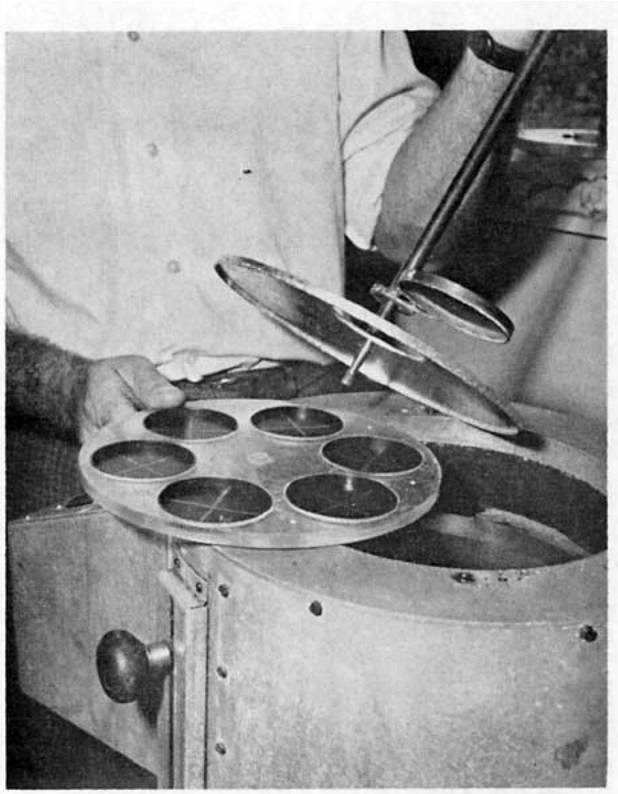

FIG. 1. Apparatus for measurement of time lag in nucleation showing the six brass trays with covering and rotating mechanism.

TABLE 1. Specific gravity of sugar solution used for ice crystal detection as a function of cold-box temperature.

Specific gravity	Temperature
1.13	−5C
1.18	−10C
1.23	−15C
1.28	−20C

TABLE 2. Acetone AgI generator. Number of ice nuclei per gram active at various degrees of supercooling.

Number of active freezing nuclei per gram	Temperature
2×10^{10}	−6C
4×10^{11}	−8C
4×10^{12}	−10C
2.5×10^{13}	−12C
10^{14}	−14C
3×10^{14}	−16C
7×10^{14}	−18C
10^{15}	−20C

No corrections have been applied to the results to account for natural nuclei in the atmosphere as the number of crystals formed from the silver iodide was greatly in excess of the natural nucleus count.

Measurements of the total number N, of the silver iodide ice nuclei per gram active at temperatures T, ranging from −6C to −20C were also made. The same experimental arrangement was used for the burners as in the time lag measurements, but the cold chamber had one large tray of sugar solution in it instead of the six-tray device used before.

3. Results

The numbers of ice nuclei per gram found active at various temperatures for the aerosol obtained from the

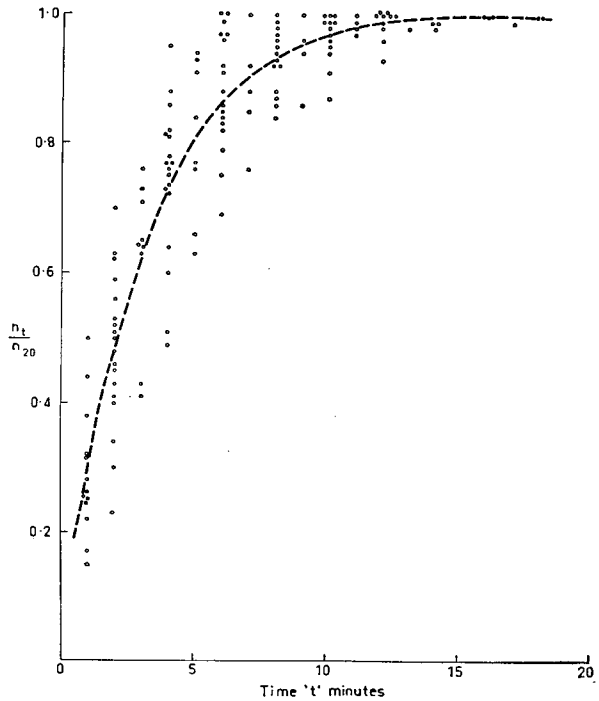

FIG. 2. The ratio of number of ice crystals formed in time t to that formed in 20 minutes in the temperature range −8C to −9C. AgI nuclei produced in acetone generator.

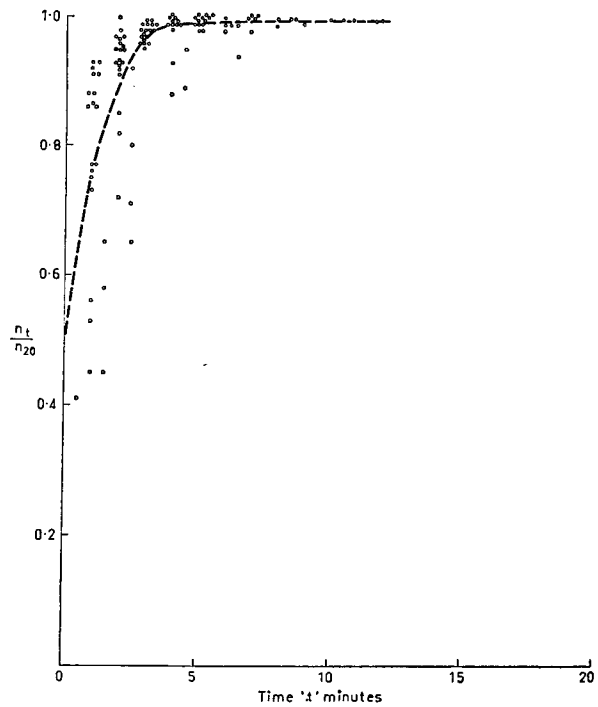

FIG. 3. The ratio of number of ice crystals formed in time t to that formed in 20 minutes in the temperature range −15C to −16C. AgI nuclei produced in acetone generator.

acetone burner, are given in Table 2. The kerosene burner produced approximately half these numbers. The curves obtained from plotting the results are similar in shape to each other and to those of other workers (Isono *et al.*, 1960; Smith and Heffernan, 1954).

For the time-lag measurements, Fig. 2 shows n_t/n_{20}, the ratio of the number of crystals formed in time 't' to that formed in 20 minutes, as a function of the time 't' for the range of temperatures −8C to −9C. Fig. 3 shows the corresponding set of measurements in the temperature range −15C to −16C. Both curves show clearly the lag in nucleation which occurs with the AgI nuclei. The time lag is also seen to be greater at the warmer temperatures.

Similar results were obtained when nuclei formed by the kerosene burner were used for the study.

In all four cases the curves followed reasonably closely the same law as that of Warner and Newnham's data viz.,

$$n_t/n_{20}=A\,(1-e^{-t/B}).$$

The constants A and B of the equation are presented in Table 3. The values B represent the time constants with which the n_{20} values are approached asymptotically.

All these time constants are less than the value of 6.3 minutes obtained for natural nuclei at −22C by Warner and Newnham and the approximate 5-min value obtained for Vonnegut's silver iodide data.

The time constant at −8.5C is longer than that at −15.5C for both burners. Table 3 also shows that there is a consistent increase in the time lag for the nuclei produced by the kerosene burner compared with those of the acetone generator. This might be caused by such things as differences in generation temperature, particle size distribution or presence of hydrocarbon contaminants.

It is of interest to note in Fig. 3 that nucleation has virtually ceased after 10 to 11 minutes. This is in contrast to the 50 minutes as observed by Vonnegut and the 20 minutes observed for the natural nuclei. At the higher temperatures, for both burners, there are still significant numbers of crystals falling out up to 15 but not after 18 minutes. The observation by Vonnegut of continued nucleation up to 52 minutes at −17C may be related to the different method of AgI aerosol production.

4. Discussion

It has been suggested by Fletcher that the experimental scatter in values of n_t/n_{20} as observed byWarner and Newnham for natural freezing nuclei can be explained by the variation of nucleus activity distribution in the atmosphere. By this theory, the variation is signified by changes in the values of a parameter β, where β is defined by the expression $N_0=\lambda e^{-\beta T_0}$. In this expression N_0 is the number of nuclei having a characteristic nucleation temperature T_0 and λ is a constant.

For silver iodide, differentiation of the N-T curves

TABLE 3. Values obtained for constants in equation. $n_t/n_{20}=A(1-e^{-t/B})$

	Temp.	Constants A	B
Acetone burner	−8.5C	1.01	3.1
	−15.5C	1.01	0.9
Kerosene burner	−8.5C	1.08	4.1
	−15.5C	1.03	1.8

obtained from data in Table 2, gives the corresponding N_0' curves. These show that for any particular value of T_0' there is a value of β' represented by the slope of the curve at that point. The primed letters are used for the experimental AgI data.

β' changes with temperature in the following way; T_0' between −16C and −20C, average slope $\beta'=0.08$, T_0' between −12C and −16C, average slope $\beta'=0.19$, and T_0' between −8C and −12C, average slope $\beta'=0.46$. Hence the time lag at different temperatures should, if Fletcher's theory is to hold for the AgI case, increase with increase in temperature. This has been observed as shown in Table 3 for both acetone and kerosene burners. However the corresponding values of β' and the other constants of the equations are not in agreement numerically.

5. Conclusions

Time lag occurs in nucleation of ice crystals by silver iodide particles over the range of temperatures −8C to −16C. The time lag has a characteristic form in good agreement with that observed for natural nuclei and is in qualitative agreement with Fletcher's theory. The average time constant for the apparent lag at −15.5C is 1.4 minutes, which is less than that found for natural nuclei by a factor of 4.5. There is evidence of more time lag for particles of silver iodide produced with a kerosene burner than those from an acetone generator.

The time constant varies with the temperature of nucleation having an average value of 3.6 minutes at −8.5C. This temperature effect is in agreement with the predictions of theory.

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