DENSITY OF THE VAPOR – GAS MEDIUM IN THE BOUNDARY LAYER OF A SUBLIMING BODY

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The vacuum sublimation process has been investigated. Data on the density distribution in the layer adjacent to a subliming body, obtained using ionizing radiation, are presented. A new mechanism of the evaporation process is proposed.

In view of the development of sublimation technology, studies of the drying mechanism are of particular importance. The determination of the nature of the density distribution in the medium surrounding a subliming body should prove useful in this connection.

In planning our experiments we started from the widely accepted theory of diffusion evaporation [1,2]. The rate of evaporation into a vacuum is usually calculated from Knudsen's formula

$$j_m = \alpha_i (P_{\text{sur}} - P_c)/(2\pi R T_{\text{sur}})^{0.5}. \qquad (1)$$

Unfortunately, this formula does not express the evaporation process accurately enough, and the calculation of the evaporation of a substance consisting of complex molecules requires the introduction of special coefficients [3].

According to the kinetic theory, the three states of matter – solid, liquid, and gaseous – are distinguished only by the proximity of the molecules and the intensity of their motion, and the temperature of a substance reflects the degree of random thermal motion of its component molecules. Disturbance of the energy balance leads to a phase transition. In this case the molecules of the evaporated substance acquire all the properties characteristic of gas molecules and are subject to known kinetic and thermodynamic laws.

In the course of evaporation in a not very high vacuum, in the process of collision between the evaporating molecules and the molecules of the medium a vapor–gas layer is formed at the surface [3]. This layer also offers the chief resistance to mass transfer during evaporation. The determination of its parameters is of great importance. It may be assumed that starting from the pressure gradients and the density gradients in the space surrounding the evaporating body one can determine the rate of removal of material from the surface, since a definite relation exists between these three quantities [4].

There are well developed methods for determining the density and pressure. But in our case the use of mechanical probes is undesirable, since the introduction of a foreign body may distort the flow. Moreover, if the density of the medium is low, the usual methods of visualization, based on changes in the index of refraction, are unsuitable [5]. This shortcoming can be eliminated if ionizing radiations, whose wavelength is five to six orders less than that of visible light, are used for recording the densities.

The use of ionizing radiations is based on the attention of the particle flux from a plane-parallel source as they pass through a chamber containing the evaporated material. In accordance with Bethe's formula, for a given substance the attenuation of the intensity of beta radiation is proportional to the density. This makes it possible to obtain a quantitative, as well as a qualitative, characteristic of the process of evaporation in a vacuum. In the twenties Glocker and Traub established a linear relation between the density of a photographic emulsion and the exposure to ionizing radiation. Further research has shown that such a relation exists for low and medium densities. It differs from the corresponding relation for exposure in visible light, which is not linear, as a result of the existence of a different sensitivity threshold for different grains [6].

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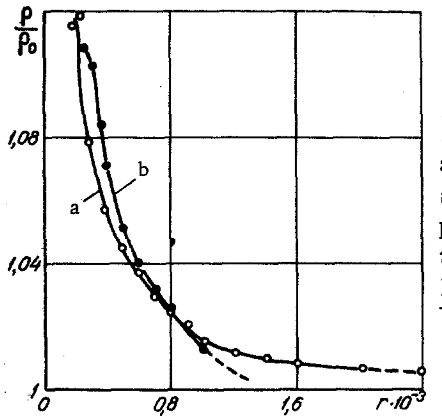

Fig. 1. Density distribution around a subliming body (naphthalene sphere) in a vacuum: a) ambient pressure 66.66 N/mm^2, temperature of medium 291°K; b) 133.32 N/m^2 and 293°K, respectively.

Collisions with gas molecules reduce the initial intensity of the ionizing particle flux. The attenuation obeys a linear absorption law

$$\frac{\partial I}{\partial X} = -\rho\mu X. \tag{2}$$

The density field may now be investigated as follows: a plane-parallel source of β-radiation of known intensity is installed in the vacuum chamber parallel to a cassette with x-ray film of the necessary sensitivity. Between them is placed the substance whose sublimation process is being investigated. A screen is introduced in front of the source. When the equilibrium evaporation rate has been reached, the cassette and the screen are opened. All these operations are performed in a darkened room. The exposure depends on the sensitivity of the film and the characteristics of the source. It is chosen so that the total β-particle flux falls in the range $(0.5\text{–}5.0)\cdot 10^6$ particles per cm^2.

Various sources, differing in energy and type of radiation, were employed. To obtain a quantitative characteristic of the process we made a calibration for the dependence of the degree of blackening of the film on the density of the medium.

The measurements are made on the linear interval of the curve representing the degree of blackening versus the intensity of the β-particle flux. The radiograms obtained are interpreted by means of a microphotometer or similar instrument.

For an axisymmetric flux the attenuation analysis is based on Abel's integral equation, which for the local density of the gas [7] has the form:

$$\rho_r = \rho_s + \frac{1}{\pi\mu}\int_r^{R_s} \frac{d}{dy}\ln I \frac{dy}{\sqrt{y^2 - r^2}}. \tag{3}$$

The values of $[d/dy]\ln I$ are determined from the experimental data. The density in the undisturbed region is determined by means of a manometer. The attenuation factor μ must be determined in advance for a given source and a given apparatus geometry by means of special measurements – calibrations – at different pressures.

For greater convenience, Abel's formula can be reduced to a form similar to the equation used in shadow and interferometric studies [8]:

$$\rho_{i,z} = \rho_s + \frac{1}{\pi\mu R_s}\sum_{j=i}^{n-1}\left[\ln I_n(z) - \ln I_j(z)\right]\tau_{ij}$$
$$\left(I_n(z) = I(R_s, z)\right). \tag{4}$$

The components of the triangular matrix are given by the following formulas:

$$\tau_{ij} = \begin{cases} \omega_{ii} & (j = i), \\ \omega_{ij} - \omega_{ij-1} & (j \neq i), \end{cases} \quad \omega_{ij} = n\ln\frac{j + 1 + \sqrt{(j+1)^2 - i^2}}{j + \sqrt{j^2 - i^2}}. \tag{5}$$

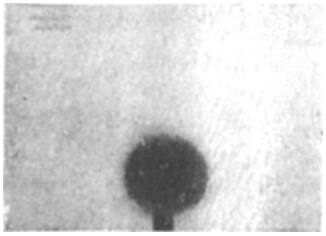

Fig. 2. Evaporation of a naphthalene sphere in a vacuum. Flow visualization with β-radiation.

Thus, to determine the density it is necessary to measure the fall in the intensity of the ionizing particles in the sections for various chords of the axisymmetric region. In our case only the inner zones are of special interest. However, in (4) the summation must always extend from the inner i zones to the outer n – 1 zone for each z.

The experiments were performed on spheres of naphthalene and ice. The pressure in the vacuum chamber varied from 0.5 to 4 mm Hg. The diameter of the spheres was 14-25 mm. The temperatures of the evaporating material and the surrounding medium were monitored with copper – constantan thermocouples.

The results of the measurements of the variation of the density of the medium with distance from the subliming body are plotted in Fig. 1.

Experiments with different substances showed that during sublimation a layer of increased density is formed around the evaporating material (see Fig. 2). At a distance of 0.25-0.30 mm from the body the density of the layer rises sharply.

The sharp increase in the degree of blackening observed close to the surface of the body may be attributed to the roughness of the surfaces of the ice and the naphthalene. In the case of a parallel flux of ionizing particles the projecting parts cause an apparent increase in optical density on the film. Similarly, in analyzing the developed film in ordinary photometers, one cannot reduce the size of the slit without loss of accuracy. In photometric scanning of a photographic image with a beam of decreasing area a the grain noise increases according to Selwyn's law $\sigma_D\sqrt{a}$ = const and reduces the number of gradations determinable. At the same time, a slit size 0.5 × 0.5 mm is perfectly sufficient for the purposes of the experiment. The results obtained by scanning the field from different directions proved to lie within the limits of accuracy of the measurements and indicate the good reproducibility and repetitive character of the variation of the density fields.

It is clear from the figures that the change of density corresponds to a weak shock wave, i.e., is analogous to the change of density associated with compression and expansion waves. The observed shock can occur close to the surface of the body because of the large increase in volume accompanying phase transformation (in a vacuum of about 0.1 mm Hg the volume increases by a factor of approximately 10^7) and collisions between the flux of evaporating molecules and the molecules of the ambient medium, since as the mean velocity of the evaporating flux we can take the velocity at which the momentum the molecules carry away is equal to that carried away by molecules with a Maxwellian distribution [9]. This produces expansion and compression waves of the weak shock type [10] with a source of mean originating from individual points of the surface.

On the basis of the values obtained for the density ratio we can theoretically calculate the relative change of temperature and pressure at the site of the local density rise. From the nature of the change in the surrounding layer we can derive an explanation of the formation of fine particles of evaporated material around a subliming body. As a result of this mass transport mechanism a layer of increased density is formed. The process is accompanied by a local rise in temperature. Heat is transferred to the surrounding medium and the body by conduction and radiation. Subsequently, upon relaxation, the pressure and temperature in the surrounding layer fall. This causes a normal process of condensation. The retardation of the heat transfer processes in the vapor–gas medium still further intensifies the condensation of vapor, which is also precipitated in the surrounding space. In their turn, the molecules returning to the surface of the body may cause a local change in temperature, as a result of which at individual points on the surface liquid phase may be formed. Its partial evaporation (owing to the greater expenditure of energy on evaporation and retardation of the heat transfer processes) may be accompanied by a process of formation and growth of crystal of the evaporated substance. All this may distort the original evaporation surface with all the consequences this entails (leaching, spalling, etc.), but has little effect on the gas dynamics of the process [10].

The mechanism of the heat and mass transfer processes, accompanied by the formation of weak shocks, indicates that an increase in the temperature of the evaporating material (other things being equal) should most powerfully intensify the evaporation process. This applies particularly to evaporation into an atmosphere of light monatomic gas and probably into a medium that absorbs the evaporated molecules. The existence of a denser layer provides physical confirmation of the superiority of shortwave infrared heating for intensifying drying processes and of high-frequency heating over other heating methods [11]. This follows both from the selective nature of the absorption of infrared radiation and high-frequency heating and from the "protective" action of the shock layer. It is known that (at certain frequencies) infrared radiation can penetrate to a certain depth into the evaporated material with relatively little attenuation in the surrounding vapor–gas layer. In the case of a convective heat supply, on the other hand, the high-density layer acts as a barrier to the heat flux.

NOTATION

J_m	is the mass of material subliming per unit time per unit surface;
α_i	is the evaporation coefficient;
R_0	is the universal gas constant;
M	is the molecular weight of vapor;
P_c	is the pressure in vapor cloud at distance equal to mean free path from surface;
R	is the gas constant, $R = R_0/M$;
T_{sur}	is the surface temperature;
P_{sur}	is the saturated vapor pressure at surface temperature;
I	is the particle flux intensity;
X	is the coordinate along flux axis;
ρ	is the gas density;
μ	is the mass attenuation factor;
ρ_r	is the unknown radial density;
ρ_s	is the density in undisturbed region;
R_s	is the radius of effective nucleus of disturbance;
ρ_{iz}	is the local density;
n	is the number of annular zones of axisymmetric region;
ρ/ρ_0	is the ratio of density in boundary layer to general density in evaporation chamber;
r	is the distance from investigated point to axis of disturbance region, m;
y	is the coordinate of cross section of disturbance zone;
i, j	are the zone numbers.

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