SOME ASPECTS OF THE MECHANISM OF SUBLIMATION AND FORMATION OF ICE CRYSTALS UNDER VACUUM CONDITIONS

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Certain features of the formation and growth of ice crystals during sublimation under vacuum conditions are discussed. The theory of volume evaporation is confirmed by means of high-speed motion-picture photography.

The growth of natural ice crystals on various evaporation surfaces was examined in [1, 2], in which the authors described observations of the growth of ice filaments and whiskers formed by ablimation in saturated and undersaturated atmospheres. They established that ice whiskers usually appear in the course of the evaporation of individual crystals at an ice temperature T = 251–263°K. The ice whiskers or filaments are treated as active centers of sublimation and ablimation.

Our object was to investigate the mechanism of sublimation and formation and growth of ice crystals at the surface of a body.

The mechanism of sublimation and ice crystal formation was studied in a vacuum chamber at an ice temperature T = 220–240°K using high-speed motion-picture photography. In these experiments we used spheres of ice 80 mm in diameter prepared from distilled water, distilled water colored with fuchsin, and ordinary tap water. For illuminating the surface of the ice we used electric-lamp condenser illuminators, which simultaneously served as radiant energy sources.

In the experiments we recorded the formation of ice crystals of various shapes and lengths (from tenths of a millimeter to several millimeters) at the sublimation surface. Under the influence of the sublimation and ablimation processes the shape of the ice crystals underwent various changes. Moreover, at the surface of ice prepared from ordinary tap water, apart from ice crystals, filaments of biological origin appeared.

Our observations of the formation of an ice nap show that it appears instantaneously at the sublimation surface, it being possible in a number of cases to observe the continuing growth of an individual ice whisker as a result of elongation of the root portion with conservation of the characteristic configuration of all the visible part of the whisker. Ice whiskers usually appear from cracks and microcracks and also at the boundary between the depressions formed in the surface during the sublimation process. The whiskers sometimes begin to oscillate at high frequency and variable amplitude. Usually the oscillating whisker breaks away and escapes with the vapor flow. However, cases in which the oscillations cease and are then reexcited are observed.

These phenomena are well illustrated by a sequence of photographs (see Fig. 1). In some cases little "ridges" in the form of arcs attached at the ends are formed on the surface of the ice. The vapor flow causes these to break and the free ends assume a radial orientation.

In addition to oscillatory motions of the particles, it was possible to observe cases of rotation of an entire crystal complex at speeds up to 70 rpm for up to 20–30 revolutions; under these conditions the crystal complex may cease to rotate and begin a new rotation in the other direction. The oscillatory motions of the whiskers and the rotation of crystal complexes among a large number of stationary filaments indicate that the sublimation process is nonuniform over the surface, proceeding at different local rates. The nonuniform

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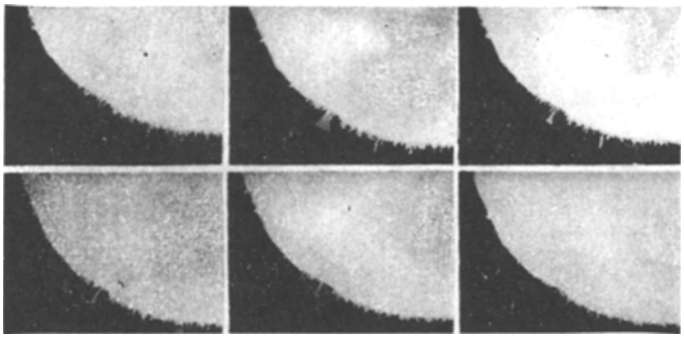

Fig. 1. Appearance and oscillation of an ice particle with variable amplitude up to complete separation.

local character of the sublimation of ice is also indicated by the presence of shallow depressions over the entire surface of the subliming sphere.

The surface of the ice is always rough as a result of the numerous submicroscopic, microscopic, and even macroscopic irregularities, projections, capillaries, and cracks. The cracks formed in the subliming material under vacuum conditions act as Knudsen cells, from which vapor can escape. Moreover, as detected in the experiments, ice contaminated by various inclusions evaporates at lower rates than does "pure" ice obtained from distilled water. In this case the differences in sublimation rates can be attributed to the presence of adsorbed inclusions.

In the presence of sublimation in the molecular-viscous and viscous regimes of state of the gas an important role is played by diffusion in the vapor phase. Therefore, in order to establish the mechanism of growth of whiskers and crystals during evaporation it is desirable to use a high vacuum, in order to avoid taking into account the effect of diffusion on the kinetics of the growth process or introducing the necessary diffusion corrections.

The mechanism of origin and the growth kinetics of an ice nap or crystals on the surface of a body may be very different. However, we will consider only the most characteristic features of this growth mechanism, namely: the origin and growth of whiskers from the vapor phase including absorption, surface diffusion to the end of the whisker, and the growth of the end.

The process of evaporation of ice or other substances is not a one-sided one. Sublimation (evaporation) is accompanied by ablimation (conversion of vapor into ice). Energetically, the individual areas of the surface of the body are not the same for sublimation and ablimation owing to the presence of absorbed inclusions (impurities). Certain areas are characterized by intense sublimation, others by ablimation. As a result of this two-sided process the surface layer becomes nonuniform.

Clearly, such a mechanism of crystal origination and growth in the presence of ablimation will be typical only under conditions of supersaturation. In this case the adsorption of dislocation impurities, which depends on time, is a source of whisker formation. Near a dislocation source pure monomolecular stages are generated. In the case of adsorption of impurities they may combine, and if the combination is characterized by circular symmetry, we get a whisker in which the symmetrical advance of the macroscopic stage becomes a prismatic face. If the crystal grows as a thin platelet, the impurities adsorbed during growth are nonuniform, and the impurity gradient creates shear stresses. These stresses force the platelets to slip parallel to the crystal axis of least dimension and hence generate a line of spiral dislocations. The faces of the ice crystal grains may be a source of these dislocation.

Another cause of the growth of an ice nap and crystals is obviously the factor of expulsion of liquid films from cracks and microcracks in the ice. As shown in [3], the crystallization of water vapor in an open crack in ice through an intermediate liquid phase is observed at negative ice temperatures. In this case we not only detected a change in the forms of the liquid phase but also noted its sudden displacement in the crack. We also detected the presence of a water film on spheres of ice in an atmosphere saturated with water vapor at an ice temperature T = 259°K.

The effect itself consisted in the ice spheres being brought into contact and then, after a certain time, separated. The normal component of the adhesion force was measured and its dependence on various

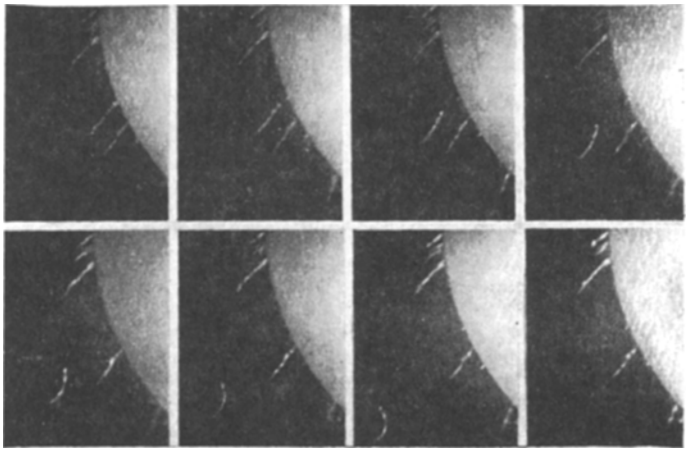

Fig. 2. Motion of ice particle after separation from the surface of a sphere.

conditions investigated. At the moment of separation the turn of the spheres in the vertical plane was registered and the angle of rotation measured. Thus, the findings of this and other experiments can be explained only by assuming the presence of liquid films at the surface of the ice crystals.

Under natural conditions of crystallization of ice from aqueous solutions it is often possible to observe that the growing ice crystals have a transverse dimension that gradually increases in the direction of the plane of contact with the water. This is indirect proof that water can climb up the lateral faces of a growing crystal in film form. This creep effect was confirmed experimentally in [4]. Thus, we now have sufficient evidence to suggest that a liquid water film on the surfaces of ice crystals is a genuine possibility.

In the experiments the crystallization of water from open microcracks in the ice through an intermediate liquid phase was observed at ice temperatures at which, it would seem, a liquid phase ought not to exist. However, on the illuminated surface of the ice we distinctly observed the sudden ejection of liquid from the microcracks and the formation of a nap of ice crystals of different configuration and length.

As a check, we performed experiments on the sublimation of colored ice, obtained by dissolving fuchsin in distilled water. Since in the sublimation process the condensate is pure ice free from any impurities, it is possible to judge from the change in the coloration of the surface what mechanism of crystal formation is most characteristic under certain conditions.

Observations of the state of the surface showed that in the case of saturated or supersaturated vapor (vacuum pump shut off, no removal of ice vapor) transparent fibers appear at the surface of the colored ice, i.e., the nucleation and growth of ice crystal take place as a result of ablimation of the vapor.

Under conditions of undersaturation (maximum rate of removal of vapor from vacuum chamber) the surface of the ice is covered with reddish crystals that appear instantaneously. In the transition regime from the undersaturated to the supersaturated state the two forms of the mechanism of ice crystal nucleation are equally probable.

With regard to the formation of a nap on the illuminated surface of the ice under conditions of undersaturation we may make the following assumption: the radiant energy flux, focused by means of the ice crystals in certain closed microvolumes between the crystals, causes a local change in the temperature gradient and pressure. These changes lead to the formation of open microcracks in the surface of the ice in which liquid water films may exist on the faces of the crystals. The supercooled liquid films are ejected from the fissures and cracks by the local pressure drop and instantaneously undergo a liquid–ice phase transition, forming a nap of threadlike, radially directed ice crystals. The whiskers and filaments of ice acquire their radial direction under the influence of the pressure drops near the surface of the ice resulting from the sublimation process.

In the ablimation zones the ice crystal complexes projecting into the boundary layer separate from the surface and escape into the surrounding medium. In this case the mass flux j (rate of evaporation) includes not only vapor but also very fine solid particles. Since the heat flux is determined from the mass flow rate ($q = rj$), we obtain exaggerated values of the specific heat flux and hence the heat transfer coefficient. In their motion the particles that separate from the surface gradually evaporate (evaporation of particles in boundary layer) (Fig. 2). The greatest ejection of particles into the surrounding medium takes place at a pressure of about 1 mm Hg. Therefore, in this region the maximum value of the heat transfer coefficient is observed.

The escape of ice particles is assisted by the stress associated with thermal slip. The ice evaporates not only from the surface but also from a certain volume (evaporation zone). In the evaporation zone there is a temperature gradient of the order of 1.5 deg C/mm. This gradient creates slip diffusion. As a result the surface gas in the pores and capillaries moves in the direction of the temperature gradient. At the same time, the walls of the pores and capillaries are being subjected to the resultant of the molecular pressure. These forces are capable of destroying the porous structure of the ice. Considerably greater temperature gradients occur in the ablimation zones, where the particles project into the gas boundary layer, since considerable heat of ablimation is released during the condensation of the vapor. Therefore the molecular pressure forces act not only normal to the surface of the body but also along the surface. As a result of the action of all these forces solid particles separate from the surface and escape into the boundary layer.

The escape of solid particles was experimentally detected in connection with the sublimation of ice. The photographs in Fig. 2 show the subliming material in the process of evaporation. The ablimation zones, in the form of fibers which then separate and move in the surface layer of moist gas, are clearly visible. During their motion these particles gradually evaporate.

The observed oscillations of the fibers also confirm the presence of molecular pressure in association with thermal slip. The oscillation of the fibers is analogous to the Brownian motion of a particle at the surface of a liquid. The reason for these motions is the same: nonidentical momenta acquired by the particle from molecular collisions.

Thus, the theory of volume evaporation in the gas boundary layer is confirmed by direct experiments.

From the trajectory of the ice particle, whose mass is approximately equal to $2 \cdot 10^{-10}$ kg, it is possible to determine its velocity. As calculations showed, the velocity of such a particle varies from 0.07 m/sec at the surface to 0.36 m/sec at a distance of approximately 14 mm from the surface at an ambient pressure $p = 40$ N/m^2. From the velocity of the particle it is possible to determine the density of the vapor–gas medium in which it moves. Calculations show that the density of the vapor–gas mixture varies along the normal from the surface of the body from $0.35 \cdot 10^{-3}$ kg/m^3 at the surface to $0.31 \cdot 10^{-3}$ kg/m^3 at a distance of 2.5 mm. The pressure at the surface of the body varies correspondingly.

Thus, supersaturation conditions are created near the surface of the body. These experimental data made it possible to postulate a new mechanism of heat and mass transfer in the vapor–gas boundary layer. The considerable increase in volume associated with sublimation (of the order of 10^6 times at $p = 0.1$ mm Hg) results in an effect similar to an explosion with the formation of a quasishock wave (molecular expansion wave). The intense rarefaction in the wave zone produces condensation or, more accurately, ablimation of the vapor with the formation of ice particles attached to the surface of the body. The distribution of the particles is associated with the motion of the molecular waves in the presence of mass source (sublimation of the body).

Calculations of the motion of these waves based on statistical methods fully correspond with the experimentally observed picture of a sharp change in the density of the surface medium. Moreover, it follows from the theory of formation of molecular expansion waves that in the sublimation zones the vapor pressure is less than the saturated vapor pressure at the given temperature. At certain pressures it is about 60% of the corresponding saturated vapor pressure.

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