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SECOND AUTUMN WORKSHOP ON
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CLOUD PHYSICS AND
ATMOSPHERIC ELECTRICITY

B. Vonnegut

State University of New York at Albany
Albany, U.S.A.

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SCIENCE

Abnormal Polarity of Thunderclouds Grown from Negatively Charged Air

C. B. MOORE, B. VONNEGUT, T. D. ROLAN, J. W. COBB, D. N. HOLDEN, R. T. HIGNIGHT, S. M. MCWILLIAMS, AND G. W. CADWELL

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G. W. CADWELL

Experiments were carried out in New Mexico to determine whether the electrification processes that lead to the formation of lightning in clouds are influenced by the polarity of the charges in the air from which the clouds grow. The normal, positive space charge in the sub-cloud air was reversed by negative charge released from an electrified wire, suspended across a 2-kilometer-wide canyon. On more than four occasions when the clouds over the wire grew and became electrified, they were of abnormal polarity with dominant positive charges instead of the usual negative charges in the lower part of the cloud. The formation of these abnormally electrified clouds suggests both that the electrification process in thunderclouds can be initiated and that its polarity may be determined by the small charges that are present in the atmosphere.

ALMOST AS SIGNIFICANT AS BENJAMIN Franklin's demonstration that lightning is a form of electricity is his observation "that the clouds of a thunder-gust are most commonly in a negative state of electricity, but sometimes in a positive state" (*1*, p. 42). Electrical measurements that have since been made all over the world confirm his finding and show that in nearly all thunderstorms there is a dominant negative charge in the lower part of the cloud. Measurements from airplanes (*2*) and balloons (*3*) show that there is usually also a dominant positive charge in the upper part of these clouds.

This strong bias of polarity has important consequences. The upper, positive part of the dipole attracts negative charge from the upper atmosphere to the top of the cloud by conduction. The lower, negative part of the dipole exports negative charge to the earth by lightning and by point discharge. As a result of these processes, the approximately 1000 thunderstorms that are continuously in progress over the earth bring about 1 kA of negative charge from the atmosphere to the earth. This current, as Wilson (*4*) perceived, is responsible for continuously maintaining a negative charge of about 0.5×10^6 C on the earth and an equal positive charge in the atmosphere.

Modern observations also confirm Franklin's finding that clouds are "sometimes in a positive state." During the usual thunderstorm, negative (downwardly directed, fine weather) electric fields beneath a cloud occur briefly, just after cloud-to-ground lightning (*5*), during gushes of heavy rain, and in the dying stage of the storm (*6*). Occasionally, storms occur that are electrically different from the usual ones. Gunn (*7*) reported several storms that produced sustained electric fields at the ground comparable in intensity to ordinary storms, but these fields were in the downwardly directed, fine weather direction with dominant positive charge aloft. This observation shows that the thunderstorm charge distribution can occasionally be the opposite of that usually encountered. Imyanitov *et al.* (*8*) have reported that the upper parts of some storm clouds have negative instead of positive charge. Data obtained from lightning-detecting networks by Orville *et al.* (*9*) and Rust *et al.* (*10*) provide evidence for the existence of storms that are abnormal in that most of the cloud-to-ground discharges bring down positive instead of negative charge (*9*, *10*).

A requirement of any theory of electrification is to explain why, with few exceptions, the electrical dipole in the cloud develops with positive charge uppermost and negative charge below. The various thunderstorm electrification mechanisms proposed can be divided into two classes, depending on the explanations for this charge distribution.

According to the first class, which is based on the so-called "induction," "influence," or "feedback" theories of thunderstorm electrification, the polarity of the dipole is determined by the polarity of weak space charges or electric fields that may be present in the atmosphere during the development of the cumulus cloud before it becomes a thunderstorm. It is possible that a cumulus cloud behaves as a high-voltage influence machine, such as the Kelvin water dropper (*11*) and similar devices developed later (*12*). If a cumulus cloud becomes electrified by a similar mechanism, the polarity of the thunderstorm will be determined by the polarity of the weak charges that are carried up into the

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C. B. Moore, T. D. Rolan, J. W. Cobb, D. N. Holden, R. T. Hignight, S. M. McWilliams, G. W. Cadwell, Langmuir Laboratory, New Mexico Institute of Mining and Technology, Socorro, NM 87801.
B. Vonnegut, Atmospheric Sciences Research Center, State University of New York at Albany, Albany, NY 12222.

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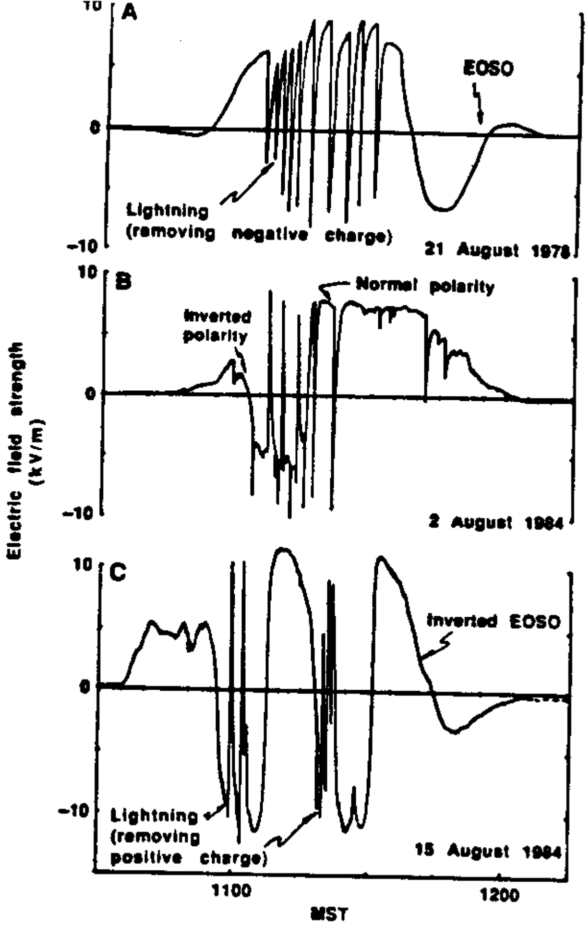

Fig. 1. Comparison of electric field records under a storm of normal polarity and under the abnormal ones observed during the experiments. (A) Normal polarity thunderstorm. [The time axis for (A) is not at the same MST as for (B) and (C), but the axes time ticks are all at 5-minute intervals.] (B) Inverted polarity thunderstorm. Record on 2 August 1984, showing electric fields of anomalous polarity produced by first of two thunderclouds. (C) Inverted polarity thunderstorms. Record on 15 August 1984, showing electric fields of anomalous polarity produced by two successive thunderclouds.

cloud and that initiate the electrification process during the early stages of the cloud's development. The air from which a cumulus cloud grows almost invariably contains the slight positive space charge present in fine weather. Therefore, if an influence mechanism is active and electrification occurs, positive charge will be in the upper, and negative charge in the lower, part of the cloud. Examples of cloud electrification mechanisms that are initiated by preexisting charges or fields include those based on inductive charge transfer between colliding cloud particles (*13*), on selective ion capture by falling precipitation (*14*), and on the formation of screening layers of charged particles at the cloud surface that are transported by convection to form charged regions (*15*).

According to the second class of mechanisms, the initial space charge and electric fields play no part in the development of electrification. In these mechanisms, the polarity of the charge separation process is determined by other variables, such as the phase, concentration, temperature, size, surface characteristics, or purity of colliding or breaking cloud particles. Mechanisms of this type include those based on breaking drops (*16*), glazing of ice particles (*17*), and ice impaction (*18*).

Both classes of explanations must also account for the exceptions—how it is possible that occasionally a thundercloud has negative instead of positive charge uppermost. With mechanisms of the first class, a thundercloud of inverted polarity could develop if the air it grows from contained negative instead of positive space charge. Though uncommon, this is sometimes the case in dust storms (*19*), over breaking freshwater waves (*20*), over waterfalls (*21*), and in the vicinity of another cloud that has already become electrified (*22*). The polarity of the feedback process may also be determined by other factors such as electric fields of external origin or fields developed from within the cloud by the falling of electrified precipitation.

A cloud of inverted polarity could form with the second class of mechanisms if changes occurred in variables, such as cloud particle population, temperature, or impurity concentrations, that reversed the polarity of the charge acquired by precipitation. Saunders *et al.* discussed such a possibility (*23*).

The predictions of influence mechanisms can be tested by determining whether the incidence of clouds having dipoles of inverted polarity is increased if the air from which they grow is artificially supplied with negative space charge. Negative, or positive, charge in the form of ions can be introduced into the atmosphere by corona discharges from an elevated wire that is maintained at a high d-c potential (*24*). Sufficiently large amounts of negative space charge can be released to reverse the polarity of the space charge and electric field for distances up to several kilometers downwind of the wire (*25*).

To our knowledge, before the work reported here, the most extensive experiment to determine the effects produced on clouds by the release of negative space charge was carried out during 1960 in central Illinois (*26*). During that experiment, when the atmosphere was unstable and fine weather cumuli were forming, observations from an airplane instrumented with electric field and charge-measuring equipment showed that space charge released from the wire and carried up into the clouds caused significant changes in the electrical properties of the clouds. When positive charge was released, the upper part of the cloud became positive, and the lower part became negative. When negative charge was released, the upper part of the cloud became negative and the lower part became positive. Evidently the charge carried into the cloud by updrafts attracted the opposite sign of charge by conduction from the surrounding clear atmosphere. This charge was then carried by downdrafts to form the charge center in the lower part of the cloud. The electric field intensities above the modified clouds were as great as 400 V/m. Though these fields were several times more intense than those produced by unaffected clouds nearby, they were weak compared to those in a thunderstorm.

These Illinois experiments showed that the polarity of electrification of a fine weather cumulus can be determined by the polarity of the space charge in the air from which the cloud forms. Under the wind conditions at the time, however, none of these clouds ever grew and became a thundercloud over the charge source.

Further studies in New Mexico were carried out during the summers of 1984 and 1985 to determine whether the inverted dipole observed when negative charge was being released would persist and intensify if the cloud grew and became a thunderstorm. Langmuir Laboratory in the Magdalena Mountains near Socorro, New Mexico, was chosen as the site for these experiments. The probability that a thundercloud will form in that area is higher than at most other locations. Because the speed of the wind there is often low, clouds sometimes form and develop into a thunderstorm without moving more than a few kilometers. Equally important, electric field records made over the past 20 years show that in the summer when an isolated cloud near the laboratory develops and becomes a thunderstorm, the lower part of the cloud invariably carries a negative charge.

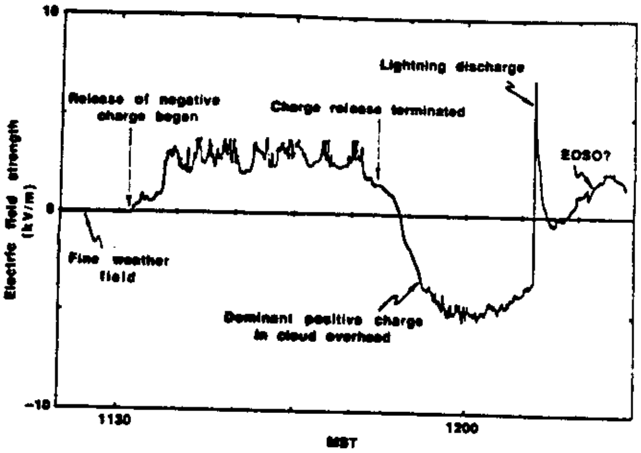

Fig. 2. Record showing electric fields of anomalous polarity produced by a small thundercloud on 24 July 1985. The lightning discharge, which was 2 km to the east of Langmuir Laboratory, removed the positive charge from the cloud.

The technique used to release negative charge in New Mexico was similar to the earlier one in Illinois. A 2-km-long wire was suspended on insulators between two mountain peaks. The catenary, approximately 400 m above the canyon floor, released negative ions by corona discharge when it was raised to a high negative potential with a d-c power supply. With the usual winds of a few meters per second, the flux of charge emitted into the atmosphere was of the order of 400 μA when the wire potential was about 120 kV.

Each morning when cumulus clouds began to form under the influence of solar heating, the apparatus was put into operation. Negative charge was released from the wire until the clouds nearby became so strongly electrified they threatened to produce lightning that could damage the power supply.

Measurements made downwind of the wire before a cloud formed showed, as in the Illinois experiments, that beneath the plume of space charge the polarity of the electric field had been reversed and its intensity had increased by tenfold. The area affected by the charge release was small, probably no more than a few square kilometers. As experiments have shown, the charge leaks to ground at a rate determined by the electrical time constant of the ambient atmosphere (*25*). Near Langmuir Laboratory the relaxation time was of the order of 3 minutes, so the charge would leak away if it were not rapidly carried into the cloud where the time constant is much longer.

An array of six field meters extending along the mountain ridge for 2 km was used to measure the electric fields of thunderclouds. Data from this equipment were supplemented by other electrical observations, which included the field changes produced by lightning and measurements made from an instrumented airplane and a free balloon carrying an electric field meter.

On several days during the period of the 1984 experiment, clouds developed into thunderstorms near or over the source of negative charge. On two of these days (2 and 15 August), the humidity was so high that the base of the cloud forming over the mountain was below the summit, and the upper portions of the electrified catenary were in the clouds. On these days the negative space charge released from the wire reversed the atmospheric electric field over the summit for 40 minutes or more, and then, as the clouds developed above, all of the field meters began to indicate an intensifying positive charge overhead. A few minutes later (on each day), lightning discharges to ground occurred near the wire and removed positive charge from the cloud overhead. A second, similar, cloud-to-ground flash occurred about 3 minutes after the first one on each of the 2 days. The electric field records for these two storms are shown in Fig. 1. For comparison, the record for a natural thunderstorm is shown, which, being of normal polarity, had negative charge in the lower part of the cloud and produced several lightning flashes that lowered negative charge to ground.

On 2 August, the anomalous, positive charge in the lower part of the cloud that formed over the site extended over a distance of more than 2 km during a horizontal penetration by the instrumented airplane. The plane started this penetration at 1101 MST and flew from north to south at an altitude of 4700 m. In a continuing penetration through another cloud to the southeast, indications of negative instead of positive charge above the airplane were recorded. At 1110:25 MST, a third lightning discharge to ground again removed positive charge from the lower part of the cloud over the site. This cloud then merged with two larger clouds of normal polarity that had been growing about 2 km away, the one to the southeast and another to the north. The combined system produced three more cloud-to-ground discharges of normal polarity that removed negative charge from the lower regions of the merged clouds before they began to dissipate.

On 15 August, the active cloud overhead subsided after its second anomalous discharge; its electric field thereafter exhibited the first part of the "end-of-storm oscillation" (EOSO) signature in which the charge in the upper part of the thundercloud dominates the surface electric field as the cloud descends and inverted convection occurs (*6*). The remarkable feature on 15 August was that the upper charge during this EOSO was negative instead of the normal positive polarity. Before the end-of-storm sequence was completed, a second cloud turret developed over the east end of the cable, and it too was inverted in polarity, producing three cloud-to-ground discharges that removed positive charge from the cloud's lower regions. The second cloud then subsided and again exhibited an inverted, EOSO, electric field signature.

The instrumented airplane flew through the top of the first turret around 1058 MST at an altitude of 7770 m. The rotation of the electric field vectors as the airplane approached and then penetrated the cloud turret indicated the presence of a dominant negative charge just beneath the plane. (A later analysis of the electric field record during this pass suggests that about 1 C of negative charge was involved.) The electric field intensified abruptly as the aircraft entered the turret and weakened similarly as it departed; this behavior may have been produced by a screening layer of positive charge around the negatively charged cloud top.

The instrumented free balloon (at an altitude of 5500 m) indicated the presence of positive charge between the balloon and the earth. A vertically scanning Doppler radar on the mountain top showed strong downdrafts and precipitation falling from near the cloud top to the cloud base.

One interpretation of these observations is that the upper negative charge came from 2 C or more of negative charge released into the cloud base by the electrified wire during the growth of the cloud. The positive charges in the lower regions of the cloud may have been derived from the positively charged screening layers around the cloud top carried downward by downdrafts and by falling precipitation.

The charge release experiment at Langmuir Laboratory was repeated during the summer of 1985. Though far fewer clouds that were suitable for experimentation formed than in 1984, anomalous distributions of charge were again observed in clouds growing from the region of negatively charged air. Several clouds growing over the negative charge source developed extensive regions containing positive charge in their lower portions. An example is shown in Fig. 2. The measurements reported for 1985 were made with ground-based equipment because the instrumented airplane and balloon systems used in 1984 were not available.

It is conceivable that the abnormal polarity of electrification exhibited by these storms may have been an unusual natural occurrence that was not related to the artificial release of negative space charge during the growing period of the thundercloud. This is unlikely, however. Observations in this region of New Mexico over the past 20 years show that this polarity of electrification very rarely, if ever, occurs naturally in isolated clouds. Of the approximately 1000 thunderstorms whose electric fields have been observed, no isolated cloud above us has exhibited abnormal polarity. That three abnormal storms would have occurred by chance during a 2-week interval seems highly improbable.

The idea that the electrified wire powered by less than 100 W could influence the development of a thundercloud that produces 100 MW may at first strain credulity. However, if the electrification of a thundercloud is brought about by a feedback process similar to that acting in a laboratory influence machine, this growth of charge in the thundercloud can reasonably be expected. In describing his laboratory experiments, Kelvin (*11*, p. 69) wrote, "It is curious, after commencing with no electricity except a feeble charge in one of the jars, only discoverable by a delicate electrometer, to see in the course of a few minutes a somewhat rapid succession of sparks pass in some part of the apparatus . . . ." Just as his apparatus supplied with mechanical energy was capable of multiplying the "feeble charge in the jar" until it produced sparks, so the growing cloud supplied with energy from the atmosphere should be able, by electrostatic induction, to multiply either naturally occurring positive space charge or artificially introduced negative charge until the resultant electric field becomes sufficiently intense to produce lightning. The fine weather electrical process, which may usually initiate thunderstorm electrification, involves a current of only 1 μA and a power of <1 W for each square kilometer.

That the charge released from the wire could have influenced the polarity of the much larger charges forming later in the thundercloud indicates that the electrification process can be of the "feedback" or "influence" kind. It appears that on some occasions enough of the negative charge from the wire is carried up into the cloud to overbalance the other factors that normally determine the electrical polarity of thunderclouds.

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Production of Ice Crystals by the Adiabatic Expansion of Gas

BERNARD VONNEGUT
General Electric Research Laboratory, Schenectady, New York
July 15, 1948

IN experiments on a supercooled cloud produced in a home freezer, V. J. Schaefer[1] showed that at temperatures of -38.9°C or lower water vapor spontaneously forms ice crystals in very large numbers. By the adiabatic expansion of air in a Wilson cloud chamber, B. M. Cwilong[2] found, similarly, that ice crystals were produced at temperatures below -35°C. Simple and interesting experiments can be performed by a combination of these two techniques.

A child's pop gun fired into a supercooled cloud in a cold chamber produces very large numbers of ice crystals. The adiabatic expansion of the air as it is released from the gun reduces its temperature to below -38.9°C, with the consequent production of large numbers of ice crystals. If the cork is not put into the gun tightly enough, the temperatures produced are above -38.9°C and no ice crystals result.

In order to rule out the possibility that the loud noise from the pop gun might have caused nucleation, a mixture of potassium chlorate and sulfur was exploded in the supercooled cloud. Although the report was far louder than the pop gun, no ice crystals were observed.

A bottle of carbonated beverage having sufficient pressure produces large numbers of ice crystals when it is suddenly opened in a supercooled cloud. Bottles of carbonated drinks kept in the freezing compartment of a household refrigerator often become supercooled. Frequently, these bottles do not freeze until the cap is removed. If such a bottle is watched as the cap is removed, many ice crystals can be seen to form at the surface of the liquid and spread throughout the bottle. A miniature snow storm produced in the gas in the neck of the bottle starts the crystallization of the contents. It has been observed that a bottle of supercooled beverage can be caused to freeze by tapping the surface of the container. Such a tap undoubtedly causes adiabatic compression and expansion of any minute bubbles in the liquid which could momentarily reduce their temperature to below -38.9°C, thus starting the formation of ice crystals.

The vapor trails which sometimes stream off the propeller tips and wings of airplanes flying at low temperatures probably are similar to the foregoing phenomena. As the propeller or wing passes through the air, it causes adiabatic expansion of the air in certain regions. If the temperature of the atmosphere is sufficiently low, this expansion will momentarily reduce the temperature to a value at which ice crystals form spontaneously. If the atmosphere is supersaturated with respect to ice, these ice crystals will grow into a visible vapor trail.

The surprisingly large number of ice crystals produced by the rapid expansion of even a small quantity of air can be shown by bursting a small rubber balloon in a supercooled cloud. A balloon about 1.5 mm in diameter when burst in a supercooled cloud at -20°C produces at least 3×10^7 snow crystals, or about 1.6×10^{10} crystals per cc of expanded air.

Experiments under carefully controlled conditions are being conducted in this laboratory by V. J. Schaefer to determine quantitative relationships between the number of crystals produced and the temperature, pressure, volume, and humidity of the expanded air.

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Importance of Including Time in the Specification of Ice Nucleus Concentrations

B. VONNEGUT
State University of New York at Albany, Albany, NY 12222

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It is generally recognized that the number of ice crystals that will be nucleated by foreign particles in a supercooled cloud is dependent not only on temperature, but also on time (Vonnegut, 1948; Vonnegut, 1949; Turnbull, 1950; Fletcher, 1958; Warburton and Heffernan, 1963; Isaac, et al., 1972; Schaller and Fukuta, 1979; Baldwin and Vonnegut, 1982; DeMott et al., 1983; Wang and Vonnegut, 1984). Notwithstanding, in most measurements of ice nucleus concentrations, such as those recently reported by Bowdle et al. (1985), only the supercooling, or supersaturation with respect to ice, is specified. In accordance with the prevailing custom, no information is provided concerning the *time* that the particles were exposed to supersaturated conditions.

In the case of measurements made at low temperatures on fast acting nuclei, such as silver iodide particles, this failure to specify time may have some justification, for practically all of the particles will serve as nuclei during even a brief exposure in a supercooled cloud. According to Langer and Rodgers (1975), whose technique was used, at −20°C the silver iodide particles acted to nucleate ice crystals "immediately." This is consistent with Vonnegut's (1949) estimate that at this temperature half of the silver iodide particles present will initiate ice crystal formation every few seconds.

On the other hand, the time of exposure cannot be neglected when measurements are made at higher temperatures and much longer intervals may be required for a particle to initiate ice formation. In this case the time interval required for nucleation may be much greater than the time of the test. For example, even silver iodide, which acts faster than most atmospheric nuclei, has been estimated to have a half life as long as hours at −13°C and days at −10°C (Vonnegut, 1949). When the half life is long, the fraction of particles that forms ice crystals over a period of an hour or more in a natural cloud may be many times larger than the fraction that acts in the brief time involved in many nucleation determinations. Failure to take this into consideration may be one of the several reasons that the concentration of ice crystals in a supercooled cloud is sometimes larger than the measured concentration of ice forming nuclei (Mossop, 1985).

Evidently, comparisons between the concentration of ice crystals in a supercooled cloud and the measured concentration of ice nuclei are valid only if the times of exposure as well as the temperatures are equivalent. It is desirable that Bowdle et al., and others who report measurements of ice nucleus concentrations, supply not only the temperature and supersaturation to which the nuclei were exposed, but also the time. This will provide some indication of the natural conditions for which their measurements are relevant.

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

BERNARD VONNEGUT AND MARK BALDWIN

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

BERNARD VONNEGUT AND MARK BALDWIN[1]

State University of New York at Albany, Albany, NY 12222

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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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[1] Present affiliation: Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195.

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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.

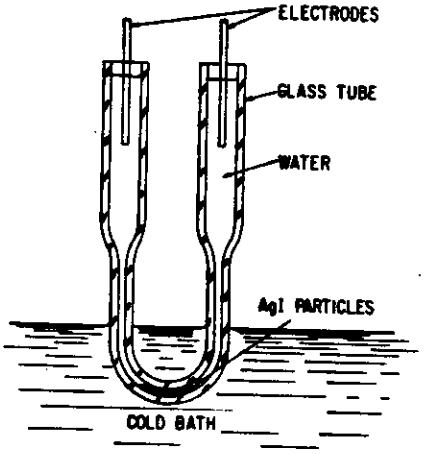

FIG. 1. Schematic diagram of glass capillary U-tube used for freezing experiments. The glass capillary tube is approximately 0.5 mm in diameter, and is submerged to a depth of 10 mm.

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.

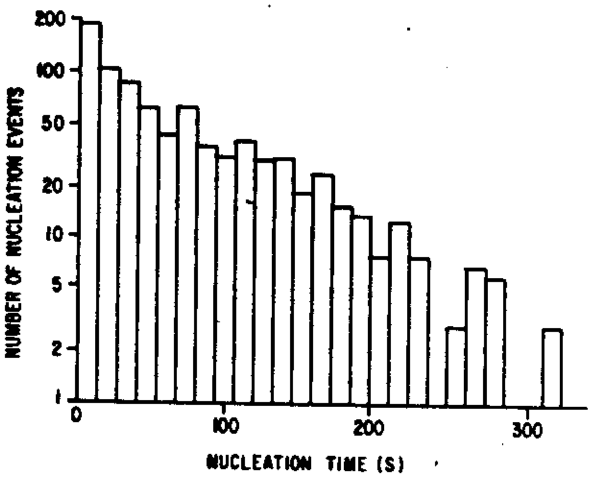

FIG. 3. Histogram on logarithmic scale showing how frequently the sample remained supercooled for various time intervals after being immersed in the bath at −5.5°C.

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

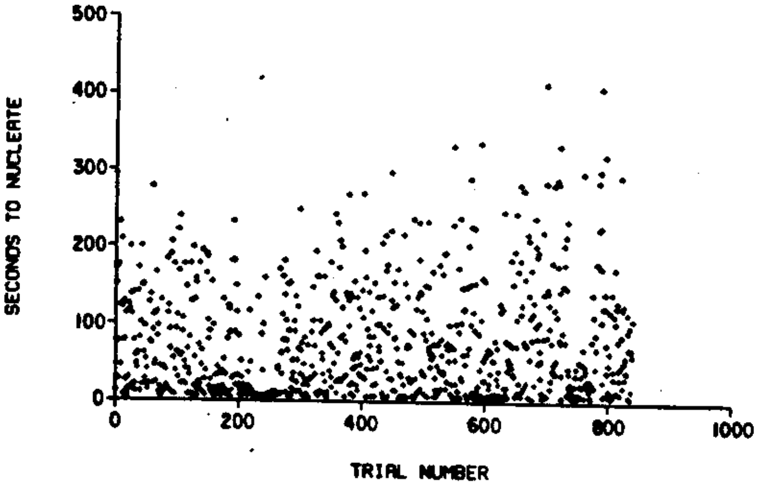

FIG. 2. Time intervals that elapsed before nucleation took place at −5.5°C.

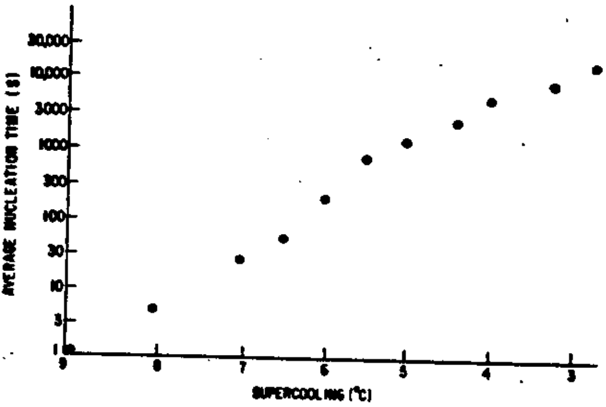

FIG. 4. Plot on a logarithmic scale illustrating the rapid increase in the average time elapsing before nucleation with increasing temperature. The average time lapses at the lower temperatures are based on hundreds of freezing events. Those at the higher temperatures, because they require much longer 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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Ice Nucleation by Solid Solutions of Silver-Copper Iodide

Abstract. *The lattice misfit between ice and silver iodide can be reduced by partial substitution of copper atoms for silver atoms in the silver iodide lattice. The best crystal match is obtained with a composition of CuI-3AgI, which corresponds to the most active silver-copper iodide nucleation catalyst.*

Vonnegut and Chessin (*1*) showed that a solid solution of 30 mole percent AgBr in AgI causes nucleation in supercooled water at about half the supercooling required for nucleation by pure AgI. According to the nucleation theory of Turnbull and Vonnegut (*2*), this improved nucleation ability can be attributed to the fact that while the AgI crystal lattice is 1.5 percent larger than that of ice, the lattice of a solid solution with 30 mole percent AgBr in AgI is only 1.0 percent larger. Presumably AgI-AgBr solid solutions with even smaller lattice misfits should be even better nucleation catalysts. However, 30 mole percent is apparently the limit of solubility of AgBr in the AgI lattice, so 1.0 percent is the minimum lattice disregistry that can be obtained with AgI-AgBr solid solutions. The disregistry, δ, is defined as $(a - a_0)/a_0$, where a and a_0 are the respective lattice parameters of the catalyst and ice along similar low index planes.

In searching for solid solutions of AgI for which we could control the lattice parameter, our attention turned to CuI-AgI. We have prepared CuI-AgI solid solutions, each having a lattice parameter smaller than that of pure AgI by two techniques. The first was direct fusion at a pressure of 10^{-2} torr and a temperature of 20°C above the melting point of the solid solution, about 600°C. The second involved dissolving the proper proportions of reagent grade CuI and AgI in hydriodic acid and then boiling off the solvent. The crystal class of the resulting solid solutions is face centered cubic, but in the (111) plane the crystal structure is similar to that of ice in the (0001) plane. The lattice spacing in the (111) plane is given by $a\sqrt{2}/2$, where a is the edge of a unit cell in the cubic system. The x-ray data in Fig. 1 show that by varying the mole percent of CuI in AgI, a solid solution can be made to have any lattice spacing from 4.58 to 4.28 Å measured in the (111) plane. This range in lattice spacings corresponds to lattice disregistries with respect to ice ranging from 1.5 percent to − 5.2 percent. Since CuI and AgI are not appreciably soluble in water (10^{-5} and 10^{-8} mole/liter, respectively), they have a negligible effect in depressing the freezing point of the water.

To determine their relative effectiveness as nucleation catalysts, powdered samples of about 0.5 g of CuI-AgI were sealed in dilatometers containing approximately 1 g of distilled water, and the freezing temperature was observed when they were cooled in a vigorously stirred bath. The temperature was measured with a Beckman thermometer with an accuracy of 0.01°C and was lowered at a rate of 0.5°C min^{-1} (*3*). The water was singly distilled and had a conductivity of 3×10^{-6} ohm^{-1} cm^{-1}.

Figure 2 shows the observed threshold nucleation temperature as a function of composition for ten samples of both the fusions and the precipitates. The fusions were tested after having been in water for about 1 month. The precipitates were tested immediately after having been immersed in water. Reduction of the cooling rate from 0.05° to 0.01°C min^{-1} produced no observable differences in threshold nucleation temperatures.

Figure 3 shows the smallest observed supercooling for the CuI-AgI fusions and precipitates, as a function of lattice disregistry with respect to ice. The disregistry is computed for the (111) plane of the CuI-AgI solid solution and the (0001) plane of ice. Vonnegut and Chessin's data for the AgI-AgBr solid solutions are also shown, along with Turnbull and Vonnegut's theoretical curve for coherent nucleation.

The fact that the temperature of − 2.5°C we measured for nucleation in the presence of pure CuI is appreciably higher than the value of − 15°C reported by Mason and Hallett (*4*) probably can be attributed to the very different conditions under which the observations were made. That the CuI-AgI catalysts precipitated from HI were generally more active than the fused CuI-AgI catalysts could be due to particle size, decay of the fused samples, or the effect described by Bigg (*5*) where small concentrations of HI can raise the nucleation temperature. Although the reasons for the difference are not clear, the parallel nature of the data in Fig. 3 suggests that the difference is uniform.

Turnbull and Vonnegut (*2*) advanced a simple theory for nucleation catalysis based on the assumption that the interfacial energy between ice and a nucleation catalyst is a minimum when nucleation is coherent. Coherent nucleation occurs when the lattice of the forming crystal matches the lattice of the catalyst and can be likened to crystal growth. If the lattices are slightly mismatched, nucleation may still be coherent, but the resulting elastic distortion will increase the bulk free energy of the forming embryo. Consequently, the supercooling necessary for nucleation increases by an amount pro-

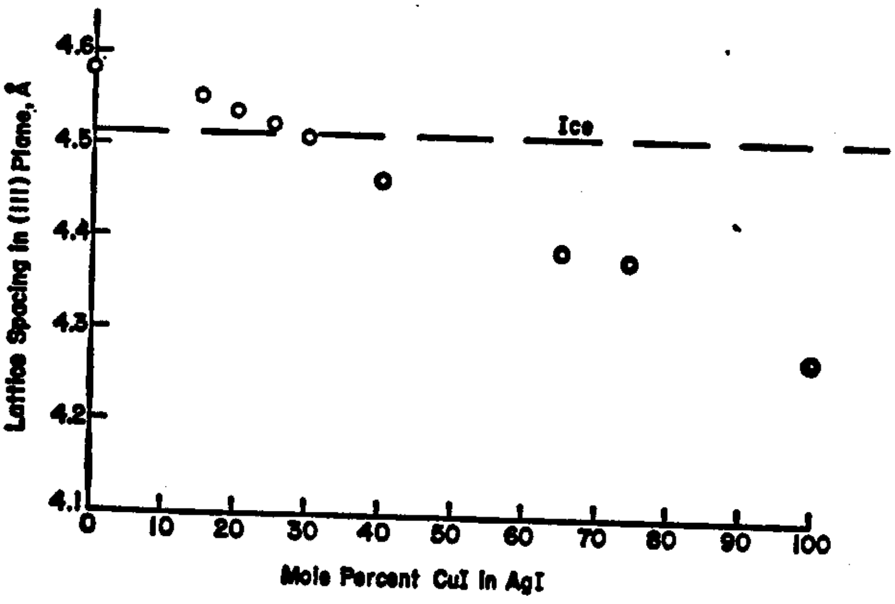

Fig. 1. Lattice parameter as a function of mole percent CuI in AgI.

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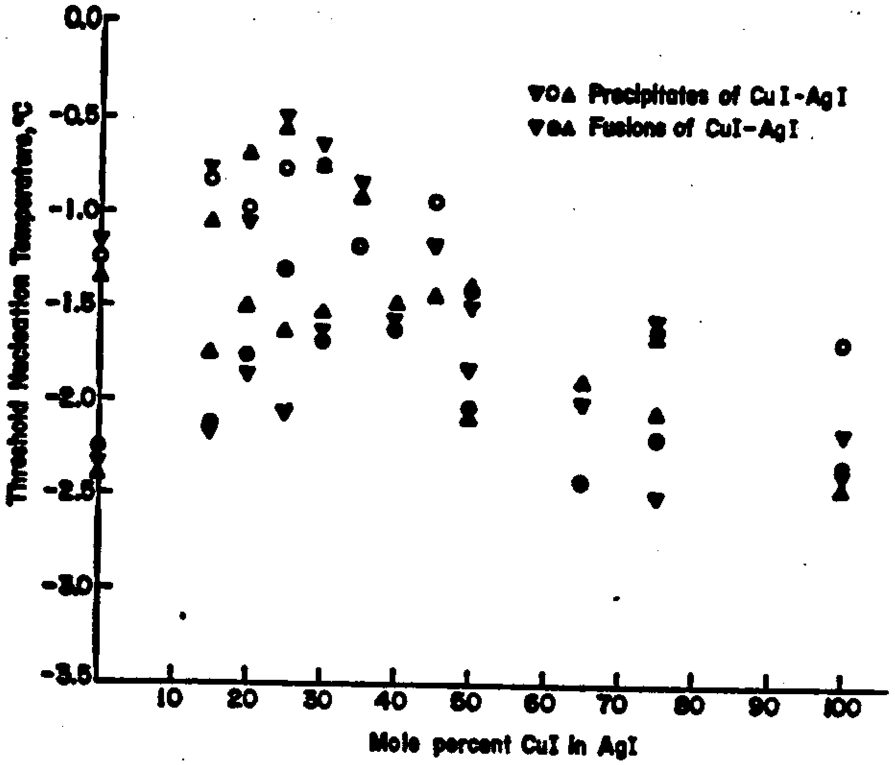

Fig. 2. Threshold nucleation temperature as a function of composition.

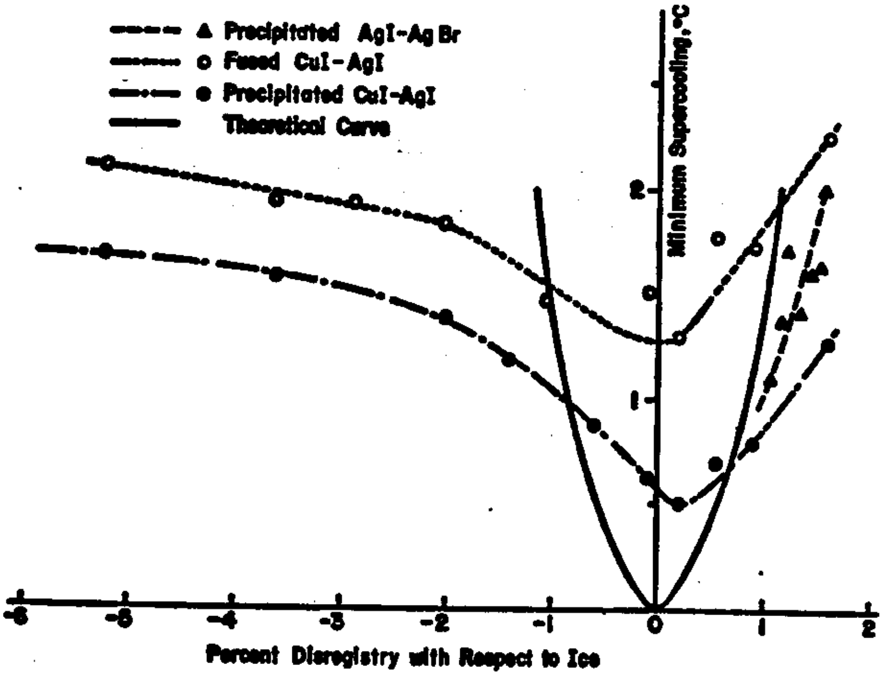

Fig. 3. Smallest observed supercooling as a function of percent lattice disregistry for CuI-AgI data and AgI-AgBr data (*1*), along with Turnbull and Vonnegut's (*2*) theoretical curve.

portional to the square of the disregistry.

The symmetry of the data in Fig. 3 suggests that catalysts with a positive disregistry have about the same nucleating ability as those with an equal negative disregistry. This result agrees with Turnbull and Vonnegut's prediction that $\Delta T = k\delta^2$, where ΔT is the supercooling, δ is the disregistry, and k is a constant. However, for our data the supercooling does not approach 0°C as the disregistry tends to zero, but instead reaches a minimum of about 0.5°C. In their derivation Turnbull and Vonnegut neglected other factors, such as particle size and adsorption, which could cause additional supercooling. When other nucleation parameters are taken into account, as suggested by Fletcher (*6*), the equation for coherent nucleation can be written as

$$\Delta T = k\delta^2 + \Delta T_1$$

where ΔT_1 is the supercooling due to the combined effect of any nucleation parameters independent of the disregistry. The parallel nature of the data in Fig. 3 tends to confirm this type of relation.

Coherent nucleation theory predicts that nucleation will become incoherent for large disregistries where the bulk free energy of ice formation is less than the free energy required to distort the ice lattice to fit the catalyst lattice. If nucleation is not coherent, Turnbull and Vonnegut predict a linear relation between the disregistry and the supercooling. The data for the CuI-AgI catalysts in Fig. 3 show a sharp dip in supercooling between lattice disregistries of ± 1.5 percent. This region could correspond to coherent nucleation. The region between − 1.5 and − 5.2 percent disregistry could correspond to incoherent nucleation, as the supercooling is a fairly linear function of the disregistry.

Richard E. Passarelli, Jr.
Department of Atmospheric Science, State University of New York at Albany, Albany 12222
Henry Chessin
Department of Physics, State University of New York at Albany
Bernard Vonnegut
Atmospheric Sciences Research Center, State University of New York at Albany

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7. We thank E. Barreto, D. C. Blanchard, N. R. Gokhale, and C. W. McCutchen for their helpful comments and suggestions, and E. Nagle for making the dilatometers. Supported in part by Office of Naval Research contract N00014-71-C-0156; in part by Air Force Cambridge Research Laboratories, Office of Aerospace Research, contract F19628-68-C-0057; and in part by National Science Foundation grant GI-34732.

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NUCLEATION OF SUPERCOOLED WATER CLOUDS BY SILVER IODIDE SMOKES[1]

BERNARD VONNEGUT

General Electric Research Laboratory, Schenectady, New York

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ABSTRACT

Measurements have been carried out in a cold box on the nucleation of ice formation in supercooled clouds by silver iodide smoke particles. The smokes were produced by atomizing an acetone solution of silver and ammonium iodides into a hydrogen flame.

The measurements show that ice crystals do not form immediately on the silver iodide particles. The silver iodide can be regarded as greatly increasing the probability of ice crystal formation. The number of effective nuclei which can be produced per gram of silver iodide varies from about 10^{13} at −10°C. to 10^{16} at −20°C.

INTRODUCTION

About a year and a half ago, it was found that silver iodide smokes had the property of causing snowflakes to form in a supercooled cloud (5). It is believed that silver iodide particles are good nuclei for ice formation because of the close resemblance of their crystal structure to that of ice. Experimentation has been under way to learn more about the production and behavior of these smokes. The work to be described in this account should be regarded as preliminary. The techniques and apparatus used in the work frequently leave much to be desired in the way of precision. The results are tentative and await confirmation by better experiments. This work, despite the uncertainties in it, nevertheless sheds light on the mechanism of nucleation and suggests new experiments and improved techniques for giving a more complete picture of the phenomena associated with nucleation by silver iodide.

APPARATUS AND TECHNIQUES FOR MEASUREMENTS ON SMOKES

Wind tunnel

In order to determine the output of a source of silver iodide smoke, it is necessary to secure a sample of smoke for testing that is a known fraction of the total output. This was accomplished by diluting the output of the smoke generator with a large known flow of air, and taking a known volume of this dilute smoke for testing. The smoke generator was placed in front of a ¼-horsepower electric fan, 3 ft. in diameter, which sucked the smoke along with a large volume of air into a crude wind tunnel 4 ft. square in cross-section and 24 ft. long. The stirring action of the fan and the turbulence in the tunnel mixed the smoke with

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[1] Presented at the Symposium on Aerosols which was held under the joint auspices of the Division of Physical and Inorganic Chemistry and the Division of Colloid Chemistry at the 113th National Meeting of the American Chemical Society, Chicago, Illinois, April 22, 1948.

the air to produce a more dilute smoke, which was discharged at the other end of the tunnel where samples were taken. When a heavy white oil smoke was introduced into the tunnel, it appeared to be quite uniformly mixed and diluted as it left the tunnel. The rate of flow in the tunnel, as determined by measuring the velocity with a vane-type anemometer, was 4×10^6 cm.^{3} per second.

Of the silver iodide smokes used, all except the ones having the largest particle size were completely invisible under the conditions of the experiment. The smokes having the largest particles were quite transparent and of a pale blue or purple appearance in the sunlight.

Smoke sampling and diluting syringe

In many of the cases, only a fraction of 1 cc. of the smoke from the tunnel is needed for a test. Precipitation on the walls of a container of this size would be very rapid. Therefore, a syringe was constructed for taking a sample of the smoke and diluting it quantitatively to any desired amount. The syringe (figure 1) consists of a metal tube 3 in. in diameter with a piston and leather washers which can be moved back and forth a fixed distance. A sample of smoke was taken with the syringe and then diluted to the desired concentration by moving the piston in and out the requisite number of times in smoke-free air, upwind from the tunnel.

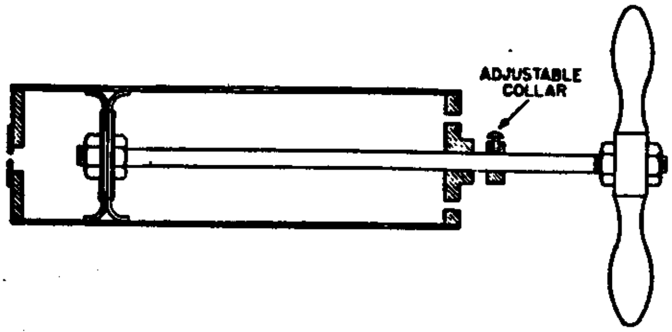

FIG. 1. Smoke sampling and diluting syringe

Cold chamber

The early measurements on the number of nuclei contained in silver iodide smokes were made using Schaefer's technique (3). A measured volume of smoke was introduced into a supercooled cloud in a home freezer and the number of snow crystals produced per cubic centimeter was visually estimated.

This technique has been slightly modified in the more recent work and the apparatus used is shown in figure 2. The tests were carried out in a brass cylinder 15 in. high and 12 in. in diameter having walls ½ in. thick to provide good thermal conductivity.

This chamber, which was closed at the bottom, was maintained at a low temperature by placing it in a 4 cu. ft. home freezer. The freezer thermostat was used to regulate the temperatures. A supercooled cloud was maintained in the refrigerated cylinder by evaporating water from wet paper toweling wound around a 15-watt electric heater placed in the lower part of the cylinder. A hinged masonite lid was used to close the top of the cylinder during tests. The temperature at the top of the cylinder was found to be about 2°C. warmer than at the bottom. The minimum temperature obtainable in the chamber was −20°C. In future experiments, it is highly desirable that lower temperatures be obtainable and that provisions be made for better temperature regulation.

Smokes were tested by introducing them from the sampling syringe into the supercooled cloud in the cylinder. A stack of cold microscope slides was placed in the bottom of the cylinder. The snowflakes produced by the action of the smoke settled on the bottom of the cylinder and on the topmost microscope slide. At intervals 2 min. apart the slide on which the snow had fallen was removed, thus exposing the slide beneath. The slide which was removed was then examined under a microscope kept in the freezer. By means of a Whipple eyepiece, the number of flakes collected per square millimeter in a 2-min. period was counted. When the rate of snowfall had dropped to a low value, the total number of flakes which had fallen per square millimeter was determined by adding the numbers which had fallen in each 2-min. sample. The total number of snow crystals which would have been produced by the entire output of the generator could then be calculated from the area of the bottom of the cylinder, the volume and dilution of the smoke introduced, and the volume rate of production of the smoke.

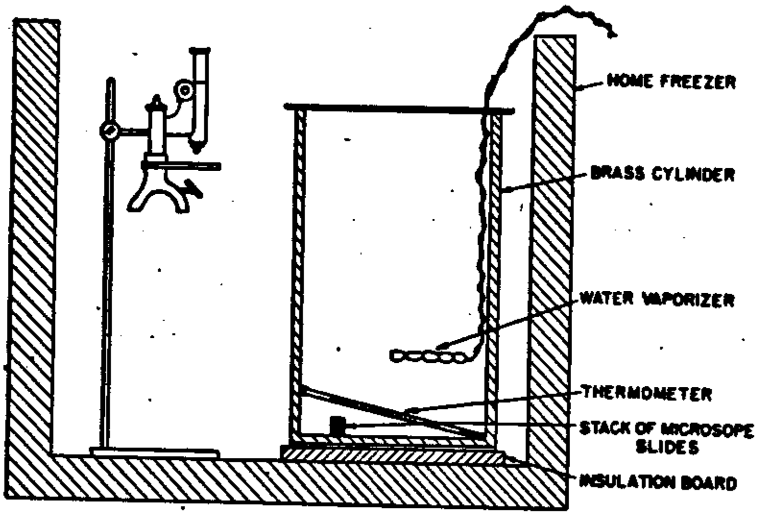

FIG. 2. Apparatus for counting nuclei in smoke

Electron microscope examination of smoke

Smokes being tested were examined with the electron microscope to determine their appearance and particle size. Samples of smoke were precipitated on a Formvar film supported on a fine wire screen, by moving it for about a minute in and out of the smoke stream about 3 ft. from the generator. The smoke stream at this point is still quite warm. The sample screen, because it is in the smoke only a moment at a time, remains cool so that thermal precipitation may play a part in the collection of the smoke.

Under these conditions of precipitation, it is quite likely that particles of a certain size may be selectively precipitated, so that the sample obtained is not entirely representative of the smoke. A more reliable method would be desirable so that more trustworthy data could be obtained.

The smoke samples were photographed using the electron microscope. Determinations of the particle size and the number of particles per cubic centimeter of material were made from these photographs.

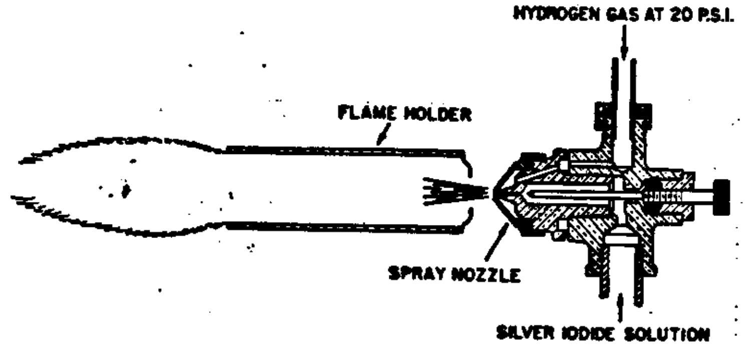

FIG. 3. Silver iodide smoke generator

Smoke generator

The smokes used in these tests were produced by a smoke generator constructed from a commercial compressed-air atomizing nozzle of the sort used for paint spraying and humidifying (Binks No. 174). The generator is shown in figure 3. Compressed hydrogen gas at 20 lb. per square inch was applied instead of air to the air inlet of the nozzle and a solution of silver iodide was used as the liquid to be sprayed. The hydrogen stream as it left the nozzle was ignited. The heat of the flame vaporized the silver iodide in the spray into a gas which, upon mixing with the atmosphere, condensed into a smoke of small silver iodide particles. In order to prevent the hydrogen flame from being blown out by the wind, a flame holder consisting of a piece of ¾-in. pipe 2½ in. long was placed ½ in. from the spray nozzle. At a pressure of 20 lb. per square inch, the spray nozzle used about 3 cu. ft. of hydrogen per minute (measured at atmospheric pressure).

Silver iodide solutions

Although silver iodide is very insoluble in water and organic liquids, it is quite soluble in acetone or water solutions containing a soluble iodide such as sodium or ammonium iodide. The solutions used in this work were made by dissolving 200 g. of silver iodide and 100 g. of ammonium iodide in a mixture of

750 cc. of acetone and 250 cc. of water. A dilute solution was also used which was made by diluting the above solution to ten times its volume with acetone. Solutions can be diluted any desired amount with acetone; however, dilution with water causes precipitation of the silver iodide. Ammonium iodide was used in the solutions for these experiments because it probably is completely decomposed in the hydrogen flame, thus leaving a smoke of uncontaminated silver iodide.

The rate at which silver iodide was fed into the smoke generator was varied by controlling the rate of flow of solution by adjusting the valve on the nozzle and by using solutions of different concentrations.

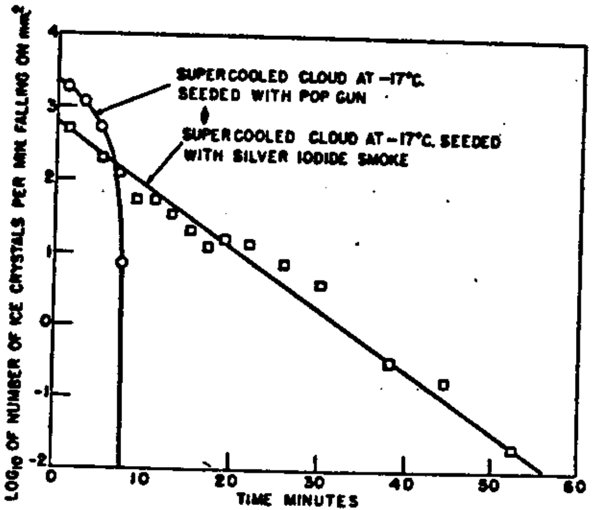

FIG. 4. Comparison of seeding with silver iodide smoke and seeding with popgun

EXPERIMENTAL RESULTS

Decrease in rate of snow formation after seeding

There was found to be a large difference in the behavior of the supercooled cloud when it was seeded with the low-temperature air produced by a popgun and when it was seeded with silver iodide smoke. From figure 4 it can be seen that although many snow crystals were produced by the low temperature from the popgun, all of these crystals had precipitated to the bottom of the container at the end of 10 min. When the cloud was seeded with silver iodide smoke, however, a measurable number of ice crystals were still precipitating at the end of almost an hour. The rate of snowfall decreases to one-half each 2 or 3 min. This rate of decrease was not found to vary significantly with temperature or with the particle size of the smoke although, as will be seen, the total number of snow crystals varied over several factors of ten, depending on the temperature of the supercooled cloud.

Precipitation of smoke in syringe

One possible source of error in these experiments is that which might be caused by coagulation and precipitation of the smoke in the sampling syringe. In order to evaluate this rate of disappearance, tests were made in which small smoke samples were withdrawn from the syringe after it had been in the syringe for varying periods of time. The number of effective nuclei in a sample of smoke was found to decrease by one-half every 20 min. The time required to take, dilute, and discharge a sample into the cold chamber was never more than a minute or two, so that the changes in the smoke occurring during this time were not large.

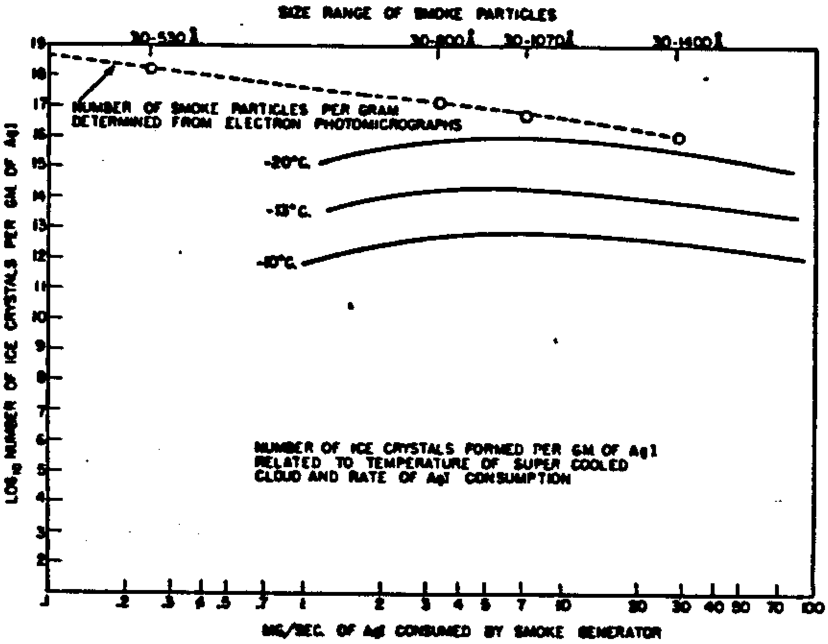

FIG. 5. Number of ice crystals formed per gram of silver iodide related to temperatuer of supercooled cloud and rate of silver iodide consumption.

Number of ice crystals per gram of silver iodide

The results of experiments carried out with different settings of the smoke generator and in supercooled clouds at different temperatures are shown in figure 5. In this graph, the results are also given for the electron microscope examination.

Electron photomicrographs were made of four different samples of smokes. A hundred or more particles in a representative section of each photograph were measured, and a graph was made of the number of particles as a function of their diameter. All of the smokes examined showed a large number of particles having a diameter of about 30 Å., which is the smallest particle observable with the microscope. It, therefore, seems probable that in these smokes there are many more particles which were too small to be resolved. By neglecting these invisible particles, it was possible to estimate the minimum number of particles formed per gram of silver iodide by dividing the number of particles in a representative section of a photograph by the sum of their masses computed on the assumption that they were spheres having the same density as silver iodide crystals. Figure 6 shows electron photomicrographs of two typical smokes.

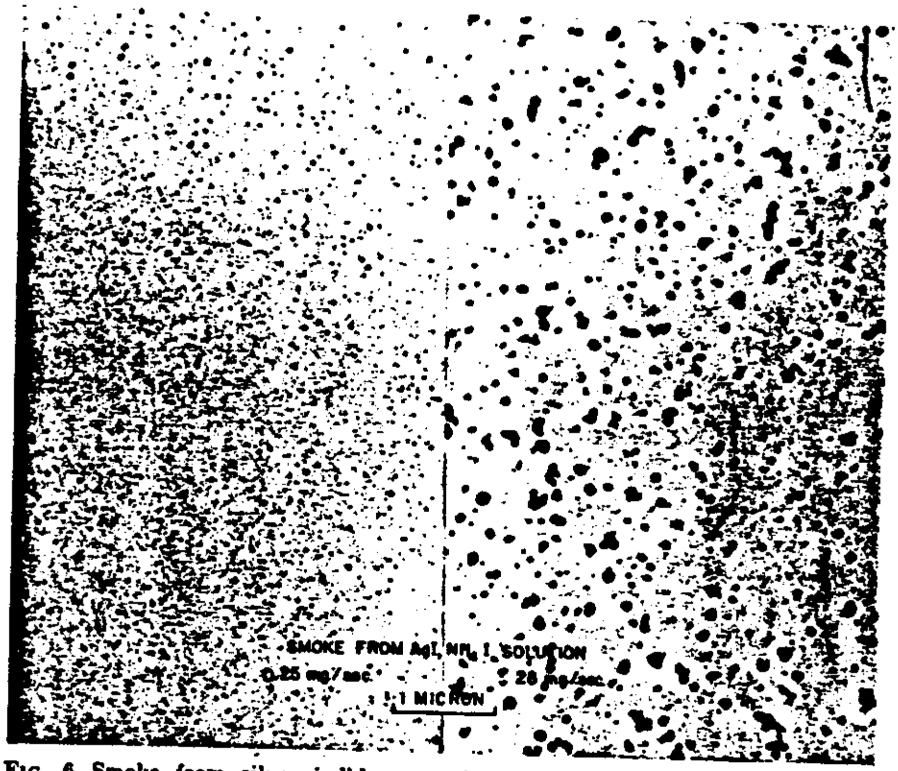

FIG. 6. Smoke from silver iodide–ammonium iodide solution. (a) 0.25 mg./sec.; (b) 28 mg./sec.

DISCUSSION OF RESULTS

The work thus far is not of sufficient scope to give straightforward answers to many questions which arise concerning the mechanism of silver iodide nucleation. It is the purpose of this discussion to venture some possible explanations for the experimental observations.

Formation of ice crystals

Figure 4, which shows the number of snow crystals precipitating per minute after seeding, illustrates a significant difference between the behavior of a cloud seeded with silver iodide and one seeded by a popgun. Seeding with a popgun or dry ice produces very large numbers of small ice crystals by cooling a small region of the cloud to a temperature at which spontaneous nucleation takes place. These ice crystals then mix with the cloud and grow at the expense of the supercooled water drops. From figure 4 it can be seen that although a large number of ice crystals is produced by the popgun, all of these crystals have precipitated out at the end of 10 min. Now if all of the silver iodide particles put into the cloud formed ice crystals at the time they were introduced, they, too, should have precipitated out at the end of 10 min. However, at the end of almost an hour, ice crystals are still precipitating. This leads one to the conclusion that all of the silver iodide particles do not form ice crystals immediately and that even at the end of half an hour or more, appreciable numbers of silver iodide particles have not yet formed snow crystals and are still present in the cloud.

There are various possible explanations for the time required for silver iodide particles to initiate the formation of ice crystals in a supercooled cloud. One possibility is that in order for an ice crystal to form on a crystal of silver iodide, a certain critical number of water molecules must by chance arrange themselves on its surface in the structure of ice. According to this explanation, a silver iodide particle would not act as a nucleus until this event took place. The presence of a silver iodide surface might be regarded as merely greatly increasing the probability of the formation of ice.

If we take a simplified view of the theory of nucleation as advanced by Gibbs, in supercooled water or in a region supersaturated with respect to ice, the water molecules by chance, from time to time, arrange themselves in the lattice of crystalline ice. If these minute aggregations are smaller than a certain size, their vapor pressure is greater than that of the supersaturated region and they are unstable and break up. If, on the other hand, they are larger than a certain size, their vapor pressure is such that they are stable and continue to grow. The lower the temperature, the smaller will be the critical size necessary for stability. Schaefer (4) found, using clean air free of dust, that the rate at which nuclei form is very low at temperatures above −38.9°C. However, in the presence of a silver iodide surface, it is possible, because of the close similarity between ice and silver iodide, that the probability of the chance formation of a nucleus is greatly increased and is large even at temperatures as high as −10°C.

Another way of looking at the phenomenon is to consider the growth of an ice crystal as the formation of a crystal of ice on ice. We know that this takes place with the greatest ease. The formation of ice on a large surface of ice requires the formation of very little new ice surface; hence there is little change in surface energy. For every new ice surface formed, an almost equal ice surface is covered up. However, when a new ice surface is formed in the absence of any other surface, large amounts of surface energy are required relative to the free energy decrease in the formation of the interior of the new phase. Because of the close similarity of ice and silver iodide, the formation of ice on a silver iodide surface probably involves only a small amount of surface energy, and therefore the chances of this taking place are good.

The lower the temperature, the smaller will be the critical size of a stable nucleus. Because the critical size is small at low temperatures, the chances of a nucleus forming are, in general, better. Hence, the rate of nucleus formation is generally greater at low temperatures.

Another possible explanation for the time required for silver iodide particles to form ice crystals can be based on the assumption that the silver iodide particles produced by the generator are not all in the hexagonal form which is similar to ice. Possibly they might exist in a metastable condition as a supercooled liquid or as some other modification. In this case, the rate at which they react to form ice crystals would be determined by the rate at which they transform into the stable hexagonal form. However, it appears for several reasons that this factor is probably not large in these experiments. It has been found that the silver iodide smokes used in these tests will nucleate silver iodide solutions supersaturated with respect to the hexagonal form and that the crystals which result are of the hexagonal variety. The number of such nuclei in a given volume of smoke is of the same order of magnitude as the number of particles determined by the electron microscope. It, therefore, seems probable that at room temperature most of the smoke particles are of the hexagonal structure. In addition one would expect, if the rate-determining factor involved the transformation of the silver iodide particles themselves, that smokes aged for a period of time at low temperature would show a different rate of falling off of ice crystal formation when they are put in a supercooled cloud. This has not been observed.

Another possibility is that the formation of an ice crystal under the influence of a silver iodide particle can take place only in the liquid phase. In this case, the rate of ice crystal formation might be limited by the rate at which silver iodide particles entered into supercooled water drops. This could occur either by diffusion of the particle to the drop or by condensation of a drop on a particle. It has been found that when a suspension of silver iodide particles in water is sprayed into a supercooled cloud, ice crystals are formed. It is therefore probable that silver iodide particles can act as nucleating agents in a drop of liquid water. However, it has not been definitely established that this is a necessary condition for silver iodide to act. If we assume this to be the rate-governing factor in these experiments, we are faced with the problem of explaining the large effect of temperature on the total number of ice crystals produced. As will be discussed later, the variation of the number of ice crystals produced with temperature can be explained on the basis that the rate of nucleation increases greatly with decreasing temperatures. There is no reason to expect that the rate at which particles enter water drops is particularly temperature-sensitive. It is quite possible that the time required for a particle to enter a water drop is of considerable importance in these experiments, but it is probably not the most important rate-governing factor.

The interpretation of results is further complicated by the possibility that small particles of silver iodide smoke may dissolve in water drops before they have a chance to start the formation of an ice crystal. At 25°C. the solubility of silver iodide in water is about 1×10^{-8} moles per liter (1). A water drop 10 microns in diameter on this basis should be capable of dissolving a silver iodide particle about 100 Å. in diameter. The solubility should be somewhat greater for particles of this small size. However, the effect of particle size should be counteracted to some extent by a decreased solubility at the lower temperatures. If these factors are of importance, the kinetics of the nucleation may be dependent to a large extent on the rate of solution of the silver iodide particles in the water drops.

The author is inclined to favor the explanation that the rate of ice crystal formation is governed primarily by the rate of spontaneous ice nucleus formation on the silver iodide particles.[*] In some as yet unreported experiments on the nucleation of supercooled water and supercooled tin, the author measured at constant temperature the rate of solidification of systems composed of a number of independent supercooled drops. It was observed that the drops did not all freeze at once but froze at a rate which steadily decreased with time. This rate of freezing increased greatly as the temperature was lowered. In these experiments, foreign particles and surfaces were present which undoubtedly served as foreign nuclei. The time required for these drops to freeze could be best explained on the basis of the chance formation of stable nuclei on the foreign surfaces. It seems reasonable to believe that in the case of nucleation by silver iodide similar phenomena play a dominant rôle.

If we proceed on the assumption that silver iodide merely increases the rate of the chance formation of spontaneous ice crystals, it is possible to come to some conclusions as to the magnitude of the rate and its dependence on temperature. Some of the particles of silver iodide introduced into the cold chamber undoubtedly become lost as potential nuclei by precipitation on the walls of the chamber. The rate of precipitation on the walls is probably large because of thermal diffusion resulting from the 15-watt heater in the vaporizer. One would expect the rate at which particles disappear by precipitation on the walls to be proportional to the concentration of the particles. On the basis of this assumption, the concentration of particles would decrease exponentially with time. If the rate of snow formation is proportional to the concentration, this too should decrease exponentially with time. This is experimentally observed to be the case.

On the basis of the foregoing assumptions, one can analyze the situation mathematically.

If c is the number of silver iodide particles per unit volume at a time t then:

$$\frac{dc}{dt} = -(K_1 + K_2)c \qquad (1)$$

where K_1 is the rate at which the silver iodide particles form ice crystals and K_2 is the rate at which they are being removed from the cloud by precipitation or other causes. By integrating equation 1 we obtain an expression for the concentration c at any time:

$$c = c_0 E^{-(K_1+K_2)t} \qquad (2)$$

where c_0 is the concentration at time $t = 0$. If N is the number of ice crystals formed per unit volume, then

$$\frac{dN}{dt} = K_1 \cdot c = K_1 c_0 E^{-(K_1+K_2)t} \tag{3}$$

which when integrated gives for the number of crystals formed at time t:

$$N = \frac{K_1 c_0}{K_1 + K_2} \cdot 1 - E^{-(K_1+K_2)t} \tag{4}$$

Or when precipitation is complete

$$N = \frac{K_1}{K_1 + K_2} \cdot c_0 \tag{5}$$

or

$$\frac{N}{c_0} = \frac{K_1}{K_1 + K_2} \tag{6}$$

The fact that the rate at which the rate of snowfall decreases with time is not greatly influenced by temperature, while the total number of crystals produced increases by a large factor with a small temperature decrease, indicates that at higher temperatures K_2 is far greater than K_1. This is another way of saying that at higher temperatures the rate at which the silver iodide particles form snowflakes is so small that a large majority of them precipitate on the container walls before they have a chance to form snow crystals. At −20°C. the number of snow crystals obtained approaches the number of particles determined from the electron microscope, so that it is reasonable to assume that at this temperature most of the smoke particles form snowflakes.

If we assume that the rate at which precipitation decreases with time at the higher temperature is determined solely by K_2, then K_2 computed from the curve in figure 4 is approximately 6×10^{-3} per second. From the data in figure 5, N_1 and c_0 can be estimated and from them and the above value for K_2, values for K_1 for different smokes at different temperatures can be computed.

These values expressed as half-life in hours are as follows:

SILVER IODIDE	RANGE OF PARTICLE DIAMETER	HALF-LIFE	
		−15°C.	−10°C.
mg./second	*Å.*	*hours*	*hours*
1.5	30–700	5.5	173
7.5	50–1070	1.9	75
37.5	130–1400	1.4	67

If these data are extrapolated on the assumption that the log of the nucleation changes linearly with the reciprocal of the absolute temperature, we find that at −5°C. the half-life is several years, while at −20°C. it is a few seconds, and at −25°C. a few milliseconds.

This large effect of temperature on the nucleation rate is of the same order of magnitude as that observed in the measurements on supercooled water drops and on supercooled tin drops.

The curves in figure 5 show a maximum for the number of nuclei produced per gram of silver iodide at a certain rate of silver iodide consumption. This is probably because at a low rate of consumption, the particles produced are so small that their reaction rate is small and many of them precipitate out before they have a chance to serve as nuclei. At high rates of consumption, the particles formed are larger and react more rapidly, but because they are larger, fewer are formed per gram of silver iodide.

Diffusion coefficients of smoke

An average diffusion coefficient for the silver iodide smoke can be calculated from measurements made on the rate at which the smoke precipitates on the walls of a container. In the experiments which were made to find the rate at which the number of nuclei falls off as a function of the time the smoke is held in the sampling syringe, it was found that the half-life of the smoke was about 20 min. This was for a smoke produced when the generator was consuming 20 mg. of silver iodide per second.

Langmuir (2) has derived the following expression for the rate of precipitation of a smoke of diffusion coefficient D on the walls of a container having a volume V and an internal area A with slight convection caused by a slightly higher temperature at the bottom than the top:

$$\frac{\mathrm{d} \ln c}{\mathrm{d}t} = \frac{0.64 A D^{2/3}}{V} \tag{7}$$

where c is the concentration of the smoke at any time t.

Using this equation the diffusion coefficient is calculated to be approximately 6×10^{-6}.

Langmuir (2) has also given the following expression for the diffusion coefficient as a function of particle radius:

$$D = \frac{2.04 \times 10^{-16}}{a^2} + \frac{1.18 \times 10^{-11}}{a} \tag{8}$$

where a is the particle radius.

According to this expression, the diffusion coefficient 6×10^{-6} corresponds to a particle diameter of 400 Å. This is in reasonable agreement with the measurements from the electron microscope, which show this smoke to have a particle diameter ranging from 30 Å. to 1400 Å. with a median diameter of about 300 Å.

As has been shown, K_2, or the rate of disappearance in the cold chamber of silver iodide particles from causes other than nucleation, is about 5.7×10^{-3} per second.

Using the diffusion coefficient of 6×10^{-6} and equation 7, it can be calculated that the smoke concentration should fall at a rate of 1.3×10^{-4} per second. This is far less than the observed rate of decrease, K_2, which was found to be 5.7×10^{-3}. This calculation, of course, does not take into account the thermal diffusion caused by the vaporizer heater in the cold chamber, which would be expected to increase greatly the rate of precipitation on the walls.

Using the diffusion coefficient it is possible to estimate the rate at which the concentration of the smoke decreases because of precipitation on the water drops of the supercooled cloud. It can be shown that the rate of change of concentration due to this cause is given by the relation

$$\frac{d \ln c}{dt} = -4\pi D r_0 Q \tag{9}$$

where r_0 is the radius of the water drops and Q is the number of drops per cubic centimeter.

If we assume the liquid water contents to be 1 g. per cubic meter and the drop radius to be 5 microns, the rate of change of concentration from this cause is 3.6×10^{-4}.

SUMMARY

Measurements have been carried out on the nucleation of supercooled water clouds by silver iodide smokes. The smokes were produced by spraying a solution of silver iodide into a hydrogen flame. The particles of the smokes were found by electron microscope examination to range in diameter from 30 Å. to 1400 Å. The number of ice crystals produced per gram of silver iodide was determined as a function of the temperature of the supercooled cloud and the rate of introduction of silver iodide into the flame. Yields of ice nuclei of as high as 10^{16} per gram of silver iodide were obtained when the supercooled cloud was at −20°C. At −10°C. the same smoke produced only $10^{12.7}$ ice crystals per gram.

It has been found that silver iodide particles do not react immediately to form ice crystals when they are put into a supercooled cloud. Ice crystals were found to be still forming at a measurable rate 50 min. after a silver iodide smoke was introduced into a supercooled cloud. It is believed that fewer ice crystals are produced at higher temperatures than at lower temperatures, because the silver iodide particles react more slowly to form ice crystals and most of them precipitate on the walls of the cold chamber before they have time to react.

According to this interpretation of the results, the rate of reaction at −13°C. is thirty or forty times that at −10°C.

The author wishes to thank Dr. Irving Langmuir and Dr. Vincent J. Schaefer for their very helpful counsel and suggestions in this work. He is grateful to Mr. E. Fullam for making the electron microscope examinations and photographs and to Mr. Kiah Maynard and Mr. Duncan Blanchard for invaluable help in testing the smokes.

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The Nucleation of Ice Formation by Silver Iodide

B. VONNEGUT
General Electric Research Laboratory, Schenectady, New York
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Silver iodide particles have been found to serve as nuclei for the formation of ice crystals in super-cooled water and in water vapor super-saturated with respect to ice. It is believed that silver iodide serves as a very effective nucleus because it very closely resembles ice in crystal structure. Both dimensions of the unit cell of ice and silver iodide are the same to within approximately one percent. The maximum temperature at which the silver iodide particles serve as nuclei is approximately −4°C for particles one micron in diameter, and −8°C for particles 100 Angstrom units in diameter. A silver iodide smoke generator has been constructed which consumes 1 mg of silver iodide per second and produces 10^{11} effective nuclei per second.

V. J. SCHAEFER of this laboratory has recently reported that super-cooled liquid water clouds spontaneously transform from water to ice when the temperature is −35°C or lower. He observed that at temperatures as low as −20°C, the addition of fine particles of a wide variety of substances was without effect on the super-cooled cloud.[1]

B. M. Cwilong,[2] using a Wilson cloud chamber, found that moisture in clean air is precipitated as a cloud of ice crystals if the temperature during the expansion drops to −35.0°C or lower and the air is super-saturated with respect to ice at this temperature. He observed that the ice crystals were formed even though the expansion ratio was far less than that necessary to produce the formation of liquid water drops. Cwilong observed that if "ordinary atmospheric air" is used, ice crystals form at −27°C, and that if the air is "artificially contaminated with tobacco smoke," the limiting temperature is −23°C. He found "crystalline dust" to be no more active than "amorphous dust" in producing ice crystals.

Following Schaefer's work, experiments were made using Schaefer's apparatus and technique to see whether particles of substances very similar to ice in crystal structure might not serve as nuclei for ice formation at temperatures closer to the freezing point.

A search was made through x-ray crystallographic data for substances resembling ice as closely as possible in crystal system, space group,

TABLE I.

Substance	System	Space group	Lattice constant	
Ice	hex.	D_{6h}^4	4.535	7.41*
AgI	hex. ZnO	C_{6v}^4	4.585_6	7.490**
PbI$_2$	hex.	D_{3d}^3	4.54	8.86

* William H. Barnes, Proc. Roy. Soc. London A125, 670–693 (1929).
** N. H. Kolkmeijer, W. J. D. von Dobbenburgh, and H. A. Boekehoogen, Proc. Amsterdam 31, 1014–1027 (1928).

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[1] V. J. Schaefer, "The production of ice crystals in a cloud of supercooled water droplets," Science 104, 457–459 (1946).

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and dimensions of unit cell. Two substances were chosen which are listed in Table I along with ice for comparison.

These crystalline substances were tested to see if they would act as nuclei for the formation of ice when dusted as a powder into a super-cooled water cloud in Schaefer's apparatus at a temperature of −20°C.

Silver iodide was without apparent effect; however, the introduction of lead iodide powder caused the formation of a number of ice crystals in the super-cooled cloud. It appeared that far fewer ice crystals formed than would have been expected from the number of particles of lead iodide introduced.

The supposition that the lead iodide particles acted as nuclei because one of the dimensions of its unit cell was almost the same as that for ice was discarded when V. J. Schaefer discovered that iodiform crystals and iodine vapor behave in a similar way. The orthorhombic structure of iodine bears little relation to the structure of ice.

Later, investigations were made on the nucleating effect of smokes produced by electric sparks between electrodes of various metals. It was discovered that a single spark between silver electrodes in the presence of iodine vapor produced many thousands of times as many ice nuclei as lead iodide particles or iodine vapor alone. It was then found that silver iodide smoke, produced by heating silver iodide on a hot filament or by dispersing it in a flame, produced enormous numbers of nuclei. The failure of the initial experiment using silver iodide powder is attributed to the fact that the sample used was badly contaminated with soluble salts, a fact not known at the time. Powdered silver iodide without this impurity has since been found to serve as nuclei for ice formation.

It is believed that silver iodide acts as a very effective nucleus for the formation of ice crystals because it very closely resembles ice in crystal structure. It can be seen that both dimensions of the unit cell of ice and silver iodide are the same to within about one percent.

According to Dr. D. Harker of this laboratory, the arrangements of the atoms in the unit cells of ice and of silver iodide are almost identical despite their different space groups. The structure of ice is the same as that of silver iodide with the oxygen atoms occupying positions corresponding to the silver and iodine atoms. In silver iodide, each silver atom is bonded tetrahedrally to four iodine atoms. In ice each oxygen atom is bonded tetrahedrally, through hydrogen bridges, to four oxygen atoms.

Iodine vapor alone, or fine silver particles alone are without appreciable effect in forming ice crystals at a temperature of −20°C. If the experiment is carried out using iodine vapor alone in a system closed to the atmosphere of the laboratory, iodine vapor soon loses its property of nucleating a super-cooled cloud. It is believed that iodine compounds and iodine vapor act to produce nuclei by reacting to form silver iodide with minute traces of silver in the laboratory atmosphere. Such traces of silver might be caused by sparks from electrical equipment using contacts made of silver or copper that contains silver. Exceedingly small amounts of silver introduced into a super-cooled cloud in the presence of iodine vapor cause the formation of very large numbers of nuclei. One breath of air blown over a silver wire heated red will produce many millions of ice nuclei if it is introduced into a super-cooled cloud containing a small amount of iodine vapor.

Experiments are being made on methods for the production of silver iodide smokes consisting of very large numbers of very small particles. The most effective method found thus far for the production of such smokes is the following. A cotton string coated with silver iodide is fed at a fixed rate into an oxyhydrogen flame which vaporizes the silver iodide. A few inches away from the point at which the silver iodide is introduced, the flame is rapidly quenched by blowing a strong jet of compressed air through it. The blast of air quickly cools and dilutes the vaporized silver iodide in the flame so rapidly that it condenses to form an invisible smoke of very small silver iodide particles. Measurements have been made which show that a generator of this sort produces ice nuclei at the rate of approximately 10^{15} per second with the consumption of one milligram of silver iodide per second. Mr. E. F. Fullam has examined particles of this smoke with the electron microscope and found that they are of the order of 100 Angstrom units in diameter. One milligram, it can be computed, should yield about 3×10^{14} particles. The discrepancy between the two values may be caused by the fact that a portion of the silver iodide introduced into the flame may form a few very large particles or may form particles which for some reason are not effective nuclei.

It has been found that the effectiveness of the silver iodide particles as ice nuclei depends to a certain extent on the size of the particles. The smoke made by the oxyhydrogen flame technique has a particle size of the order of 100A diameter. This smoke does not cause large numbers of crystals to form until the temperature is −8°C or lower. Smokes made by vaporizing silver iodide from a hot wire have a particle size of the order of one micron and are effective at −4°C or below. A piece of silver iodide several millimeters in diameter placed in water in a test tube makes it difficult to super-cool the water to temperatures below about −3.5°C.

Recently the effect of silver iodide smoke was tried near Schenectady on a thin layer of supercooled fog at a temperature of −4°C. The smoke was produced by evaporating silver iodide on the surface of an electrically heated wire coil. The liquid water fog was transformed into small ice crystals for a distance of at least 150 feet from the point where the smoke was generated.

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VARIATION WITH TEMPERATURE OF THE NUCLEATION RATE OF SUPERCOOLED LIQUID TIN AND WATER DROPS

Bernard Vonnegut

From the General Electric Research Laboratory, Schenectady, N. Y.

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INTRODUCTION

In investigations of the kinetics of the formation of a new phase, it is important to learn at what rate nuclei, or centers of formation for the new phase, make their appearance. It is possible to investigate the rate of nucleation by observing single masses of material during and after a phase transformation. However, in many cases it is difficult to separate the kinetics of nucleation from the kinetics of the growth of the new phase after nuclei have made their appearance. The nucleation of a substance can often be more easily studied by dividing it into a large number of small mutually independent particles and observing as a function of time the number of particles which have undergone transformation. The time required for a particle to change from one phase to another once a nucleus has formed will, in general, be proportional to the first power of the particle radius. The chance that a nucleus will form will generally be proportional to the second or third power of its radius. Therefore, by making the particle sufficiently small, the time required for the occurrence of a nucleus can be made large in relation to the time required for the particle to transform once a nucleus has appeared. It is advantageous to make nucleation measurements on systems containing a sufficiently large number of particles to be easily treated statistically.

Preliminary investigations have been on the nucleation of supercooled tin and supercooled water. Observations were made at constant temperatures on the freezing rate of systems composed of large numbers of supercooled drops.

EXPERIMENTAL METHODS AND RESULTS

Nucleation of Supercooled Liquid Tin

In the experiments on tin, the samples were prepared from a fine tin powder (obtained from Eimer and Amend) consisting of small spheres of tin ranging in diameter from approximately 1 to 10 μ.

The first determinations of the rate of nucleation of supercooled tin drops were made using X-ray diffraction measurements. The sample of

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tin powder was mixed with a Bakelite varnish and spread as a film on a glass slide. The slide was mounted in a small electric furnace built to fit on a Philips X-ray diffraction apparatus. The apparatus was adjusted to give a strong diffraction line of the crystalline tin powder. The sample was then heated above its melting point (231.89°C.) to 240°C. At the melting point, the diffraction line of the solid tin disappeared. Hydrogen gas was run through the furnace to prevent oxidation of the sample. After having been heated above the melting point, the sample was cooled and held at some temperature below its freezing point. The rate at which the supercooled particles crystallised was determined by measuring the rate at which the intensity of the diffraction line of solid tin returned to its former value. The results of a typical experiment are shown in Fig. 1. It was soon found that the rate of nucleus formation was greatly increased by a small decrease in temperature and that the temperature control was not sufficiently sensitive to permit measurements with any accuracy.

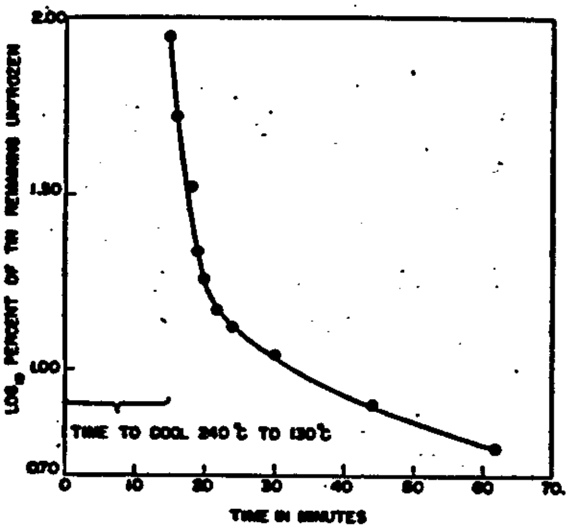

FIG. 1. Fraction of tin drops remaining unfrozen as function of time at 130°C., from X-ray data.

A different apparatus was then set up in which the rate at which the tin particles solidified could be measured by the rate at which their volume changed. When liquid tin crystallises, its volume decreases by about 5%. The tin powder was first heated in air for about 0.5 hr. at 150°C. to give it a thin coating of oxide to separate the particles. It was sealed into a bulb of a dilatometer (see Fig. 2). The dilatometer was then pumped out and baked at a pressure of less than 1 μ to remove any gas. "Octoil S" was then distilled into the dilatometer under vacuum. A measurement of the rate of nucleation was made by first heating the bulb to a temperature above the melting point of tin (265°C.), and then placing it in a silicone oil constant temperature bath. The rate of nucleation was determined by observing the rate of volume decrease as measured by the motion of the "Octoil S" along a graduated capillary tube. A long capillary tube was used in the first experiments, but it was found that appreciable error was caused by the slow drainage of the liquid from the walls of the tube. This difficulty was minimized by using the oil reservoir shown in Fig. 2. During the melting of the sample, the tube was held at an angle so that the liquid covered the end of the capillary tube. When the sample had been cooled to almost the desired temperature, the tube was tipped so that the excess liquid ran away from the end of the capillary tube, thus forming the meniscus in a convenient position.

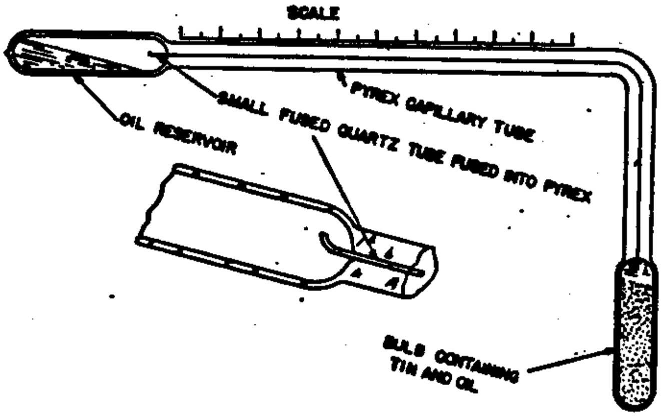

FIG. 2. Dilatometer.

The results of the experiments are shown in Fig. 3. The time has been plotted on a log scale to condense the curves for runs made over a long time interval. If the chances of a nucleus occurring in each tin particle were exactly the same and were independent of the length of time it had been supercooled, one would expect the rate of nucleation to decrease exponentially with time. The curves show clearly that in these experiments this is not the case. The fraction of the unfrozen portion of the sample crystallizing per unit time steadily decreases with time. Some drops nucleate more rapidly than others, probably because they are either larger than the others or because they contain certain impurities which increase the probability of nucleus formation. The data obtained should be interpreted as the behavior of supercooled tin with whatever impurities were present. It is probable that tin, free of impurities, if it could be obtained, might behave very differently.

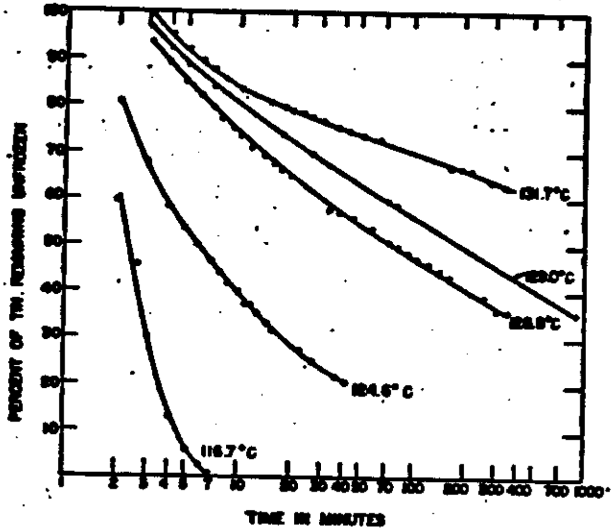

FIG. 3. Fraction of tin drops remaining unfrozen as a function of time from dilatometer data.

One of the most striking features of the data is the very great effect of temperature on the rate of nucleation. A decrease in temperature of 7° causes a 60-fold increase in the nucleation rate. In observations on the rate of nucleation of supercooled water clouds in the presence of silver iodide smoke, the author has observed a similar large negative temperature coefficient (1). For a given smoke the rate of ice crystal formation was approximately 30 times greater at −13°C. than at −10°C.

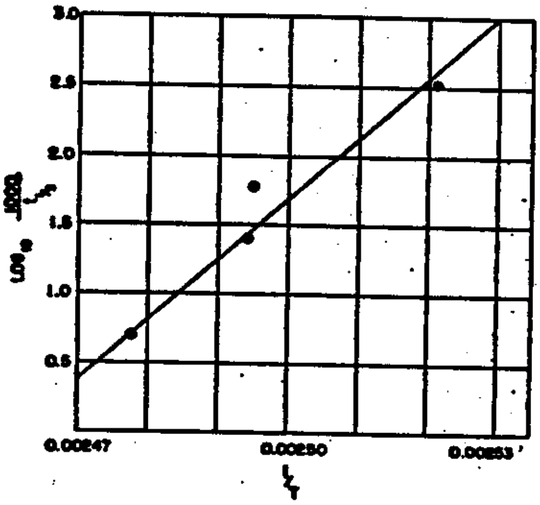

FIG. 4. Nucleation rate of tin drops as a function of temperature.

An approximate value for the activation energy of the nucleation reaction can be computed from the data in Fig. 3. The log of the reciprocal of the time required for $\frac{1}{2}$ of the sample to freeze was plotted against the reciprocal of the absolute temperature to give the curve in Fig. 4. This corresponds to an activation energy of -2×10^5 calories. The data taken at 116.7°C. have not been used because nucleation at that temperature proceeds so rapidly that most of the sample is frozen by the time its temperature has come to equilibrium with the constant temperature bath.

The fact that the tin particles had widely differing diameters greatly limits the deductions which can be obtained from these experimental results. Not only is the probability of nucleus formation far larger in a large drop than in a small one, but the freezing of a large drop would produce a far greater effect on the diffraction of the X-rays or the volume of the system than would the freezing of a small drop. The data, therefore, probably reflect primarily the behavior of the larger drops.

It is highly desirable that future experiments be conducted on samples containing drops that are as nearly identical as possible.

Nucleation of Supercooled Water

The author first attempted to measure the nucleation of supercooled water in experiments conducted while at the De-icing Research Laboratory at M.I.T. An emulsion of water drops suspended in lubricating oil was cooled to −29°C. with the expectation of measuring the nucleation rate by the rate of volume increase. This method was not successful, because the solubility of water in the oil was sufficiently large that diffusion rapidly took place from the unfrozen to the frozen drops.

Some preliminary studies on water have been made in this laboratory using a variation of the above method. In these experiments, 64 drops of distilled water, weighing approximately 3 mg. each, were placed in a square pattern on a polished chromium plated metal plate.

On the recommendation of V. J. Schaefer of this laboratory, the chromium surface of the metal plate was covered with a thin film of polystyrene by dipping it into a solution. This had been found by Schaefer to lower the temperature to which the water could be supercooled. The plate with the drops on its surface was then placed on a thermostated copper block at some temperature below freezing. To prevent impurities in the air from settling on the water drops, the plate was covered with a piece of plate glass which rested on a raised rim on the copper block. The heat transfer between the block and plate was sufficient to bring the drops on the plate to the temperature of the block in less than 1 min. The number of unfrozen water drops was measured as a function of time

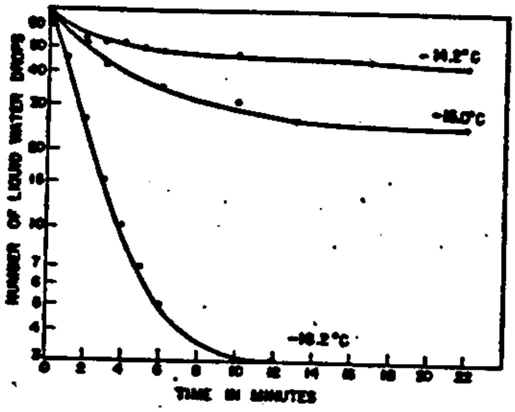

FIG. 5. Fraction of water drops remaining unfrozen as a function of time.

by visual observation. Fig. 5 is a curve showing the nucleation of the drops at various temperatures.

Despite precautions to keep the water drops free of impurities, it is certain that they were contaminated by foreign material from the atmosphere and by the surface of the plate which increased the rate of nucleation. Here again the data would probably be far different for completely pure water. The striking feature of the data is again the large negative

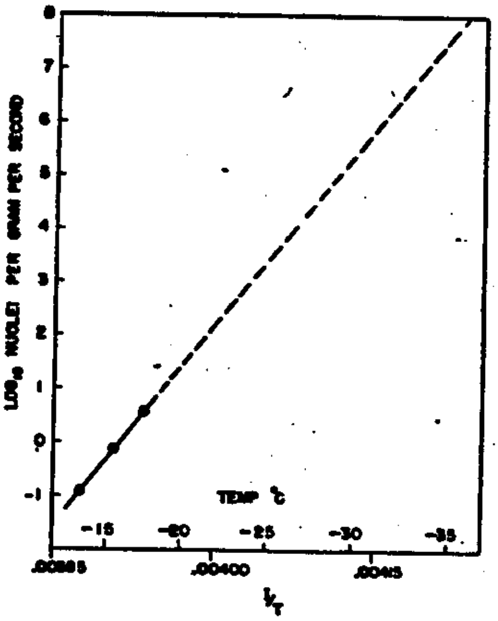

FIG. 6 Nucleation rate of water drops as a function of temperature.

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temperature coefficient which characterized the results of the experiments on supercooled tin and on a supercooled cloud seeded with silver iodide.

The data for the freezing of water drops given in Fig. 5 can be interpreted in terms of the rate of nucleus formation per gram of water. Fig. 6 relates the rate of nucleus formation per gram to the reciprocal of the absolute temperatures. The rate of nucleation was calculated from the times required for the first 22 drops to freeze at the various temperatures. The energy of activation computed from the slope of the curve in Fig. 6 is $- 1.6 \times 10^5$ cal. It is interesting to extrapolate these data for comparison with observations made by Schaefer (2, 3) in his experiments on supercooled clouds. If it is assumed that the liquid water content in the cloud in the cold box is of the order of .1 g./m.^{3}, at a temperature of −25°C., according to these data ice crystals should be appearing at the rate of about 10^4/sec. Actually, with clean air at this temperature, no crystals are observed. It is not until the temperature falls below − 39.0 ± 0.1°C. that many crystals begin to form. The rate of nucleation in the water drops on the metal plate is much larger than that in the water drops in a cloud, probably because of the nucleating effect of the surface of the plate and chance impurities.

The sudden appearance of large numbers of ice crystals when the temperature is −39°C., or lower, indicates that in Schaefer's experiments the increase in nucleation rate with decreasing temperature must be even greater than that found in this work.

Acknowledgments

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Summary

X-ray diffraction, dilatometric, and visual techniques are described for measuring the extent of crystallization of systems composed of many small mutually independent volumes of supercooled liquid. Preliminary measurements on supercooled liquid tin and supercooled water show their rate of nucleation has a very large negative temperature coefficient corresponding to an activation energy of the order of $- 2 \times 10^5$ calories.

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