Journal of Engineering Physics and Thermophysics, Vol. 74, No. 2, 2001

THEORY AND CALCULATION OF THE CONDENSATION GROWTH OF A DROPLET IN PURE VAPOR AND IN A VAPOR–GAS MIXTURE

K. M. Aref'ev,[a] **Yu. G. Belostotskii,**[b] **and A. M. Koshelev**[b]

UDC 533.24

Consideration is given to the theory of condensation as applied to the liquefaction of gases. Numerical calculations of the growth of a droplet using methane as an example revealed the decisive role of heat removal from its surface to the ambient medium in condensation from both a pure vapor and a vapor–gas mixture. It is shown that for very low supersaturations of the vapor, radiative heat removal can prevail over convective heat removal.

Liquefaction of gases, especially of natural gas composed mainly of methane, is an important technical problem. With the aim of refining the ideas of the process of liquefaction, it is appropriate to analyze the features of the condensation growth of a droplet with allowance for heat and mass transfer. This precisely is the subject matter of the present work.

Let us consider the condensation growth of a single droplet under invariable conditions in the ambient medium. We assume that the rapid processes of nucleation [1, 2] and initial growth are already over. For the subsequent retarded growth the droplet has an initial diameter δ_0 of the order of 10^{-7} m that is larger than the mean-free path of vapor molecules. For a droplet of this diameter and for larger droplets we can disregard the Laplace pressure and assume that the pressure of a saturated vapor above the droplet is the same as above a plane surface. To calculate the condensation growth of such droplets, we can use the following equations of material and heat balance:

$$\rho_{\text{liq}}\, d\,(\pi\delta^3/6)/d\tau = \pi\delta^2 g_{\text{v}}\,, \tag{1}$$

$$\rho_{\text{liq}}\,(C_{p\text{liq}} - C_{p\text{v}})\, d\,[(\pi\delta^3/6)\,(T_{\text{dr}} - T_{\infty})]/d\tau = \pi\delta^2\,[r_{\text{tabl}}\, g_{\text{v}} - \alpha\,(T_{\text{dr}} - T_{\infty}) - q_{\text{rad}}]\,, \tag{2}$$

where $\alpha = \text{Nu}\lambda_{\text{v}}/\delta$ is the coefficient of heat transfer to the ambient medium.

It is approximately adopted that the time-variable temperature of the liquid phase of the droplet T_{dr} is constant at a given instant in its radius, since usually $\lambda_{\text{liq}}/\lambda_{\text{v}} \approx 10$, on the average, i.e., $\text{Bi} = \text{Nu}\lambda_{\text{v}}/\lambda_{\text{liq}} \approx \text{Nu}/10$ and the assumption made is fulfilled in practice, especially for Nu = 2 (the droplet is sessile relative to the medium). Allowance for the influence of surface effects and the variability of the temperature inside the droplet in its growth in a pure vapor is made in [3]. In [4], the influence of dissolved substances on the evaporation and growth of water droplets under atmospheric conditions is considered. This influence is shown to be substantial, for example, in condensation on sea-salt particles.

---

[a] St. Petersburg State Technical University, St. Petersburg, Russia; email: talalov@twonet.stu.neva.ru; [b] St. Petersburg Electronic and Computer Technologies, St. Petersburg, Russia; email: belost@elco.spb.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 74, No. 2, pp. 164–170, March–April, 2001. Original article submitted January 29, 2001.

1062-0125/01/7402-0487$25.00

The specific heat of condensation $r_{\text{tabl}}(T_{\text{dr}})$ corresponds to reckoning the enthalpy from the phase-transition temperature (i.e., from the temperature T_{dr} in the approximation used), which conforms to the values given in the tables of thermophysical properties. The quantities ρ_{liq}, $C_{p\text{liq}}$, and $C_{p\text{v}}$ in the expected ranges of variation of T_{dr} change not very appreciably, and we will consider them to be constant. The condensing vapor has the temperature T_{dr}; therefore, in formula (2), the difference $(C_{p\text{liq}} - C_{p\text{v}})$ appears as the specific heat. Upon rearrangements, Eq. (2) with account for Eq. (1) acquires the form

$$\rho_{\text{liq}}\,(C_{p\text{liq}} - C_{p\text{v}})\,(\delta/6)\,d\,(T_{\text{dr}} - T_{\infty})/d\tau = rg_{\text{v}} - \alpha\,(T_{\text{dr}} - T_{\infty}) - q_{\text{rad}}\,, \tag{3}$$

where

$$r\,(T_{\text{dr}}, T_{\infty}) = [r_{\text{tabl}}\,(T_{\text{dr}}) - (C_{p\text{liq}} - C_{p\text{v}})\,(T_{\text{dr}} - T_{\infty})] \tag{4}$$

is the specific heat of condensation in reckoning the enthalpy from the temperature T_{∞}.

If the influence of the thermal inertia of the droplet is disregarded, i.e., if the left-hand side of Eq. (3) is set equal to zero, the droplet temperature can be established as

$$pg_{\text{v}} = \alpha\,(T_{\text{dr}} - T_{\infty}) + q_{\text{rad}}\,. \tag{5}$$

A change (a growth) in the diameter of the droplet with time can be found from solution of Eq. (1).

The validity of the approximation made follows from the fact that for lowered temperatures T_{dr} that are close to the temperature T_{∞} the intensity of condensation increases while the removal of heat is low. It is expended to a large measure on heating the liquid phase in the droplet. The time of increase in the temperature T_{dr} to values close to those corresponding to condition (5) is small as compared to the time of droplet growth.

In determining the density of the vapor flow g_{v} involved in condition (5) and in the remaining equations written above, it should be borne in mind that the value of g_{v} the minimum possible under certain conditions is determined by the known Hertz–Knudsen formula [2]. If we disregard the small difference of the ratio $T_{\text{dr}}/T_{\text{b}}$ from unity, which is insignificant for subsequent calculations, this formula can be written in the following form:

$$g_{\text{v}} = af\sqrt{M/(2\pi RT_{\text{dr}})}\;P\,(Y_{\text{b}} - Y_{\text{dr}})\,. \tag{6}$$

Here $a = 2/(2 - f)$ is the correction [5] for the influence of the vapor flow to the droplet surface that distorts the Maxwellian distribution of molecules by velocities (the distribution has been adopted in deriving formula (6)). The quantity g_{v} decreases as Y_{dr} and Y_{b} approach each other with increase in the temperature T_{dr}, since Y_{b} corresponds to the saturation state for this temperature. In the case of a pure vapor, in formula (6) we should set $Y_{\text{b}} = 1$. Formula (6) is said to express the kinetic resistance of phase transition. In the absence of this resistance g_{v} could be arbitrarily large (being limited only by the remaining conditions of the problem).

It is noteworthy that the velocity of the vapor v_{v} at the condensation surface cannot exceed a velocity comparable with the velocity of sound. Otherwise, a substantial gasdynamic resistance to the motion of the vapor develops. The calculations of condensation considered below have been performed as applied to a methane vapor and to a mixture of methane with nitrogen. The physical properties of methane were taken based on the data of [6, 7]. The evaluations performed for the velocity of sound showed that, on the average, it equals 300 m/sec for methane in the temperature range 111–138 K. Even if we take $v_{\text{v}} = 30$ m/sec, with allowance for the vapor density $\rho_{\text{v}} \approx 10$ kg/m^3 (corresponding to a pressure of $5.89 \cdot 10^5$ Pa of a saturated vapor of methane at a temperature of 138 K) we have quite an appreciable gasdynamic resistance, $\rho_{\text{v}} v_{\text{v}}^2 \approx 10^4$ Pa. The considered resistance will be negligible for much smaller velocities of the vapor. In dropwise condensation, this occurs because, owing to the superheating of a droplet and Y_{dr} approaching Y_{b}, the vapor velocities can be unities, tenths, and even hundredths of a meter per second. The vapor velocity can reach larger values in the film condensation of metals on a cooled surface with intense removal of heat (in addition, when the thermal conductivity of the liquid is high).

Turning back to consideration of the condensation growth of a droplet in a pure vapor or a vapor-gas mixture, we note that the condensing coefficient f for methane in formula (6) can be taken equal to unity, since the values of f for nonpolar substances differ little from unity [2, 8].

The droplet will be considered to be sessile relative to the medium. Therefore Nu = 2, i.e., $\alpha = 2\lambda_{\mathrm{v}}/\delta$. In this case, the convective heat transfer coincides with the heat transfer by conduction through an unbounded vapor or vapor-gas layer. For a high content of gas we should introduce the mean-effective value instead of λ_{v}. However, a more significant role in heat transfer by conduction is played by the mixture layers adjacent to the droplet, where the vapor fraction is higher than at a distance. Therefore, in order to keep the computation from becoming too complicated owing to a possible excess of accuracy, throughout the following discussion we will use precisely the values of λ_{v} referred to the temperature T_{dr}.

For increased values of g_{v} we should additionally apply a correction for the influence, on heat transfer, of the expenditure of heat on warming-up the vapor flow to the droplet surface. The corresponding correction factor can be obtained by using a differential equation of stationary heat conduction for a fixed spherical layer of the medium around the droplet. In this equation, account should be taken of the influence of the vapor flow on the temperature profile. Upon the integration performed with allowance for the invariability of the total flow rate of the vapor through a spherical surface of all radii we obtain the following expression for the heat flux by conduction from a droplet to the ambient medium (in terms of unit surface):

$$q_{\mathrm{h}} = \frac{2\lambda_{\mathrm{v}}}{\delta}\,(T_{\mathrm{dr}} - T_{\infty})\,\frac{b}{1 - \exp(-b)}\,,$$

where $b = C_{p\mathrm{v}} g_{\mathrm{v}} \delta / 2\lambda_{\mathrm{v}}$.

To the droplet, the convective heat flux

$$q_{\mathrm{conv}} = C_{p\mathrm{v}}\, g_{\mathrm{v}}\,(T_{\mathrm{dr}} - T_{\infty}) = \frac{2\lambda_{\mathrm{v}} b}{\delta}\,(T_{\mathrm{dr}} - T_{\infty})$$

is carried with the vapor flow. The resultant heat flux from the droplet surface is

$$q = q_{\mathrm{h}} - q_{\mathrm{conv}} = \frac{2\lambda_{\mathrm{v}}}{\delta}\,X\,(T_{\mathrm{dr}} - T_{\infty})\,,$$

where

$$X = b \exp(-b)/[1 - \exp(-b)] \tag{7}$$

is precisely the sought correction factor. The effective value of the heat-transfer coefficient will be $\alpha = 2\lambda_{\mathrm{v}} X/\delta$.

When $b \to 0$, $X \to 1$; when $b \to \infty$, $X \to 0$. For certain intermediate values of b:

b	0.05	0.1	0.5	1	3	5
X	0.98	0.95	0.77	0.58	0.16	0.03

In the majority of calculations done below for a condensation growth of methane droplets, the values of X changed from 0.94 to 0.98.

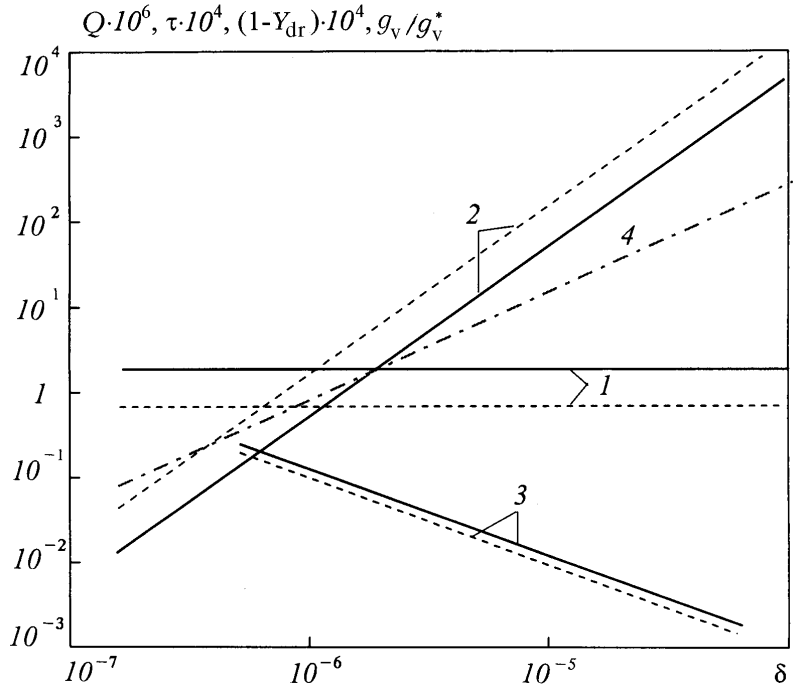

Fig. 1. Calculated quantities vs. droplet diameter for the condensation of a pure vapor of methane: 1) $Q\cdot10^6$ kg/(m·sec); 2) $\tau\cdot10^{-4}$ sec; 3) $(1-Y_{dr})\cdot10^4$; 4) g_v/g_v^*, where g_v^* is the value of g_v for $\delta = 10^{-6}$ m (for pressures of $5.89\cdot10^5$ and $1.96\cdot10^5$ Pa, $g_v^* = 2.09$ and 0.63 kg/(m^2·sec), respectively). The solid lines denote a pressure of $5.89\cdot10^5$ Pa; the dashed line denotes a pressure of $1.96\cdot10^5$ Pa; the dash-dot line shows the absence of the dependence on pressure.

To determine the density of the flux of radiative heat removal from the droplet surface (in W/m^2), we use the expression

$$q_{rad} = 5.775 \cdot 10^{-8}\,\sigma T_{dr}^4 . \tag{8}$$

The emissivity factor of the droplet surface σ is close to unity (for example, for water $\sigma \approx 0.96$ [9]). In the subsequent discussion, we will adopt $\sigma = 1$.

Let us calculate the condensation growth of a droplet using methane as an example. For calculating the condensation of a pure vapor we use formula (5) with account for the dependence (4) of r on temperature, and also Eq. (1) and expressions (6)–(8).

To close the system of equations, we use the approximation of the experimental data of [5, 6] on the pressure of a saturated vapor of methane as a function of temperature.

The condensation growth of methane droplets in a pure vapor at a temperature of $T = 111$ K were calculated for two pressures: $P = 5.89\cdot10^5$ Pa ($T_s = 138$ K) and $P = 1.96\cdot10^5$ Pa ($T_s = 119.7$ K) for the above magnitude of the condensing coefficient $f = 1$. For comparison, in individual cases the calculations were done for $f = 0.3$. Calculation results for $f = 1$ are presented in Fig. 1. In the δ range of $3\cdot10^{-7}$ to 10^{-4} m embraced by the calculations, it turned out that the value of the vapor-flow density g_v at the droplet surface can be expressed by the dependence

$$g_v = Q/\delta , \tag{9}$$

where Q is a constant equal to $2.09 \cdot 10^{-6}$ and $0.63 \cdot 10^{-6}$ kg/(m·sec) respectively for the above two pressures. This dependence also holds for higher values of δ.

Upon the substitution of expression (9) into Eq. (1) and integration on condition $\delta_0^2 << \delta^2$ (if, for example, $\delta_0 \approx 10^{-7}$ m) we obtain, just as for the case of evaporation of a droplet [10–12], a linear dependence of δ^2 on time, i.e., Sreznevskii's law:

$$\delta^2 = 4Q\tau / \rho_{\text{liq}} \,. \tag{10}$$

In addition to the results of Fig. 1, we give more values of the ratio $\Delta T / \Delta T_{\text{m}}$, where $\Delta T = T_{\text{dr}} - T_{\infty}$ is the superheating of the droplet that exists under the conditions of the problem and $\Delta T_{\text{m}} = T_{\text{s}}(P) - T_{\infty}$ is the maximum possible superheating of the droplet that corresponds to the condition of saturation at its surface for a prescribed pressure of the vapor. For $P = 5.89 \cdot 10^5$ Pa, $\Delta T = 138 - 111 = 27$ deg, while for $P = 1.96 \cdot 10^5$ Pa, $\Delta T = 119.7 - 111 = 8.7$ deg. In both cases, the values of $\Delta T / \Delta T_{\text{m}}$ in round numbers are as follows:

δ, m	$3 \cdot 10^{-7}$	10^{-6}	10^{-5}
$\Delta T / \Delta T_{\text{m}}$	0.99	0.999	0.9999

For higher values of δ, the ratios $\delta T / \Delta T_{\text{m}}$ must be even closer to unity. Thus, with a very small error the values of g_v can be calculated (disregarding radiative heat removal) using the simple expression

$$g_{\text{v}} = \alpha \Delta T_{\text{m}} X / r \,, \tag{11}$$

in calculating by which we obtain practically the same values $g_{\text{v}}\delta = Q$ as above. The radiative heat removal had no appreciable effect in all the calculations done for a pure vapor at pressures prescribed in these calculations.

We also note that, despite the small changes in $\Delta T / \Delta T_{\text{m}}$, the quantity $(1 - Y_{\text{dr}})$ changes with δ substantially (Fig. 1), which is due to the strong dependence of $Y_{\text{dr}} = P_{\text{vs}}(T_{\text{dr}})/P$ on the temperature T_{dr}.

The decrease in f to 0.3, as the calculations showed, has practically no effect on the values of g_{v}, Q, and τ, since $(1 - Y_{\text{dr}})$ accordingly increases. The reason is the appreciable decrease in Y_{dr} with a small decrease in the temperature T_{dr}.

Let us pass to calculating the growth of a droplet in condensation from a mixture of a vapor with a noncondensable (permanent) gas. The condensation of methane from natural gas that contains an admixture of nitrogen (an average of 1 vol.% but can be up to 5 vol.% or higher) is one example of practical importance [13]. Also, there are traces of inert gases and small admixtures of gases condensing earlier than methane (other hydrocarbons, carbon dioxide, etc.). Sometimes the admixtures of condensing hydrocarbons can be relatively high (up to 5–10 vol.% and even to 15 vol.% or higher), which has a substantial effect in the initial stage of liquefaction. Below, we will take into account only the admixture of nitrogen.

Because of the occurring diffusion resistance the intensity of condensation can to a certain measure decrease. A formula for the diffusion transfer in evaporation or condensation was obtained even by Stefan [10, 14]. In calculations of the evaporation and growth of droplets and also of fogging [10, 2], and diffusional burning of droplets [11, 12], account is taken of the Stefan flow, which is frequently of decisive importance. In condensation on cooled surfaces, the Stefan flow substantially increases the intensity of the process, for example, in isolation of the vapor of metals from mixtures with inert gases or nitrogen [15].

As applied to a calculation of the droplet growth in condensation of a vapor from a mixture with a noncondensable gas for a low vapor fraction, the density of the diffusion vapor flow is determined by the formula

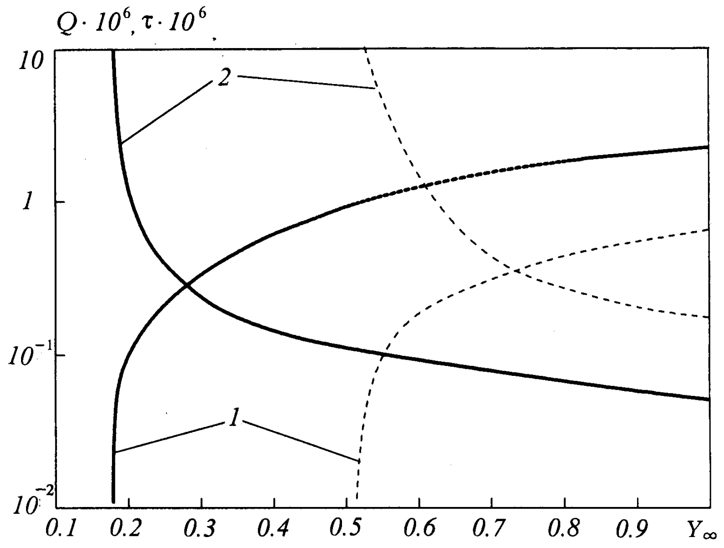

Fig. 2. Calculated quantities vs. relative vapor content Y_∞ in condensation in a mixture of methane vapor with nitrogen: 1) $Q \cdot 10^6$ kg/(m·sec); a) $\tau \cdot 10^3$ sec. T_∞ = 111 K. The solid lines denote a pressure of $5.89 \cdot 10^5$ Pa; the dashed lines denote a pressure of $1.96 \cdot 10^5$ Pa.

$$g_{\text{v}} = \alpha_D \frac{PM}{RT_{\text{av}}} (Y_\infty - Y_{\text{b}}) \,.$$

For arbitrary vapor fractions, in accordance with the Stefan conclusions a certain Y is replaced by $[-\ln(1 - Y)]$, i.e., the action of the above-mentioned Stefan flow toward the condensation surface is taken into account. Allowing for this and substituting the value $\alpha_D = \text{Nu}_D D/\delta$, we can, as is usually done, write for the case of arbitrary vapor fractions

$$g_{\text{v}} = \frac{\text{Nu}_D D}{\delta} \frac{PM}{RT_{\text{av}}} \ln [(1 - Y_{\text{b}})/(1 - Y_\infty)] \,. \tag{12}$$

Much as in the calculations of the condensation of a pure vapor, the droplet will be considered to be sessile. Therefore $\text{Nu}_D = 2$ (just as Nu = 2). The value of the diffusion coefficient of the methane vapor in nitrogen was calculated from the first approximation to the theory of Enskog and Chapman [16]. It is established that

$$D = 0.33 \, (T_{\text{av}}/110)^{1.8}/P \,, \quad \text{m}^2/\text{sec} \,.$$

The second and higher approximations lead to insignificant differences.

The value of Y_{b} is found from a comparison of the values of g_{v} from formulas (6) and (12), i.e., is established with allowance for the kinetic and diffusion resistances. This was done in the calculations. However, if formula (6) is not used, even for high vapor fractions without an appreciable error we can calculate g_{v} using formula (12) with the replacement of Y_{b} by Y_{dr} in the latter, since usually these quantities differ little and in logarithmic operation the error is concealed.

Figure 2 presents the values (resulting from calculations) of the parameter Q involved in formula (10), which still holds, and the times of growth of the droplet τ for $\delta = 10^{-6}$ m versus the relative content of the methane vapor Y_∞ in the mixture with nitrogen at a temperature of the medium of 111 K and pressures of $5.89 \cdot 10^5$ and $1.96 \cdot 10^5$ Pa.

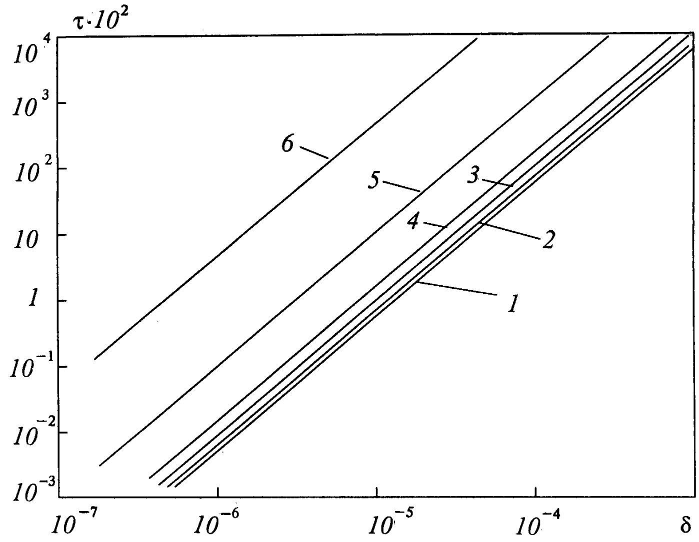

Fig. 3. Calculated dependences of the time of growth of a methane droplet $\tau \cdot 10^2$ sec on the droplet diameter δ for different vapor fractions Y_∞ in a mixture of methane vapor with nitrogen: 1) $Y_\infty = 0.99$; 2) 0.9; 3) 0.7; 4) 0.5; 5) 0.2; 6) 0.175. $T_\infty = 111$ K.

Figure 3 gives the times of growth of the droplet versus the diameter for a pressure of $5.89 \cdot 10^5$ Pa and a temperature of the medium of 111 K for different values of Y_∞. From the given results, it is obvious that for values of Y_∞ close to 0.99 the condensation intensity decreases little with decrease in Y_∞. We note that when $Y_\infty = 0.99$ and $Y_\infty = 1$ (pure vapor) the results practically coincide, and formula (11) still holds. Moreover, in approximate calculations, this formula can also be used for lowered values of Y_∞, for example, for $Y_\infty = 0.9$ with an understating of $g_{\rm v}$ by ~1% of a more exact value. For lower values of Y_∞, formula (11) can be used with the replacement of the quantity $\Delta T_{\rm m}$ by ΔT that correspond to the prescribed values of Y_∞. According to the complete numerical calculations made, the ratio $Q/\Delta T$ changes not very appreciably with decrease in Y_∞. For $P = 5.89 \cdot 10^5$ Pa, even with a decrease in Y_∞ to 0.7, this ratio decreases only by approximately 4%. For $P = 1.96 \cdot 10^5$ Pa, the values of the ratio $Q/\Delta T$ are close to such for $P = 5.89 \cdot 10^5$ Pa (6–4%). All this suggests that the resistance to the removal of the heat of condensation from the droplet surface to the ambient medium rather than the resistance to the diffusion supply of the vapor to the droplet is predominant. Therein lies one fundamental feature of the condensation growth of a droplet in a vapor-gas mixture. The same can be said about the resistance to the droplet growth in a pure vapor. As is obvious from the results considered above and as is confirmed by formula (11), it is the resistance to the removal of heat released on the droplet surface rather than the kinetic resistance of phase transition, i.e., constraint of the flow by formula (6), that is decisive in this case.

So, to at least $Y_\infty = 0.9$ and somewhat lower, simple calculations of $g_{\rm v}$ by formula (11) using the correction (7) are possible followed by computations of all the remaining quantities that govern the process. At the same time, it is known that in the most efficient liquefiers of natural gas with reciprocating expanders or turboexpanders the degree of liquefaction owing to the warming up of the gas by condensation heat release does not exceed 8–12% (and in expanderless throttle liquefiers it does not exceed 1.8–3%). Thus, even in expander liquefiers Y_∞ can decrease to only 0.9 or somewhat lower.

Because of the expansion of the gas in liquefiers, the total pressure decreases. Therefore, the values of Q will decrease for this reason, too. If the expansion is not very rapid, i.e., if in a time of droplet growth of about 10^{-4}–10^{-3} sec the pressure fails to change appreciably, data (see Fig. 2) for a fixed pressure can be used directly. For the case of rapid expansion, Eqs. (1), (5)–(8), and (12) and dependence $P_{\rm vs}(T)$ used can be

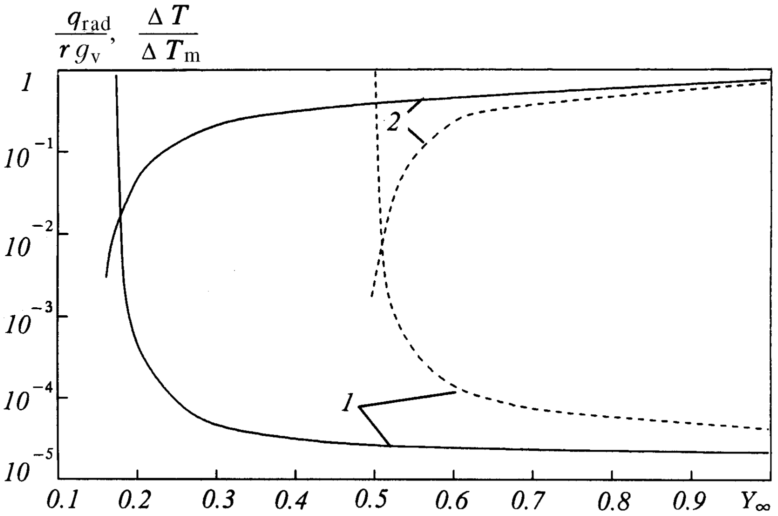

Fig. 4. Calculated dependences of the relative radiative heat removal q_{rad}/rg_v and the superheating of a droplet $\Delta T/\Delta T_m$ on the relative vapor fraction Y_∞ in a mixture of methane vapor with nitrogen: 1) q_{rad}/rg_v; 2) $\Delta T/\Delta T_m$. T_∞ = 111 K. The solid lines denote a pressure of $5.89{\cdot}10^5$ Pa; the dashed lines denote a pressure of $1.96{\cdot}10^5$ Pa. For the former pressure ΔT_m = 27 deg, for the latter pressure ΔT_m = 8.7 deg.

included in the general system of equations with allowance for expansion. In all cases, a formula that determines the intensity of formation of liquid-phase nuclei is necessary for complete calculation of the process of liquefaction. As such a formula, it is reasonable to use Ya. I. Frenkel's formula [1] yielding, as is shown in [2], a better agreement with experimental data for water than, for example, the formula of Becker and Dering. According to the calculation by Ya. I. Frenkel's formula, for methane the supersaturation $S \approx 2.5$ at a temperature of 111 K will be critical, i.e., the nuclei of the liquid phase will begin to develop. For a pressure of $1.96{\cdot}10^5$ Pa at the same temperature, the supersaturation $S \approx 2$ is subcritical. Should the methane pressure with holding of the temperature be $5.89{\cdot}10^5$ Pa the supersaturation $S \approx 6$ will be supercritical with an intensity of nucleation of about 10^{22} $\text{cm}^{-3}{\cdot}$ sec^{-1}. In this case, a corresponding injection of methane is required to hold the pressure. For a methane pressure of $4{\cdot}10^5$ Pa and still the same temperature 111 K when the supersaturation $S \approx 4$ is also supercritical, the intensity of nucleation decreases by 10 orders of magnitude.

In order to close the system of equations we should use the equations of balance of mass and heat for a vapor-gas mixture for one specific case or another. Subsequent calculations will make it possible to determine the droplet size, the degree of liquefaction, and the time of reaching the equilibrium regime as the droplets cease to grow. Similar calculations are beyond the scope of this work. Here we give only a formula which replaces relation (10) for the general case:

$$\delta^2 = (4/\rho_{liq}) \int_0^\tau Q(\tau)\, d\tau .$$

The relationship between Q and τ is determined by the dependences of P and Y_∞ on τ in expansion of the gas in a liquefier.

For a more complete description of Q as a function of P, we add to the results (see Fig. 2) the calculated values of Q in kg/(m·sec) according to the same method for P = $4{\cdot}10^5$ Pa at T_∞ = 111 K for several values:

Y_∞	0.7	0.8	0.9	0.99
$Q \cdot 10^6$	1.05	1.22	1.36	1.53

It turns out that in this range of Y_∞ values the dependence $Q(Y)_\infty$ is close to a linear one, just as in Fig. 2 for $P = 5.89{\cdot}10^5$ Pa (recall that the values of Q are represented there on a logarithmic scale).

In all the calculation results considered above, the convective heat transfer substantially dominated the radiative heat transfer. The fraction of the radiative release of heat from a droplet $q_{\text{rad}}/rg_{\text{v}}$ is very small up to $Y_\infty \approx 0.2$ for $P = 5.89{\cdot}10^5$ Pa and to $Y_\infty \approx 0.52$ for $P = 1.96{\cdot}10^5$ Pa (Fig. 4). Below the indicated values of Y_∞ the superheating of the droplet ΔT and accordingly the convective heat transfer decrease sharply; therefore, the radiative heat transfer begins to dominate. In the limiting cases that correspond to $Y_\infty \approx 0.171$ for $P = 5.89{\cdot}10^5$ Pa and to $Y_\infty \approx 0.514$ for $P = 1.96{\cdot}10^5$ Pa, we can disregard convective heat removal and consider that the heat of condensation is practically totally removed from the droplet by radiation. For such cases, i.e., when the condition $\alpha\Delta T << q_{\text{rad}}$ is fulfilled, Eq. (1) for q_{rad} = const and $r\rho_{\text{liq}}$ = const (since the droplet temperature is constant) yields the following formula:

$$\delta - \delta_0 = 2q_{\text{rad}}\,\tau/(r\rho_{\text{liq}})\,,$$

where q_{rad} corresponds to relation (8).

In accordance with the written formula, the droplet will grow very slowly because of the low value of q_{rad}. We give results of calculating the growth of a single droplet of methane with the initial diameter $\delta_0 = 10^{-6}$ m at $T_{\text{dr}} \approx T_\infty = 111$ K and the partial pressure of the vapor $P_{\text{v}\infty}$ held constant in the ambient medium:

τ, sec	0.1	0.5	1	2	3
δ/δ_0	1.01	1.05	1.1	1.2	1.3

It is obvious that, for example, if the droplet is given a time of 1 sec for growth, its diameter will increase by only a factor of 1.1 but its volume (or mass) proportional to δ^3 will increase by a factor 1.33 now, etc. We give more results of evaluating the ratio $P_{\text{v}\infty}/P_{\text{vs}}(T_\infty)$ (i.e., supersaturation of the vapor at a large distance from the droplet) that corresponds to the calculations done. Let the total pressure of a mixture of a methane vapor with nitrogen be $P = 5.89{\cdot}10^5$ Pa. Then according to the condition of saturation at the temperature $T_{\text{dr}} = 111$ K we have $Y_{\text{dr}} = 0.171$. When formula (12) with $Y_{\text{b}} = Y_{\text{dr}}$ is used, we obtain that $P_{\text{v}\infty}/P_{\text{vs}}(T_\infty) \approx 1 + 0.8{\cdot}10^{-5}$. For the pressure of the mixture $P = 1.96{\cdot}10^5$ Pa when $Y_{\text{dr}} = 0.514$ for the saturation corresponding to 111 K, similarly to the foregoing we have $P_{\text{v}\infty}/P_{\text{vs}}(T_\infty) \approx 1 + 2{\cdot}10^{-6}$. In the case of simultaneous condensation on many droplets, such supersaturations can rapidly disappear and the process will cease unless a vapor is added.

We also note that heat can be released directly from the droplet by phase-transition radiation, at least in the stage of nucleation [17]. In review [17], in particular, results of an investigation [18] are also discussed in which the effect of a strong supertemperature radiation of water boiling up at atmospheric pressure has been detected experimentally. The intensity of radiation from the water–glass interface in the region of wavelengths of 1.7–1.8 μm exceeded the intensity of black body radiation by approximately a factor of 100. Thus, energy radiation can occur in opposite phenomena – condensation and boiling. In [18], the detected radiation is explained by the rearrangement of bonds between water molecules in clusters. All this confirms the assumption of [19] of the propagation, in natural phenomena, of energy radiation inherent in many processes which occur in opposite directions.

In conclusion, we note that with a rapid expansion of the vapor-gas mixture in the liquefier and the attainment, as a result, of a high supersaturation, a considerable mass of the vapor can be expended on forming the nuclei of a liquid phase. Subsequently the droplet growth practically ceases, since droplets can grow to large sizes only with a relatively slow expansion [20]. If the removal of the occurring phase-transition radiation using a system of mirrors or a flow laser is provided [21], the degree of liquefaction of the gas can be increased. In the experiments on an air-liquefaction unit conducted by Yu. G. Belostotskii et al. at the St. Petersburg Academy of Cold, the presence of the mentioned radiation was detected in the mouth of the nozzle of a Joule–Thomson throttle. This phenomenon can be used for raising the capacity of devices intended for the industrial production of a liquefied natural gas.

NOTATION

ρ_{liq}, density of the liquid; δ, droplet diameter; τ, time; g_{v}, density of the vapor flow at the droplet surface; $C_{p\text{liq}}$ and $C_{p\text{v}}$, specific heats of the liquid and the vapor at constant pressure; T_{dr}, droplet temperature; T_{∞}, temperature of the medium at a distance from the droplet; r_{tabl}, specific heat of condensation in reckoning the enthalpy from the phase-transition temperature; q_{rad}, density of the radiative heat flux from the droplet surface; Nu, thermal Nusselt number; λ_{v} and λ_{liq}, thermal conductivities of the vapor and the liquid; Bi, Biot number; r, specific heat of condensation in reckoning the enthalpy from the temperature of the medium; f, condensing coefficient; R, universal gas constant; P, pressure of the medium; $Y_{\text{b}} = P_{\text{v.b}}/P$, $P_{\text{v.b}}$ is the vapor pressure at a distance from the droplet surface of the order of the mean-free path of molecules; T_{b}, temperature at the same distance; $Y_{\text{dr}} = P_{\text{vs}}(T_{\text{dr}})/P$, $P_{\text{vs}}(T_{\text{dr}})$, pressure of saturated vapor at the droplet surface at temperature T_{dr}; T_{s}, saturation temperature; α_D, coefficient of diffusion mass transfer; Nu_D, diffusional Nusselt number; D, diffusion coefficient; $T_{\text{av}} = (T_{\text{dr}} + T_{\infty})/2$, average temperature; M, molecular mass of the vapor; $P_{\text{v}\infty}$, partial pressure of the vapor at a distance from the droplet; $P_{\text{vs}}(T_{\infty})$, pressure of saturated vapor at temperature T_{∞}; $S = P_{\text{v}\infty}/P_{\text{vs}}(T_{\infty})$, supersaturation of the vapor. Subscripts: 0, initial value; liq, liquid; v, vapor; dr, droplet; rad, radiative; b, boundary value; h, heat-conducting; conv, convective; m, maximum value; av, average value; tabl, tabulated value; D, diffusional; s, saturated.

REFERENCES

1. Ya. I. Frenkel', *Kinetic Theory of Liquids* [in Russian], Leningrad (1975).
2. A. G. Amelin, *Theoretical Principles of Fogging in Vapor Condensation* [in Russian], 2nd edn., Moscow (1966).
3. A. L. Itkin, *Prikl. Mekh. Tekh. Fiz.*, No. 1, 89–95 (1987).
4. I. N. Ivchenko and A. V. Terzyan, *Teplofiz. Vys. Temp.*, **23**, No. 2, 402–405 (1985).
5. R. Ya. Kucherov and L. É. Rikenglaz, *Zh. Éksp. Teor. Fiz.*, **37**, No. 1, 125–126 (1959).
6. V. S. Chirkin, *Thermophysical Properties of Materials: Manual* [in Russian], Moscow (1959).
7. N. B. Vargaftik, *Handbook of Thermophysical Properties of Gases and Liquids* [in Russian], Moscow (1963).
8. A. P. Andreev, in: *Temperature Regime and Hydraulics of Steam Generators* [in Russian], Leningrad (1978), pp. 116–145.
9. S. M. Shorin, *Heat Transfer* [in Russian], Moscow–Leningrad (1952).
10. N. A. Fuks, *Evaporation and Growth of Droplets in a Gaseous Medium* [in Russian], Moscow (1958).
11. L. A. Vitman, B. D. Katsnel'son, and I. I. Paleev, *Spraying of a Liquid by Atomizers* [in Russian], Moscow–Leningrad (1962).
12. V. V. Pomerantsev, K. M. Aref'ev, D. B. Akhmedov, et al., *Principles of Practical Theory of Combusion* [in Russian], 2nd edn., Leningrad (1986).
13. R. D. Margulov, R. I. Vyakhirev, I. A. Leont'ev, and A. I. Grishchenko, *Exploitation of Deposits with a Complex Composition of Gas* [in Russian], Moscow (1988).

14. D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics* [in Russian], 3rd edn., Moscow (1987).
15. K. M. Aref'ev, A. R. Lesyuis, B. M. Khomchenkov, and L. Sh. Tsemekhman, *Inzh.-Fiz. Zh.*, **27**, No. 5, 825–832 (1974).
16. J. Hirschfelder, C. Curtiss, and R. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, New York (1954).
17. A. P. Smirnov and S. A. Sall', in: *Fundamental Problems of Natural Science*, Vol. II, *Ser. Problems of Investigation of the Universe*, Issue 22, St. Petersburg (2000), pp. 186–210.
18. W. R. Potter and J. G. Hoffman, *Infr. Phys.*, **8**, 265–270 (1968).
19. Yu. G. Belostotskii, *Single Basis of the Universe* [in Russian], St. Petersburg (2000).
20. G. É. Zarnitskii, É. É. Markovich, E. A. Muronov, and V. G. Pikin, *Ref. Sb. VNIIÉGazprom.*, No. 8, 21–24 (1972).
21. Yu. G. Belostotskii and A. P. Smirnov, *Method of Liquefaction of Gas and a Liquefier That Realizes This Method,* Description of the Invention, RF Patent No. 2125216 (1999).