UDC 536.423.4

CALCULATION OF THE CONDENSATION COEFFICIENT

D. A. Labuntsov

Inzhenerno-Fizicheskii Zhurnal, Vol. 8, No. 6, pp. 820-821, 1965

In certain conditions, the rates of condensation and evaporation processes depend on the kinetics of the phase transition itself. In calculating such processes, data on the coefficients of condensation (evaporation) are necessary, since these reflect the relative rate of interphase molecular transfer [1, 2].

In [3] an attempt was made to use the concepts of quantum mechanics in calculating these coefficients, all individual features of the structure of the condensed phase being ignored. The analysis is based on two characteristics only: the kinetic energy of the vapor molecule and the heat of phase transformation. The strangeness of this formulation becomes obvious, if it is considered that, on the one hand, never before have quantum-mechanical effects been acknowledged to be important in the problem examined and, on the other, that any classical analysis requires a more or less detailed model of the condensed phase [1, 2].

It is also necessary to point out that the final relation of [3] appears strange in view of the absence of a quantum constant. Therefore, in particular, a transition in the limit to classical mechanics is impossible, although it is known [4, 5] that such a transition must exist for a physically correct quantum-mechanical formulation.

Any comparison of the relations presented in [3] with previous studies is therefore impossible in principle.

In connection with the topicality of the problem of evaluating coefficients of condensation (evaporation) in a number of important practical areas, the above points deserve to be considered in somewhat greater detail.

It is known [5] that under the conditions of interaction of moving particles with a force field, estimation of the significance of quantum-mechanical effects is very easy. It reduces to a comparison of the energy of the particle E with the quantity $\hbar^2/2ma^2$, where a is the spatial scale of appreciable change in the force field (potential energy of interaction). In this case a quantum-mechanical description of the interaction is found to be necessary when $E \ll \hbar^2/2ma^2$, whereas when $E \gg \hbar^2/2ma^2$ the interaction takes place in accordance with the laws of classical mechanics. In examining the collision of vapor molecules with molecules of the surface layer of condensed phase, the quantity a can be assumed to be of the order of the intermolecular distances in the condensed phase, i.e., $a \simeq (m/\rho)^{1/3}$.

The kinetic energy of the vapor molecules $E = 3/2kT$. Then the ratio

$$2mEa^2/\hbar^2 = 3mkT\,(m/\rho)^{2/3}/\hbar^2. \tag{1}$$

Calculations show, that for all real cases this ratio is substantially greater than unity. Thus, for water T = 300°K ratio (1) is $\sim 3 \cdot 10^3$, for sodium T = 1000°K, $\sim 2 \cdot 10^4$, etc.

From this it follows that the problem in question belongs among the phenomena that obey the laws of classical mechanics. All known theoretical investigations [1, 2] have proceeded on this basis.

Quantum-mechanical analysis, carried out without violation of the condition

$$2mEa^2/\hbar^2 \gg 1, \tag{2}$$

must lead to the same results as the classical solution.

In [3] the "condensation" of a vapor molecule is treated as transition of the particle from a region of zero potential energy (vapor) to a region of negative potential energy (condensed phase). This completely ignores the processes of collision of vapor molecules with molecules of the surface layer of the condensed phase and, consequently, the possibility of reflection of impinging vapor molecules. Therefore, if the quantum-mechanical description [3] had been constructed without regard for condition (2), the result would have been the obvious (for such an idealized formulation) answer: the condensation coefficient is identically equal to unity. All molecules flying in the direction of the condensed phase would enter its zone of attraction and inevitably (collision and reflection excluded) go over into the liquid region.

However, in [3] it is groundlessly assumed that the nature of the change in potential energy at the phase interface is discontinuous. Hence, the dimension of the zone of appreciable change in potential energy is equal to zero ($a = 0$), and condition (2) is hopelessly infringed, for now

$$2mEa^2/\hbar^2 \equiv 0.$$

This abstract case (equivalent to an infinitely large value of the quantum constant) is devoid of physical meaning in relation to the processes considered.

REFERENCES

1. O. Knake and I. N. Stranskii, UFN, no. 2, 1959.
2. B. Pol, Raketnaya tekhnika, no. 9, 1962.
3. N. N. Kochurova, IFZh, no. 3, 1964.
4. L. D. Landau and E. M. Lifschitz, Quantum Mechanics [in Russian], Fizmatgiz, 1963.
5. V. G. Levich, Yu. A. Vdovin, and V. A. Myamlin, Course in Theoretical Physics [in Russian], 2, Fizmatgiz, 1962.

2 October 1964

Krzhizhanovsk Power Engineering Institute, Moscow

UDC 536.423.4

ON THE CALCULATION OF THE CONDENSATION COEFFICIENT

N. N. Kochurova

Inzhenerno-Fizicheskii Zhurnal, Vol. 8, No. 6, pp. 822-823, 1965

In the theory of evaporation the condensation coefficient f is equal to the ratio of the number of condensing molecules to the total number of vapor molecules striking the surface of the condensate. Theoretical and experimental studies of the condensation coefficient [1-3] show that it is determined by the change in the energy state of molecules during phase transition and on the purity of the surface of the condensed phase.

The basic idea of reference [3] consists in the application of the solution of the "barrier problem" of quantum mechanics to the calculation of the condensation coefficient.

In this formulation of the problem, the difficulties of constructing a model of the process that fully corresponds with reality are reduced to determining the height and shape of the barrier. The first of these is determined by the activation energy (which is not always equal to the heat of vaporization), the second comprises determination of the barrier width.

For a clean surface of the condensed phase, the condensation coefficient is determined by the change in the energy state of the molecules during phase transition.

Collision of vapor molecules with condensate and the possibility of reflection of the incident vapor molecules are determined by the transmission and reflection processes at the boundary between two regions of different potential. Here, in each specific case of a barrier of a certain shape and width and also for different relationships between the total energy and the height of barrier, it is necessary to use the corresponding solution of the Schroedinger equation.

Reference [3] presents an example of calculation of the condensation coefficient in the case when the activation energy is equal to the heat of vaporization and the total energy is greater than the height of the barrier. In this case the condensation coefficient is treated as the probability of molecules crossing the boundary between regions of different potential. The manifestation of the quantum effect (nonzero reflection) is then determined by the width of the transition region. Increase in the width of the transition region causes the reflection to tend to zero.

Since the question of the shape of the barrier is a topic of special investigation for each substance, in order to estimate condensation coefficient in the first approximation the width of the transition region was assumed equal to zero. With the above assumptions (activation energy equal to the heat of vaporization and width of transition region equal to zero) the condensation coefficient was calculated for a number of substances at different temperatures. The values of the condensation coefficient were found to be close to one and exactly equal to one at the critical temperature.

When the width of the transition region is taken into account, the condensation coefficient will tend to one. This result corresponds to the value $f = 1$ obtained in Hertzfeld's classical examination of the problem [4] and by a number of other authors [1, 2]. Moreover, experimental determinations of the condensation coefficient, in conditions close to the conditions of the assumed model, also give values close to one [6].