

The necessity of determining the condensation or evaporation rate of liquid drops arises in the study of numerous processes in meteorology, physical chemistry, and gas-dynamics. At the present time, the experimental study of these quantities is rather difficult, particularly for small drops, consisting of several thousands of molecules. The available theoretical methods [1-3] make it possible to calculate the growth rate of spherical drops under certain special restrictions imposed on the nature of the investigated process. Unfortunately, in none of the studies mentioned did the authors analyze the effect of their specific assumptions on the final result.

The problem of determining the growth rate of spherical drops, found in a medium of natural vapor, is solved in the present paper. Particular attention is paid to the problem of how the variation in drop internal energy with time and thermal conductivity of the drop affect its growth rate and temperature.

1. Basic Equations. Consider a spherical drop surrounded by natural vapor. The temperature T_0 and vapor pressure p_0 at infinite separation from the drop are constant. Initially, at $t = 0$, the drop has a radius R_0 . We introduce the spherical coordinate system r, φ, θ with origin at the center of the drop, and assume that the temperature profiles in the drop and in the vapor are spherically symmetric. Thus, the temperature inside the drop varies by some law $T = T(r)$.

We write the balance equations of mass and energy. Taking into account the low compressibility of the liquid, we assume that its density ρ depends on temperature only. Then

$$\begin{aligned} dM/dt &= S\Pi_M, \quad dU/dt + pdV/dt = S\Pi_Q, \\ M &= \int_0^R 4\pi r^2 \rho(r) dr, \quad U = \int_0^R 4\pi r^2 e(r) \rho(r) dr + S[\sigma - T_s d\sigma/dT_s], \\ V &= (4/3)\pi R^3, \quad S = 4\pi R^2, \quad \Pi_M = m_1(N^+ - N^-), \quad \Pi_Q = m_1(Q^+ - Q^-), \end{aligned} \quad (1.1)$$

where $M, U, e,$ and V are the mass, internal and specific internal energy, and the volume of the drop; S and T_s , area and temperature of its surface; σ , surface tension coefficient; m_1 , mass of the vapor molecules; and $\Pi_M, \Pi_Q, N^\pm,$ and Q^\pm , total and specific mass and energy fluxes at the drop surface. The superscripts plus and minus refer to molecules flying toward and from the drop, respectively. In deriving (1.1) it was assumed that the liquid drop contains a sufficient number of molecules, so that the concepts of temperature, pressure, and density make sense, and one can separate between the bulk and surface portions.

To find the temperature profile in the drop we find the self-similar quasistationary solution of the thermal conductivity equation

$$\frac{\partial T}{\partial t} - \frac{\alpha_T}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial T}{\partial r} = 0.$$

We assume that the liquid, the drop material, is at rest. We introduce the dimensionless variable $\tau = T/T_*(t)$ ($T_* = (1/V) \int_0^R 4\pi r^2 T dr$ is the drop temperature averaged over the volume),

and assume that $d\tau/dt = 0$ [4]. The boundary conditions are stated at the center and at the surface of the drop. Since from a physical point of view the center of the drop is not a singular point, the regularity condition $\partial\tau/\partial r|_{r=0} = 0$ must be satisfied at its location. The temperature gradient at the drop surface is related to the thermal flux Π_Q by the Fourier law $\lambda\partial T/\partial r = \Pi_Q$. It can then be shown that the temperature profile for this regime is given by the relations

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$$\begin{aligned} T(r) &= \Pi_Q R^2 \operatorname{sh} lr / [(LR \operatorname{ch} lR - \operatorname{sh} lR)r\lambda], \quad \mu^2 < 0, \\ T(r) &= \Pi_Q R^2 \sin lr / [(LR \cos lR - \sin lR)r\lambda], \quad \mu^2 \geq 0. \end{aligned} \quad (1.2)$$

Here $\mu^2 = -3\Pi_Q/(R\lambda_*)$, and l is determined from the solution of the transcendental equation

$$\lambda T_s = \Pi_Q(R, T_s)R \operatorname{sh} lR / (LR \operatorname{ch} lR - \operatorname{sh} lR), \quad \mu^2 < 0. \quad (1.3)$$

Thus, knowing T_s , R , Π_Q , and the thermal conductivity coefficient λ , one can calculate the temperature $T(r)$ at any point of the drop.

Using (1.2), we find a system of differential equations for determining the time dependences of R and T_s . We assume that $\rho = \rho_1 - \rho_2 T$ (ρ_1 and ρ_2 are constant). Denoting by L the specific condensation heat, one can then obtain:

$$e = c_p T - L - \rho_2 p T / \rho^2 \approx c_p T - L, \quad (1.4)$$

where it has been taken into account that far from the critical point $\rho_2 p T / \rho^2 \ll L$, and c_p is the vapor heat capacity at constant pressure. Using the definitions of M , U , and T_* in (1.1) and (1.2), we have

$$M = V(\rho_1 - \rho_2 T) = V\rho(T_*). \quad (1.5)$$

Similarly we obtain from (1.1)-(1.5) under the assumption $L = \text{const}$

$$U = S\Sigma - LM + V\{c_p T_* \rho_1 - (3/2)c_p \rho_2 \Gamma^2 (\operatorname{sh} 2lR/2lR - 1)/R^2\} = S\Sigma - LM + VF. \quad (1.6)$$

Here $\Gamma = \Pi_Q R^2 (\operatorname{ch} lR - \operatorname{sh} lR)^{-1} / \lambda = RT_s / \operatorname{sh} lR$; F denotes the expression in the curved brackets, and $\Sigma = \sigma - T_s d\sigma/dT_s$. Finally, we note that the pressure p in the drop can be found from the equilibrium condition $p = p_v + 2\sigma/R$, where p_v is the vapor pressure above the drops.

One can now express $\dot{R} = dR/dt$ and $\dot{T}_s = dT_s/dt$ explicitly:

$$\begin{aligned} \dot{R} &= (z_1 y_2 - z_2 y_1) / \varphi, \quad \varphi = x_1 y_2 - x_2 y_1, \\ \dot{T}_s &= (x_1 z_2 - x_2 z_1) / \varphi, \quad z_1 = \Pi_M, \quad z_2 = \Pi_Q + L\Pi_M, \\ x_1 &= \rho(T_*) + (R/3) \partial \rho(T_*) / \partial T_* \cdot \partial T_* / \partial R, \quad T_* = 3T_s / (lR)^2 (lR \operatorname{ch} lR - 1), \\ x_2 &= F + (R/3) \partial F / \partial R + p + 2/R(\Sigma - \sigma), \quad y_1 = (R/3) \partial \rho(T_*) / \partial T_* \cdot \partial T_* / \partial T_s, \\ y_2 &= (R/3) \partial F / \partial T_s + \partial \Sigma / \partial T_s. \end{aligned} \quad (1.7)$$

The derivative $\partial l / \partial R$ and $\partial l / \partial T_s$ are found by differentiating (1.3) with respect to R and T_s , and l is found by solving (1.3).

We make the following comment. In [2, 3], along with the energy equation appearing in (1.1), the following relation is used:

$$\Pi_Q + L\Pi_M = 0. \quad (1.8)$$

We derive it from (1.1) by neglecting the work of the expanding drop ($pdV/dt = 0$), surface effects ($\sigma = 0$), and assuming $\rho = \text{const}$. Since by (1.4) $e \approx c_p T - L$, then

$$\begin{aligned} U &= \int 4\pi r^2 e \rho dr = \rho(c_p T - L)V = M(c_p T - L), \\ S\Pi_Q &= dU/dt = dM/dt(c_p T - L) + M c_p dT/dt. \end{aligned}$$

At low temperatures $c_p T \ll L$, whence

$$S\Pi_Q + L S\Pi_M = M c_p dT/dt \quad \text{or} \quad \Pi_Q + L\Pi_M = \rho R/3 \cdot c_p dT/dt. \quad (1.9)$$

It is easily seen that (1.8) follows from (1.9) if $\Pi_Q + L\Pi_M \gg \rho R/3 \cdot c_p dT/dt$. This assumption, however, is not obvious.

2. Calculation of the Mass and Energy Fluxes. To solve (1.7) it is necessary to know the fluxes N^\pm and Q^\pm and the vapor pressure above drops p_v . We assume that the vapor consists of a monatomic gas. The quantities mentioned can then be found by solving the Boltzmann equation, which in spherical coordinates is

$$\partial f / \partial t + v_r \partial f / \partial r + (v_\phi^2 + v_\theta^2) / r \cdot \partial f / \partial v_r - (v_\phi v_\theta / r \operatorname{ctg} \theta + v_r v_\phi / r) \partial f / \partial v_\phi +$$

$$+ (v_0^2/r \operatorname{ctg} \theta - v_r v_0/r) \partial f / \partial v_0 = \int (f' f_1' - f f_1) d\Omega.$$

Consider the process of drop growth in the quasistationary approximation $\dot{R} \ll 2kT_0/m_1$, assuming that $(T_s - T_0)/T_0 \ll 1$. In this case, $\partial f / \partial t = 0$, and the problem admits linearization.

To solve the linearized stationary Boltzmann equation, we use the Lees moment method [5], in which the molecular distribution function over velocities is assumed to be discontinuous at each point of velocity space. A conic surface with a center at the given point and forming tangents to the drop surface partitions all velocity space into two subspaces. We assume that at each subspace f is a linearized locally Maxwellian function, while the superscripts minus and plus denote the regions inside and outside the conic surface introduced. Thus,

$$f^\pm = f_0(1 + \varphi) = f_0[1 + v^\pm + (C^2 - 3/2)\tau^\pm], \quad (2.1)$$

where φ^+ and φ^- are the linear corrections to the distribution function, $f_0 = (\rho_0/m_1)(\eta/\pi)^{3/2} \exp(-C_0^2)$; $\rho_0 = p_0/(AT_0)$; $C_0^2 = \eta(v - u)^2$; $\eta = m_1/2kT_0$; τ^\pm and v^\pm are corrections to temperature and density: $\tau^\pm = T^\pm/T_0 - 1$; $v^\pm = \rho_v^\pm/\rho_0 - 1$. In the latter relations, T^\pm and ρ_v^\pm are the temperature and vapor density in the corresponding subspaces.

Multiplying successively the Boltzmann equation by m_1 , $m_1 v_r$, $m_1 v^2/2$, and $m_1 v^2 v_r/2$, and integrating over the whole velocity space, one obtains a system of four moment equations in the unknown corrections v^\pm and τ^\pm [2, 6]. In this case the integral over the whole velocity space is represented as a sum of integrals over the corresponding subspaces, and it is assumed that $u = O(\tau^2)$.

Two approaches were used in calculating the moments of the collision integral. In the first approach the function f in the integrand expression was expanded in a series in Sonin polynomials $S_{3/2}^p$, multiplied by C_r , and the expansion coefficients were selected by the equality condition of the moments of this expansion to the moments of the original distribution function [7]. In the present study we retained the first two terms of the series, and to determine the coefficients we selected the moments u_r and q_r (q_r is the radial component of the thermal flux vector). In the second case we used the ellipsoidal model of [8]. It can be shown that the first three moments Δm_1 , $\Delta m_1 v_r$, $\Delta m_1 v^2/2$ vanish due to conservation laws, while

$$\Delta m_1 v^2 v_r/2 = [2(v^+ - v^-) - 7(\tau^+ - \tau^-)]D/r^2. \quad (2.2)$$

In this case we have for the collision operator of the ellipsoidal model $D = -(4/15)k p_0 T_0 R^2 / (m_1 \pi \lambda_c)$, while for the model of [7], $D = -(2/15)\rho_0^2 R^2 \Omega^{(2.2)} / (m_1^2 \eta^{3/2} \sqrt{\pi})$, where λ_c is the molecular mean free path, where $\Omega^{(2.2)}$ is the standard notation of [8], with the $\Omega^{(2.2)}$ value depending on the choice of the interaction potential of vapor molecules.

As boundary conditions we use the fact that for $r \rightarrow \infty$ the vapor temperature and pressure equal T_0 and p_0 , and $u = 0$. At the surface of the drop we provide the mass and energy accommodation coefficients

$$\alpha_m = (N^+ - N^-)/(N^+ - N_s^-), \quad \alpha_Q = (Q^+ - Q^-)/(Q^+ - Q_s^-). \quad (2.3)$$

Here N_s^- and Q_s^- are the mass and energy fluxes of the molecules, which, following reflection from the drop or evaporation from its surface have a temperature T_s and density ρ_{sv} , equal to the equilibrium density of saturated vapor above drops of a given radius R . Since an ideal gas is being considered, $\rho_{sv} = p_e/(AT_s)$, where A is the gas constant, p_e is the equilibrium vapor pressure at the surface of the drop, which can be found from the Kelvin equation $p_e = p_\infty(T_s) \exp[2\sigma/(\rho AT_s R)]$.

It is known that a drop in equilibrium with a surrounding vapor is called a critical nucleus, whose radius is denoted by r_* . Thus,

$$R = r_*(T_s, p_e). \quad (2.4)$$

Solving the system of moment equations with given boundary conditions, we obtain

$$\begin{aligned} \tau^+ &= j/(2r), \quad v^+ = -\tau^+, \quad \tau^- = \tau^+ + C_1, \quad v^- = v^+ + C_2, \\ j &= d(2C_2 - 7C_1); \quad d = (4/5)m_1 D / (k p_0 T_0); \end{aligned} \quad (2.5)$$

where

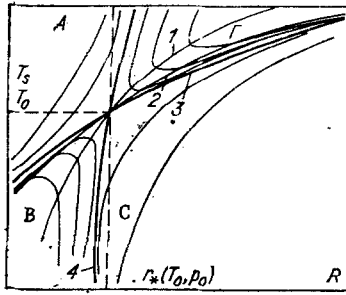


Fig. 1

$$v^+(R) = -aC_2 - bC_1; \quad a = d/R, \quad b = -(7/2)d/R;$$

$$C_1 = [(1-a)\tau_s - av_s]/(1+b-a);$$

$$C_2 = [b\tau_s + (1+b)v_s]/(1+b-a);$$

$$\tau_s = T_s/T_0 - 1; \quad v_s = \rho_{sv}/\rho_0 - 1.$$

It can be shown that the expression $1 + b - a$ vanishes only when $R < 0$, i.e., the system of moment equations always has a unique solution.

It follows from kinetic theory [9] that

$$N^\pm = \int f^\pm v_r dv, \quad Q^\pm = \int f^\pm (1/2) v^2 v_r dv. \quad (2.6)$$

Substituting (2.5) into (2.6), and assuming $r = R$ (since we are interested in fluxes at the surface of the drop), we finally have

$$N_s^- = N_* (1 + v_s + \tau_s/2), \quad Q_s^- = Q_* (1 + v_s + (3/2)\tau_s), \quad Q_* = 2AT_0 N_*, \quad (2.7)$$

$$N_* = p_0/(2\pi m_1 k T_0)^{1/2}, \quad N^+ = N_* (1 + v^+(R) + (1/2)\tau^+(R)),$$

$$Q^+ = Q_* (1 + v^+(R) + (3/2)\tau^+(R)), \quad \Pi_M = \alpha_m m_1 N_* (v^+ - v_s + (1/2)\tau^+ - (1/2)\tau_s),$$

$$\Pi_Q = \alpha_Q m_1 Q_* (v^+ - v_s + (3/2)\tau^+ - (3/2)\tau_s), \quad \rho_{sv} = p_e/(AT_s).$$

For $R \rightarrow \infty$, we have from (2.5) $\tau^+ \rightarrow \text{const}$ and $v^+ \rightarrow \text{const}$. In this case the velocity space degenerates from a discontinuous into a continuous one. Thus, the Lees method becomes unsuitable for solving similar problems for large-size drops.

3. Stability and Limiting Cases. Consider the stability of system (1.7). This problem is intimately related to clarifying the validity limits of the model developed. We establish when Eqs. (1.1) can be solved in the form (1.7). For this it is necessary and sufficient that the Jacobian $\varphi = x_1 y_2 - x_2 y_1$ is nonvanishing. We put $\sigma = \sigma_1 - \sigma_2 T_s$, where $\sigma_1, \sigma_2 = \text{const}$. Consider special cases: in the first (SC1), $\rho_2 = 0$, $T(r) = \text{const}$, and $\varphi = c_p \rho_1^2 > 0$, and, in the second (SC2), for $T(r) = \text{const}$, $\varphi = c_p \rho^2 R/3 + (p + 2\sigma_2 T/R)R\rho_2/3 > 0$. In the general case, due to the complicated dependence of φ on R and T_s , this fact is not obvious. However, a numerical study for water and argon has shown that $\varphi > 0$ in the whole temperature and pressure region, in which separate existence of liquid and gas phases is possible. The values of the constants appearing in the thermophysical dependences for water and argon are given in Table 1, where μ is the molecular weight, d and p_1 are the constants

TABLE 1

Medium	μ , kg/mole	ρ_1 , kg/m ³	ρ_2 , kg(m ³ ·K)	$\sigma_1 \cdot 10^3$, N/m	$\sigma_2 \cdot 10^3$, N/(m·K)	b , R	d	$p_1 \cdot 10^6$, Pa	λ , J/(m·sec·K)	$\rho_*^{(2,2)}$	$\sigma_0 \cdot 10^{10}$, m
Water	18,02	1110	0,4	128,0	0,19	5338	28,26	1	0,684	2,50	2,52
Argon	39,95	2620	13,8	29,5	0,196	685,4	7,85	10 ⁶	0,126	1,75	3,40

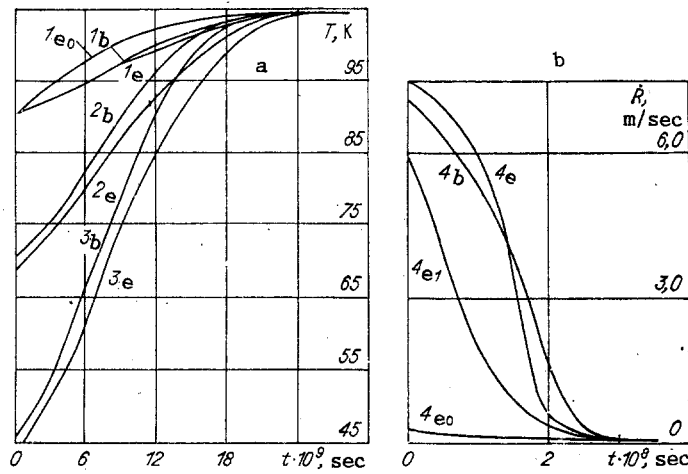


Fig. 2

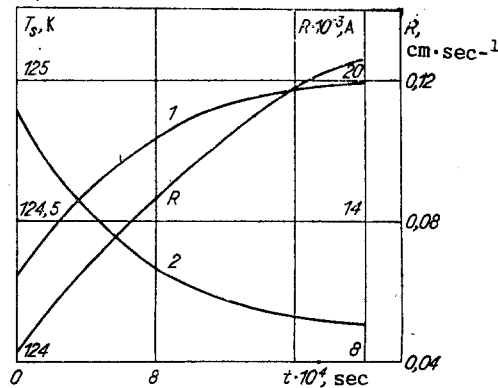


Fig. 3

of the Clausius-Clapeyron equation for determining the saturated vapor pressure $p_{\infty}(T) = p_1 \cdot \exp(d - L/(AT))$, $\Omega_{*}^{(2.2)} = \Omega^{(2.2)}/(2\sigma_0^2 \sqrt{AT_0 \pi})$, and σ_0 is a parameter of the interaction potential of solid spheres. In this case $\Omega^{(2.2)}$ was selected for the Lennard-Jones (6-12) potential (argon) and for the Keesom potential (water), and was assumed to be independent of T_0 .

We find the stationary points of system (1.7), for which it is required to solve the system of equations $\dot{R} = 0$ and $\dot{T}_S = 0$.

3.1. Critical Size Nucleus. It is seen that the condition $\dot{R} = 0$, $\dot{T}_S = 0$ is satisfied for $z_1 = z_2 = 0$, corresponding to $\Pi M = \Pi Q = 0$ and $\tau_S = \nu_S = 0$. Hence we have $T_S = T_0$, and from (2.4) $p = p_0$, $R = r_{*}(T_0, p_0)$. The point T_0, r_{*} corresponds to the case in which the drop is a critical nucleus in equilibrium with the surrounding vapor.

In studying the stability of the point T_0, r_{*} it seems that for the models considered of the collision operator is is always unstable. It corresponds by its physical meaning to the critical radius known from thermodynamics.

3.2. Integral Curves (1.7). We establish the behavior of the integral curves (1.7), for which purpose for given T_0 and $s_0 = p_0/p_{\infty}(T_0)$ we construct the curves $T_1 = T_1(R)$ and $T_2 = T_2(R)$, along which \dot{R} and \dot{T}_S vanish. They are shown schematically in Fig. 1 (curves 1 and 2), but the exact calculations verify this behavior. It follows from Sec. 3.1 that both curves intersect at the point $T = T_0$, $R = r_{*}(T_0, s_0)$. Thus, all possible states in which the drop has a radius R and surface temperature T_S can be divided into four regions. In region A, $\dot{T}_S < 0$, $\dot{R} < 0$; B, $\dot{T}_S < 0$, $\dot{R} > 0$; C, $\dot{T}_S > 0$, $\dot{R} > 0$; D, $\dot{T}_S > 0$, $\dot{R} < 0$. The study performed has shown that the point T_0, r_{*} is a singular point of the "saddle" type. The separatrix 3 partitions the regions mentioned and practically coincides with curve 2 ($\dot{T}_S = 0$), and the separatrix 4 is a line of critical radii. All drops whose initial size in Fig. 1 is left of this line evaporate, and all those on the right grow. Thus, the concept of criti-

cal size can be generalized to the case in which the temperatures of the drop and the vapor differ from each other.

The analysis of the behavior of integral curves makes it possible to make several comments:

Under nonvarying external conditions in the vapor (T_0 , p_0 are constant) there exist drops with $R < r_*$, which increase to infinity in their evolution process.

There exist drops with $R > r_*$ which evaporate in the evolution process.

Thus, account of nonisothermicity can lead to a change in the nature of the flow process of drop growth or evaporation.

4. Test Calculations and Model Comparison. In test calculations the system (1.7) was integrated numerically for given T_0 , p_0 as well as R_0 and T_{S0} at moment $t = 0$. It was assumed that $\alpha_m = \alpha_Q = 1$ for argon, and the remaining required constants were selected from Table 1.

Figure 2a, b shows the dependences obtained from the solution of systems SC1, SC2, and (1.7) of T_S , T_* , T_N , and \dot{R} (lines 1-4) on t (T_N is the temperature of the center of the drop, the subscript e is the ellipsoidal model of the collision operator, b is the model of [7], 0 is SC1, and 1 is SC2). The initial conditions for this calculation are: $T_0 = 90^\circ\text{K}$, $s_0 = 3$, $p_0 = 3 \cdot 10^5$ Pa, $r_*(T_0, p_0) = 8.42 \cdot 10^{-7}$ mm, $R_0 = 1000r_* = 8.42 \cdot 10^{-7}$ mm, $T_{S0} = T_0 = 90^\circ\text{K}$. As follows from the calculations, the nonuniformity of the temperature profile in this drop can consist of 14°K . In this case, account of thermal conductivity leads to a noticeable change in \dot{R} , while the results can differ by orders of magnitude. At time of order 10^{-7} sec the temperature profiles are balanced in this drop.

Figure 3 shows results of calculations with the same initial data, carried out by the model of [2] (curve 1 is T_S , 2 is \dot{R}). The results differ greatly from those shown in Fig. 2, which is related to the use of the energy equation (1.8).

It is seen from Fig. 2 that the replacement of the ellipsoidal model of the collision operator by the model of [7] leads to variations in T_S by 2-3% and a change in \dot{R} by up to 40%.

Similar calculations, carried out with the same initial data but with $R_0 = 9r_*$, showed that for such small drops inclusion of thermal conductivity is unimportant.

It is of interest to explain the effect on \dot{R} and T_S of the choice of the thermophysical dependences. It is seen from Fig. 2 that account of the temperature dependence of the liquid density leads to a variation of T_S within 2-5% and of \dot{R} by a factor of 30. Thus, for exact calculations of \dot{R} it is necessary to take into account the real thermophysical drop properties.

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