THE INFLUENCE OF THE CONTENT AND CONCENTRATION OF CERTAIN IONS IN AQUEOUS SOLUTION ON THE ICE SUBLIMATION MECHANISM

D. P. Lebedev and V. N. Zhukov

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The effect of various ions on the process of crystallization (desublimation) on the sublimating surface of samples of polycrystalline ice in a vacuum with radiant heat supply is studied. Extremal effects of great crystal growth were discovered upon change in the pH of the polycrystal (liquid phase) and for certain ions in the ice crystalline lattice.

The majority of works devoted to the mechanism of sublimation have not touched upon the question of the role of the surface structure of the sublimating ice; the sublimating ice is assumed to be merely an emitter of vapor molecules which does not interfere with the sublimation process by structural changes. However, as our studies [2] have shown, this widely adopted approach essentially schematizes the physical picture of the process and is unable to give a proper presentation of it.

The goal of the study described below was to investigate the effect on the ice–water sublimation mechanism of the presence and concentration of inorganic components and, in particular, the role of ions of such components, which could aid or hinder crystal formation (desublimation) on the surface of the

TABLE 1. Ion Content of Water Samples

Water sample	Ca^{+2}			Mg^{+2}		Na^{+1}	
	mg/liter	$\% \cdot 10^4$	mg·equiv/liter	mg/liter	$\% \cdot 10^4$	mg/liter	$\% \cdot 10^4$
Water from Moscow River*	61,5	61,5	—	14,2	14,2	—	—
Tap water	6,5	6,5	3,25	—	—	3	3
Distillate	—	—	0,16	—	—	0,076	—
Bidistillate	0,12	0,12	0,06	—	—	0,51	0,51

Water sample	SO_4^{-2}		Cl^-		SiO_3^{-2}		Fe^{+3}	
	mg/liter	$\% \cdot 10^4$	mg/liter	$\% \cdot 10^4$	mg/liter	$\% \cdot 10^4$	mg/liter	$\% \cdot 10^4$
Water from Moscow River*	5,6	5,6	2,3	2,3	7,15	7,15	—	—
Tap water	—	—	—	—	—	—	0,075	0,075
Distillate	—	—	—	—	—	—	0,075	—
Bidistillate	—	—	—	—	—	—	0,005	0,005

*Data taken from Heat Technology Handbook [in Russian] Vol. 1, Énergoizdat (1960).

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TABLE 2. Ion Content and pH of Solutions Studied

Cation	Working substance	Working substance in soln., %·10^4	Portion of cations in solution * mg/liter	Portion of cations in solution * %·10^4	Portion of anions in solution mg/liter	Portion of anions in solution %·10^4	pH
Ca^{+2}	$CaCl_2 \cdot 6H_2O$	32,4 6,0	6,62 0,72	6,62 0,72	16,2 1,81	16,2 1,81	6,82 6,85
Mg^{+2}	$MgSO_4$ (crystalline)	35,0 100,0	7,0 20,0	7,0 20,0	35,0 100,0	35,0 100,0	5,71 5,76
Fe^{+3}	$FeCl_3 \cdot 6H_2O$	25,0 50,0	5,0 10,0	5,0 10,0	14,5 29,0	14,5 29,0	3,61 3,54

*Including given ion content in bidistillate.

sublimation ice layer. Moreover, in the course of the study, the qualitative effect of the pH of the liquid solution on the intensity of desublimation, and on the average height and shape of the ice crystals formed on the surface of the sublimating polycrystal, was shown.

These questions are completely uninvestigated, and only in certain works on the practice of crystal growth, under completely different conditions, is there mention of the necessity of clarifying them [1].

The ice samples for experimental investigation were prepared from water containing varying contents of dissolved salts and bases. Investigations of the sublimation of these samples were conducted with a radiant heat supply, making extensive use of macrophotography.

It is evident from Table 1 that typical tap water contains various inorganic impurities in the form of dissolved salts and bases. Using these data and also on the basis of qualitative semimicroanalysis conducted by the water and fuel technology faculty of the Moscow Energy Institute for the content of Ca^{2+}, Fe^{3+}, and Na^+ ions, solutions with a known content of each of these ions, were prepared. In order to exclude the influence of certain other ions, the samples were prepared from a bidistillate. Table 1 presents the results of qualitative semimicroanalysis of this bidistillate for basic ion content. After preparation of the samples, the solution pH was determined by the potentiometer method. Glass was used for the measurement electrode; calomel for the reference electrode. An LPU-01 high resistance potentiometer with scale calibrated in pH units was used as the measuring device.

Table 2 presents the characteristics of the solutions studied.

After preparation of the solutions, the samples were poured into special containers of dimensions 80 × 50 × 5 mm and frozen at atmospheric pressure in a refrigerator. Thereupon sublimation of the polycrystalline ice so obtained was studied in a vacuum chamber with radiant heat supply [2].

The sublimation process took place due to the presence of a temperature gradient (or corresponding pressure gradient) produced by plastic deformation of the polycrystal. Depending on the sample thickness

TABLE 3. Effect of Solution pH on Crystal Growth

pH	Experimental parameters T_e, °C	P_c, mm Hg	W_e, W	T_w, °C	Description of process
2,5	114	0,5	28	13	Individual needle-shaped crystals observed on surface, average height, δ~70μ. Growth region – separate surface zones (Fig. 1b).
4,0	117	0,5	30	13	Creeping dendritic crystals, average height δ~180μ growing over entire surface (Fig. 1c)
10,0	120	0,5	32	12	Over entire surface dendritic crystals grow up to δ~1100μ (Fig. 1d)
12,5	114	0,5	30	13,5	Needle-shaped crystals transform into "petal-shaped" (crystals with apparently fused tops). Crystal density on surface decreases. Crystal height reaches δ~500μ (Fig. 1e)
Bidistillate	116	0,5	27	13	Small individual crystals. Crystal density in sample center greater than at edges (Fig. 1a)
Tap water, pH=6.4	120	0,5	30	13	Individual dendritic stellate crystals, height to δ~500μ (Fig. 1f)

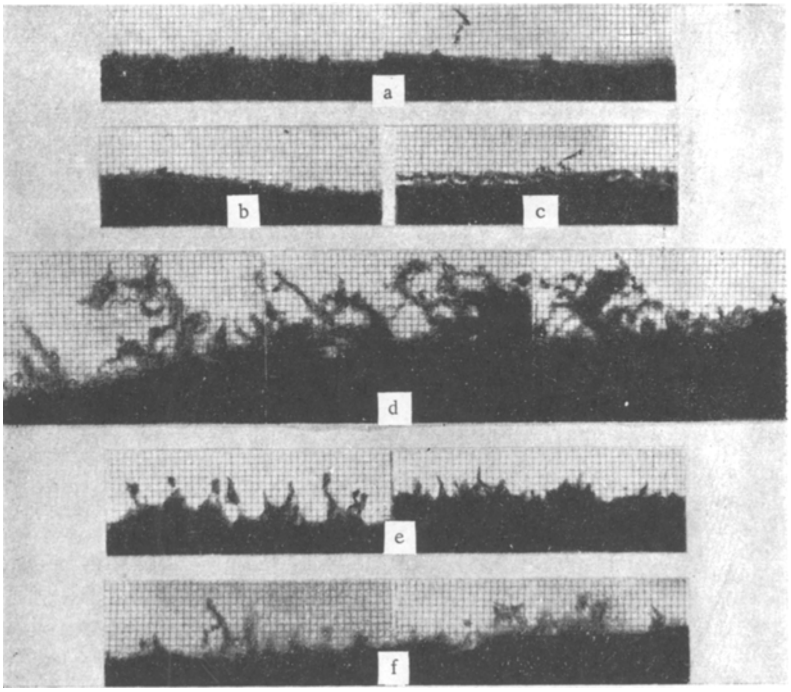

Fig. 1. Effect of liquid sample pH on crystal growth on sublimating surface with radiant heat supply: a) pH = 2.0; b) 2.5; c) 4; d) 10; e) 12.5; f) 6.4.

and the values of the heat flux and vacuum, the intensity and character of the sublimation process change significantly. In these experiments we also observed the process noted by us earlier [2], desublimation (crystal formation on the surface of the sublimating ice layer).

As sequential macrophotography showed, inclusion of various ions in the crystalline ice lattice significantly changes the picture of surface crystal growth and the sublimation mechanism.

On the basis of chemical analysis of the bidistillate and study of the sublimation process it was possible to determine that crystal growth depends on the pH value in the liquid sample (the preliminarily frozen polycrystal). The effect of solution pH on crystal growth is shown in Table 3 and Fig. 1.

At a sublimator pressure P_c = 0.5 mm Hg, ≃66.6 N/m^2, and black radiator screen temperature T_e = 120°C, no crystal growth occurs on the sublimating surface of the polycrystal prepared from double-distilled water (pH = 2). Under the same conditions with increase in bidistillate pH to 4 (see Fig. 1), some crystal growth is noted (up to $\delta \simeq 180\ \mu$), and for pH = 10 significant dendritic crystal growth is observed (up to $\delta \simeq 1100\ \mu$). On all photographs the grating spacing is 70 μ. Further increase in pH to 12.5 leads

TABLE 4. Influence of Ions (Additions) on Crystal Growth

Salt (base)	Cation concentration	Experimental parameters				Description of process
		T_e, °C	P_c, mm Hg	W_e, W	T_w, °C	
$CaCl_2$	0.6 mg·equiv /liter	120	0,5	30	13	Spherical crystals up to 150 μ form on the surface (Fig. 2a)
$MgSO_4$	7 mg/liter	128	0,5	30	11	Growth of very fine crystals (δ_{max} = 100 μ) (Fig. 2b)
$FeCl_3$	5 mg/liter	114	0,5	29	12	Fine dendritic crystals to 80 μ (Fig. 2d)
$FeCl_3$	10 mg/liter	118	0,5	31	13	Crystal density on surface increases. Crystals of several types formed (needle-shaped, spicular, block). Height to 500 μ (Fig. 2e)
$Ca(OH)_2$	0.6 mg·equiv /liter	118	0,5	30	13	Individual crystals some distance apart. Height to 80 μ (Fig. 2c)

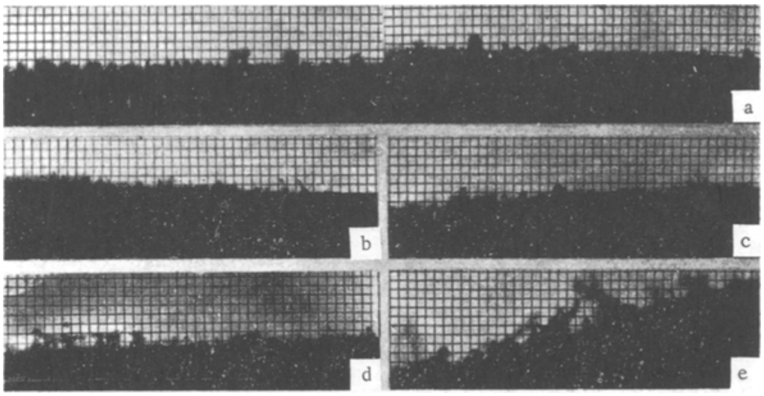

Fig. 2. Effect of certain ions on crystal growth: a) $CaCl_2$; b) $MgSO_4$; c) $Ca(OH)_2$; d) $FeCl_3$, 5 mg/liter; e) $FeCl_3$, 10 mg /liter.

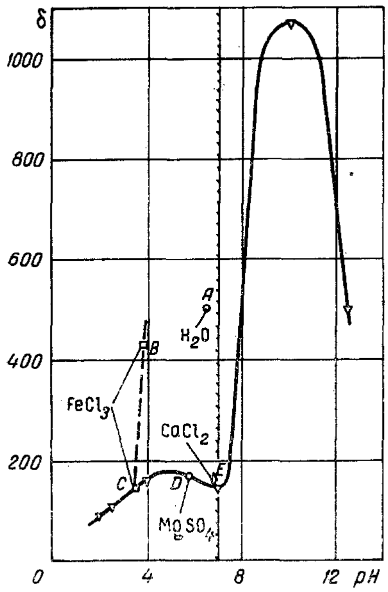

Fig. 3. Average height δ (μ) of ice crystals on sublimating surface as a function of pH of polycrystalline ice (liquid sample).

to decrease in crystal growth on the sublimating surface. At the same time the clearly defined crystal form transforms into a "petal-shape." The sublimation process ceases to be purely molecular (with sublimation of exclusively individual ions from the surface) and leads to growth (desublimation), breakage, and carrying off from the surface of crystals, dependent on the pH.

If the curve of crystal height vs pH (Fig. 3) is constructed, it will have two maxima at pH = 5 and pH = 10, with a minimum at pH = 7. In [1] the authors indicate a critical pH value for growth of $Li_2SO_4 \cdot H_2O$ crystals, located in the range 6.5-6.7, as well as the impossibility of crystal growth for pH deviations of more than 0.25.

The influence of various ions on crystal growth is shown in Table 4. The presence of Ca^{2+} and Mg^{2+} ions produces no significant effect on growth (Fig. 2b, c) and agrees well with the curve of crystal height against pH (Fig. 3). However, it must be noted that the addition of Ca^{2+} ions creates a curious new spherical crystal form on the sublimating surface (Fig. 2a).

Thus, like different pH values, additions of various ions can affect the form of the growing crystal, in particular, the development of defined faces.

Fe^{3+} ions in concentrations greater than 5 mg/liter in the bidistillate solution have a significant effect on the growth of dendritic crystals on the sublimation surface. Thus, at a concentration of 10 mg/liter the average crystal height reached $\delta \approx 430\ \mu$ (Fig. 2e). It should be noted that on the surface of the polycrystal prepared from tap water with pH = 6.4, the average crystal height reached $\delta \approx 500\ \mu$. In the graph (Fig. 3), point A for tap water does not lie upon the $\delta = f(\mathrm{pH})$ curve of the bidistillate, which is evidently associated with the influence of other ions (in particular, Fe^{3+}) included in the crystal lattice.

The experiments conducted indicated, in a sufficiently convincing manner, that crystal growth on the sublimating surface in a vacuum occurs not from the liquid phase (protrusion of liquid films [3]), but from the gaseous phase, due to defects in the crystalline lattice of the polycrystalline ice. The significant differences in crystal height and the dependence of their forms on the pH value and the inclusion of various ions in the liquid sample indicate the existence of differing conditions of molecular interaction on the sublimation surface (fields of concentration, supersaturation, etc.).

These complex conditions show the necessity of considering, along with them, the equally complex analytical formulation of the external sublimation problem. The experiments conducted show that in principle the process of sublimation of ice under the effect of radiant heat does not occur unambiguously, but depends on the chemical composition of the ice and on the thermodynamic conditions. It must also be noted that existing concepts regarding the influence on crystal growth of residual air, entering the sublimator due to leakage (in attempts to maintain a given vacuum) are unfounded. In these experiments leakage of air in the working regions was practically excluded; the maintenance in the sublimator of a vacuum and an atmosphere of pure water vapor was accomplished by means of automatic valves located in the vacuum pump connections.

NOTATION

T_e is the measurement screen temperature;
P_c is the sublimator pressure;
W_e is the radiator electrical power;
T_w is the sublimator wall temperature.

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