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Abstract

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ON THE QUESTION OF MEASURING THE CONDENSATION COEFFICIENT

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Numerous experimental works ([1,2]) have been devoted to the measurement of the condensation coefficient α. Depending on the vapor pressure p_0 of the substance under study, experiments are carried out either by measuring the rate of evaporation into a vacuum, followed by calculation of the coefficient α from Langmuir' s formula

$$\tau_0 = \alpha p_0 (2\pi mkT)^{-1/2}, \tag{1}$$

or by measuring the rate of evaporation and the vapor pressure p at the phase boundary and calculating α by means of the Hertz-Knudsen formula

$$\tau = \alpha (p_0 - p)(2\pi mkT)^{-1/2}. \tag{2}$$

The first method is used for substances with $p_0 \lesssim 0.1$ mm Hg, the second for substances with higher vapor pressure.

In the present work it is shown that formula (2) must be used with caution, since it is valid only in the limiting case $\alpha \ll 1$. The error is connected with the fact that, in deriving (2), no account was taken of the convective motion of vapor away from the surface during evaporation or toward the surface during condensation, which always accompanies these processes, as well as of the temperature jump at the vapor-liquid interface.

Allowance for these effects in slow evaporation (i.e., when the evaporation rate is much smaller than the rate of evaporation into a vacuum at the same temperature) for the case in which the condensation coefficient α and the accommodation coefficient β are equal to unity was made in the authors' work ([3]). By analogous reasoning it is easy to show that, for arbitrary values of these coefficients, the expression for the particle flux density must be written in the form

$$\tau = \alpha \frac{p_0}{\sqrt{2\pi mkT_0}} - \alpha \frac{p}{\sqrt{2\pi mkT}} + \alpha \frac{\tau}{2}, \tag{3}$$

where T_0 is the temperature of the liquid surface, T is the temperature of the vapor at the surface, τ is the flux density of vapor molecules, and m is the mass of a molecule.

With the aid of simple transformations, neglecting terms quadratic in τ/τ_0, we obtain

$$\tau = \frac{2\alpha}{2-\alpha}\frac{1}{\sqrt{2\pi mkT_0}}\left\{(p_0 - p) - \frac{p_0}{2}\frac{T_0 - T}{T_0}\right\}. \tag{4}$$

To determine the temperature jump $T_0 - T$, let us write the expression for the energy flux density Q. By analogy with (3) we find that, near the evaporation surface, the amount of heat carried by molecules moving toward the surface is equal to

$$Q^- = \frac{p}{\sqrt{2\pi mkT}}\left[2kT + U(T)\right] - \frac{Q}{2}, \tag{5}$$

where $U(T)$ is the internal energy of a molecule at temperature T.

The flux of molecules moving away from the surface consists of two parts: evaporated molecules and molecules scattered by the surface upon collision with it. The latter molecules constitute the fraction $(1-\alpha)$ of the flux incident on the surface. The exchange of energy between them and the liquid is characterized by the accommodation coefficient introduced by Knudsen,

$$\beta = \frac{T_r - T}{T_0 - T}, \tag{6}$$

where T_r is the effective temperature assigned to the molecules scattered by the surface.

Taking the above into account, the amount of heat carried by the molecules moving away from the surface is

$$Q^+ = \alpha\frac{p_0}{\sqrt{2\pi mkT_0}}\left[2kT_0 + U(T_0)\right] + (1-\alpha)\left[\frac{p}{\sqrt{2\pi mkT}} - \frac{\tau}{2}\right]\left[2kT_r - U(T_r)\right]. \tag{7}$$

The density of the heat-energy flux is equal to

$$Q = Q^+ - Q^-. \tag{8}$$

On the other hand, neglecting the contribution of thermal conductivity, which is usually insignificant for the present problem, we may write

Fig. 1

Figure 1: Fig. 1

$$Q = c_{pT}0\tau. \tag{9}$$

With the aid of (5)–(9), after elementary transformations we find

$$T_0 - T = \frac{\sqrt{2\pi mkT_0}}{2p_0} \frac{\tau\left[c_{pT}0 - 2kT_0 - U(T_0)\right]}{(c_v + k/2)[\alpha + \beta(1-\alpha)]}. \tag{10}$$

Substituting (10) into (4), we finally obtain

$$\tau = \varkappa\alpha \frac{p_0 - p}{\sqrt{2\pi mkT_0}}, \tag{11}$$

where

$$\varkappa = \frac{2}{2 - \alpha + \alpha\left[c_p - 2k - U(T_0)/T_0\right]/2[\alpha + \beta(1-\alpha)](c_v + k/2)}.$$

The dependence of $\varkappa$ on α for the particular case of a monatomic gas ($U(T_0) = 0$) at $\beta = 1$ is shown in Fig. 1. As $\alpha \to 0$, $\varkappa \to 1$, and (11) becomes the Hertz-Knudsen formula. However, when $\alpha \sim 1$, neglect of $\varkappa$ leads to a substantial error.

In all works on the measurement of α carried out at high vapor pressures, the results were processed with the aid of the Hertz-Knudsen formula. Therefore those of them which led to the value $\alpha \sim 1$ must be reconsidered.

Fig. 1

For an experimental verification of the considerations presented here, it would be of interest to compare measurements of the condensation coefficient of one and the same substance with $\alpha \sim 1$, carried out under conditions of evaporation into vacuum and of slow evaporation. As far as the authors know, such measurements are lacking.

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Note: Figure translations are in progress. See original paper for figures.