RATE OF SUBLIMATION OF ICE AT LOW PRESSURES

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Sublimation of ice in a rarefied atmosphere at $P = 1\text{-}1600\ \mathrm{N/m^2}$ is examined. The ice evaporation coefficients at different pressure in a vacuum chamber are determined.

Evaporation from the solid state (sublimation) at low pressure is of great interest for various branches of industry. Evaporation is directly implicated in such technological processes as molecular lyophilization and distillation, sorption and desorption, etc.

The evaporation rate is usually characterized by the evaporation coefficient, expressed as the ratio of the evaporation rate in vacuum to the maximum rate determined from the Hertz formula. An analysis of the values of the evaporation coefficients in [1] shows that the values of the ice evaporation coefficients given by different authors vary in a wide range – from 0.07 to 1. Hence, a further investigation of this question is of great theoretical and practical interest.

According to molecular-kinetic theory the evaporation rate in the case of unilateral evaporation from a surface in contact with its saturated vapor, when the surface and vapor have the same temperature T, is given by the equation

$$j_t = \alpha_e P_s \frac{1}{\sqrt{2\pi RT}}. \tag{1}$$

Equation (1) can be used to determine the evaporation rate in cases where the temperature T of the evaporation surface corresponds to fairly low vapor pressures ($P_s < 10\ \mathrm{N/m^2}$). When the substance evaporates into a vapor with pressure at the phase interface $P_p < P_s$, the evaporation rate is given by the equation

$$j_t = \alpha_e (P_s - P_p) \frac{1}{\sqrt{2\pi RT}}. \tag{2}$$

It is assumed in equation (2) that the vapor molecules are identical with the molecules on the surface of the evaporating solid and that processes like association, dissociation, or any other process involving chemical changes do not occur. It is also assumed that the density of the vapor cloud is low enough to ensure that no significant diffusion resistance is offered to the emitted molecules. If any other gas is present above the evaporation surface, additional effects which reduce the value of α_e occur. If an inert gas of low density is present over the evaporation surface the partial pressure of the evaporated vapor molecules can be taken as P_p. It is rather difficult in practice to determine the partial pressures and temperatures of the evaporated molecules and inert gas molecules, especially in the region adjoining the surface.

An increase in the partial pressure of the inert gas or vapor leads to an increase in the diffusion resistance. When solids evaporate in process equipment with walls of limited size, allowing the formation of a vapor cloud over the evaporation surface, the resistance due to collision of molecules with the apparatus walls must be taken into account as well as the diffusion resistance. These and certain other factors reduce the experimental value j_e in comparison with its actual value j_t. The evaporation rate also depends considerably on the purity of the evaporation surface, since contamination of subliming surfaces reduces the evaporation probability. This probably accounts for the large differences in the values of α_e obtained by different authors. Most subliming materials (ice, etc.) are not homogeneous and consist of a multiplicity of microscopic crystals or grains with strictly individual properties. In some cases the structural unit of ice

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is called a grain, and not a separate crystal, since it has a complex substructure and consists of numerous parallel plates. The orientation and the size of crystals at an ice surface vary considerably, since their formation depends on external factors.

In crystals of macroscopic size there are always numerous deviations from the ideal structure, or defects in the crystal lattice. Such defects include the absence of one or more atoms from the crystal lattice, spots where individual parts of the crystal are slightly apart, foreign atoms which have gained access to the crystal lattice in some way, and so on.

Reduction of the ice temperature leads to a reduction of the size of the inclusion-filled units. The units have the form of long orderly directed (radially in spherical specimens) cylinders (channels) of varying cross section. In addition, ice usually contains numerous small spherical air bubbles formed by the air dissolved in the water and released by freezing. The higher the freezing rate, the greater the increase in the amount of air trapped in the ice. In the case of sublimation of inhomogeneous crystalline substances in a vacuum the loss of mass will not be uniform over the whole surface, and because of the difference in orientation of the crystals relative to the energy source the loss from the surface of some crystals will be greater, and from others will be less. This nonuniformity of sublimation leads to an increase in the roughness of the surface and the formation of small depressions or cavities on it.

The observed variation of the surface state of subliming ice raises the question of what is the effective evaporation area: the geometric area or the total area, including the roughness. Melville [2] investigated the effect of surface roughness on the evaporation rate of some metals. His calculations of the evaporation coefficient showed that when $\alpha_e = 1$ the surface roughness has no effect, but when $\alpha_e < 1$ roughness increases the evaporation rate. It was shown experimentally in [3] that if the drilling of a large number of holes in metal specimens did not lead to an increase in evaporation rate, the coefficient α_e was close to unity.

We carried out experiments to determine the effect of ice surface roughness on the evaporation rate with two pressures in the chamber (1 and 65 N/m^2) in steady-state conditions. The test specimens were spheres 80 mm in diameter made of ice by different freezing methods.

Sublimation from the surface of the spheres was uniform, since a uniform supply of energy was provided. Surface roughness was created by drilling numbers of holes [from 50 to 300; hole sizes (diameter × depth) 1×6, 2×6, and 2×11 mm] in the surface of the sphere. The drilling of 300 2×11 holes more than doubled the surface area of the specimen. To assess the effect of roughness we compared the evaporation rates of two specimens – one with holes and a control, without holes. At the center of the two bodies there were spherical electric heaters of equal power connected in parallel. The investigations were conducted with different internal heat fluxes; the temperature gradients along the walls of the holes varied from 150 to 200 deg/m.

The experimental and control specimens were weighed separately on a VLTK-500 balance in a vacuum chamber, so that the spheres were in identical thermodynamic conditions. Since the ratio of the area of the sphere to the area of the cubical chamber was a low value (less than 0.01) we could assume that the chamber was sufficiently large to ensure that there was no distortion of the true picture of sublimation. These investigations showed that the presence of cylindrical holes on the surface of an experimental specimen with and without a temperature gradient did not lead to an increase in the evaporation rate.

Since diffusion resistance can be neglected at pressure $P = 1\ N/m^2$, and the chamber walls are sufficiently far from the evaporation surface to ensure that it is unlikely that molecules reflected from the walls will land on the ice surface, we used equation (1) to determine α_e. The coefficient α_e for ice with surface temperature $T = 214.6°K$ ($P_s = 1.33\ N/m^2$) was 0.07. In the same external conditions, but in the presence of an internal energy source leading to an increase in the surface temperature and, hence, the sublimation rate, there was some increase in α_e – to 0.11. At higher pressures ($P \gg 1\ N/m^2$), when a vapor cloud of high density formed over the ice surface, the coefficient α_e was determined from equation (2). In this case the coefficient α_e decreased from 0.07 to 0.002 when the pressure increased from $P = 1$ to $P = 1600\ N/m^2$. Thus, as distinct from [3], where an increase in surface roughness led to an increase in evaporation rate when $\alpha_e < 1$, in our case the evaporation rate for subliming ice was independent of the surface roughness when $\alpha_e \ll 1$.

The sublimation rate, other conditions being equal, depends on the energy supplied to the evaporating substance. Many features of the heat supply, however, are still obscure. It is extremely difficult to investigate the heat transfer theoretically and this is an insoluble problem at present. Experimental investigations so far have been directed mainly towards direct measurement of the individual energy fluxes between the surroundings and the ice surface. In compiling the heat balance we considered four energy fluxes: 1) the heat flux brought to the ice by conduction; 2) convection; 3) radiation; 4) heat loss due to the phase transition.

To determine the separate components of the heat flux expended on sublimation we used the method in which individual heat fluxes are excluded. For instance, the radiative or convective heat flux component was excluded by equalization of the temperature of the subliming surface and the vacuum chamber walls, or the subliming surface and the surrounding vapor–gas atmosphere. The experiments were conducted in a wide range of temperature ($T = 200$–$370\,^\circ K$) and pressure ($P = 1$–$1600\ N/m^2$).

An analysis of the results of the investigations indicated that convective heat transfer in a rarefied atmosphere is very slight and does not become appreciable until $P > 100\ N/m^2$. The free motion due to inhomogeneity of the temperature and concentration distributions in the chamber volume causes an insignificant flux of heat to the surface.

In view of the convective heat transfer relationship $q = \alpha_c \Delta T$, on the basis of the heat balance equation in a wide temperature range in the vacuum chamber α_c does not vary and is numerically equal to unity. While the radiative heat transfer coefficient increases linearly with increase in the temperature head the convective heat transfer coefficient is constant, i.e., the main role in heat supply in sublimation in a vacuum is played by the radiative component of the heat flux [4].

Since convection decreases at low pressure, while the heat transfer between the body surface and vapor cloud continues, the concept of the convective heat transfer coefficient α_c does not correspond with its classical definition. It would be more correct to characterize heat transfer in a vacuum by the thermal accommodation coefficient α_t. The convective heat transfer between the solid surface and vapor will then be proportional to the accommodation coefficient and the difference in temperature of the surface and vapor. It should be noted that the coefficient α_t, found experimentally from the formula,

$$\alpha_t = \frac{T_3 - T_1}{T_3 - T_2},$$

was found to be unity for ice. This result is of great theoretical interest, since it shows that, although the ice evaporation coefficient is very low ($\alpha_e = 0.002$–0.11) the transfer of energy between the molecules and the evaporation surface is complete, i.e., one can assume that vapor molecules with energy E_1 moving towards the surface of a solid with energy $E_2 < E_1$ condense on the surface and give up their excess energy to it. It should be noted that for ice even at pressure $P \sim 100\ N/m^2$, when there is an appreciable amount of inert gas in the atmosphere, the accommodation coefficient α_t is also equal to unity. In view of this we can propose the following mechanism of heat transfer from a vapor–gas medium to an evaporation surface.

Owing to the rapid mass release (due to the energy of the radiant flux or the internal heat source) the solid surface emits a flux of vapor molecules, the energy of which at a distance of several molecular mean free paths becomes equal to E_1, the energy of the molecules of the vapor-gas mixture. Some of the vapor molecules with energy E_1 are reflected onto the surface, where they condense and give up their excess energy $E_1 - E_2$ to the body, i.e., sublimation is accompanied by condensation of reflected molecules. This heat transfer mechanism is characteristic of the case where the vapor cloud over the evaporation surface contains very few inert gas molecules. If there is an inert gas over the surface, then for $\alpha_t = 1$ the inert gas molecules must give up all their excess energy when they collide with the evaporation surface. Thus, for the case $\alpha_t = 1$ only these two mechanisms of interaction of molecules with the surface are characteristic.

An analysis of the interaction of vapor molecules with the walls of cylindrical holes in ice shows that in fine cylindrical holes evaporation proceeds "on its own" at low intensity, i.e., static equilibrium between the evaporating and condensing molecules is established. Evaporation in fine holes can be likened to the radiation of a blackbody (closed cavity with fine slit), where the entrance and exit of the beam are hindered.

NOTATION

j_t	is the theoretical mass evaporation rate, $kg/m^2 \cdot sec$;
j_e	is the experimental evaporation rate, $kg/m^2 \cdot sec$;
P_s	is the water vapor saturation pressure, N/m^2;
P_p	is the partial pressure of vapor in gaseous medium, N/m^2;
T	is the temperature, °K;

R	is the gas constant, J/deg · kmole;
α_e	is the evaporation coefficient;
α_c	is the convective heat transfer coefficient, W/m^2 · deg;
α_t	is the thermal accommodation coefficient;
q	is the specific convective flux, W/m^2;
E_1	is the energy of molecules in vapor cloud;
E_2	is the energy of molecules on evaporation surface;
P	is the pressure in chamber, N/m^2;
T_1	is the mean temperature of molecules reflected from solid, °K;
T_2	is the mean temperature of molecules corresponding to temperature of solid surface, °K;
T_3	is the temperature of molecules incident on solid, °K.

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