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STUDIES OF CUBIC ICE CRYSTALS

Final Report to the Office of Naval Research

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Dr. William Hoppel, Acting Program Manager

by

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EXECUTIVE SUMMARY

This three-year study, conducted for the Innovative Science and Technology Program of the Strategic Defense Initiative Organization through the Office of Naval Research, has produced a number of interesting findings of consequence to the atmospheric sciences. More important, the discovery of one phenomenon--that ionic salts which are present undergo differential ion inclusion into the ice phase of growing ice crystals--results in the explanation of many ice crystal initiation, growth, and interaction processes. These include ice crystal aggregation, morphology and symmetry, secondary ice crystal formation, and coupled oxidation-reduction reactions in growing ice crystals. Implications of these processes involve atmospheric pollution processes, planetary oxygen atmosphere generation, Antarctic ozone depletion processes, and ore bodies of atmospheric origin. Potential roles in thunderstorm electrification can be seen.

It is anticipated that these discoveries in ice crystal growth phenomena will apply equally well to crystal growth processes in general. (AU)

This report was compiled from reviewed publications and conference preprints. Some duplication of procedures and theory will therefore be evident.

This study, while primarily conducted under SDIO and ONR sponsorship, was also partially funded by the National Oceanic and Atmospheric Administration, in areas relevant to their program. The Atmospheric Science Center of the Desert Research Institute provided technical support and cloud chamber upkeep and maintenance.

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1. INTRODUCTION

The original focus of the study was to experimentally investigate ice crystal structure and habit, relevant to the question of the shapes of crystals in noctilucent clouds. However, after the discovery, by this group, of electric charge distributions (electric multipoles) in growing ice crystals containing low concentrations of ionic salts, and with the approval of the Contract Managers (Dr. James Hughes, and later Dr. Paul Twitchell), we pursued studies of the charge distributions in growing ice crystals and how they affect ice crystal initiation, growth, interaction, and chemical reactions. This final report for the three year period, 1986-1989, therefore describes the work we performed and our results relevant to electric multipoles in growing ice crystals.

Initially, we surveyed the configurations of ice crystal junctions in aggregates of two to six crystals grown in the cloud chamber. The junctions were classified according to their geometry, an approach that several investigators have pursued previous with spatial crystals in an effort to learn about the crystallographic nature of the branches. However, our efforts were designed to determine whether the postulated charge distributions could be manifested through some influence on the geometry of the crystal junctions. Our hypothesis in the study was that solutions with higher magnitude freezing potentials would exhibit a larger percentage of T-shaped ice crystal junctions. Our experimental results confirmed the hypothesis, and we can find no other reason to explain why low concentrations of dissolved salts in growing ice crystals should affect the configurations of junctions so strongly.

In the course of the study of aggregation, we happened to notice that we could distinguish the solutions used in particular runs on the basis of the details in ice crystal shapes. We performed a few, qualitative analyses of the effects of solutes on the shape and found that, in general, the solutions with higher freezing potentials were the ones which produced the most elaborately shaped ice crystals at -16°C. An exception to this tendency, which we pondered for awhile, was the ammonium carbonate solution. Sometimes, the solutions would result in highly elaborate crystals, and other times it would yield very simple crystals. We tentatively concluded that the ammonium carbonate reacted with atmospheric carbon dioxide (CO_2) to produce ammonium bicarbonate (NH_4HCO_3), which has a lower freezing potential. Hydrogen ion concentration also has a pronounced effect on ice crystal morphology. Low pH solutions yielded consistently simple crystal shapes, while high pH solutions yielded consistently elaborate crystals. When we compare this with the results of Workman and Reynolds for acid solutions, which all yielded negligible freezing potentials, we conclude that the pH also has effect on the freezing potential and shape of crystals. This line of research is being continued under separate sponsorship.

It is interesting to correlate freezing potential with ice crystal shape, but it is much more satisfying to devise a process by which the observed phenomenon can be achieved. To that goal, we postulate that, at the growing ice crystal interfaces (located at the growing edges of the crystal), the rejected charge, which is of higher magnitude with higher freezing potential solutions, is manifested in a liquid layer and is therefore somewhat mobile (although constrained by geometry and surface tension). Thus, we postulate that growing crystals with higher freezing potential solutions have higher magnitudes of charge at the growing interfaces, and that the repulsive electric forces tend to maximize the growing interfacial length (create instabilities rather than permit the growth to follow the crystallographic directions).

It is interesting that this concept, that electric forces and surface tension act to control the ice crystal morphology (detailed shape and form), not only explains the variety of crystal shapes that were observed in the cloud chamber (and the tremendous diversity of crystal shapes in the real atmosphere), but also explains the symmetry which is present in natural crystals. Without the electrostatic forces present to attract condensed water molecules to the growing edges, there is no compelling reason why ice crystals should be either symmetrical or so highly non-spherical.

Section 2 describes the theory of electric multipoles in growing ice crystals containing inorganic salts. The theory has thus far been entirely developed within our group, and requires further study. Also, the theory, being in its infancy, does not yet have the polished mathematical formalism.

Section 3 describes the interaction of two ice crystals with electric multipoles, including the aggregation phenomenon. Included in this section are the results of our cloud chamber tests that tested (and supported) the hypothesis of electric multipoles in growing ice crystals.

Section 4 describes our studies of one of the manifestations of ice crystal growth, namely ice crystal morphology. Ice crystal morphology is the detailed shape and form of the crystal, as contrasted to what is called the ice crystal habit, which is the expression of the crystal overall aspect ratio, with minimal regard to details. Habit is concerned primarily with a-axis or c-axis growth, and is coded descriptively (a-axis crystals including plates, sector plates, stellar ice crystals, and dendrites, and c-axis crystals including needles and columns). This section looks beyond the overall aspect ratio, to examine the effects of dissolved inorganic salts on the details manifested in growing ice crystals.

Section 5 describes our studies of secondary ice formation--the formation of ice crystals in the atmosphere without the benefit of precursor ice nucleating substances. Our research in this area is new, and has been limited by the time and resources at our disposal.

Section 6 describes our studies of chemical reactions in growing ice crystals containing ammonium and/or halide ions. It begins with a subsection on the theory of electrochemical-like, coupled oxidation-reduction reactions arising from a charge separation in growing crystals, and follows with our experimental studies and results.

Section 7 presents some of the implications of the research presented in sections 2 through 6. In section 8, we present additional discussion regarding the research. Section 9 presents a short summary of the major findings and conclusions of the study.

The research was conducted with funding from the Innovative Science and Technology Program of the Strategic Defense Initiative Organization, through the Office of Naval Research. Our Program Managers, Dr. James Hughes, Dr. Paul Twitchell, and Dr. William Hoppel, have all been most enthusiastic and supportive of our research. We also acknowledge the support of the National Oceanic and Atmospheric Administration through a NOAA-Nevada cooperative program that ran parallel to the ONR study, and of the NOAA Program Manager, Dr. Roger Reinking. Mr. Lawrence G. Young of the Atmospheric Sciences Center of DRI contributed materially to the research program through extensive discussions regarding ionic separation phenomena and the observed electrical and chemical effects. Finally, we acknowledge the gracious support by the Dr. Joseph Warburton, Executive Director of the Atmospheric Sciences Center of the Desert Research Institute.

Without such a team effort, this very fruitful and exciting line of research would not have accomplished so many significant results.

2. THEORY OF ELECTRIC MULTIPOLES IN GROWING ICE CRYSTALS

Workman and Reynolds (1950) investigated electrostatic potential differences which arose across the ice-water interface during freezing of dilute aqueous solutions of ionizable salts. Their results have been substantiated and extended in laboratory experiments by other researchers (Gross, 1968). These investigations have conclusively demonstrated that differential incorporation of ions into the ice crystal lattice gives rise to the potential difference across the growing ice crystal interface.

For example, when a solution containing 10^{-5} equivalents per liter of sodium chloride (NaCl) is frozen, the chloride ion (Cl^-) is partially incorporated into the ice and the sodium ion (Na^+) remains with the water. This results in a potential difference of 30 V across the ice-water interface, with the water positive relative to the ice. For a 10^{-5} normal solution of ammonium sulfate [$(NH_4)_2SO_4$], the ammonium ion (NH_4^+) is largely incorporated in the ice and the sulfate ion (SO_4^{-2}) is almost completely rejected, resulting in a potential difference of 61 V across the interface, with water negative relative to ice. Figure 1 depicts the separation of ions during freezing and the development of a potential difference across the growing ice interface.

Additional studies of freezing potentials (Gross, 1968; Pruppacher, et al., 1968) have reported different potential differences across the ice-water interface. The potential difference is clearly a function of the solute content (chemical species and concentration) in the freezing solution, as shown in each

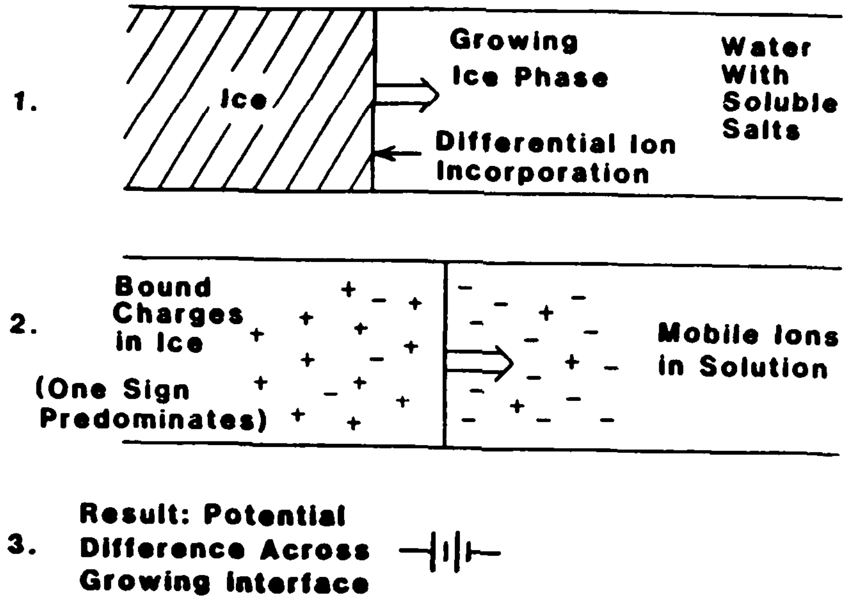

Fig. 1 Conceptual diagram of formation of potential difference across growing ice interface.

experiment. It is also a function of the freezing conditions, namely the geometrical configuration and the rate of freezing.

Ice is a protonic semiconductor: protons are more mobile in the ice lattice than are electrons. Ice is also a conductive dielectric. This presents difficulties in making accurate electrical measurements across the ice-water interface. Gross and McGehee (1988) only recently devised a layered-capacitor method for measurements of dielectric relaxation and dc conductance in ice.

Different ions may be incorporated into the ice crystal lattice in different ways. Some, particularly ammonium ion, are believed to be incorporated into ice by substituting an ammonium ion for a water molecule in the ice crystal lattice. On the other hand, halide ions (fluoride, chloride, bromide and iodide) are believed to be incorporated into the interstitial "holes" between oxygen atoms in the ice crystal structure, which are aligned along the c-axis of the crystal.

Even when pure, distilled deionized water is used, a small potential difference may develop across the growing ice interface, since water ionizes. Larger values, sometimes noticed, may be the result of incorporation of carbon dioxide and ammonia from the air. Unless special precautions are taken, some ammonium carbonate will be present in the water.

Workman and Reynolds found the strongest freezing potentials at salt concentrations between 10^{-5} and 10^{-4} N, which correspond roughly to those typically found in atmospheric clouds and precipitation. When ice crystal growth stops, the potential difference decays. The decay may be due either to proton migration within the ice lattice, which eventually recombines charges across the ice-water interface, or, as we have found during this research program, to electron transfer, which leads to oxidation-reduction reactions. Thus, the process is a dynamic one, requiring the growth of the ice crystal lattice to differentially incorporate ions.

The Workman and Reynolds experiments were conducted with the ice-water interface growing in one direction, due to the geometry of the apparatus in which the water is frozen. In atmospheric ice crystals, growth proceeds more or less symmetrically. Needles and columns grow along their c-axis in two opposite directions, and plates and dendrites grow along their a-axes in six directions, more or less in a plane.

By visualizing each growing ice interface as maintaining a potential difference, as a result of a charge separation due to the differential ion incorporation (by analogy with the Workman-Reynolds effect), and by superimposing this onto the geometry of a growing ice crystal, we postulated that the pattern of the charge distribution in growing ice crystals could be represented by an appropriate electric multipole, with one dipole across each growing interface (Figure 2).

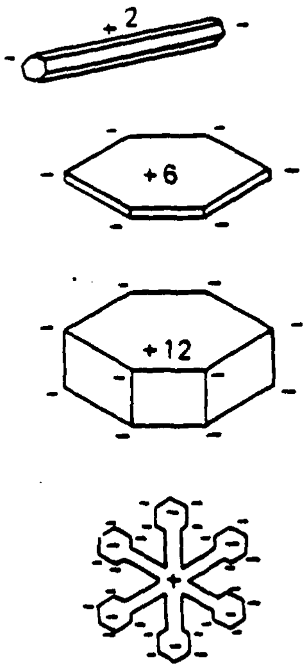

Fig. 2 Representation of charge configuration in ice crystals.

The next four sections present our laboratory studies in different cloud physical phenomena: aggregation, ice crystal morphology, secondary ice formation, and chemical reactions in growing ice crystals. In each instance, we are able to explain the observations by the postulates of differential ion incorporation in the ice phase and electric multipoles in growing ice crystals. Additionally, although the concept of internal charge distribution in atmospheric ice crystals is quite new, we have found substantial evidence in the crystal growth literature that similar phenomena observed in other types of crystals may also be the result of charge distributions. If this is substantiated, then we have discovered a broad, perhaps universal, feature of the crystalline growth of substances.

3. ICE CRYSTAL INTERACTIONS (AGGREGATION)

3.1 PROBLEM STATEMENT

The onset of aggregation among ice crystals is an important evolutionary milestone in a supercooled atmospheric cloud. The yet-unanswered questions of when aggregation commences, how fast it occurs, and what factors affect the rate of aggregation, are highly relevant to the overall understanding of the development of various types of precipitation. Our present understanding of the onset of aggregation, and of aggregation rates in general, is presently too sparse to obtain reliable numerical calculations of the evolution of precipitation in ice-bearing clouds.

The initial aggregation event, between two single crystals, often results in a T-shaped aggregate, whereby the tip of one crystal joins at the center of the largest face of the other, frequently at angles close to 90 degrees (Odencrantz et al., 1968; Smith-Johanson, 1969). The two-crystal aggregates are not to be confused with spatial crystals (Lee, 1972), which arise by diffusion growth from a polycrystalline ice crystal, or from an impurity on the existing crystal surface. The appearance of more T-shaped aggregates in the Yellowstone Field Research Experiments when silver iodide nuclei (2AgI-NaI) were used, as opposed to when dry ice was used for nucleation, indicated that something about silver iodide/sodium iodide acted such that the initial aggregates were strongly oriented toward point-to-center (Magono and Tazawa, 1972).

Our investigation of the nature of ice crystal aggregation--particularly a curiosity of why T-shape crystals are sometimes so prevalent--began with an assessment of the forces involved during the interaction: namely, aerodynamic, inertial, gravitational, and perhaps electrostatic.

The first three forces--aerodynamic, inertial, and gravitational--always act during an ice crystal interaction in the atmosphere. The non-spherical geometry of ice crystals also gives rise to crystal tilting, and hence to gliding and, perhaps, to associated fluttering or tumbling of the crystals as a result of their overall aerodynamic interaction. With such variations in the free-fall behavior of single crystals, one would anticipate that the configuration of initial aggregates would be happenstance, and consequently would tend toward a random distribution of possible orientations. Liquid layers on crystals near 0°C would not affect the distribution of orientations, although tangling of dendritic branches might affect the distributions near -16°C.

Aerodynamic, inertial, and gravitational forces affect the interactions of water drops (Grover and Beard, 1974), and affect ice crystal riming and scavenging of aerosols (Pitter and Pruppacher, 1974; Martin et al., 1981). The effects of these forces, and the initial positions and orientations of the ice crystals, on ice crystal aggregation varies with the size and shape of the ice crystals. However, these forces cannot account for the frequently-observed point-to-center orientations of crystal junctions in aggregates. Therefore, since these orientations are more frequent than we surmise would occur by chance, we suggest that these orientations are the result of the action of other forces during ice crystal interactions.

Electric forces involve a variety of possibilities. Schlamp et al. (1976) investigated the effects of the external electric field intensity and the net charges on two interacting water drops. Although similar studies have considered the effects of net charges, but not of external electric fields, on aerosol scavenging by ice crystals (Martin et al., 1981), the combined effects of electric fields and charges on ice crystal interactions are still unknown.

Only electrostatic forces might lead to an ordered configuration of crystals in aggregates, such as the point-to-center orientations previously noted. The action of net charged crystals does not lead to such configurations; nor does a postulated charge distribution consisting of dipoles on crystals, as might be induced by external electric fields of sufficient strength. The lowest order charge distribution on a crystal which could lead to a point-to-center charge distribution is a linear quadrupole. This configuration would yield results consistent with the observations of T-shaped aggregates. Electric multipole charge distributions, however, have effects only in their immediate vicinity. The electric field of a linear quadrupole diminishes as r^{-4} at a distance from the needle, and that of a high moment would vary even faster at a distance from a plate or dendrite. However, in the immediate vicinity of either shape of crystal, the electric fields are high and nonuniform. The effect of electric multipoles on aggregation relies on other forces to bring the crystals into close, but otherwise non-colliding, proximity.

Although many initial aggregates form otherwise, the evidence indicates an increased likelihood for T-shaped aggregates to form when ionizable salts are intentionally introduced into the cloud. This led us to examine precisely how the Workman-Reynolds effect, which relates the freezing potential of water to the soluble ions present, might be extended to an atmospheric ice crystal, and what the consequences of such might be.

Workman and Reynolds (1950) investigated an electrical phenomenon which arises during the freezing of bulk water with low concentrations of salts present.

Their laboratory studies, investigating the freezing of bulk samples of dilute ionic solutions, demonstrated that an electrical potential difference arises across a growing ice crystal interface as a consequence of differential ion incorporation into the ice crystal lattice. They noted that the magnitude of the potential difference, which has been termed the Workman-Reynolds effect, is related to the chemical content (the ionic species and concentration) and to the rate of growth of the ice crystal. Although attempts have been made to relate this phenomenon to cloud electrification, Pruppacher and Klett (1978) note the difficulty of achieving physical charge separation by means of this mechanism.

Cloud chamber work by Odencrantz and coworkers (Odencrantz and Buecher, 1967; Odencrantz, 1968; Odencrantz et al., 1968) provided additional evidence of the action of various solutes on ice crystals. They demonstrated that low concentrations of organic vapors affected ice crystal habit, and their charged wire apparatus results showed that ice crystals were preferentially attracted to one or the other polarity. They attributed this phenomenon to net charging of ice crystals.

3.2 EXPERIMENTAL

A series of laboratory experiments was conducted in the DRI 6.7 m^3 cloud chamber (Figure 3). The chamber has been described previously (Steele et al., 1981). It was operated at atmospheric pressure and constant temperature. The temperature was brought to a constant, sub-zero value, and was maintained by computer-controlled feedback from thermocouples to refrigeration system valves. Experiments were conducted at temperatures from -2°C to -30°C. The average temperature was maintained within 0.5C° throughout any run, and the instantaneous

(1 per second) readings of each of four thermocouples placed at various positions within the chamber were all within 1C° of the average.

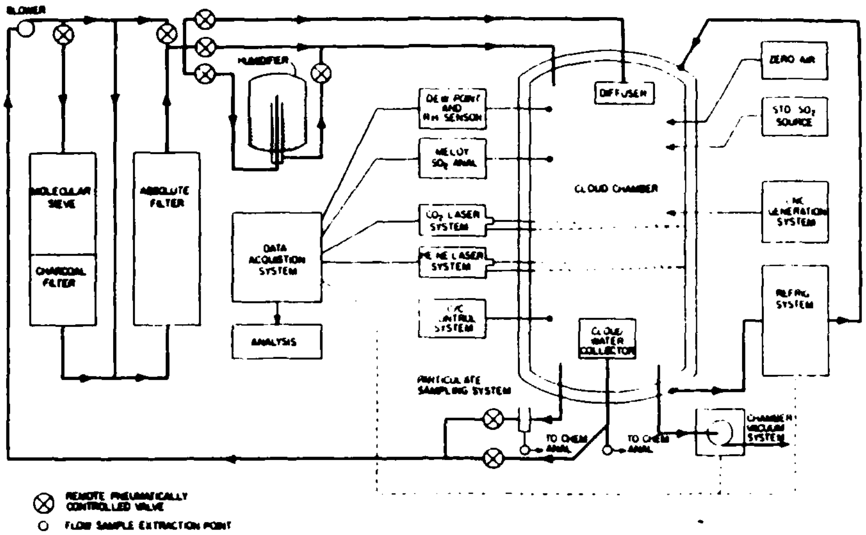

Fig. 3 Desert Research Institute cloud chamber facility.

Liquid water clouds containing 10^{-4} N solutions of various dissolved salts were produced using an ultrasonic nebulizer. This technique produced drops with extremely small net electric charges, of sizes up to about 20 μm diameter. Solutions of sodium chloride (NaCl), ammonium sulfate [$(NH_4)_2SO_4$], and ammonium carbonate [$(NH_4)_2CO_3$] were tested.

The liquid water content of the cloud chamber was monitored using a laser transmissometer calibrated for liquid water content (Gertler and Steele, 1980).

The nebulizer was operated until the liquid water content reached a steady value, typically in the range between 1.4 and 2.5 g/m^3.

Ice nucleation was initiated by adiabatic expansion of moist compressed air using an air pistol. Droplet freezing occurred by an undetermined mechanism; perhaps either as a result of the transient supercooling or by contact with ice embryos. Ice was visible within 75 to 90 s after the compressed air pulse was triggered. Ice crystal samples were collected on clean glass slides and removed from the cloud chamber two minutes after nucleation for microscopic investigation. The slides were placed on the microscope stage in an enclosure held at -20°C, and photographs were taken of several areas on the slide.

The electric nature of the ice crystals was investigated using a device shown in Figure 4. The device consists of two stages. The top stage is an induction ring, 34 mm in diameter and 19 mm in length, patterned after one devised by Gunn (1949). It is used to determine whether any drops or ice crystals possess high net charges. It is connected to an amplifier, and is capable of sensing the passage of charged drops or ice crystals with magnitude in excess of 1 fC (10^{-15} C). In principle, however, we expect any measured charges to be due to net charges on ice crystals, since droplets initiated by ultrasonic nebulization have extremely low initial charges and since the Rayleigh instability limits the magnitude of electrostatic charges on liquid drops. For example, a 20 μm diameter drop (the maximum size we expect, from photographs of rimed drops on ice crystals), would possess a charge substantially below the absolute limit of 1fC, and thus would not be detected. Electrostatic charges on natural, precipitating snowflakes and ice crystals have been previously measured by Magono and Orikasa (1966) and by Burrows and Hobbs (1970). The mean values they detected were several hundred femtocoulombs per snowflake.

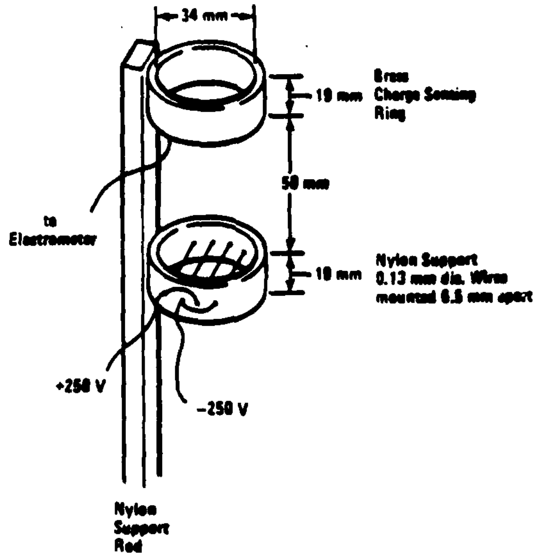

Fig. 4 Ice crystal charge measurement device.

The second stage of the electric detection device consists of four 0.13 mm diameter wires, mounted horizontally in parallel, 6.5 mm apart, resembling the device used by Odencrantz and Buecher (1967) and Odencrantz (1968). Wires 1 and 3 were charged positively, and wires 2 and 4 were charged negatively. The voltages applied to the wires were +/- 250 V. Odencrantz claimed this apparatus indicated the sign of the net charge on ice crystals. In his experiments, the crystal preferentially collected on the wires of one polarity only.

The present experiments were conducted to investigate the effects of solutes in growing ice crystals on the orientations of ice crystals in aggregates. In this manner, they were used to test the hypothesis of electric multipoles in growing ice crystals.

Since the freezing of sodium chloride and ammonium sulfate solutions in bulk result in oppositely polarized electric potentials across the growing ice interface, we followed a suggestion of Dr. B. Vonnegut (State University of New York, Albany) to conduct another experiment. Two nebulizers were used to generate the supercooled water cloud in the chamber, with a 10^{-4} N solution of ammonium sulfate in one and a 10^{-4} N solution of sodium chloride in the other. Initially, this produces a mixture of cloud droplets, half containing NaCl, the other half containing $(NH_4)_2SO_4$. The low rate of collision and coalescence of cloud droplets 10 to 20 μm diameter, in the absence of strong external electric fields or electric charges, causes us to believe that the populations intermixed in the chamber, but did not significantly coalesce with each other, during the experimental run.

The object of this "dual cloud" experiment was to test the postulate with regard to how oppositely polarized ice crystals aggregate. If ice crystal electric multipoles are all the same polarity (all ice crystals contain the same salts), then one would expect the proportion of T-shaped junctions to increase with the electric multipole strength, and for point-to-point junctions to correspondingly diminish with increasing electric multipole strength. However, if the cloud consists of equal numbers of ice crystals of both polarities, then one would expect an increase in the number of point-to-point junctions, due to aggregation of two oppositely-polarized crystals.

3.3 AGGREGATION RESULTS

The microphotographs were examined to count the various types of aggregate orientations. Each microphotograph viewed an area about 4.9 mm^2 on the slide.

Ice crystal aggregates of two to six crystals were analyzed, classifying each individual junction of crystals.

Examination of the photographs indicated a variety of orientations where two crystals make contact. Since analysis was limited to situations where the crystals were not highly three-dimensional, thus projecting beyond the plane of focus, the initial analysis was restricted to temperatures of -4° to -6°C, and -12°C. Aggregates with T-shaped junctions were observed at all temperatures between -4° and -30°C. However, at -4° and -6°C, all crystals are columns or needles. Single crystals and aggregates of two almost always lie flat on the slide, and most aggregates of up to six crystals are sufficiently in focus to determine how the crystals are oriented at their junctions. Similarly, at -12°C, the crystals are thin hexagonal plates which usually lie flat when they land on the slide. Aggregates of two to six crystals are easily discerned and classified.

For the needles and columns at -4° to -6°C, examples of the categories selected for orientations are shown in Figure 5. T-shaped aggregates are characterized by right angles between the individual crystals, and the junction occurs at the center of one crystal. Junctions at other angles, or off-center, were called lambdas, since they approximately resembled the Greek letter. Point-to-point junctions were those which joined two crystals at their ends, and which exhibited an obtuse angle. End-to-end junctions with acute angles were classified as vees. The final category of crystal junctions was reserved for other orientations. Most of these were crossed crystals.

The hexagonal plates present at -12°C were similarly classified, as shown in Figure 6. T-shaped aggregates were characterized by right angles and intersection of one crystal's edge at the center of the other's basal plane. Off-center or tilted (not right angles) junctions were classified as lambdas, following the example in the needle habit analysis. Crystals oriented edge-to-edge, with angles up to 90°, were classified as vees, and those with obtuse angles were classified as point-to-point junctions. A final category was reserved for other orientations. Most of these were overlapping crystals.

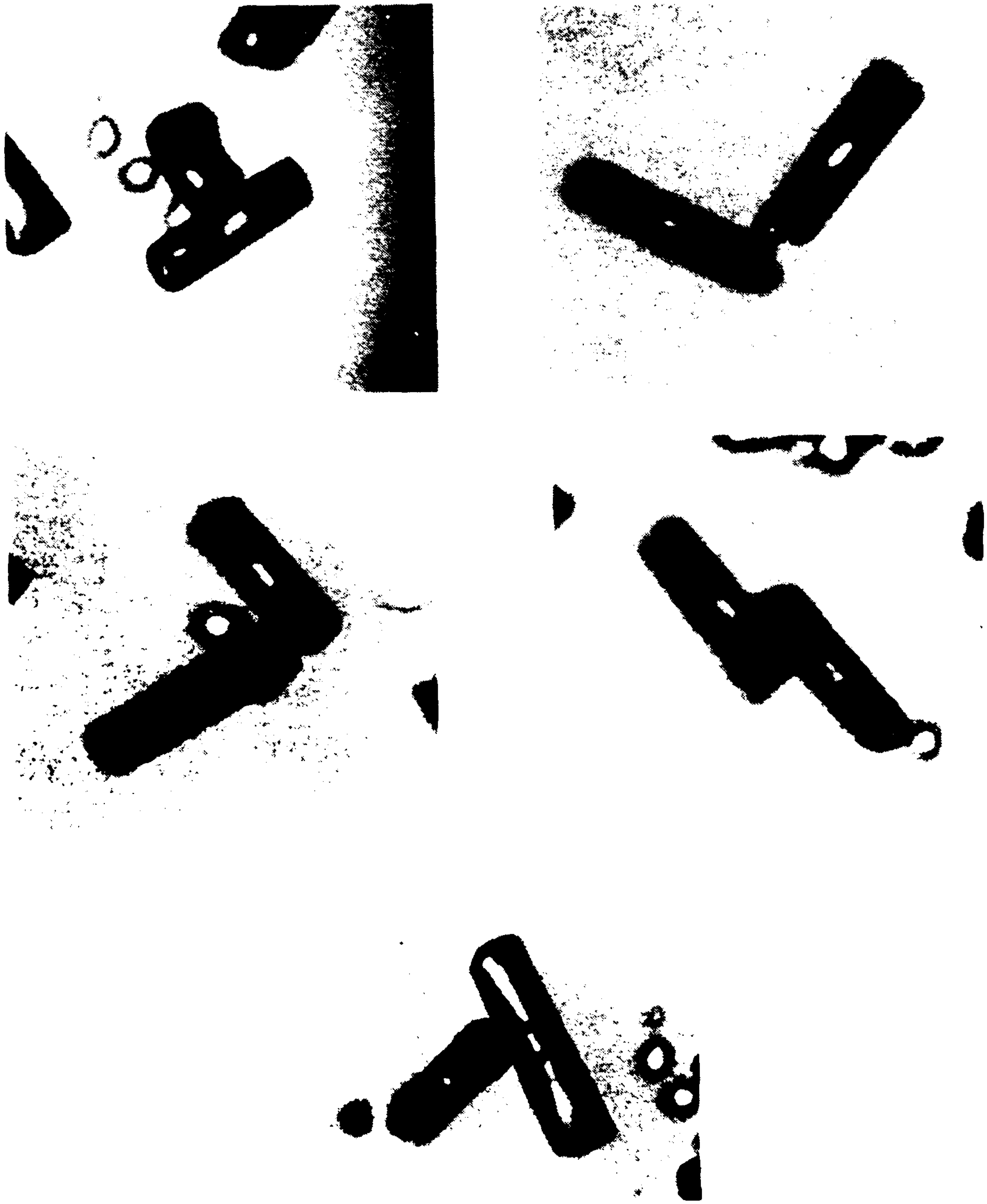

Fig. 5 Examples of junction categories for needles and columns.

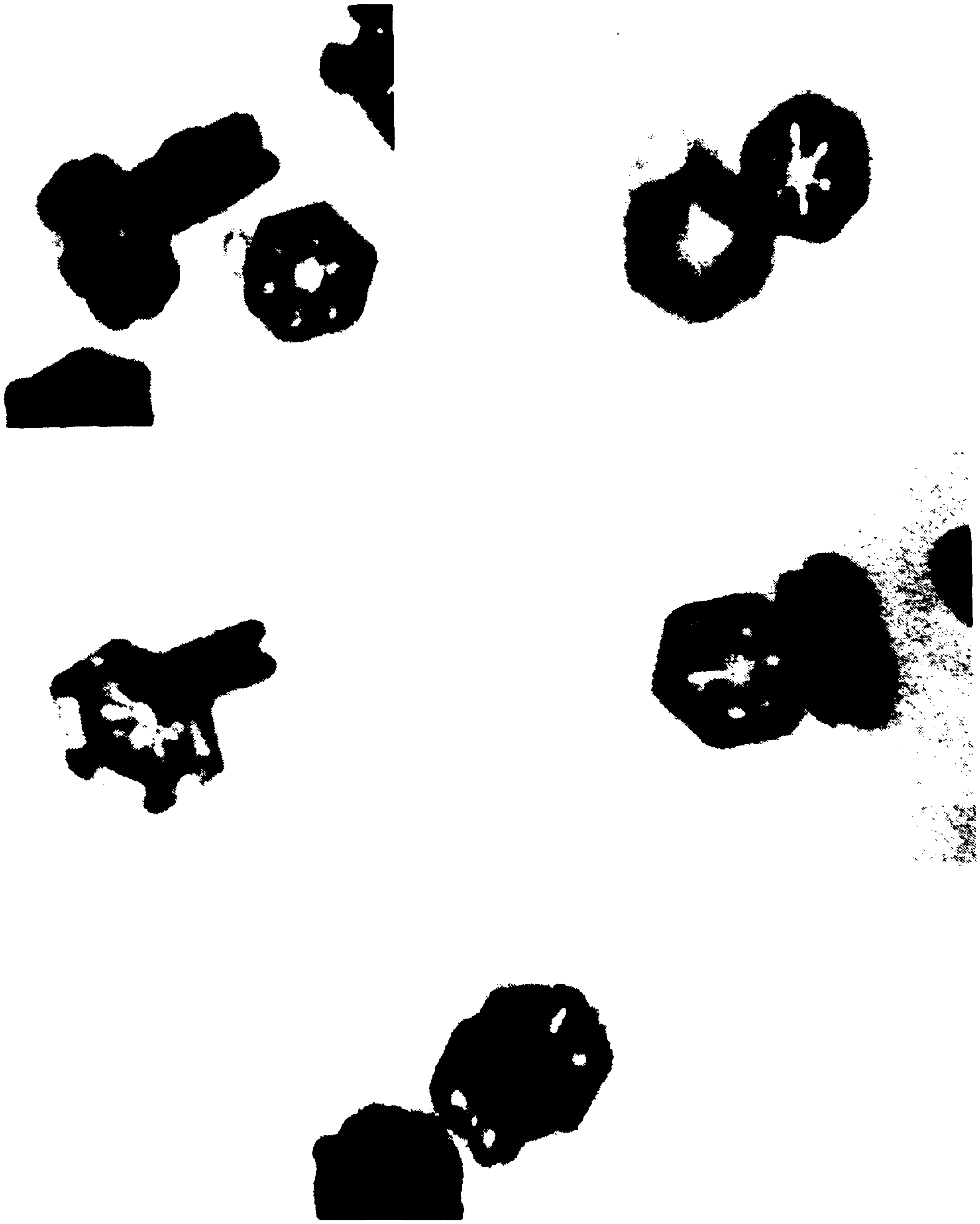

Fig. 6 Examples of junction categories for plates.

The classification scheme was designed to study the relative frequencies of crystal orientations at the junctions of pairs of ice crystals in aggregates. If ice crystals aggregate in the absence of electric forces, then gravity, aerodynamic flow, and inertia influence the interaction. For plate-like crystals, aerodynamic forces act during the interaction to tilt the crystals, causing them to glide horizontally while a restoring force acts to stabilize their orientation. This tends to yield butterfly-shaped aggregates (vees or lambdas); the combined action of aerodynamic and inertial forces does not provide any compelling reason for T-shaped junctions to form between two crystals.

Two quantities were devised to test the electric multipole theory using the data. The first, R1, is the percentage of T-shaped junctions observed. If crystal interactions were not influenced by electrical effects, then we would expect a low percentage of T-shaped junctions and R1 would be low. On the other hand, if electric multipoles strongly influence the orientation of ice crystals in aggregates, then R1 will be higher. R1 thus serves as an indicator of the influence of electric multipoles on aggregation. The second quantity, R2, is the ratio of point-to-point junctions to T-shaped junctions observed. This quantity is used to investigate the results of the dual-cloud experiments.

The concentrations of ice crystals generated and the resultant rates of aggregation were not quantitatively determined in these experiments. The primary objective was to test the hypothesis of electric multipoles influencing the geometry of the junctions of crystals in the aggregate.

Table 1 contains the results of experimental cases at -12°C, differing only in the types of ionic salts in solution. Only 15 percent of the aggregate junctions were T-shaped when distilled deionized water was used. When sodium chloride solution was used, only a slight increase in R1 was noted, but the ammonium sulfate solution cases exhibited a high percentage of T-shaped junctions--nearly half of all ice crystal junctions in aggregates.

The dual-cloud experiment resulted in the percentage of T-shaped junctions being intermediate to that when either of the two solutions was studied alone. There were almost equal numbers of T-shaped crystal junctions and point-to-point junctions (R2=0.89). The value of R2 is considerably higher for the dual cloud experiment than it is for either of the individual solution clouds.

Table 1

Summary of Ice Crystal Aggregation Junction Types

Plate-Like Crystal Aggregates (-12 C)

Solute	Tees	Lambdas	Vees	Pt-Pt	Other	R1[1]	R2[2]
(Deionized)	6	5	16	9	4	0.15	1.50
Sodium Chloride	9	13	20	4	4	0.18	0.44
Ammonium Sulfate	31	12	6	7	8	0.48	0.23
Dual[3]	18	8	9	16	1	0.35	0.89

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[1] R1 is the ratio of Tees to sum of all types of junctions.

[2] R2 is the ratio of Pt-Pt to Tee junctions.

[3] Dual cloud consists of sodium chloride solution droplets and ammonium sulfate solution droplets.

Table 2 presents the results for experimental runs at -4° and -6°C in the columnar growth regime. The results for distilled, deionized water show relatively few T-shaped junctions (only 16 percent). When the sodium chloride solution case is investigated, it again shows a modest increase in R1. The ammonium sulfate solution causes a much stronger tendency for T-shaped junctions to occur. This strong tendency is also reflected in ammonium carbonate solution cases. Both the ammonium salt solutions revealed lower values of R2.

Table 2

Summary of Ice Crystal Aggregation Junction Types

Needle Crystal Aggregates (-4 to -6 C)

Solute	Tees	Lambdas	Vees	Pt-Pt	Other	R1[1]	R2[2]
(Deionized)	7	13	8	11	4	0.16	1.57
Sodium Chloride	9	7	8	6	5	0.26	0.67
Ammonium Sulfate	8	4	0	3	0	0.53	0.32
Ammonium Carbonate	45	21	10	10	11	0.46	0.22
Dual[3]	31	40	4	29	4	0.40	0.94

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1 R1 is the ratio of Tees to sum of all types of junctions.

2 R2 is the ratio of Pt-Pt to Tee junctions.

3 Dual cloud consists of sodium chloride solution droplets and ammonium sulfate solution droplets.

When the dual-cloud experimental runs were conducted, the results again showed nearly equal numbers of point-to-point and T-shaped junctions, as was observed at -12°C.

The charged wire apparatus was used to examine the electrical nature of the crystals. The first stage was capable of measuring net charges in excess of about 1 fC. The experimental durations ranged from 3 to 6 minutes, during which time the crystals grew and fell out to the chamber floor. Throughout that period of time, there were no detectable charges on the initial water drops, and no detectable net charges on the ice crystals. The second stage of the apparatus, with four parallel wires of alternating polarity, yielded the interesting results. There was ice crystal collection on the positive wires when ammonium salts were used to generate the cloud, and on the negative wires when sodium chloride was used, regardless of temperature. The interpretation of these electrical results is presented in the next subsection.

3.4 DISCUSSION

The results, shown in Tables 1 and 2, indicate a consistent pattern in the orientations of ice crystals in aggregates. For distilled deionized water cases, the predominant configurations are vees and point-to-point junctions. For sodium chloride solution cases, there is a slight increase in the proportions of T-shaped aggregates. When ammonium sulfate solutions are used, the T-shaped aggregates become the most frequently observed junction configuration, and the tendency switches from point-to-point and vee junctions to T-shaped and lambda junctions. Finally, when the dual-cloud case is examined, the orientations are mostly T-shaped and point-to-point junctions, with almost equal numbers of the two types.

For needles and columns, the effects of aerodynamic flow and inertia are expected to modify a random orientation of aggregated junctions which would results from differential rates of gravitational settling acting alone. The random orientation of junctions would result primarily in crosses, involving neither crystal's tips (fitting the 'other' category in the present analysis). Thus, we interpret the results of the deionized water case to indicate that aerodynamic and inertial effects skew the distribution toward one that contains significantly more tip junctions than cross junctions. Just how these junctions are distributed with regard to angle and position is not known at the present, but aerodynamic and inertial forces do not inherently compel aggregation junctions to be point-to-point or well-formed T-shaped junctions, so we would expect a low percentage of these categories under purely aerodynamic interaction conditions.

The increase in percentage of T-shaped junctions observed when ammonium salts were dissolved in the nebulized cloud water was interpreted as evidence in support of the postulated electric multipoles in growing ice crystals. If the orientation effect is related to the strength of the electric multipole, then the effect is also correlated with the freezing potentials as measured in bulk solutions. Workman and Reynolds (1950) reported that deionized water, carefully prepared and handled, had freezing potentials of only a few volts, while sodium chloride solution exhibited a freezing potential of +30 volts, ammonium sulfate exhibited a freezing potential of -61 volts, and ammonium carbonate exhibited a freezing potential of -109 volts.

Our observations of ammonium sulfate and ammonium carbonate solutions, throughout the course of the sponsored program, revealed that ammonium sulfate was a consistent and strong solution for electric multipoles (i.e., as manifested in the effects of aggregation, morphology, and secondary ice production), while ammonium carbonate solution was highly variable. We surmise that the variability of ammonium carbonate solutions may have been due to a reaction with atmospheric CO_2 to form ammonium bicarbonate. In the next section, on ice crystal morphology, we present some experimental data which substantiates this surmise.

The dual-cloud experiments are consistent with the existence of ice crystals with electric multipoles of both polarities, since the aggregates exhibit a percentage of T-shaped junctions intermediate to the values for the individual solution cases, and since the aggregates exhibit a percentage of point-to-point junctions which suggests that oppositely polarized electric multipoles in crystals also affect aggregation.

The present results therefore support the concept of electric multipoles in growing ice crystals. The postulate is consistent with both the observations of orientations of ice crystal junctions in aggregates and the results of crystal collection on the charged wires.

Martin et al. (1981) numerically found that electrostatic charges on small ice crystals of less than 1 a^2 e.s.u., where a is the crystal semi-major axis length in centimeters, were insufficient to affect the efficiencies of ice crystal riming. The crystal semi-major axis lengths in the present experiments were typically 100 μm (10^{-2} cm). Thus, crystals in our experiments with net charge of less than .01 e.s.u. (3.3 pC) would not be expected to have enhanced electrostatic riming efficiencies. Since net charges were below the detectable limit of the device we used (5 fC), and are over a thousand times smaller than the minimum required for enhanced riming, we do not expect the net charges on the ice crystals in the chamber to be strong enough to affect aggregation.

The electrical field generated by oppositely charged parallel wires is highly nonuniform. The work by Odencrantz used such an apparatus as a measure of ice crystal net charge polarity. Although our net charge ring indicates that ice crystals were charged less than 5 fC (since we recorded no signals, probably less than 1 fC), calculations show that the charged wire apparatus could differentially collect crystal with net charges down to approximately 0.05 fC for small needles, in the absence of electric multipoles. However, our observations of crystal collection on the wires differed from those of Odencrantz. Odencrantz and Buecher (1967) found, for ice crystals grown from a steam generator fog, that the polarity of the charge inverted seven times between -4 and -20°C. Their results are inconsistent with the ice crystal habit chart they present to explain their findings, since they have one or more polarity inversions within a single habit, and occasionally do not have inversions across temperature boundaries between habits.

Our results of collection on the charged wires with a cloud of deionized water were similarly inconsistent. Perhaps, as reported by Workman and Reynolds (1950), trace amounts of ammonia and carbon dioxide in air act to produce variable freezing potentials in pure water. The charged wire results with solutes present, which always showed ice crystal collection on the positive wires when ammonium salts were used to generate the cloud, and on the negative wires when sodium chloride was used, support the postulate of electric multipoles in growing ice crystals.

A hypothetical electric dipole (no aerodynamic effects), falling in a field created by an assembly of charged wires, would orient in the electric field and would then migrate toward the closest wire. However, an ice crystal, consisting of multiple dipoles and experiencing aerodynamic forces, would behave slightly differently. The edge of the crystal closest to a wire would experience the strongest electric field, and would react to either repulse or attract the crystal to that wire. If it is attractive (the outer charge polarity opposite to that of the wire), the wire would have an enhanced probability of collecting the crystal. If it is repulsive, the wire acquires a reduced probability of collecting the crystal.

One significant question that arises concerns the magnitude of the electric multipoles in growing ice crystals, how they are attained, and how strong the resulting electric fields are . This matter remains a topic for future studies.

The question of ion migration in such strong electric fields causes one to consider the mechanisms for maintenance of the charge distribution in growing ice crystals. Indeed, when ice crystal growth stops in the linear freezing of dilute solutions in bulk, the potential difference across the growing interface rapidly decays (Workman and Reynolds, 1950). Thus, the potential difference must be maintained by a dynamic process, intimately linked to the growth of the ice interface.

The rate of ice crystal aggregation is proportional to the square of the ice crystal concentration, multiplied by the collision efficiency. There is considerable disagreement in the literature on the effect of temperature on collision efficiency. The present results support those of Latham and Saunders (1970), who found collision efficiency to be independent of temperature.

One of us (WGF) investigated silver iodide aerosols for ice nucleation yields and rates for several years using the Colorado State University isothermal cloud chamber. The chamber provides a supercooled liquid water cloud of distilled deionized water at water saturation and at constant temperature. As ice forms, the crystals grow and fall ont glass slides for counting. The chamber rarely produced ice crystal aggregates; only an occasional two-crystal aggregate was encountered, even with ice crystal concentrations in excess of 1000 per liter, for observation periods of several tens of minutes. We interpret these observations to indicate an inherently low collision efficiency for small, salt-free single ice crystals growing at water saturation.

In the present experiments, the net electrostatic charges on crystals were below 1 fC, and were insufficient to influence aggregation. Yet, we readily observed the onset of aggregation after only a few minutes, with liquid water contents comparable to those used at Colorado State University, and with a range of ice crystal concentrations which were less than the higher concentrations observed in the Colorado State University cloud chamber. The most notable difference in the two experimental conditions was the careful use of distilled deionized water at Colorado State University and the use of water with 10^{-4} N concentrations of ionizable salts in the present study. On this basis, we surmise that not only do electric multipoles in growing ice crystals influence the orientations of aggregates, but they also influence the rate of aggregation during the first few aggregation events.

4. ICE CRYSTAL GROWTH (MORPHOLOGY)

4.1 INTRODUCTION

In studies of the growth of ice crystals, little attention has been paid to the influence of naturally occurring ionic salts--such as sodium chloride or ammonium sulfate--on the shapes and habits of growing crystals. This is interesting, especially since studies by Vonnegut (1948a), Hallett and Mason (1958a,b), and Odencrantz (1968) all found that low concentrations of organic vapors affected ice crystal habits, and since Nakaya (1955) reported that the ambient aerosol had confounded his studies of crystal habit. It was generally concluded that vapors influence crystal habit and morphology because they are irreversibly absorbed on various crystal surfaces, although the surface dependence of this absorption has not yet been fully explained. In crystal growth literature, low concentrations of ionic and/or non-ionic impurities have been shown to affect crystal habits and morphology (Van Hooke, 1961).

Some details of the variation of ice crystal habit with temperature differ slightly among investigators (Nakaya, 1955; Hallett and Mason, 1958; Kobayashi, 1961; Wang and Fukuta, 1984). Such details deserve further analysis for clarification. Our preliminary studies show that certain trace contaminants may be responsible for these differences.

Despite the common knowledge that ice crystals possess six-fold symmetry, there is no good explanation for the reason this is so (Maddox, 1985). Microscopic studies by many researchers have confirmed the approximate six-fold symmetry, but there is frequently some visible imperfection in the exact symmetry, such as slightly different details present on the dendritic branches on a crystal. Mortley (1985) suggested that electrostatic forces may be more reasonable an explanation of crystal symmetry. Whatever mechanism is responsible for crystal shape should, reasonably, have some built-in process which acts to maintain crystal symmetry.

The temperature-supersaturation diagram of ice crystal phase (Pruppacher and Klett, 1978) is difficult to reconcile with observations of the many different crystal shapes, insofar as the former suggests that the habit is determined by *only two* parameters. The temperature-supersaturation diagram offers no indication of how perturbations of habit allow so many different crystal shapes to exist. In light of this, it is interesting that crystal growth literature has long considered habit to be a function of *three* parameters--temperature, supersaturation, and impurities (Strickland-Constable, 1968). Reconciliation of these two attitudes is sought. Our belief is that the overall ice crystal habit, characterized by the aspect ratio (2a/c), is more strongly influenced by the temperature and supersaturation, while details of the crystal surface, which are investigated as ice crystal morphology, are more dependent on incorporated foreign ions.

4.2 EXPERIMENTAL

At the Desert Research Institute (DRI) in Reno, Nevada, investigations of the effects of chemical composition in cloud water on the ice phase processes of growth and interaction were conducted using the DRI 6.7 m^3 cloud chamber.

The cloud chamber is equipped with thermocouples for measuring temperature within 0.2°C, a dew point hygrometer for measuring relative humidity, a laser transmissometer for measuring the liquid water content of the chamber (Gertler and Steele, 1980), and a computer-controlled refrigerant regulator for maintaining accurate temperature control of the chamber. The experiments were conducted at ambient pressure (about 850 mb) and constant temperature.

Water clouds were generated with ultrasonic nebulizers, using 10^{-4} N solutions of sodium chloride, ammonium sulfate, ammonium chloride, sulfuric acid, and sodium nitrate--soluble substances with ions commonly detected in cloud and precipitation water. The concentrations of ions in the cloud water are similar to those found in natural clouds and precipitation (e.g., Berge, 1988). The liquid water content at the beginning of a run was varied between about 1 and 2.5 g/m^3. The drop size distribution was determined from photography of drops falling on the microscope slides. Typical size of such drops is about 10 - 20 μm diameter. Drops generated by ultrasonic nebulizers have very low electrostatic charging; our efforts to detect electrostatic charges yielded no signals, indicating that, if present, electrostatic charges on drops were below the level of detection of our unit (< 5 fC).

When the liquid water content had stabilized in the cloud chamber, ice was nucleated by adiabatic expansion of moist air, in the manner described by Vonnegut (1948b). This caused immediate ice formation without the introduction of other chemical substances. After the initial ice formation, there were no remaining nuclei to function at later times, as is invariably the case when contact freezing or condensation freezing nuclei are introduced to glaciate the cloud. This technique simultaneously nucleates of all the ice crystals, so the starting time of ice crystal growth is known. The ice crystals grew at the expense of the supercooled drops, which usually resulted in a predominantly ice cloud after several minutes. The large crystals were limited in their residence time in the chamber, and typically fell out before they reached 500 μm maximum extent.

Glass microscope slides were uncovered shortly after nucleation, and removed for microscopic analysis three minutes after nucleation. Sometimes, additional slides were exposed at such time and removed at subsequent 3-minute intervals. Microscope slides were placed on a microscope stage in a cold chamber at -20°C, to prevent melting and to minimize metamorphosis of crystals.

4.3 RESULTS

Ice crystal morphology refers to the physical shape and form of the ice crystal. In studies of natural ice crystals, researchers have used morphology to indicate rimed crystals and graupel, ice crystal aggregates, and fragments of ice crystals. In the present studies, however, ice crystals grew in the cloud chamber for only a few minutes before their increasing fall speed caused them to settle out, so these morphological studies are limited to studies of ice crystal habit and details of shapes which are normally classified within a single habit. Riming and aggregation, although noted in the chamber tests, are not considered in the morphological context in this work because they describe morphological features of collections of hydrometeors, while we are considering the properties of single hydrometeors.

Our interest in ice crystal morphology centered on the question of how soluble ionic salts in ice crystals affect the details of ice crystal shape. The emphasis of the study was observation of the effects of different ionic salts on the ice crystal morphology.

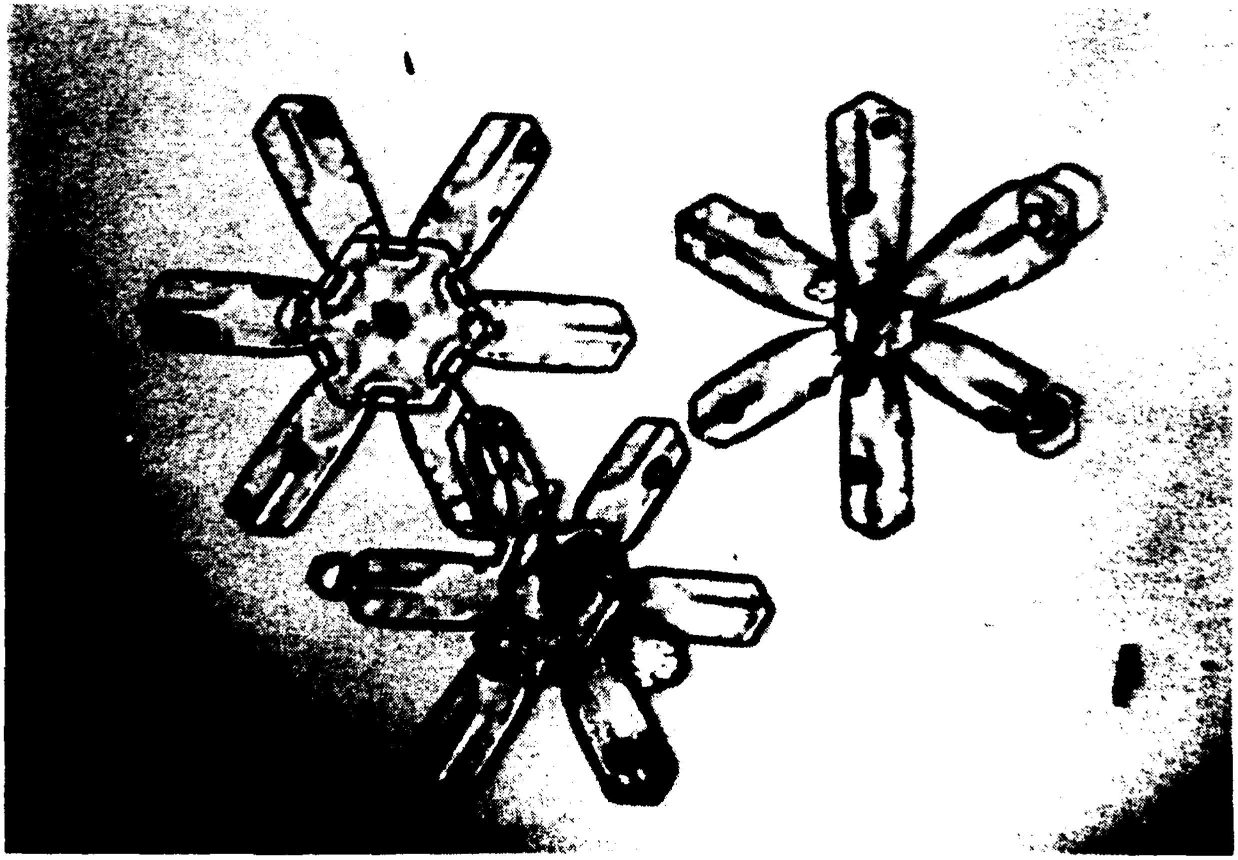

Fig. 7 Crystals grown from deionized water at -16°C.

One of our studies investigated the effect of different solutes in cloud water on ice crystal shapes at -16°C. Experiments involving 10^{-4} N concentrations of sodium chloride (NaCl), sodium nitrate ($NaNO_3$), ammonium sulfate [$(NH_4)_2SO_4$], ammonium carbonate [$(NH_4)_2CO_3$], and sulfuric acid (H_2SO_4) in supercooled cloud water were compared with those conducted with deionized water. The crystals formed from each of these different aqueous solutions all possessed dendritic habit, but contained specific, reproducible differences.

Crystals grown from deionized, distilled water clouds grew to be dendritic crystals, with each branch consisting of straight, parallel sides, very few features, and an apex of 120 degrees flanked by two straight edges (Figure 7).

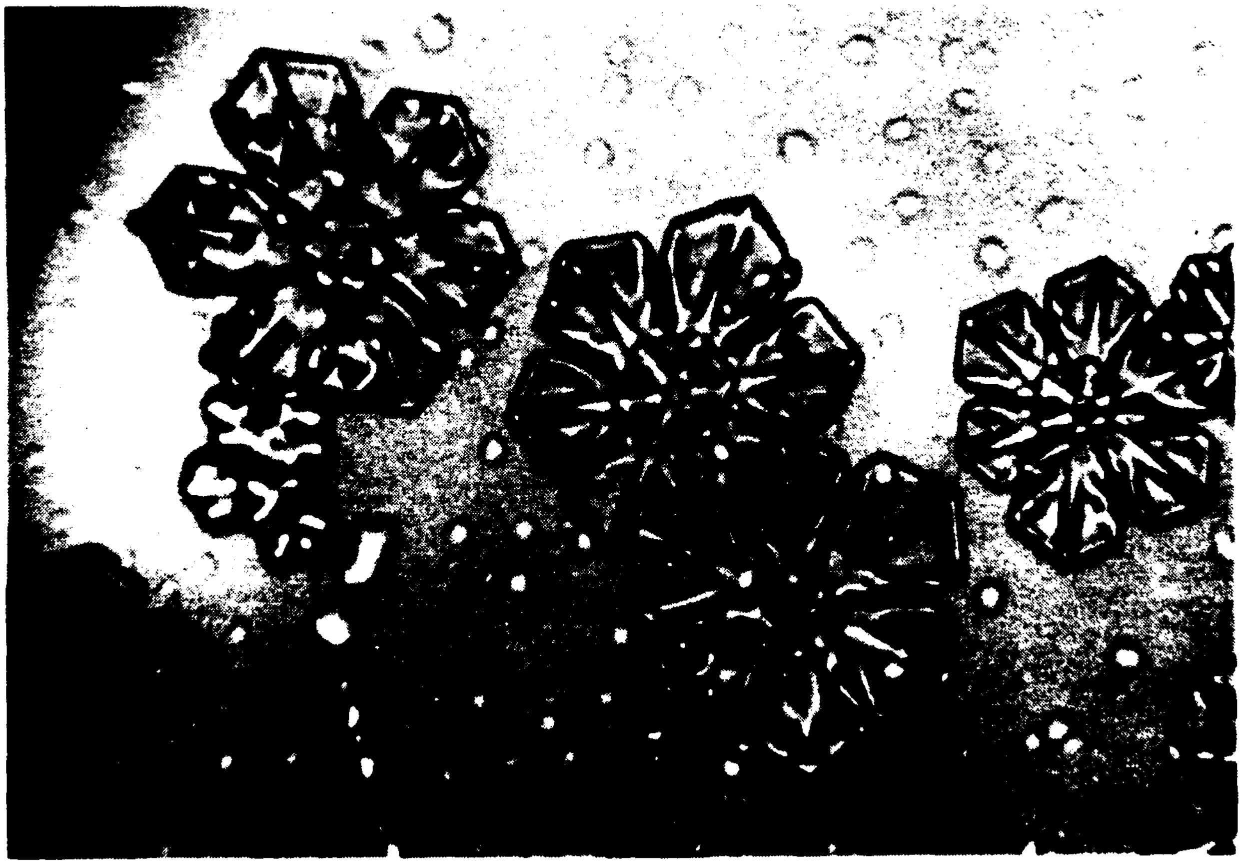

Fig. 8 Crystals grown from solutions of sodium chloride at -16°C.

Crystals formed in sodium chloride solution clouds were distinct sector plates, with broad sectors and three distinct ribs at the termination of each branch (Figure 8). The ribs consist of a central rib and two lateral ribs, with apex angles of 110 to 120 degrees.

Ice crystals formed in ammonium carbonate solution clouds grew as narrow branched stellar crystals with frequent lateral branches from the central branch (Figure 9). As a result of this morphology, the individual branches were approximately equal width through most of their length, terminating with angular edges to an apex at the central rib.

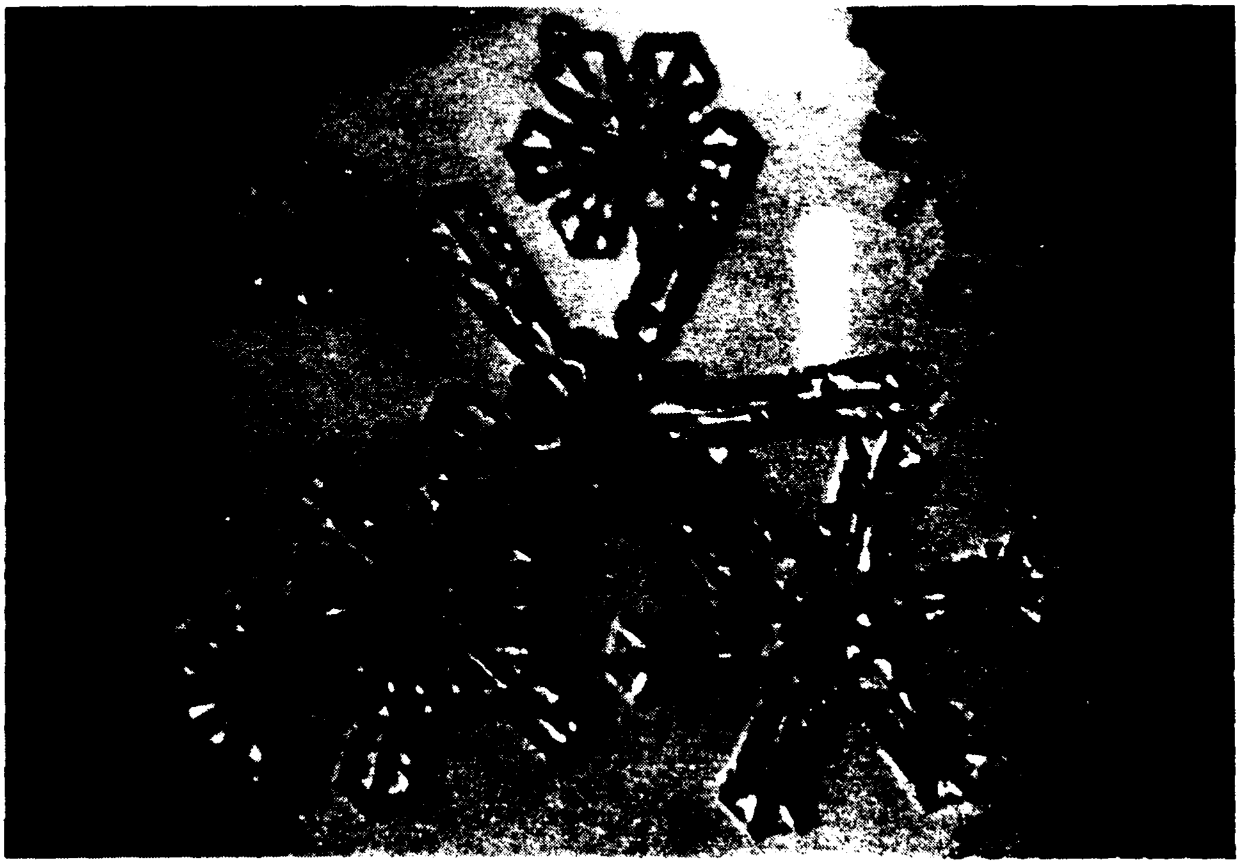

Fig. 9 Crystals grown from solutions of ammonium carbonate at -16°C.

Ice crystals formed in sulfuric acid solution clouds grew as narrow branched stellar crystals with straight, parallel sides (similar to the characteristic for deionized water), but with distinct undulations along the sides of the branches, which had a tendency to evolve into the initial side branches as the main branches acquired lengths of over 100 μm (Figure 10).

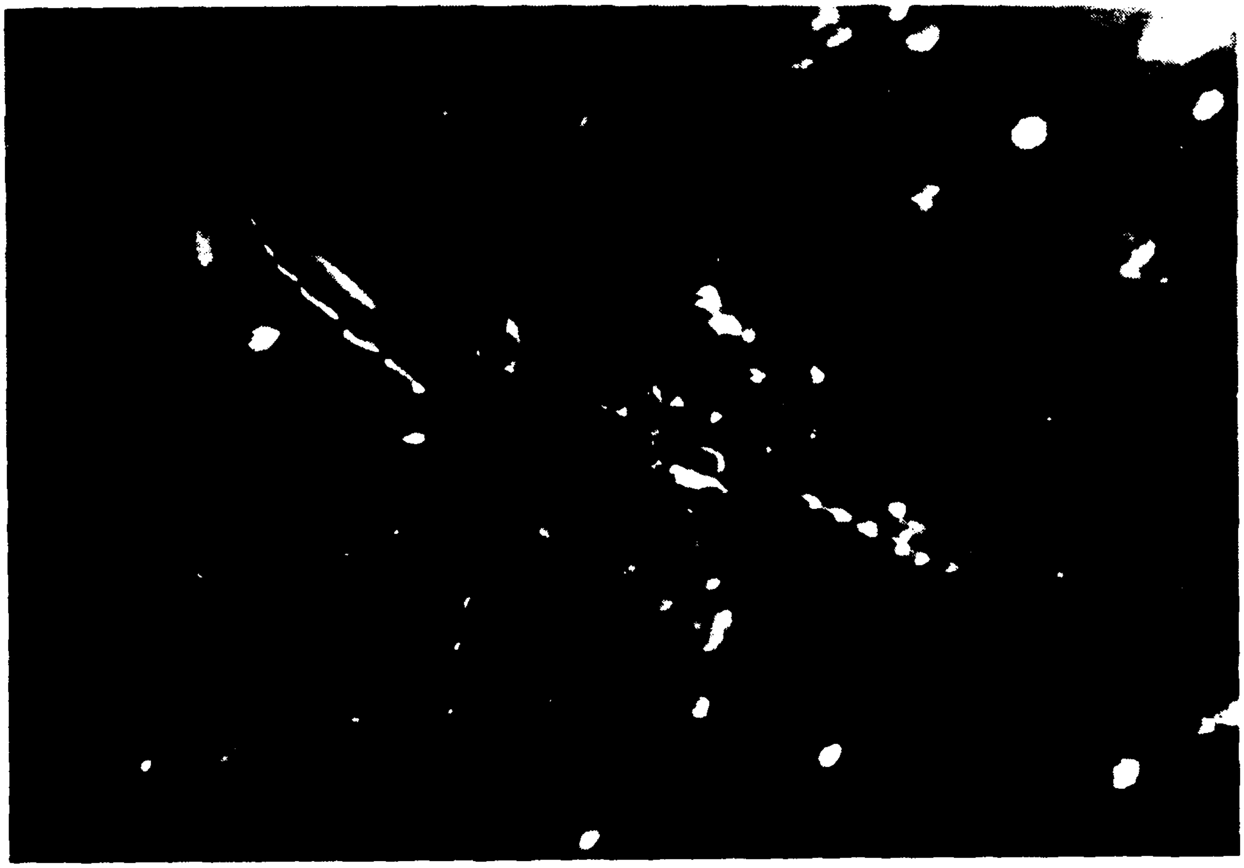

Fig. 10 Crystals grown from solutions of sulfuric acid at -16°C.

In another study, close to the transition temperature between two habits, differences of ice crystal habit were found to be dependent on the solutes present in the cloud water at fixed temperatures. The transition temperature between warm columns and plates, that is, the point where the aspect ratio, 2a/c, goes from less than 1 to greater than 1, was found to be -8°C for ammonium sulfate solutions, and -9°C for sodium nitrate solutions (Figure 11).

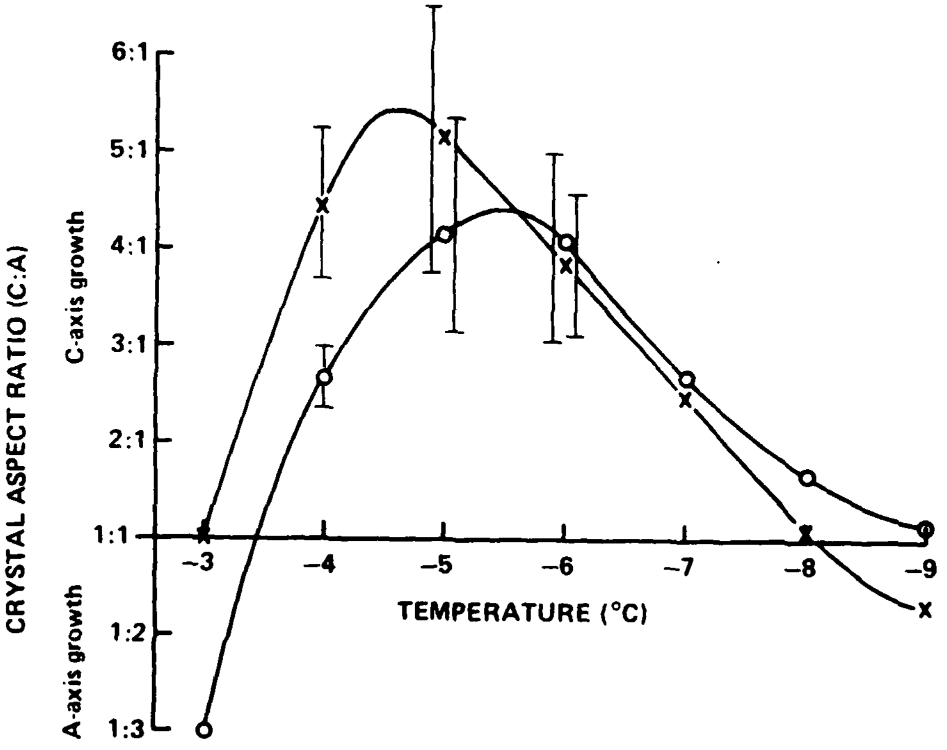

Fig. 11 Ice crystal aspect ratios for ammonium sulfate **X** *and sodium nitrate* **O** *solutions.*

5. ICE CRYSTAL INITIATION (SECONDARY ICE FORMATION)

Some of the experimental runs yielded ice crystals which were similar. The size distribution was narrow, and the morphological features were consistent for all the crystals observed. These runs lasted for less than ten minutes, in which the crystals grew at the expense of the supercooled water droplets and fell out to the chamber floor. Other runs, however, had a different set of features. These runs produced a polydisperse size spectrum of crystals which were far more numerous and had more variation of morphological features. These other runs also lasted longer. On the basis of four independent types of observations, noted below, we postulated that a secondary ice formation mechanism was active. Secondary ice formation was noted only in experiments involving ionic salts in ice crystals which were growing and aggregating. The following independent observations led us to the conclusion that secondary ice formation occurred:

1. **Visual inspection of ice crystals in microphotographs** yielded some cases in which the crystals were of similar size and morphology, and other cases where the crystals exhibited a broad size distribution and at least two dominant shapes. The broad distribution cases always arose later in the experimental run, but did not always appear. The smaller ice crystal sizes in the broad distribution cases are consistent with those ice crystals being nucleated later in the experiment. These smaller crystals resembled the morphology of crystals grown from deionized water clouds, which is contrary to observations of narrow distribution cases.

   Figure 12 contrasts the two types of size distributions and their corresponding morphological details.

Fig. 12 Contrast of size distribution and morphological results for (A) experimental run without secondary ice formation; and (B) experimental run with secondary ice formation.

2. **The duration of ice crystals in the cloud chamber was noted.** After ice was nucleated to initiate an experimental run, the ice crystals grew in the cloud chamber and fell out. The duration of the ice crystal fallout in the chamber was visually monitored. In some cases, the duration was short, often lasting only 5 to 7 minutes. This time span is consistent with the growth of ice crystals at water saturation to sizes in excess of 500 μm, and their fall speeds in excess of 50 cm/sec at the larger sizes. The gentle air motions in the chamber are insufficient to keep the crystals aloft. In the broad size distribution cases (noted in the preceding paragraph), the duration was much longer, from 15 to 75 minutes. The smaller fall speeds of ice crystals nucleated later in the run, and the repeated formation of new ice crystals, can explain the longer durations of these experimental runs.

3. **An infrared CO_2 laser (10.2 μm wavelength) transmissometer exhibited sensitivity to very small ice crystals.** Shortly after initial nucleation, as ice crystals grew through the size of approximately the wavelength of the laser light, strong extinction of the laser beam was detected. In the short duration experiments, there was only one extinction pulse, a few seconds after nucleation, to indicate this phenomenon. In the long duration experiments, multiple extinction pulses were observed, which is consistent with the recruitment of new generations of ice crystals by nucleation some time after the initial nucleation pulse.

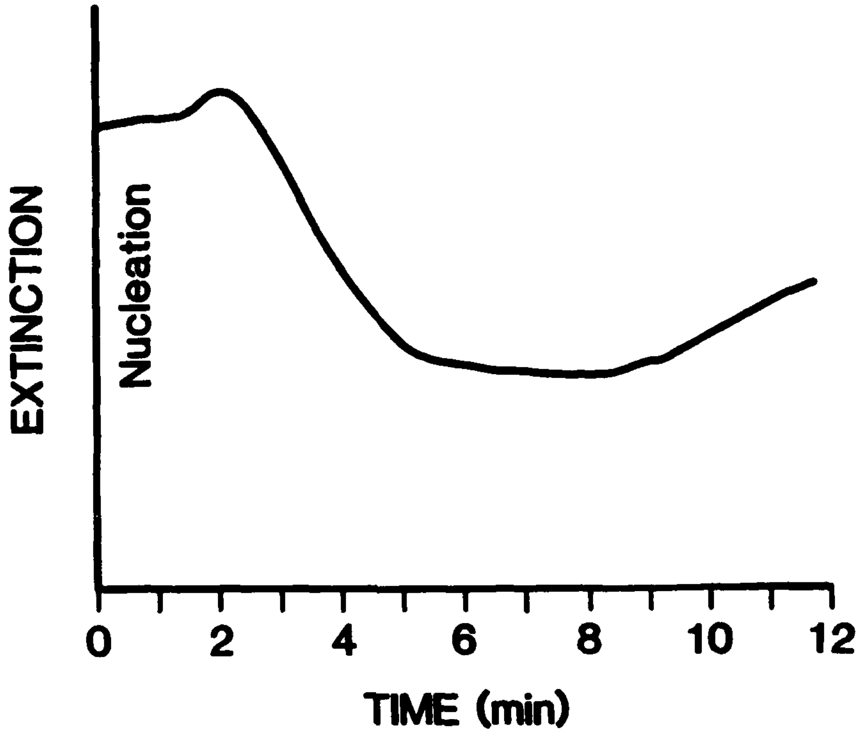

Fig. 13 Laser transmissometer trace for experimental run without secondary ice formation.

Figure 13 illustrates the attenuation trace associated with a short duration experiment. It has one attenuation pulse, just after nucleation. In contrast, Figure 14 shows the type of attenuation trace associated with longer duration runs. Occasionally, extremely strong pulses were recorded.

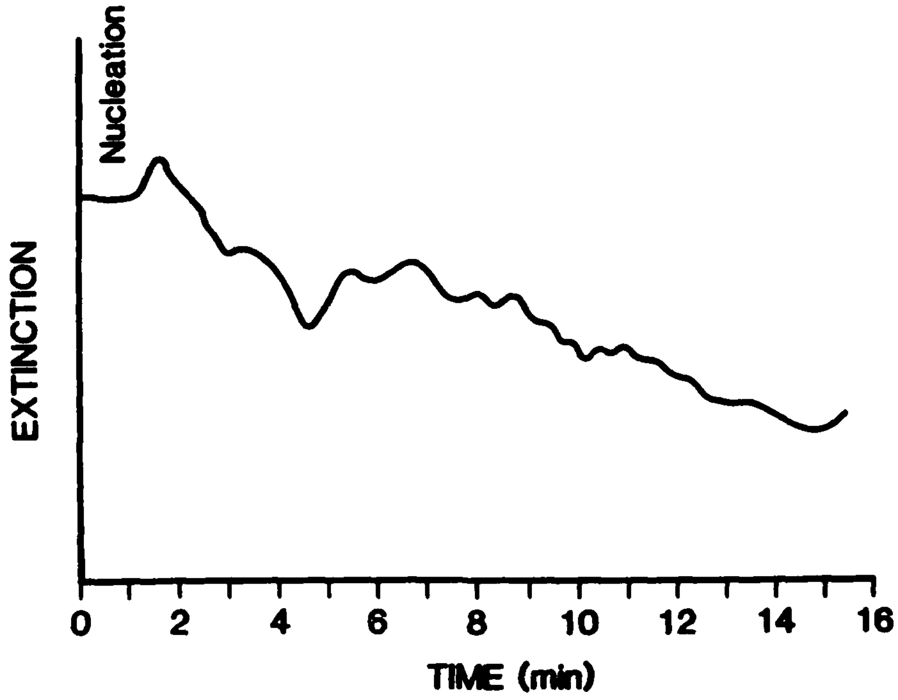

Fig. 14 Laser transmissometer trace for experimental run with secondary ice formation.

4. Some experiments used two transmissometers: a 10.2 μm wavelength CO_2 laser in the infrared and an 0.55 μm wavelength HeNe laser (Figure 15). In these, when characteristics of secondary ice nucleation (mentioned above) were detected by other indicators, the pulses of the HeNe laser attenuation preceded those of the CO_2 laser by 10 to 30 seconds. This observation is consistent with the newly-nucleated, sub-submicrometer crystals first growing through the submicrometer size, where they attenuated the HeNe laser beam, and subsequently growing through the 10 μm size, where they attenuated the CO_2 laser beam.

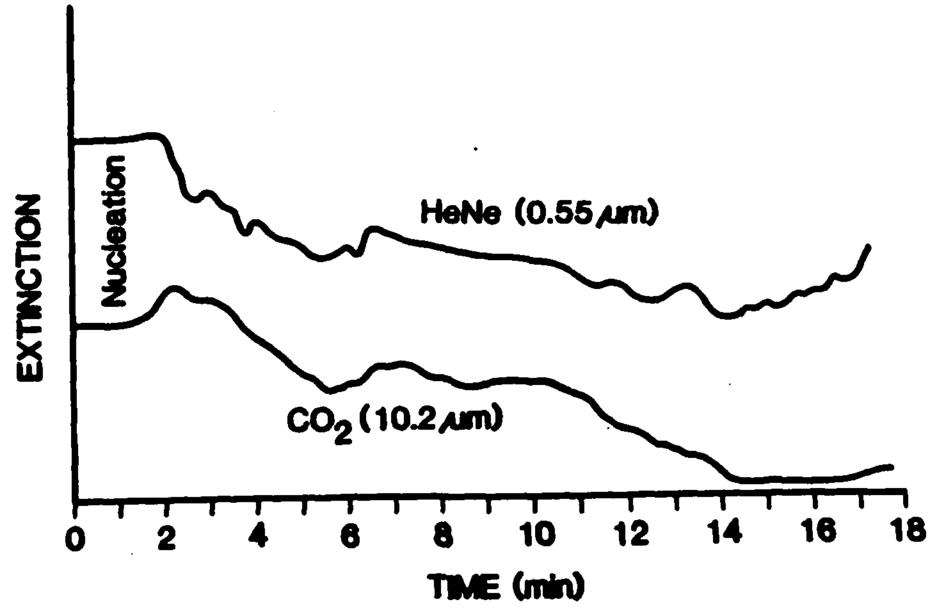

Fig. 15 Transmissometer traces for CO_2 laser (10.2 µm) and HeNe laser (0.55 µm) for experimental run with secondary ice formation.

Table 3 presents the results which describe the frequency with which secondary ice formation was detected in experiments with various chemical salts included in the cloud water. Secondary ice formation was detected at all temperatures investigated between -4 and -30°C. The highest rates of secondary ice formation occur at temperatures where the crystals are highly non-spherical, and the influence of the included chemical ions can be seen from the results. *No secondary ice formation was detected in any experiment for which very little or no ice aggregation was detected, so experiments without aggregation were not included in the table.* This eliminated more cases from the sodium nitrate solution column than from the ammonium salt solutions column.

Table 3

Summary of Secondary Ice Formation Results

	Aqueous Solution					
	Sodium Nitrate[1]			Ammonium Salts[2]		
Temp. Range (°C)	N[3]	SIF[4]	%	N	SIF	%
-4 to -8	20	14	70	19	18	95
-9 to -12	7	4	57	10	8	80
-13 to -20	7	7	100	8	8	100
-21 to -30	5	3	60	11	11	100
TOTAL	39	28	72	48	45	94

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[1] 10^{-4} N concentration sodium nitrate solution in cloud water.

[2] 10^{-4} N concentration ammonium sulfate or ammonium carbonate solution in cloud water.

[3] N: Number of experimental cases with aggregation.

[4] SIF: Number of experimental cases with secondary ice formation.

6. ICE CRYSTAL CHEMICAL REACTIONS (OXIDATION-REDUCTION)

6.1 INTRODUCTION

Atmospheric chemistry studies on in-cloud reactions have generally focused on exothermic oxidations of sulfur and nitrogen species by ozone, hydrogen peroxide, or oxygen (metal ion or carbon catalyzed) in cloud droplets. Chemical reactions occurring in the ice phase have been largely neglected. It has been argued that the rates of chemical reactions would be much slower in ice crystals than in cloud droplets.

Our recent laboratory research has demonstrated that endothermic chemical reactions can occur in ice crystals as a consequence of ice crystal growth, and can progress rapidly and efficiently. The chemical reactions observed in ice crystals are similar to electrochemical reduction-oxidation (REDOX) reactions in that they consist of coupled sets of chemical reactions occurring simultaneously. These features of chemical reactions in growing ice crystals have not been observed or previously postulated in the literature, to our knowledge. Therefore, we present some theoretical background on why they occur.

6.2 THEORETICAL

The formation of an electric potential across an ice/water interface during ice crystal growth was reported by Workman and Reynolds (1950) for freezing of dilute aqueous solutions. Their experiments, and those of others studying the phenomenon, led to the conclusion that the electric potential arises from the differential ion incorporation into the ice phase (Figure 1). Ammonium and the halide ions are preferentially incorporated. Ions such as carbonate, sulfate, nitrate, and sodium are rejected by the ice phase. The resulting effect is a potential difference across the growing ice interface, amounting to perhaps 30 volts for 10^{-4} N sodium chloride solutions, for example.

Our earlier work (Finnegan and Pitter, 1988; Pitter and Finnegan, 1989) demonstrated that the growth of freely falling ice crystals which contain halide or ammonium salts also leads to differential ion incorporation in the ice of such magnitude that it affects the ice crystal shape, the configuration of ice crystal aggregates, the rate of aggregation, and the formation of secondary ice crystals. The extrapolation of the freezing potential concept, developed by Workman and Reynolds for a single growing ice interface, to growing single ice crystals led the authors to conclude that growing ice crystals develop internal charge distributions (electric multipoles) regardless of the presence of any net charge.

The charge distribution is approximately configured such that electric dipoles exists across each growing interface (Figure 2). Since most ice crystals grow as columns, needles, thin plates or dendrites, the growing interfaces are usually quite localized, and exist primarily at the edges or ends of the ice crystals.

Chemical reactions have been observed or postulated during freezing of bulk aqueous solutions by Workman (1954), Lodge *et al.*, (1956) and Cobb and Gross (1969). We postulated that coupled oxidation-reduction reactions, quite similar to those found in bulk freezing, would occur in the growing ice crystals when appropriate chemicals were present. The oxidation-reduction reactions were postulated to occur as a direct result of the separation of ions during crystal growth. Ions are separated in a manner analogous to the separation that ions undergo in electrochemistry, except that the separation is not due to an electric field provided by external electrodes, but rather is due to the mechanisms of crystal growth which permit the inclusion of one ion rather than another into the crystal lattice.

In one of our experiments, we investigated the chemical reactions of sulfur species when a 10^{-4} N solution of ammonium sulfide, $(NH_4)_2S$, was used to create the supercooled cloud water. The concept is presented graphically in Figure 16. Initially, the solution of ammonium sulfide is located in the aqueous phase, which by an extension of Ostwald's Law of Stages we postulated to exist at the growing edges of the ice crystal. The differential ion incorporation leads to the incorporation of ammonium ions into the lattice, with nearly complete rejection of the sulfide ions. The ionic separation then leads to chemical reaction. In the aqueous solution, the sulfide ion loses six electrons, reacts with four water molecules and forms sulfuric acid and hydrogen gas, leaving two electrons. These electrons are transferred across the growing ice interface to complete the coupled chemical reactions in the ice, where the ammonium ion and

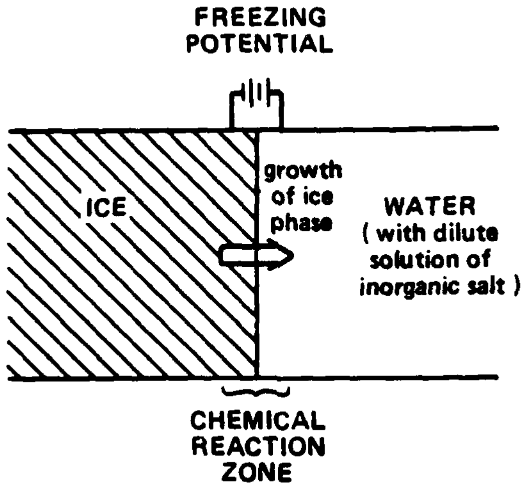

Fig. 16 Concept of oxidation-reduction reactions in growing ice crystals

water react with the electrons to form ammonium hydroxide and hydrogen gas. Thus, the result of the coupled oxidation-reduction reactions is the formation of hydrogen gas (reduction of water) and sulfate ion (oxidation of sulfide ion).

6.3 EXPERIMENTAL

Our experimental facility consists of a 6.7 m^3 cloud chamber, operated for these experiments at -16°C and ambient pressure (about 850 mb). A supercooled water cloud is generated using an ultrasonic nebulizer. We do not use pure water in the experiments. Instead, the cloud water consists of dilute (10^{-4} normal) concentrations of soluble ionic salts, to represent the atmospheric condition. When the liquid water content stabilizes between 1 and 2 g m^{-3}, we initiate ice formation by adiabatic expansion of compressed air. The ice crystals grow rapidly, at the expense of the water drops, and fall out of the chamber within five to ten minutes. The salts initially in the cloud water were found by ion chromatography to be present also in the collected ice crystals.

6.4 RESULTS

The experimental results demonstrate how rapid and efficient the chemical reactions can be in growing ice crystals. The concentrations in the ice crystals were found to differ somewhat from concentrations in the nebulized cloud water. Typically, concentrations in ice crystals were about 0.3 times the concentrations in the cloud water. Ice crystals growing from the vapor will tend to dilute the concentrations of included ions, but growing ice crystals, being efficient aerosol scavengers, also capture aerosol particles. These diluting and concentrating processes were experimentally found to be of similar magnitude.

When 10^{-4} N concentration of $(NH_4)_2S$ is contained in the cloud water, the average results of several experiments was a 61 percent conversion of S^{-2} to SO_4^{-2}. In a typical experiment, ice crystals grew and fell out over a 5 to 10 minute period after nucleation of the supercooled cloud.

In another experiment, 10^{-4} N solutions of ammonium bromide, NH_4Br, and ammonium nitrate, NH_4NO_3, were used in the cloud water. The ion chromatography could not detect the end product of the bromine, but it did detect a 13 percent loss of Br^- ion relative to the nitrate ion concentration in the ice. We hypothesize that Br^- was oxidized to bromine (Br_2), hypobromous acid (HOBr), or bromic acid ($HBrO_3$). The NO_3^- ion served as a chemical marker, and was used to determine the amount of ion incorporation into the ice crystals. Ammonium ion is preferentially incorporated into the ice crystal lattice in this system, which becomes the reducing side of the couple. Nitrate and much of the bromide ion remain in the aqueous layer, which becomes the oxidizing side of the couple.

When 10^{-4} N solutions of NH_4Br and ammonium sulfate, $(NH_4)_2SO_4$, were used, a similar analysis found a 64 percent loss of bromide ion relative to the sulfate ion concentration in the ice.

Finally, when 10^{-4} N solutions of sodium iodide (NaI) and sodium nitrate ($NaNO_3$) were used, 15 percent of the nitrate ion (NO_2^-) in the ice was *reduced* to nitrite ion during the ice crystal growth.

6.5 DISCUSSION

The results of the experiments are significant in several ways. First, the chemical reactions were found to occur rapidly when ice crystals were growing in a supercooled liquid water cloud at -16°C, but negligible amount of chemical conversion occurred when a 10^{-4} N solution of $(NH_4)_2S$ was nebulized into the chamber at temperatures above 0°C and then collected for analysis without ice crystal formation occurring. Thus, the freezing process was found to be essential for the chemical reactions to occur.

Second, the chemical reactions investigated included both oxidation and reduction reactions, and are postulated to consist of *coupled* oxidation-reduction reactions. The cloud water was prepared without including catalysts, ozone, or hydrogen peroxide, so a different oxidation mechanism than any which is usually considered for chemical reactions in clouds was operable. The observed reduction of nitrate ion to nitrite ion points out the coupled nature of the process. Ion separation explains both the oxidation and reduction reactions which were observed. When one or both of the separated ions cannot be oxidized and/or reduced, the hypothesis also requires the oxidation and/or reduction of water to form oxygen and/or hydrogen gas. The studies have not yet analyzed for the gaseous products of freezing.

For the electric multipole hypothesis to function as the mechanism responsible for the chemical reactions observed, it is crucial that liquid layers *of sufficient extent to cause dissolution and ionization of soluble ionic salts* be present on the growing surfaces of ice crystals at -16°C. Thus, the observed chemical reactions also have (yet undetermined) implications with regard to the mechanism of ice crystal growth. The internal charge distributions in growing ice crystals have previously been shown to influence ice crystal aggregation (Finnegan and Pitter, 1988), ice crystal morphology and secondary ice formation (Pitter and Finnegan, 1989), and aerosol scavenging (Pitter and Zhang, 1989). The present results, of observed chemical reactions due to the process of differential ion incorporation into the ice crystal lattice during growth, provides additional support to the electric multipole hypothesis.

If oxygen and hydrogen result from chemical reactions in growing ice, one might expect to see formation of these gases during bulk freezing. To confirm this hypothesis, we conducted a study of the bubbles in ice resulting from freezing. A sample of water containing a 10^{-4} N solution of $(NH_4)_2SO_4$ was frozen while under a vacuum. The frozen sample contained bubble tracks and streaks. While the vacuum was maintained, the sample was thawed and refrozen. The bubbles rose to the surface and were lost to the vacuum upon thawing, but more bubbles formed when the sample was refrozen. This process was continued for several cycles, with each freeze yielding approximately the same amount of bubbles in the ice sample. We concluded that the bubbles were not due to dissolved air in the water sample, but consisted of hydrogen and oxygen produced during freezing.

6.6 IMPLICATIONS

The chemical reactions in growing ice crystals have several potential implications. The oxidation of sulfide to sulfate indicates that the oxidation of sulfite to sulfate, and hence the conversion of SO_2 to sulfate ion in growing ice crystals should be readily accomplished. Further studies, in acid systems relevant to environmental air pollution and acid precipitation, and in stratospheric clouds associated with the sulfate layer, are warranted.

The oxidation of halide ions is of geochemical interest since there exist evaporite deposits of sodium nitrate containing iodates, periodates, bromates, chlorates, and perchlorates in the Atacama Desert of Chile (Ericksen, 1981). Iodates have been reported in the soils in arid regions of Antarctica (Claridge and Campbell, 1968). The question has previously been the mechanism of formation of these highly-oxidized species. The present results suggest that these oxidized species may result from oxidation, in the atmosphere, of marine aerosols during cloud glaciation processes. The present results also indicate that the rate of oxidation is highly dependent on the chemicals contained in the ice crystals. More research is required to examine this topic more completely.

The formation of oxygen as a byproduct of some chemical reactions is of interest since, it provides an additional mechanism of oxygen generation for the planetary atmosphere--a mechanism which does not require the pre-existence of certain life forms. If this mechanism is operable, then earth-like planets (planets of similar temperature, containing water, etc.) might all be expected to evolve oxygen-containing atmospheres over geological time, regardless of whether or not life evolves.

The chemical reactions related to the growth of ice crystals also bring to light the possibility of an alternate mechanism for the generation of active chlorine and bromine species involved in the Antarctic stratospheric ozone destruction. Two possible scenarios are advanced. In the first scenario, the general circulation of the Southern Hemisphere provides upwelling motion throughout most of the troposphere in the region just beyond the circumpolar vortex. Since much of the Southern Hemisphere is oceanic, it is conceivable that natural, marine aerosols (which contain significant amounts of halides) and water vapor may involved in convective storms near 60°S may, upon freezing, oxidize halogens to reactive ozone species, leading to reactive halogen species (Cl_2, Br_2, HOCl and HOBr) to the polar region. Such a scenario may be more plausible in explaining why ozone depletion at the South Pole is much more significant than its depletion at the North Pole, despite the much greater production rate of chlorofluoromethanes in the Northern Hemisphere.

The second scenario involves the atmospheric convection in the Intertropical Convergence Zone near the equator. Again, much of the earth's surface in those latitudes is oceanic. It is surmised by others that the tropical convective clouds provide most (if not all) of the tropospheric air entering the stratosphere. We advance the possibility that stratospheric clouds, which have been found associated with significant ozone depletion, may be capable of oxidation-reduction chemical reactions.

During the electrolysis of aqueous solutions of potassium chloride, sulfate, or perchlorate with a copper electrode, CO_2 bubbled through the solution was observed to be reduced to ethylene and propylene (Hori *et al.*, 1988). It is conceivable that a similar reduction of atmospheric CO_2 during ice crystal growth may be possible. If so, an explanation for a possible "missing carbon sink" in the atmospheric carbon cycle (Detwiler and Hall, 1988) and the current increase in atmospheric methane may be possible.

Gross (1968) relates a number of investigations which have studied the formation of electric potentials across the interfaces of growing crystals other than water. Costa Ribeiro (1947) investigated the potentials and currents arising during solification of carnuba wax. Krause and Renninger (1956) observed potentials of the order of a hundred volts in pentaerythritol crystals growing from a supersaturated solution. Mascarenhas and Freitas (1960) investigated the effects on naphthalene crystals, where they found that the charge transfer depended strongly on the impurity content. *We postulate therefore that electric multipoles, and consequently oxidation-reduction reactions, also occur in growing crystals other than ice.*

6.7 CONCLUSIONS

The research conducted to date on chemical and physical processes occurring during the growth of ice crystals due to the differential incorporation of ions into the ice crystal lattice, indicates that coupled oxidation-reduction chemical reactions occur very rapidly and efficiently in growing ice crystals containing dilute solutions of inorganic ionic salts (of concentrations similar to those found in clouds and precipitation).

The investigators present a variety of scientific topics which need further investigation to determine whether the postulated mechanism is generally operable and of significance.

7. IMPLICATIONS OF THE RESULTS OF THIS STUDY

a. Charge Distribution in Growing Ice Crystals

The differential incorporation of chemical ions into an ice crystal growing from supercooled water gives rise to a potential difference across the growing interface of ice (Workman and Reynolds, 1950). The sign and magnitude of the potential difference are dependent on the chemical ionic compositions, with less concentration dependence in the range of 10^{-6} to 10^{-3} N. Finnegan and Pitter (1988) postulated that electric fields in the immediate vicinity of growing ice crystals, which are strong enough to influence ice crystal aggregation, could be achieved by applying the concept behind freezing potentials to ice crystals growing from the vapor. This postulate requires the existence, at the growing interface, of a liquid layer which is sufficient to dissolve and ionize the included ionic salt; phase transition from vapor directly to solid would not support the postulate.

Ostwald's Law of Stages states that when a chemical system changes from an unstable state to a stable state, it does not tend to change directly to its most stable form, but rather first to an intermediate form which is achieved with the smallest loss of energy. Thus, we postulated that during ice crystal vapor diffusion growth, water vapor molecules change to ice by passing through the liquid phase. At present, there is no experimental evidence that the transient liquid phase at the growing ice interface does not exist for rapidly growing ice crystals.

Finnegan and Pitter (1988) postulated that the result of the vapor growth freezing potential would be the formation of an internal symmetrical charge distribution in growing ice crystals containing dilute concentrations of soluble, ionizable salts. Figure 2 portrays the charge distributions which would then arise on crystals of different habits. The ice crystal lattice acquires net charge of one sign, which is balanced by net charge of the opposite sign in the liquid layer at the growing interface of the crystal. This charge separation does not, by itself, lead to any net charging of the crystal. This model of electric multipoles in growing ice crystals is utilized in the conceptual models presented below for crystal morphology and secondary ice formation.

b. Conceptual Models

i. Ice Crystal Morphology and Symmetry

The symmetry and morphological nature of growing ice crystals are postulated to result from the action of the opposing forces of surface tension and the net electric charge contained in the liquid phase at the growing interface. The surface tension acts to form a polyhedral crystal of approximately unity aspect ratio (short column), while the electrostatic charge attempts to distribute itself to minimum energy, and thus acts in a contrary manner to surface tension. This holds even though other factors, such as vapor diffusivity and thermal conductivity of the surrounding air, also influence crystal habit (Gonda, 1980). During growth from the vapor, the ice crystal receives water vapor at all points on its surface, but the incorporation of water into the ice crystal lattice is constrained to highly localized regions at the growing interfaces. Thus, there must be a migration of the water molecules from their points of arrival on the crystal surface to the growing interfaces. The migration of the water governs the overall habit, the ice crystal symmetry, and the crystal morphology. The electric field at the non-growing surfaces of the ice crystal is strong, but inhomogeneous, and the resultant non-uniform force, electrophoresis, may be responsible for attracting mobile water molecules toward the growing tips. If one branch of a dendrite becomes longer than the rest, its electrophoretic attraction is temporarily diminished (the electric field gradient near the crystal's center is diminished) until the other branches grow to the same length, thereby establishing a feedback mechanism for crystal symmetry.

By this concept, the degree of secondary branching of dendritic arms is dependent on the amount of separated charge due to the action of the differential incorporation of chemical ions into the crystal lattice and to other processes which act to recombine the unlike charges. Where large freezing potentials are realized, the mobile layer acquires greater electric charge density, and the mutually-repulsive electric charges in the liquid layer have a greater tendency to overcome surface tension and initiate secondary branches. The structure of the secondary branches is still greatly influenced by the lattice structure though its influence on the surface tension.

Another aspect of the electrostatic-surface tension concept is the role of electrostatics in maintaining crystal symmetry. Beyond the equal partitioning of water to the branches, the electrostatic forces reinforce the straight growth of the equal-length branches away from each other at angles of 60 degrees. Of interest in this regard is a photograph of a crystal which happened to acquire seven branches (Figure 17). The branches have grown in such a manner that the six branches from the lower stellar are bent to accommodate the upper branch. The larger angles between two branches are correlated with shorter lengths of the branch directly opposite, similar to the behavior expected of electrostatic influence of the lengths of the branches. The branches thus are distorted with respect to the ice crystal lattice, in response to the influence of strong electric forces, not merely to the influence of heat and mass transport. The symmetry of an ice crystal, particularly of the stellar or dendritic habit, is postulated to result both from the influence of the crystal lattice on surface tension and from the tendency of surface-mobile electric charges (of predominantly like sign) to mutually repulse each other.

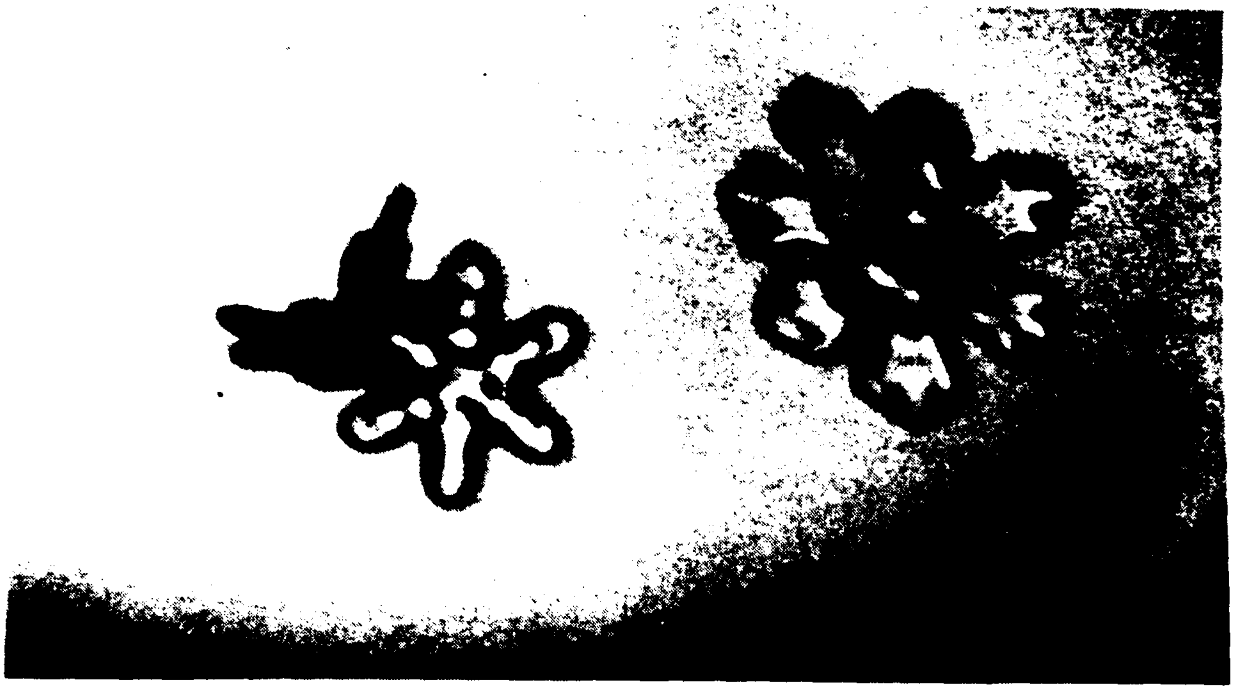

Fig. 17 Photograph of an ice crystal which has grown seven branches, and which has preserved a symmetry despite the misalignment of branches and crystal lattice structure.

ii. Secondary Ice Formation

One characteristic of the small secondary ice crystals observed in the cloud chamber is their very simple morphology, like that of crystals grown from distilled water clouds. This experimental evidence strongly suggests that the secondary ice crystals do not originate from breaking or splintering of previously existing crystals (which would contain the ions which govern the morphologies of those crystals), or from interstitial soluble particles, but are rather nucleated and grown from the vapor, virtually free of contaminant chemical ions. This experimental evidence eliminates both ice crystal fracturing and cloud droplet freezing as mechanisms of secondary ice formation. There are few alternative mechanisms left. One possibility is that nucleation occurs in a manner similar to corona discharge ice nucleation, as described by Schaefer (1968). There is also the possibility that small ion clusters of water molecules in the air are affected by a strong, but not discharging, electric field, as postulated below.

In the course of aggregation of growing ice crystals containing the electric charge distributions described previously, locally high electric fields are produced between the two crystals just prior to collision, for a short duration. During the interaction, both crystals are falling through the air, and thus subjecting the moist air between them to high, non-uniform electric fields. Strong electric fields serve to orient polar molecules, and these molecules will migrate toward stronger field intensity in non-uniform fields. The ice crystals, as they are about to collide, may generate sufficient fields to form larger clusters of water vapor molecules, perhaps about the small ions present in the air. The interaction time of clusters of water vapor molecules and the high intensity electric field is sufficiently long for ice nucleation to occur. Subsequently, the newly-formed crystals may grow by vapor diffusion until they reach detectable size. (Detectable size depends on the sampling device.)

The above mechanism is presented only as a postulate which explains the observational data of our experiments. Careful studies of supersaturated airstreams passing through strong electric fields may determine whether this mechanism is viable.

8. DISCUSSION

Several microphysical aspects related to growing ice crystals have been presented. The effects of ionizable salts present in the cloud water being incorporated into growing ice crystals are demonstrated for aggregation, morphology and symmetry, and for secondary ice formation.

The observations used in this study are of crystals grown in free-fall in an isothermal cloud chamber in a cloud formed by ultrasonic nebulization of dilute aqueous solutions of ionic salts at concentrations typically found in cloud and precipitation water.

Despite the excellent research which has been conducted into mechanisms of the development of distinct habits in ice crystals, no explanation has yet been generally accepted for the sixfold symmetry of single crystals (Maddox, 1986; Mortley, 1986), nor has work gone far beyond the specification of fundamental classes of habits, such as proposed by Magono and Lee (1966). Our studies lead us to believe that both of these problems are intimately linked to the growth processes of ice crystals, and thereby to the strong, inhomogeneous electric forces which originate on those growing crystals.

The growth mechanisms of freely-falling crystals are intimately involved in this discussion of symmetry. Several researchers (Hallett, 1961; Mason et al., 1963; Hobbs and Scott, 1965) have performed experiments on ice crystals growing on substrates which they interpret to demonstrate that the vapor arrives at the tips of dendrites, and the water then migrates toward the central area of the crystal in the quasi-liquid layer, until it freezes in.

However, Pitter (1981) utilized numerical modeling of forced convection about a model of a freely-falling ice crystal, to examine how it would grow in the absence of condensed phase motion on its surface. The results show that a growing crystal would continue to grow at virtually the same aspect ratio as a result of forced convection. Any net flow of the mobile layer water toward the center of the larger crystal faces would tend to make the crystals more spherical as they become larger--contrary to the observational data of several field studies. In addition to Pitter's work, the crystallization literature (i.e., Van Hooke, 1961) also contains experimental evidence that crystals grow by vapor absorption on the large area faces followed by migration of the absorbate to the growing edges. Therefore, on the basis of observations of the growth morphology of freely-falling crystals and supplemented with numerical simulation of the rate of vapor deposition on a crystal model, we postulate that water mass must flow from the central area of the crystal *toward* the branch tips in order to be consistent.

Secondary ice formation is recognized to occur in some cumulus clouds (Mossop et al., 1972) and occasionally in orographic winter storms (Stewart et al., 1984). Logic for ascribing secondary ice formation has been the meager supply of nuclei capable of functioning at the warm temperatures noted in the field examples. A variety of processes which result in secondary ice formation have been reported in the literature (Mossop, 1985). These secondary ice formation processes often involve physical breakup, breaking of branches during partial melting, or interaction of graupel particles or rimed crystals with drops. Several of these processes have been demonstrated in laboratory facilities using secured riming targets. None of the processes have been demonstrated to occur in cloud chambers due to interactions between freely-falling hydrometeors.

The various measurements which indicated secondary ice formation in the DRI cloud chamber were studied with the objective of varying experimental conditions to determine which factors were more important in promoting or repressing secondary ice formation. It was found that secondary ice formation occurred only when rapid ice crystal aggregation occurred, and such required rapid diffusion growth of the ice crystals. The ionic salt composition in the cloud water was found also to play a role in secondary ice formation. Ions capable of producing higher magnitude freezing potentials (Workman and Reynolds, 1950) were found to be more capable of producing secondary ice formation during an experimental run. Compact crystals (aspect ratio near 1) were less likely to produce secondary ice formation than long needles, columns, flat plates, or dendrites; the shape effect appeared to be the principal manner in which the temperature affected secondary ice formation.

The above factors do not coincide greatly with factors which have been found to influence secondary ice formation in prior cloud physics literature on this issue. However, they do link rather closely into crystal growth literature, as shown in the next paragraph.

Crystal growth literature has documented similar phenomena of crystal multiplication in supersaturated solutions. Strickland-Constable (1968) notes that the presence of crystals in supersaturated solutions may lead to the spontaneous formation of new crystals at rates much faster than homogeneous nucleation can account for. He proposes the term *crystal breeding of nuclei* to describe the phenomena. An analysis of the literature suggests several ways that breeding occurs in different systems and situations. Relevant to the case of spontaneous ice formation, Strickland-Constable's *collision breeding* describes how fresh nuclei are produced in solutions with low supersaturations during which the crystals come into contact with each other and with the container walls. He notes that while one might suggest that collision breeding is due to the simple fracture of the colliding crystals, with the resulting production of new crystallites which continue to grow, it is difficult to rectify such with the result that the number of new fragments produced by collision depends on the supersaturation. The alternative dependence of nucleation rate on supersaturation leads to two alternative views of the mechanism:

1. Collision breeding might not be due to fracture of the crystals. Nuclei might somehow be formed in the very thin layer of fluid which is trapped between the colliding crystals;
2. Collision breeding might be due to fracturing of the colliding crystals, with the production of fragments whose size range falls on both sides of the critical size, thereby introducing the supersaturation dependence.

Experimentally, Schaefer (1968) produced ice crystals using a very small, electrically conducting wire charged to about 3 kV dc in a supercooled cloud at temperatures between -8 and -15 C. He noted that the crystals grew rapidly and began to start falling, at which point they showed "brilliant interference colors similar to crystals formed by homogeneous nucleation."

It is possible that Strickland-Constable and Schaefer were exploring different facets of the same phenomenon, which is also operable in the secondary ice formation experienced in the present study.

9. CONCLUSIONS

A single phenomenon, discovered by the investigators of this project about the time of the initiation of the project, involving the differential incorporation of included ions during ice crystal growth, influences a number of ice crystal initiation, growth, and interaction processes. Knowledge of this phenomenon and the way it works helps to better understand the nature of ice crystal evolution in the atmosphere. The significant conclusions of this study, examining the various processes affected by electric multipoles in growing ice crystals, are as follows:

1. The presence of low concentrations of ionizable salts in cloud water, and subsequently in growing, freely falling ice crystals, affects the detailed morphology of ice crystal shapes;

2. The presence of low concentrations of ionizable salts in cloud water, and subsequently in growing, freely falling ice crystals, affects the nature and rate of ice crystal aggregation;

3. The presence of low concentrations of ionizable salts in cloud water, and subsequently in growing, freely falling and aggregating ice crystals, increases the probability of secondary ice formation occurring at temperatures from -4 to -30 C;

4. A conceptual model of internal charge distributions, arising as a result of the vapor growth freezing potential, has been developed to address the three phenomena noted above;

5. The electrostatic forces arising from the conceptual model charge distributions are postulated to influence ice crystal symmetry;

6. The features of the conceptual model for secondary ice formation may have application to the broader field of crystal growth, as demonstrated in the discussion on crystal breeding of nuclei; and

7. The differential incorporation of ions during ice crystal growth leads to the coupled oxidation and reduction of the ions and/or water substance.

The work presented herein is of a preliminary nature, and additional experimental studies are required to more completely describe these phenomena. Mathematical development of the theory is necessary for its application.

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