A STUDY OF GALLIUM ARSENIDE EVAPORATION, MASS TRANSFER, AND CONDENSATION IN A QUASICLOSED VOLUME WITH A TEMPERATURE GRADIENT

Yu. Z. Bubnov, M. S. Lur'e,
G. A. Filaretov, and L. N. Shendler

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Results are shown of a theoretical and experimental study concerning the processes of evaporation, mass transfer, and condensation of gallium arsenide, as an example of a strongly dissociated substance.

In [1, 2] we have developed a theory of vacuum evaporation, mass transfer, and condensation of a substance inside a cylindrical vessel – a theory based on gasodynamic expansion, with mass transfer (condensation and reevaporation) of the substance at the walls taken into account.

Here we will analyze the flow of the vapor of a completely dissociated substance inside a quasiclosed volume with a temperature gradient. Such a quasiclosed volume is established by a split graphite cylinder* under the bell jar of a vacuum apparatus.

We measured the space distribution of gallium arsenide condensate on Sital plates installed along the longitudinal axis of the vessel. The temperature profile along such a plate was in this experiment linear ($\mathrm{grad}\, T_W = \mathrm{const}$).

The pressure of saturated vapor above the gallium arsenide layer was, according to [3], never below $3 \cdot 10^{-2}$ torr with the length of free path $\lambda \ll L$ and $\lambda \ll D$ throughout the test range of evaporation temperatures from 800 to 1100°C. The flow of vapor under such conditions constituted a gasodynamic expansion with condensation and reevaporation. The flow equation for such a vapor had been derived and subsequently solved in [2]. Analytical expressions for the vapor parameters in the vessel, as functions of the space coordinates, had also been derived in [2].

In order to calculate numerically the initial values of parameters and the profiles of gasodynamic variables, one must first determine the evaporation energy for a given test substance.

The concept of evaporation energy is not applicable to gallium arsenide, because the latter is completely dissociated during evaporation. In view of this, on the basis of the critical temperature of vapor condensation on the vessel walls, we will define some effective evaporation energy according to the following expression [1]:

$$x_0 \simeq \frac{1.3\,\dfrac{RT_e^2}{E_{e,\mathrm{eff}}}}{\dfrac{dT_W}{dx}}. \tag{1}$$

Expression (1) has been derived for a diatomic vapor; for a vapor with a different atomicity the expression is almost the same [1].

In the experiment we determined the location of section x_0 up to which no condensate had precipitated on a plate, and from this distance we then calculated the effective evaporation energy. Measurements

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*Details of this quasiclosed vessel construction and of the test procedure were given in [1].

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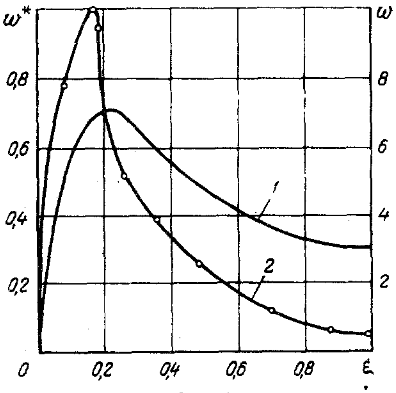

Fig. 1

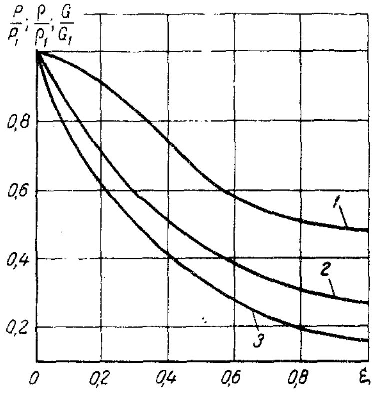

Fig. 2

Fig. 1. Condensation rate of gallium arsenide vapor (w, Å/sec), as a function of the space coordinate: 1) theoretical curve; 2) test curve.

Fig. 2. Calculated profiles: 1) flow rate; 2) density; 3) pressure of gallium arsenide vapor, as functions of the space coordinate.

made on specimens which had been prepared under various conditions of heat treatment yielded values of the evaporation energy within $E_{e,\mathrm{eff}} = 85\text{-}90$ kcal/mole.

Calculated and measured profiles of the condensation rate are shown in Fig. 1, and normalized curves of vapor parameters are shown in Fig. 2, as functions of the space coordinate in each. A comparison between calculation (Fig. 1, curve 1) and test (Fig. 1, curve 2) indicates a close similarity between both in terms of the general trend of the curves and in terms of where the condensation rate is maximum. For a quantitative comparison between calculation and test, we must define the normalizing parameter

$$w_0 = \frac{\rho_1 u_1 D}{4\rho_b\, l}, \text{ where } l = L - x_0.$$

The density and the temperature of a diatomic vapor* at the initial gasodynamic section are determined from the following relation [1]:

$$\rho_1 \simeq 0.33\rho_s(T_e), \quad T_1 \simeq 0.7T_e. \tag{2}$$

The vapor velocity u_1 is a single-valued function of the temperature T_1 [$u_1 = \sqrt{\gamma(RT_1/m)}$], while the vapor density is related to the vapor pressure according to the Mendeleev–Clapeyron law $\rho_s(T_e) = mP_s(T_e)/RT_e$.

Experimental studies have been made [3, 6, 7] to determine the pressure of saturated vapor above a gallium arsenide layer, as a function of the gallium arsenide temperature. Calculations based on the data in [3], for example, have yielded $w = 0.8 \cdot 10^{-5}$ cm/sec at $T_e = 940$°C and $\xi = 0.1$, which is by one order of magnitude higher than the test value (Fig. 1, curve 2). The reason for this is that the measured pressure above a gallium arsenide layer represents the sum of arsenic vapor pressure and gallium vapor pressure. It is well known [3, 6] that gallium arsenide dissociates completely during evaporation, while the bond energy of arsenic in gallium arsenide is less than its dissociation energy and that, therefore, the total vapor pressure above a gallium arsenide layer is determined by the pressure of arsenic vapor.†

Thus, the mass transfer of evaporated gallium arsenide inside a quasiclosed volume can be described as follows. The pressure of arsenic vapor above the initial gasodynamic section in a vessel is approximately constant and equal to the pressure of arsenic vapor at that section (no condensation of arsenic on the vessel walls occurs, because of their high temperature).

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*Gallium arsenide vapor contains mono-, di-, and tetraatomic molecules [3, 6], but the differences between their densities and temperatures at the initial gasodynamic section are small [1] so that the vapor will, therefore, be henceforth considered diatomic.

†The pressure of gallium vapor above a gallium layer (and even more so above a gallium arsenide layer) is by several orders of magnitude lower than the pressure of arsenic above a gallium arsenide layer or above an arsenic layer [3, 6].

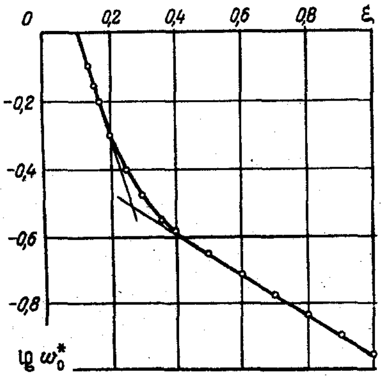

Fig. 3

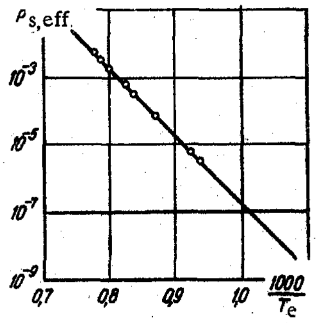

Fig. 4

Fig. 3. Test curve of the normalized parameter w_0^* as a function of the space coordinate ξ.

Fig. 4. Effective pressure of saturated gallium arsenide vapor ($P_{s,eff}$, torr) as a function of the temperature (T, °K).

Gallium molecules move through arsenic vapor, the density of the former regulating the buildup of the gallium arsenide condensate layer. Gallium and arsenic molecules, after striking the surface, move along it until they reevaporate. During collision between gallium and arsenic molecules, gallium arsenide may form according to to the reaction:

$$k\,\mathrm{Ga}_{(gas)} + \mathrm{As}_{k(gas)} \rightleftarrows k\,\mathrm{GaAs}_{(b)}, \tag{3}$$

where k = 2 or 4, depending on the atomicity of the arsenic molecules. Obviously, the probability of the forward reaction becomes higher at lower temperatures of the condensation surface. Besides, a lower temperature results in a longer "lifetime" of gallium and arsenic molecules on the condensation surface prior to their evaporation, which also increases the probability of forming gallium arsenide molecules.

Since the vapor temperature at the initial gasodynamic section drops to $T_1 \simeq 0.7T_e$, hence a stable association of gallium and arsenic molecules directly in the vapor phase is possible. The rate of this process also increases with decreasing temperature. A characteristic feature of the condensation process in a quasiclosed volume is that the density of arsenic vapor molecules is much higher than the density of gallium vapor molecules.

Thus, the processes of mass transfer and condensation in the case of gallium arsenide vapor differ substantially from the vapor flow in the case of an undissociated substance, these differences depending on both the temperature of the condensation surface and the temperature of the vapor, i.e., on the ξ-coordinate. In view of this, we introduce some normalizing parameter $w_0^*(\xi)$ which accounts for the change in flow and condensation modes along the vessel, i.e., we consider the flow of a vapor of constant composition: containing only diatomic gallium arsenide molecules with the parameters $P_{eff}(\xi)$, $\rho_{eff}(\xi)$, etc., with all deviations being due to a variation of the vapor parameters at the initial gasodynamic section.

We define $w_0^*(\xi)$ as $w_0^*(\xi) = w(\xi)/w^*(\xi)w_{0(cr)}$. Here $w(\xi)$ denotes the measured condensation rate (Fig. 1, curve 2), $w^*(\xi)$ denotes the calculated referred condensation rate of diatomic gallium arsenide (Fig. 1, curve 1), and $w_{0(cr)}$ denotes the measured condensation rate at a section near the critical one as, for example, at $\xi = 0.05$. The relation $w_0^* = f(\xi)$ is markedly exponential (Fig. 3).

Since the vapor temperature inside the vessel varies appreciably within the zone between the condensation surface and the initial gasodynamic section ($T_1 \simeq 0.7T_e$), hence the probability of association of gallium arsenide vapor molecules increases most rapidly within this zone.

The profile $w_0^*(\xi)$ of the condensation rate is $w_0^* = A_1 \exp(-B_1\xi)$ within the segment $0 \lesssim \xi \lesssim 0.2$ and $w_0^* = A_2 \exp(-B_2\xi)$ within the segment $0.4 \lesssim \xi \leq 1$ (there is a transition segment $0.2 \lesssim \xi \lesssim 0.4$ between them). The first relation is stronger and, apparently, determined by the longer "lifetime" of gallium molecules† on the condensation surface prior to their reevaporation; the second relation follows from a shift of reaction (3) toward gallium arsenide association on the condensation surface due to a drop in its

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†The "lifetime" of arsenic molecules on the condensation surface remains short along the entire vessel.

temperature. By virtue of the vapor temperature being constant inside the vessel, the relations $P_1^* = P_1^*(\xi)$, $\rho_1^* = \rho_1^*(\xi)$, and $G_1^* = G_1^*(\xi)$ follow exactly the trend of relation $w_0^* = w_0^*(\xi)$.

In order to determine the profiles of the effective parameters numerically, in the case of diatomic gallium arsenide molecules, one must know the pressure of saturated vapor above the evaporating gallium arsenide layer. Let us determine $P_{s,\mathrm{eff}} = f(T_e)$ from $w_{0(cr)}(\xi)$ with ρ_1 and T_1 for diatomic vapor:

$$P_{s.\mathrm{eff}}(T_e) = \rho_{s.\mathrm{eff}}(T_e)\,\frac{RT_e}{m_{\mathrm{eff}}} = \frac{12\rho_b\, l w_{0(\mathrm{cr})}}{D}\sqrt{\frac{RT_e}{m_{\mathrm{eff}}}}\,. \tag{4}$$

The relation $P_{s,\mathrm{eff}} = f(T_e)$, when plotted in $\log P_{s,\mathrm{eff}}$, $1000/T_e$ coordinates, appears in Fig. 4 as an almost straight line which can be described by the equation

$$\lg P_{s\,\mathrm{eff}} = \frac{A}{T_e} + B, \tag{5}$$

where $A = -20{,}300$ and $B = 13.05$.

The temperature–pressure relation for saturated vapor does adequately represent the actual relation for elemental substances and for substances not dissociating during evaporation.

NOTATION

T_e	is the evaporation temperature;
T_w	is the temperature of the vessel walls;
x	is the space coordinate measured from the bottom of the vessel up;
ξ	is the dimensionless space coordinate inside the vessel;
x_0	is the section where net condensation begins;
E_e	is the evaporation energy of the substance;
R	is the universal gas constant;
u_1	is the vapor velocity at the initial gasodynamic section;
T_1	is the vapor temperature at the initial gasodynamic section;
ρ_1	is the vapor density at the initial gasodynamic section;
D	is the vessel diameter;
L	is the vessel length;
ρ_b	is the density of the gallium arsenide layer;
P_s	is the pressure of saturated vapor;
ρ_s	is the density of saturated vapor;
γ	is the adiabatic exponent;
m	is the molecular weight;
w	is the condensation rate;
G	is the vapor flow rate.

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