FLOW OF VAPOR THROUGH A QUASICLOSED VOLUME WITH A TEMPERATURE GRADIENT

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Results of a theoretical and experimental study of the flow of cadmium sulfide vapor through a cylindrical chamber are cited, with condensation and reevaporation of vapor from the chamber walls taken into account.

In the study of the kinetics of formation of vacuum condensates in an "open" volume, the concept of transport of matter by a molecular beam is often resorted to. Given the differences between the method of preparation in a quasiclosed volume and in an "open" vacuum, this paper confronts the problem of experimental investigation of the spatial distribution of condensate thickness (condensation rate) in constructing a qualitative model of the mechanism underlying the transport of material evaporated in a quasiclosed volume.

EXPERIMENTAL METHOD

The quasiclosed volume is formed by a split graphite cylinder d = 50 mm in diameter and L = 80 mm in length (Fig. 1), the bottom functioning as an evaporator.

The end surfaces of the cylinder are heated by two distinct radiation heaters which bring about the requisite temperature distribution throughout the effective volume. Vertical grooves were machined in the side walls of the cylinder to accommodate the devitrified glass ("sitall") substrates. Sitall plates were placed in the radial cross sections (on a helical line) parallel to the base. The materials to be evaporated in the experiment were cadmium sulfide, cadmium selenide, and cadmium telluride. Since all of these materials exhibit qualitatively identical behavior, cadmium sulfide alone will be singled out in the further discussion of the experimental results. The evaporation temperature T_0 of the initial material ranged from 550 to 750°C; the temperature of the top of the chamber varied from 350 to 500°C respectively (the temperature distribution along the cylinder walls was linear). The condensation time was constant (30 min) in all the experiments.

Figure 2 shows the distribution of condensate thickness in the radial cross sections of the cylinder, determined on the vertically positioned plate. It is clear that the film thickness remains constant in each such cross section, and depends solely on the distance the particular cross section is removed from the evaporator (graphite cylinder bottom). A similar pattern was observed when the sitall substrates were laid horizontally.

The problem probed in the investigation of condensation in a closed crucible can hence be treated as a one-dimensional problem, and the distribution of the parameters of the vapor produced from the material being evaporated is investigated as a function of only one coordinate (the length of the crucible).

It is clear from Fig. 3 that condensation of vapor occurs when the temperature of the substrate falls below a certain critical temperature T_{cr}. The existence of this critical condensation temperature stems from the fact that the average "lifetime" of the particle adsorbed on the surface (prior to reevaporation) shortens with increasing temperature of the substrate, while T_{cr} increases with increasing vapor density, on the other hand [1].
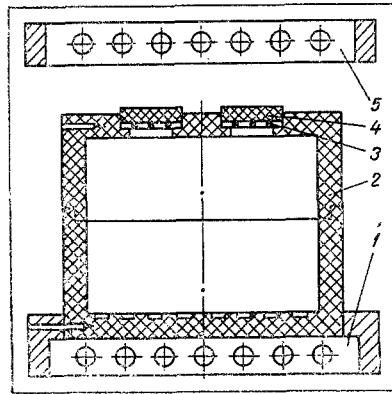
Fig. 1

Fig. 2

Fig. 1. Diagram of experimental arrangement: 1) chamber heater;
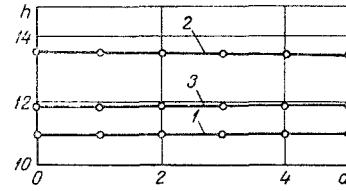2) chamber; 3) substrate; 4) graphite inserts; 5) substrate heater
unit.

Fig. 2. Distribution of thickness of condensate in radial cross sec-
tions of chamber, removed from chamber bottom by distances: 1)
30 mm; 2) 40 mm; 3) 50 mm (h, μ; d, cm).

It is clear from Fig. 3 that the ratio T_{cr}/T_0 increases linearly as the evaporation temperature T_0
rises. Figure 4 shows the distribution of condensate thickness over the length of the cylinder at
two evaporation temperatures of the cadmium sulfide. The dependence h = f(x) rises at first as the dis-
tance from the evaporator is increased, then attains a maximum and declines subsequently; the position
of the maximum shifts in the direction of the top of the cylinder as the evaporation temperature increases.
The condensate thickness increases with T_0, so that the ratio of film thicknesses at the maximum and in
the cross section of the cylinder top declines.

DISCUSSION OF RESULTS

The most interesting features of the vapor flow and condensation conditions in the quasiclosed vol-
ume are the presence of a region in the initial stage of the flow patterns where there is no layer of con-
densate at all, and the clearly defined maximum in the rate of condensation on the walls at some distance
from the evaporator (Fig. 4). To account for these features in qualitative terms, it is sufficient to assume
that the mass transfer of vapor from the walls is determined by the independent action of two distinct
factors: 1) condensation of particles from the directed flow of vapor moving along the walls of the cyl-
inder; and 2) partial reevaporation of the condensate from the walls back into the stream. The conden-
sation rate v_{co} characterizing the first factor depends on the density and temperature of the vapor and
on the velocity of the stream, while the reevaporation rate v_{re} characterizing the second factor depends
solely on the wall temperature† T_w, and this last dependence is a very sharply expressed one:

$$v_{re} = f(T) \exp\left(-\frac{T^*}{T}\right),$$ (1)

where f(T) is a much weaker function of the temperature than $\exp(-T^*/T)$.

The resulting rate of vapor condensation on the walls is determined by the straightforward equation

$$v(x) = v_{co}(x) - v_{re}(x).$$ (2)

This expression can also be restated for specific mass flows:

$$j(x) = j_{co}(x) - j_{re}(x).$$ (3)

The variable j_{re} is related to T and to $\rho_s(T)$ (e.g., see [2]) by the formula

$$j_{re}(T) = \rho_s(T)\beta\sqrt{\frac{RT}{2\pi\mu}} = \rho_0 f(T) \exp\left(-\frac{T^*}{T}\right).$$ (4)

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†We assume that the heat imparted to the wall as the vapor condenses does not affect the thermal con-
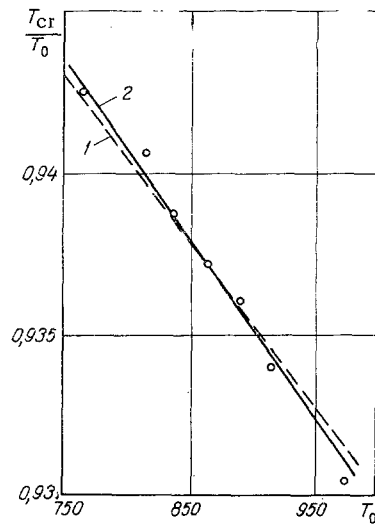ditions of the wall. The problem is treated as one of stationary condensation conditions.
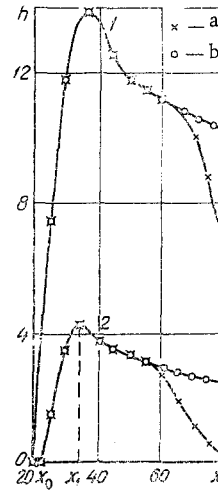
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Fig. 3

Fig. 4

Fig. 3. Theoretical (1) and experimental (2) dependence of ratio T_{cr}/T_0 on evaporation temperature of cadmium sulfide $(T_0, °K)$.

Fig. 4. Distribution of thickness of cadmium sulfide condensate over height of crucible at different evaporation temperatures: 1) $T_0 = 600°C$; 2) $T_0 = 550°C$; a) horizontal position of substrate; b) vertical position of substrate; $(h, \mu; x, mm)$.

The maximum mass flow in condensation j_{co} can be determined, by analogy with Eq. (4), as

$$j_{co}(T_v) = \rho(T_v)\beta\sqrt{\frac{RT_v}{2\pi\mu}}. \tag{5}$$

Consequently, if $j_{co}[T_v(x)] > j_{re}[T_w(x)]$, there will be no net condensation of vapor on the walls over the entire stretch of cylinder from the initial cross section (x = 0) to some cross section (x = x_0), where

$$j_{co}[T_v(x_0)] = j_{re}[T_w(x_0)], \quad T_w(x_0) = T_{cr}. \tag{6}$$

In our case, where the vapor forming in the initial cross section of the cylinder (x = 0, T = T_w = T_0) is capable of expanding freely into the surrounding space, we have, always:

$$\rho[T_v(0)] < \rho_s[T_w(0)] = \rho_s(T_0).$$

Consequently, along the initial path of vapor escape in the cylinder, with the wall temperature of the cylinder declining smoothly down from the temperature T_0, there will be no net vapor condensation, since all of the condensate becomes reevaporated from the "hot" walls.

Starting with the cross section x = x_0, some fraction of the condensable particles is retained by the surface of the walls, and with increasing distance from the evaporator this fraction increases, while the contribution made by reevaporation of particles to mass transfer on the walls diminishes abruptly because of the decline in the temperature of the walls (see Eq. (4)). The condensate layer on the walls increases, and the vapor stream begins to become depleted. Naturally, the thickness of condensate on the walls, after passing through a maximum, begins to decline. It is clear from these arguments that the linear dimension of the interval of rise in net condensation can be estimated qualitatively as the length of the effective reevaporation zone $l = x_1 - x_0$ such that the condition

$$\frac{j_{re}(x_0)}{j_{re}(x_1)} = e. \tag{7}$$

is satisfied. Substitution of Eq. (4) into Eq. (7) yields

$$\frac{\exp\left(-\dfrac{T^*}{T_{\mathrm{cr}}}\right)}{\exp\left(-\dfrac{T^*}{T'_1}\right)} = e,$$

where T'_1 is the wall temperature at $x = x_1$. After straightforward transformations, we have

$$T'_1 = \frac{T^* T_{\mathrm{cr}}}{T_{\mathrm{cr}} + T^*}.$$

Recalling that $T^* \gg T_{\mathrm{cr}}$, and expanding the function in a series in powers of T_{cr}/T^*, we find, in an approximation;

$$T'_1 \simeq T_{\mathrm{cr}} \left(1 - \frac{T_{\mathrm{cr}}}{T^*}\right). \tag{8}$$

In the case of a linear temperature gradient along the cylinder

$$T_{\mathrm{cr}} = T_0 - x_0 \frac{dT_{\mathrm{w}}}{dx}, \quad T'_1 = T_0 - x_1 \frac{dT_{\mathrm{w}}}{dx}. \tag{9}$$

Substitution of Eq. (9) into Eq. (8) yields

$$x_1 = x_0 + \frac{(\varepsilon T_0)^2}{T^* \dfrac{dT_{\mathrm{w}}}{dx}}, \tag{10}$$

where $\varepsilon = T_{\mathrm{cr}}/T_0$.

It is clear from Eq. (10) that the effective reevaporation zone becomes further removed from the evaporator to the extent that the temperature T_0 rises, and in inverse proportion to the temperature gradient along the cylinder.† This is clearly confirmed by the above experimental data. As numerical calculations and comparison with experiment have shown, the coordinate x_1 fits quite closely to the position of the maximum vapor condensation rate.

This means that we can distinguish three intervals over the entire region of dispersion of vapor in the cylinder:

1) $0 \le x \le x_0$ – reevaporation dominates over condensation and no film settles on the walls;

2) $x_0 < x \le x_1$ – condensation, while dominating over reevaporation, is accompanied by only insignificant depletion of the stream, so that the thickness of the condensate film increases with increasing distance from the evaporator;

3) $x_1 < x$ – reevaporation of material from the cylinder walls and back into the stream is virtually nonexistent, and the stream becomes depleted with partial condensation of vapor on the walls, resulting in a lessening of the thickness of condensate film with increasing distance from the evaporator.

It must be emphasized that this qualitative explanation of the observed features of condensate formation on the cylinder walls is presented without reference to the vapor flow pattern.

A quantitative description could be achieved only by attempting to cope with the vapor flow mechanisms The criterion for realization of any particular vapor flow mechanism is the relationship between the free path length (λ) of atoms (or molecules) in the vapor between collisions and the length of the effective reevaporation zone l and the linear dimensions of the chamber (length L and diameter d of the cylinder). When the evaporator temperature is high ($T_0 \sim 800$ to $1000°$K in the case of CdS) and the vapor pressure $p \sim 10^{-1}$ to 10^{-2} torr, when $\lambda \simeq (1\text{-}5)\cdot10^{-1}$ cm [3] and $\lambda \ll L$, $\lambda \ll d$ and, moreover, $l < L$, the gas-dynamic flow mechanism is realized.

In this case vapor flow comprises gas-dynamic expansion into a vacuum with condensation on the cylinder walls, and a local Maxwellian distribution of vapor particles with respect to velocities in a system

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† Note that Eq. (10) does not deal with the effect of several other factors, above all the cylinder diameter, on the value of x_1.

of coordinates moving along the cylinder walls at velocity u prevails at each point of space occupied by the vapor. In the initial (in the gas-dynamic sense) cross section, the velocity (u_1) is equal to the local speed of sound c_0 [4]

$$u_1 = c_0 = \sqrt{\gamma \frac{RT_1}{\mu}}.$$

(11)

Over the interval $0 \leq x \leq x_0$, where vapor flow takes place without condensation, the flowspeed does not vary and remains equal to c_0. When $x_0 < x$, when the flow begins to be subject to "discharge" effects because of the net condensation, the group velocity of the stream rises, and the temperature, density, and pressure of the vapor in the stream all decline [5]. Solving the gas-dynamics equations for a stationary flow with condensation and reevaporation of particles from the confining walls taken into account, in the one-dimensional approximation,† we can find the profiles of the gas-dynamics variables we are interested in. We shall not cite this solution here (that will be done in a separate article), and we need only determine the value of x_0 and the critical condensation temperature.

To do this we have to know the vapor parameters in the initial gas-dynamic cross section. This cross section is separated from the evaporation surface by a gas-kinetic layer of thickness 2λ to 3λ [6] within which the particles come to an equilibrium velocity distribution in the stream moving at the flowspeed u = c_0 because of collisions between the particles (noncentral particles in the first instance). The problem of how to search out some relationship between the particle distribution functions on the inner and outer boundaries of the gas-kinetic layer and how to determine the initial gas-dynamic parameters of the vapor as it expands into the vacuum has been solved only recently [6, 7]. We make use of these results in specifying the initial parameters of the vapor:

$$T_1 \simeq 0.7 T_0; \quad \rho_1 \simeq \rho_s (T_0).$$

(12)

Then, making use of Eqs. (4), (5), (6), (12), we get:

$$3.64 \rho_s (T_{cr}) \sqrt{T_{cr}} = \rho_s (T_0) \sqrt{T_0}.$$

(13)

In the case of a two-atom vapor, according to [2], when $\gamma = 7/5$,

$$\rho_s (T_0) = \frac{A}{T_0^{7/2}} \exp \left(-\frac{T^*}{T_0} \right),$$

(14)

where A is a constant characterizing the material to be evaporated.

We learn from Eqs. (13) and (14) that the critical condensation temperature T_{cr} can be determined from the equation

$$3.64 \exp \left(-\frac{T^*}{T_{cr}} \right) = \left(\frac{T_{cr}}{T_0} \right)^3 \exp \left(-\frac{T^*}{T_0} \right).$$

(15)

When $T_{cr} \ll T^*$, the solution of Eq. (15) can be stated in the form

$$T_{cr} \simeq T_0 \left(1 - 1.3 \frac{T_0}{T^*} \right),$$

(16)

from which we infer that, when $T_0 \ll T^*$, the critical condensation temperature does not differ too radically from the evaporator temperature.

Of course, the sublimation energy of the thin film (E) is somewhat lower than the sublimation energy of the bulk material (E). Taking this into account, we have, instead of Eq. (16),

$$T_{cr} \simeq \varkappa T_0 \left(1 - 1.3 \frac{T_0}{T^*} \right).$$

(17)

Processing of experimental data on the basis of formula (17) showed that $\varkappa = 0.983$ in our case.

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† The one-dimensionality of the problem is made clear by the constraint $\lambda \ll d$. That the vapor parameters are constant over the cylinder cross section has been confirmed experimentally (see below).

The experimental and theoretically predicted dependences (the latter using formula (17) at $\varkappa = 0.983$) of the ratio T_{cr}/T_0 as a function of T_0 are plotted in Fig. 2. It is clear in the diagram that the theoretically predicted and experimental dependences $T_{cr}/T_0 = f(T_0)$ fit closely in practice. We can also find, from formula (17), the coordinate of the cross section up to which condensation on the cylinder walls is absent. In the linear fall-off of the temperature along the cylinder $(dT_W/dx = const)$, we have

$$x_0 = \frac{T_0 - T_{cr}}{\dfrac{dT_W}{dx}},$$

and hence, when formula (17) is taken into account, we obtain

$$x_0 = \frac{T_0(1 - \varkappa) + 1.3\,\dfrac{T_0^2}{T^*}}{\dfrac{dT_W}{dx}}. \tag{18}$$

The conditions of overflow of vapor as a continuous medium flowing into a vacuum, investigated in this paper, can go over smoothly into another set of limiting conditions. When $x > x_1$, the vapor can become depleted to such an extent because of condensation on the cylinder walls that the free path length of the molecules becomes commensurate with the cylinder dimensions, and further motion of the vapor will comprise a directed molecular beam.

It is clear in Fig. 4 that the $h = f(x)$ dependence for the vertically positioned plates experiences a break, and the decrease in the thickness of the condensate as the distance to the top of the chamber becomes narrowed down takes on a more abrupt form, while the $h = f(x)$ dependence tends smoothly to saturation in the case of backing plates positioned horizontally. This is the characteristic criterion of the molecular beam, since the condensation rate for the molecular beam decreases as the condenser surface becomes further removed from the normal to the direction the beam is moving in. As the evaporation temperature rises, the replacement of the vapor flow mechanism must take place at large x values, and this has also been observed experimentally (Fig. 4).

NOTATION

x	is the coordinate reckoned from bottom of chamber;
T_0	is the evaporator temperature;
T_W	is the temperature of cylinder walls;
T	is the temperature of evaporation surface;
T_V	is the vapor temperature;
T_{cr}	is the critical condensation temperature;
E, E'	are the energy of evaporation of one mole of material at $0°K$, of bulk material and of thin film;
$T^* = E/R$	is the characteristic temperature;
R	is the gas constant;
μ	is the molecular weight of material;
λ	is the mean free path length;
ρ_0	is the density of material;
$\rho(T_V)$	is the vapor density;
ρ_S	is the density of saturated vapor;
u	is the flowspeed;
c_0	is the local speed of sound in vapor;
u_1, T_1, ρ_1	are the flowspeed, temperature, and density of vapor in initial gas-dynamic cross section;
γ	is the adiabatic exponent;
v_{co}, v_{re}	are the condensate rate and reevaporation rate;
j_{co}, j_{re}	are the specific mass flows due respectively to condensation and reevaporation;
β	is the sticking coefficient of molecules adhering to evaporation surface;
h	is the condensate thickness.

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