

The category of Conference Summary has been initiated for the following article with the hope that others of its kind will be submitted to the BULLETIN in the future. Abstracts of papers for regular AMS Meetings have been published, and will continue to be published, in the BULLETIN, but the material of many special conferences and meetings receives only the minimum coverage of a short announcement. A summary report by the chairman or a senior participant would provide valuable perspective to the entire membership; henceforth, such summaries both for special conferences and for regular meetings will be welcomed by the BULLETIN.

CONFERENCE SUMMARY

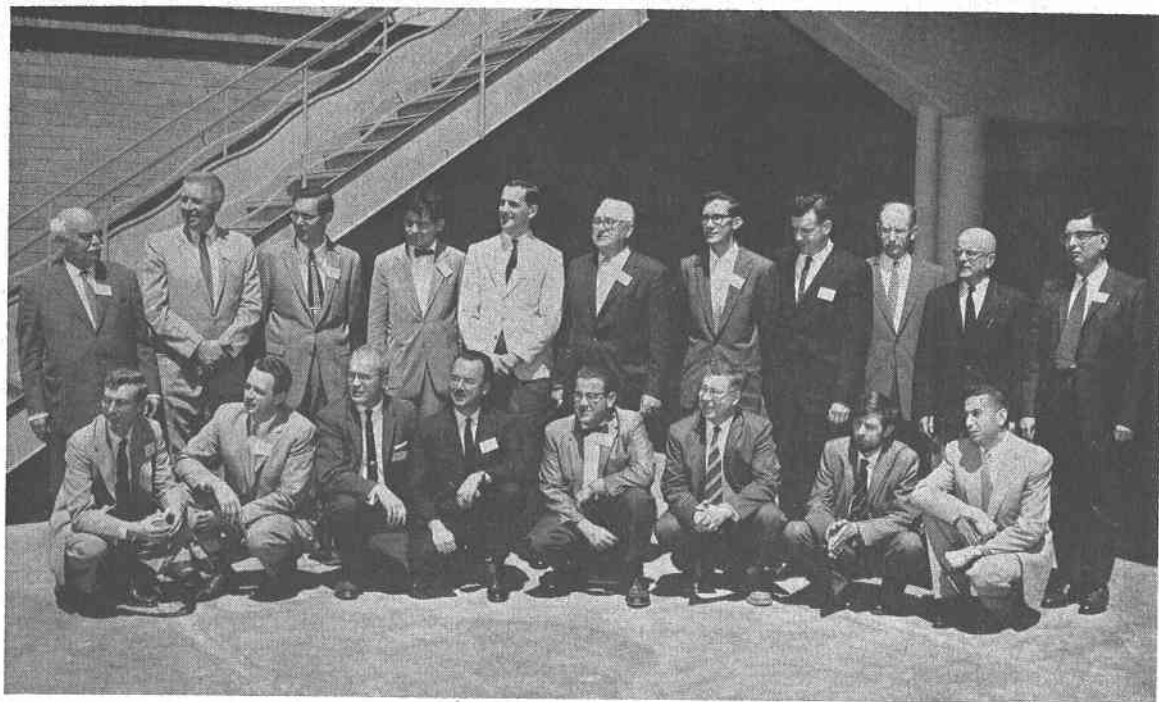
The Surface Chemistry of Ice Nucleation

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With the sponsorship of the National Science Foundation, a Conference on the Surface Chemistry of Ice Nucleation was held at The University of Arizona, 6-8 April 1961. Emphasis was placed on informality, and no formal publication of proceedings was planned. By bringing together workers in cloud physics on the one hand and surface chemistry on the other, it was hoped that useful exchange of insights and information would ensue. At the close of the Conference it seemed the consensus of the participants' opinion that this had been accomplished. Such interdisciplinary conferences (of which a recent NSF-sponsored gathering of statisticians and workers in the field of weather modification represents another example) have the great virtue, at least for the meteorologists, of showing whether the latter are proceeding in ignorance of any new techniques or fundamental points of view of an adjoining discipline. By and large the present Conference disclosed no gross blind spots in the sense of technique or principle in meteorology's current efforts to unravel its nucleation puzzles. The confrontation did elicit a comforting number of expressions of sympathy from surface chemists who obviously would not choose H_2O and AgI as their working substances if they were setting about to solve the easy problems first!

Following a welcome on behalf of NSF, given by Dr. Earl G. Droessler, the Conference extended over two days of give-and-take that stayed at a generally lively level. Mason's introductory survey of the present status of nucleation problems in cloud physics included emphasis upon the points that epitaxy must be treated as a three-dimensional and not just a two-dimensional interaction between substrate and the deposited material, that ice nucleation seems clearly to be a phenomenon occurring at preferential sites (of which growth steps on the substrate afford a common example), and that homogeneous nucleation seems now to be established as volume-dependent (but see below). His comments on surface migration of water molecules adsorbed on nucleating crystals were elaborated later by Hallett, who noted molecule migration distances of the order of 5-10 μ . Rate of advance of growth steps on the ice is found to vary inversely as step-height; hence when a shallow step overtakes a deeper step, both are suddenly slowed down to a new common growth velocity that reflects the longer unit of time required to pave one more frontal layer on the now high growth front since they must subsequently feed in common on the same flux of diffusively arriving water vapor molecules due to migration-length limitations in their feeding range.



Participants at the Conference on the Surface Chemistry of Ice Nucleation, The University of Arizona, April, 1961. Left to right, back row, standing: Sanger, Schaefer, McDonald, Halsey, Mason, LaMer, Fletcher, Fuquay, Byers, Beebe, Corrin. Front row: Hosler, Braham, Harris, Papee, Kassander, Hall, Hallett, Birstein. Not shown: Zettlemoyer, Droessler, White.

Both Schaeffer and Birstein discussed aspects of inhibition of nucleation by adsorption of organic materials. That meteorologists have now learned their lessons from the statisticians seemed to be shown by the reluctance of most participants to accept as meaningful the very small number of modification experiments Birstein reported in which ethyl amine was added to cumuli; however, no one doubted the desirability of more tests. Braham reported interesting results from the Chicago group, including Kumai's delicate electron diffraction work on individual snow crystal nuclei. The fact that about 85 per cent of all of a sample of several hundred snow crystals taken in Michigan snow showers exhibited mineral nuclei, added to Kumai's and others' previous results pointing in the same direction, seems to suggest strong likelihood that it is, in fact, the siliceous clays on which Nature chiefly depends for ice nuclei. Reports of nucleating efficiency measurements made on about 600 surface arid-region soil samples by McDonald seemed to be in accord with the Kumai results and with Mason's laboratory observations of activity of pure samples of silicates. Thus, one of the notions that appeared to be confirmed in the Conference is the long-standing

suspicion that wind-blown dusts may be a chief ice nuclei source.

New theoretical arguments that ice normally has an outer film of water-like structure were offered by Fletcher. Put in somewhat anthropomorphic terms, Fletcher's model indicates that, in the interest of reducing total energy, the outer few molecular layers of a piece of ice prefer to stay in a water-like state of sufficient molecular mobility to permit the layer to turn most of its protons inward. That ice seems to behave as if it had a liquid coating well below OC is an old idea, but Fletcher's analysis seems to have provided, finally, a quantitative thermodynamic basis for believing that it should, in fact, occur. Fletcher also placed an interesting tentative interpretation on Mason's finding that AgI nucleates via a condensation process down to -12°C but by direct deposition of vapor at constant ice supersaturation of about 12 per cent at all lower temperatures, though the argument cannot be briefly summarized here.

The question of whether homogeneous nucleation depends on some function other than the volume of subcooled water was reopened by Hosler, whose capillary tube experiments of several years ago seemed, after all the discussion was over,

to be still a poorly understood matter. Suggestions by LaMer and Mason concerning role of interactions with the glass walls of the capillaries were met by Hosler's observation that three-dimensional movies disclosed nucleation events occurring not near the walls but well within the cylinders of water; and as Fletcher noted, the surface-to-volume ratio arguments seem to fail the critics of the capillary-tube experiments. Where Mason cited Mossop's inability to duplicate the effect with hydrophilically coated capillaries, Braham noted that Hoffer's results indicate some residual size effect beyond that of volume. Perhaps LaMer's observation that, since the meteorologists problem is one of isolated water spheres, he should abjure glass tubes makes some sense, but we ought to clarify this phenomenon. More experiments and better theory must be awaited.

Other laboratory studies on nucleation and adsorption were also described by Harris, Beebe, Papee, and Corrin, and developments in AgI nuclei generators were summarized by Fuquay, with special reference to a new high-output airborne generator. Sanger followed reports on some puzzling effects of salt concentration on nucleation with descriptions of Swiss efforts to use nuclear magnetic spin resonance to follow temperature changes in molecular mobility of ice layers adsorbed on nucleants. Early results suggest that the water film on AgI is mobile, in the sense of the experiment, down to about -15°C , while water on CuO (a poor nucleant) shows proton mobility down to as low as -36°C . Further developments with this technique should be interesting.

Zettlemoyer described surface-chemical evidence that only about 7 per cent of all sites on AgI surfaces that serve as N_2 adsorption sites also function as H_2O sites. He compared this with graphite surfaces where only one in a thousand sites seemed to take up water, yet noted that those hydrophilic spots suffice to "lubricate" carbon commutator brushes in aircrafts. Zettlemoyer imagined that it may actually be advantageous in ice nucleation to have only widely spaced active sites, for then two adjacent colonies of water molecules can build up their structures without interfering sterically with each other.

At a number of points throughout this Conference, discussion returned to present confusion as to the relative efficacy of ice nucleants such as AgI when acting as freezing nuclei (nucleus inside subcooled water) on the one hand, and when acting as deposition nuclei (nucleus adsorbing water molecules directly from the vapor phase) on the

other. It has to be admitted that this long-standing question remains in need of basic study and clarification, for too many hazy features persist. Several participants cited experimental results pointing toward poorer nucleating efficiency (measured in terms of activation temperature) when a given nucleant acts as a freezing nucleus rather than deposition nucleus; and solubility of the nucleant will not explain away all of these results. From the viewpoint of cloud modification, these questions are of great practical interest for one may be unknowingly treating clouds in the wrong way in ignorance of the mechanisms here involved. A happy suggestion made by Fletcher rather more casually than its importance might prove to warrant was the idea that perhaps AgI particles when encountering subcooled drops by external Brownian capture stay on the interface and can nucleate by either or both of the mechanisms, with "their stomachs in the water and their backs in the air," so to speak. To the writer, these points of confusion and disagreement on the mode of ice nucleation illustrate more emphatically than any other points evolved in the Conference how indispensable it is to secure fundamental physical and chemical knowledge concerning each step in the nucleation processes that underlie our still vaguely understood methods of trying to modify clouds.

Halsey, in summing up the Conference, compared the meteorological problem of the Conference with that of physical metallurgy where it has taken so much money, time, and research effort to reduce appreciably the degree of empiricism of the art. He noted that the cloud physicist in his nucleation problems is confronted by aspects of the greatest unsolved problem of physical chemistry—the structure of liquids. He urged careful, and ever more careful attention to contamination problems in nucleation studies, citing slow and painful lessons that had to be learned in past years by surface chemists who were not duly pessimistic about contamination. He seemed puzzled, as a chemist, by the fact that the cloud physicist finds that such vastly different substances as a piece of clay and a piece of hydrophobic heavy-metal iodide both work as ice nucleants.

Perhaps Dr. Halsey summarized the surface chemist's view most clearly and emphatically at an earlier juncture when he noted that it is difficult enough to make progress using extremely simple adsorbed molecules (*e.g.*, inert-gas molecules) but that the poor cloud physicist is stuck with a really difficult molecule: To quote Halsey's incisive comment directly, "Water is a mess!"