SHORTER CONTRIBUTIONS

SILVER AND LEAD IODIDES AS ICE-CRYSTAL NUCLEI

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Introduction.—The effectiveness of silver iodide as an ice crystal nucleus, first discovered by Vonnegut [1], has had far reaching consequences in the field of experimental meteorology. A search for other substances which might be even more effective has been continued by various workers in the field. A survey by the writer [2], related to some of the probable natural ice nuclei, showed that soils of volcanic origin and clays from glacial deposits serve as active ice-crystal nuclei in the temperature range of − 12 to − 22C. Thus far, no naturally occurring nuclei have been discovered which work in the range of 0 to − 5C, although there is reason to believe [3] that frazil ice may be initiated by freezing nuclei active in this temperature range. No serious attempt has been made by the writer to investigate this important relationship, but it is hoped that this will be possible before long.

When Vonnegut was searching the x-ray crystallographic data for crystals having a lattice arrangement similar to ice, he found that silver iodide and lead iodide should be nearly ideal. Along the a-axis, lead iodide matched the ice dimension even better than silver iodide. Despite this fact, Vonnegut concentrated his efforts toward a study of silver iodide, since this substance had a much lower solubility in water and closely matched the ice structure along both the a- and c-axes.

By using the continuous cloud chamber [4], a comparison has been made between silver and lead iodide. Submicroscopic smoke particles of each of these substances were made by two different methods. Fig. 1 illustrates a cross section of the chamber used. In the first method, a Tesla coil was connected to a spark gap made of pure silver or pure lead electrodes. These were placed in a clean glass container, containing a few small crystals of iodine held at room temperature. When a spark discharge occurred, submicroscopic metallic particles were produced which reacted with the surrounding free iodine vapor to form particles of the iodide. Samples of the air containing this invisible smoke could then be introduced into the closed cloud chamber under easily controlled conditions.

The second method utilized a heated platinum filament, coated with a thin layer of powdered lead iodide or silver iodide. By heating the filament, small particles of these iodides vaporized to form a faintly visible bluish aerosol.

Method of comparing silver and lead iodides as ice nuclei.—With use of a suitable valve system, samples

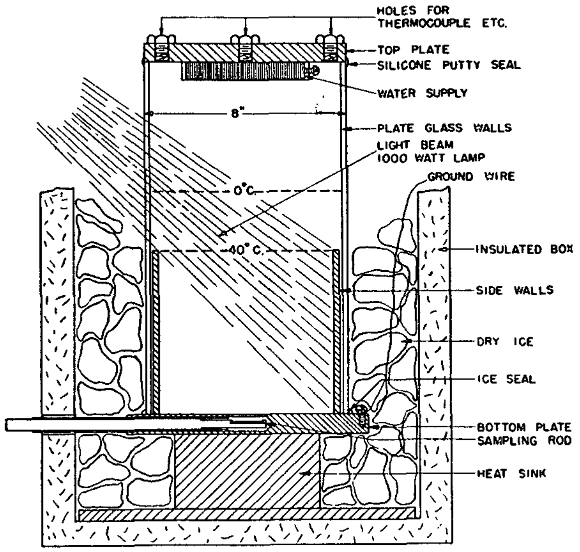

FIG. 1. Continuous cloud chamber for studying performance of nuclei under controlled conditions.

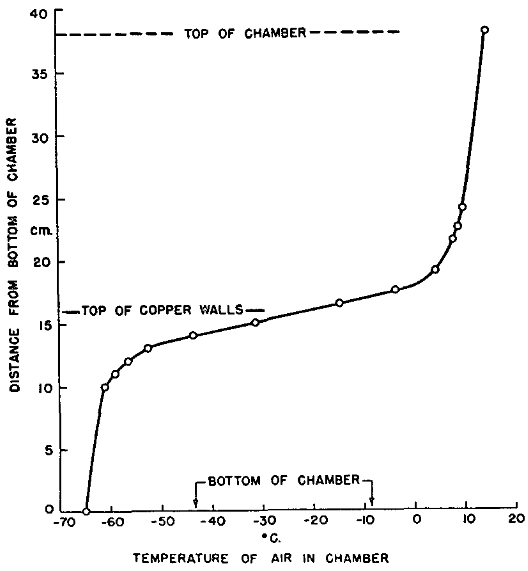

FIG. 2. Temperature profile in continuous cloud chamber.

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having a volume of a few cubic millimeters were introduced into the continuous cloud chamber. Fig. 2 illustrates the temperature distribution in the chamber. This was operated under two conditions of absolute humidity, namely, (1) supersaturation with respect to ice at − 5C, and (2) supersaturation with respect to water at + 5C. The samples were introduced at two levels in the chamber, one having a temperature of + 5C and the other about − 5C. Two inlets were used for introducing aerosol samples. In this manner, simultaneous comparisons could be made between two different materials.

Aerosol samples of silver iodide and lead iodide were prepared by the methods described previously. No appreciable differences were observed in the formation and growth of ice crystals on nuclei produced by these two different techniques. There should be considerable differences in crystal structure, since in one case the particle consists of an adsorbed layer of iodine on a metallic particle, while the other probably consists of a homogeneous crystal of the metallic iodide.

Role of silver- and lead-iodide particles as sublimation nuclei.—The first series of experiments was made under conditions in which the submicroscopic smokes were introduced into the − 5C region with the air supersaturated with respect to ice. Under these conditions, the tiny particles could serve as sublimation nuclei for ice-crystal formation if they possessed a suitable structure for such a role. Samples of silver iodide and lead iodide smokes were introduced side-by-side, to make direct comparisons.

It was found that both silver iodide and lead iodide served with equal effectiveness as sublimation nuclei at temperatures colder than about − 5C.

Role of silver- and lead-iodide particles as freezing nuclei.—A different relationship exists, however, when these two kinds of particles are compared as freezing nuclei. To do this, it is necessary to introduce aerosol samples at the + 5C level under conditions of supersaturation with respect to water. To accomplish this, it is necessary to permit all foreign nuclei to "rain out." The particles thus serve as condensation nuclei and form cloud droplets in the warm zone of the chamber. If a direct comparison is made between silver iodide and lead iodide under these conditions, both substances seem to work equally well as condensation nuclei. As they fall into the cold zone of the chamber, each water droplet which formed on a silver-iodide particle is observed to shift to an ice crystal at about − 5C [5].

The droplets formed on lead-iodide particles behave differently, however. After serving as nuclei for water-drop formation at + 5C, they fall into progressively colder air, supercool, and do not cause ice-crystal formation until cooling to about − 20C.

This difference between the effectiveness of silver iodide and lead iodide in their role as freezing nuclei may be related to the difference in solubilities of these two substances. At 0C, the solubility of PbI_2 is 4×10^{-2} g/100ml of water, and that of AgI is about 3×10^{-7} g/100ml. This difference in solubility of more than 100,000 times may account for the observed differences.

Studies of particles under the microscope.—After noting the relationships between lead and silver iodide, a different type of experiment was devised. A microscope was placed in a cold chamber and cooled to the surrounding temperature of about − 20C. Large lead-iodide crystals were made by dissolving 4 g of powdered lead iodide in a liter of boiling distilled water. Upon cooling, many very beautiful, extremely thin hexagonal crystals precipitated out of solution. Many of these crystals were so thin as to produce brilliant interference colors. Under the microscope they appear as extremely flat and featureless hexagonal plates, as shown in fig. 3. Many of these crystals gather on the surface of the water as a monolayer and appear to be hydrophobic. By lowering a clean microscope slide through the water surface, a sheet of these crystals may be easily transferred to the surface.

Suitable objective and ocular lenses were put in the microscope to give a magnification of 100. Under such conditions, 20-micron droplets are easily observed as they land on the surface of a slide, since they appear to be about 2 mm in diameter. Ice crystals produced in a supercooled cloud in the chamber by dry-ice seeding appear to be from 5 to 15 mm in diameter under the same conditions. By this method, it is quite easy to observe the effect of different types of surfaces on supercooled water droplets.

When supercooled water droplets land on a dry surface of the glass microscope slide, they immediately evaporate. If the surface is coated with a thin layer of ice, they freeze immediately. If ice crystals land on

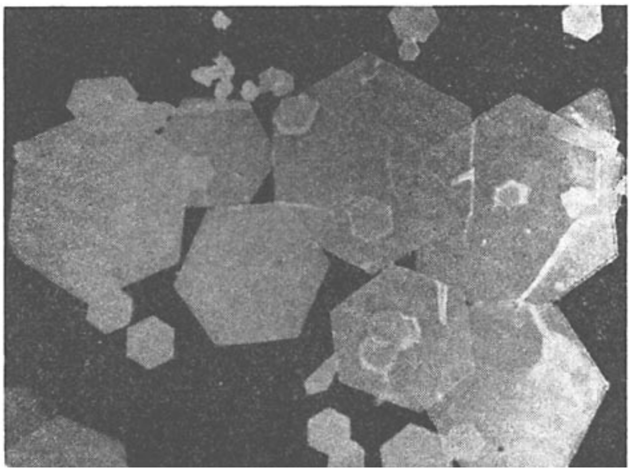

FIG. 3. Lead-iodide crystals formed in cooling water.

the clean glass surface, they remain unaffected by the heat of the microscope illuminator and persist indefinitely. A supercooled water droplet landing on one of these crystals immediately freezes.

Under such conditions, it is of interest to observe the effect of lead-iodide and silver-iodide crystals upon supercooled water droplets which contact their surfaces. An aggregation of lead-iodide and silver-iodide crystals was placed on a clean glass surface, so that comparisons could be made within the viewing field of supercooled droplets landing on (1) dry glass, (2) ice crystals, (3) silver iodide, and (4) lead iodide.

Under these conditions, the droplets evaporated after landing upon the dry glass and the flat surfaces of the lead-iodide crystals. They froze instantly on the ice crystals and the silver-iodide particles. These latter crystals were not as symmetrically formed as those of the lead iodide.

The differences observed between the freezing of the droplets were consistent with the picture that silver iodide is a good freezing nucleus but lead iodide is not.

A possible reason for the anomalous behavior of large lead-iodide crystals.—A possible explanation of the anomalous behavior, whereby a supercooled droplet evaporates before freezing while resting on the surface of a large lead-iodide crystal, has been proposed by Mr. David Turnbull of this laboratory. He pointed out to the writer that the extreme thinness of the lead-iodide crystals (which often show first-order interference colors) suggests that their thickness is a direct function of the effective size of the nuclei upon which they form, and that the flat surface which develops in the direction of the a-axis represents an area free of edges due to the termination of screw dislocations in the hexagonal plane of the crystal. These edges are necessary to inaugurate further crystal growth, either of the same material or of a closely related structural molecule due to epitaxy. If such sites are not available, further growth is inhibited. Since this is the axis of the lead-iodide crystal along which the lattice constant is nearly identical to that of ice, this hypothesis may suggest the reason why lead iodide is suitable as a sublimation nucleus but not as a freezing nucleus. The only suitable sites for growth would thus be at the edge of the hexagonal plates. Bulk water contacting such regions would tend to dissolve the active surface. Vapor water would form an ice crystal directly from the gaseous phase and thus could not cause solution. Water droplets landing on the flat surfaces of the crystals evaporate before freezing due to the absence of nucleating sites on this part of the crystal. Presumably they would freeze, or at least leave an icy residue nearby, if nucleating sites were available, since both ice crystals and silver iodide under the same conditions are effective in this respect.

Time did not permit carrying out a critical experiment in this regard. A large lead-iodide crystal should be mounted on a slide, checked for behavior with respect to liquid and gaseous water vapor, and then deformed by heat or pressure. Following deformation, the surface along the a-axis might be expected to serve as a good site for ice-crystal formation from the gaseous phase. It might also serve to initiate crystallization of water droplets, small with respect to the dimensions of the lead-iodide crystal.

Need for further studies in this field.—These interesting relationships between ice crystals, lead iodide, and silver iodide emphasize the importance of further research along such lines.

There are many methods which may be used to produce these metallic iodides as submicroscopic particles. They may be vaporized directly by heating the dry powder in a flame or on a hot surface. Solutions may be atomized directly to form a hydrosol or sprayed into a burning flame to be vaporized. Iodine vapor may be passed over silver or lead electrodes. Burnable material, such as paper, string, charcoal or coke, may be impregnated with the iodide as powder or with solutions of these materials, burned, and the vapor condensed. The effectiveness as an ice nucleus of aerosols produced by these various methods may then depend on the manner in which the individual particles form or crystallize *and* on subsequent reactions which may occur in the atmosphere as gases adsorb on them, ultraviolet light shines on them, or they in turn become part of a synergistic reaction. Many of these effects may be studied in the laboratory under controlled conditions. Most of them should be tested in the free atmosphere.

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