KINETICS OF HETEROGENEOUS CONDENSATION.

4. CONDENSATION ON CHARGED NUCLEI AND ASYMMETRY OF CONDENSATION RELATIVE TO SIGN OF CHARGE ON NUCLEUS

F. M. Kuni, A. K. Shchekin,
and K. V. Kopeikin

UDC 536.423:537.2

The principal characteristics of state of an ensemble of drops at the end of a condensation process have been calculated, including corrections for the drop curvature parameter and the work of drop formation on a charged nucleus. It is shown that the coefficients in these corrections that are related to nonelectrical and electrical parameters of the surface layer of the drop can be found from experiments on homogeneous and heterogeneous nucleation.

Previously [1-3], in the "subthreshold region of initial supersaturations," the principal stages of heterogeneous condensation were investigated. The state of supercritical drops that is reached at the end of condensation subsequently changes only as transcondensation develops; this occurs at times much longer than the time of the condensation process itself. As this state remains unchanged for a comparatively long time, it may be manifested in an experiment. Specifically this state is observed in a Wilson chamber. In contrast to the universal distribution of drop sizes that is established in the process of transcondensation [4], it depends on the work of drop formation F_ν, a function of the number of molecules of the drop ν with a given value of supersaturation of the vapor ζ (F_ν is expressed in thermal energy units kT). With logarithmic accuracy, corresponding only to a correct order of magnitude of the values, this relationship is accomplished by means of the height of the activation barrier $\Delta F(\zeta)$. For quantities that themselves change by an order of magnitude with a relatively small change in supersaturation, such accuracy is entirely adequate (in the equations, this accuracy is indicated by the symbol ~).

Of the greatest interest in the state of supercritical drops at the end of condensation is the total number of drops N in unit volume, the maximum drop size ρ_2 ($\rho \equiv \nu^{1/3}$, where ν is the number of molecules in the drop), the relative scatter of drop sizes ρ_1/ρ_2 ($\zeta_2 - \rho_1$ is the minimum size of the drops), and the time until the end of the condensation process t_2. Also, in analyzing experiments with an artifically truncated condensation time [5-8], an important characteristic of the process is the time required for formation of a size spectrum t_1, at which time the width of the spectrum of dimensions ρ_1 and the number of drops remain practically unchanged.

The influence of a charged nucleus on the work of drop formation is manifested mainly through the long-range field of electric forces. An accounting for electrical contributions to the thermodynamic parameters, with an accuracy within first-order terms with respect to the drop curvature parameter, inclusive, was carried out in [9-12]. Using [11, Eqs. (28) and (26)], for the work of drop formation F_ν we have

$$F_\nu - F_\nu^0 + F_\nu^1, \quad F_\nu^0 = -b\nu + a\nu^{2/3} + \frac{1}{2} a\nu_0\nu^{-1/3}$$

$$F_\nu^1 = -2a\nu^{1/3}\left(c_1 + \frac{1}{6}c_2 + c_5\nu^{-1/3}\right) + \frac{1}{2} a\nu_0\nu^{-2/3} \times \tag{1}$$

$$\times \left[c_1 + \frac{1}{3}c_2 - c_4 + c_7 - \frac{1}{24}(c_2 + 6c_7)\nu_0\nu^{-1} + \left(c_5 - \frac{2}{3}c_6\right)\nu^{-1/3}\right] \tag{2}$$

where ν_0 is the point of inflection of F_ν^0. Here, we have excluded the term related to work of solvation of the nucleus, which is independent of ν and hence unimportant for the kinet-

$$a \equiv \frac{4\pi\gamma_\infty}{kT} \left(\frac{3}{4\pi n_\infty^\alpha} \right)^{2}, \quad \nu_0 \equiv \frac{8\pi u_\infty q^2}{3\gamma_\infty} n_\infty^\alpha$$

$$c_1 = \left(\frac{4\pi n_\infty^\alpha}{3} \right)^{1/3} \lambda_\infty, \quad c_2 \equiv 2 \left(\frac{4\pi n_\infty^\alpha}{3} \right)^{1/3} \chi_\infty \gamma_\infty, \quad c_4 \equiv \left(\frac{4\pi n_\infty^\alpha}{3} \right)^{1/3} \frac{k_1}{2u_\infty}$$

$$c_5 \equiv \frac{4\pi}{3} q \left(\frac{d \mathcal{P}_0}{du} \right)_\infty, \quad c_6 \equiv \frac{2\pi}{3} \frac{n_\infty^\alpha k_2 q}{u_\alpha}, \quad c_7 \equiv \frac{1}{3} \left(\frac{3}{4\pi n_\infty^\alpha} \right)^{2} \frac{\gamma_\infty}{u_\infty (\varepsilon_\alpha^\alpha)^2} \left(\frac{d\varepsilon^\alpha}{d\mu} \right)_\infty \quad (3)$$

where the superscripts α and β identify parameters pertaining to the liquid and gas phases, respectively; the symbol ∞ indicates values that have been found for equilibrium with a plane interface; n is the number of molecules in unit volume: $u \equiv (1/\varepsilon^\beta - 1/\varepsilon^\alpha)/8\pi$; ε is the permittivity; γ is the surface tension; q is the charge; χ is the isothermal compressibility of the liquid phase; $\mathcal{P}_0$ is the spontaneous surface polarization; μ is the chemical potential; λ_∞ is the difference between the radii of the equimolecular surface and the tension surface in the limit of a plane interface; k_1 and k_2 are the coefficients of the induction-linear and induction-quadratic contributions to the induced surface polarization. According to [9, Eq. (44)], for $(d\mathcal{P}_0/d\mu)_\infty$ we can write

$$(d\mathcal{P}_v/d\mu)_\alpha = -\varkappa \mathcal{P}_{v\alpha}/kT, \quad \varkappa \sim 1 \quad (\varkappa > 0) \quad (4)$$

Finally, b is the chemical potential of the vapor, expressed in units of kT and referred to the value for a plane liquid/vapor interface. It is related to the vapor supersaturation by the equality $b = \ln(1 + \zeta)$. As is clear from (3), $\nu_0 \equiv \nu_0(q)$ is an even function of q; $c_5 \equiv c_5(q)$ and $c_6 \equiv c_6(q)$ are odd functions of q; the values of a, c_1, c_2, c_4, and c_7 are entirely independent of q.

The term $F_v{}^1$, in order of relative magnitude to the sum of the second and third terms in $F_v{}^0$, is no greater than the curvature parameter $c_m \nu^{-1/3}$, where c_m is understood to be the larger of the coefficients c_1 and c_2. The smallness of $c_m \nu^{-1/3}$ in comparison with unity also enables us to neglect the subsequent asymptotic corrections. Also, we will not consider corrections arising from nonequivalence between the thermodynamic ensemble in which the real drop exists and the ensemble in which F is determined. The magnitude of the corresponding corrections remain in doubt; for us it is important that these corrections have a higher order of smallness in relation to the corrections for the curvature parameter that we are taking into account. Evidently, the "unperturbed" term $F_v{}^0$ coincides with [1, Eq. (4)].

The height of the activation barrier to nucleation is determined by the relationship

$$\Delta F(\zeta) = F_{\nu_c} - F_{\nu_e} \quad (5)$$

where ν_c and ν_e are the points of the maximum and minimum of the function F_ν, corresponding to the critical drop and the equilibrium drop. Neglecting the corrections for the drop curvature parameter for the unperturbed value ΔF_0, from [1, Eq. (12)] we have

$$\Delta F_0 = \frac{1}{3} a \nu_0^2 (u_{c0}^{2/3} - u_{e0}^{2/3} + 2u_{c0}^{-1/3} - 2u_{e0}^{-1/3}) \quad (6)$$

where $u_{e0} = \nu_{e0}/\nu_0$, and $u_{c0} = \nu_{c0}/\nu_0$, with ν_{e0} and ν_{c0} satisfying the equation $(F_\nu{}^0)' \big| = \nu_{e0}$, $\nu_{c0} = 0$. For each value of the supersaturation, values of $\Delta F_0/(1/3)a\nu_0^{2/3}$, u_{e0}, and u_{c0} can be found by means of [1, Table 1]. An accounting of corrections for the curvature parameter, in view of $\exp(\Delta F) \gg 1$, can change $\exp(\Delta F)$ severalfold in comparison with $\exp(\Delta F_0)$ for a given supersaturation, and correspondingly, according to [2, Eq. (28)] and [3, Eqs. (44) and (46)], it can change the values of N, t_1, t_2, and ν_2. Consequently, these corrections are significant.

Now investigating the most interesting region of low supersaturations, we will determine the relationship $N(\zeta)$ with an accounting for corrections for the curvature parameter, having set

$$N(\zeta) = N_c(\zeta_c) \quad (7)$$

---

*Here, as a characteristic of the nucleus, there remains in F_ν only the charge of the nucleus. As shown by mass spectrometric measurements [13], F_ν' ceases to depend on the nature of the ion when $\nu \sim 10$.

where $N_0(\zeta_0)$ is the number of drops as a function of the unperturbed supersaturation ζ_0. According to [3, Eq. (46)], Eq. (7) is equivalent to

$$\Delta F(\zeta) = \Delta F_0(\zeta_0) \tag{8}$$

Now we will consider N as the independent variable in the supersaturation ζ as a function of N; then, from [3, Eq. (46)], for a given N, we have

$$\Delta F(\zeta^K) \simeq \frac{4}{3} \ln \left[\frac{\eta}{N} \left(\frac{n_\infty^\beta}{\eta} \right)^{1/4} \right], \quad \Delta F(\zeta^D) \simeq \frac{5}{3} \ln \left[\frac{\eta}{N} \left(\frac{n_\infty^\beta}{\eta} \right)^{2/5} \left(\frac{\tau_D}{\tau_K} \right)^{3/5} \right] \tag{9}*$$

Equations (6), (8), and (9) can be used with [1, Table 1] to find, for each value of N, the corresponding value of the unperturbed supersaturation ζ_0 (or chemical potential b_0). We will now determine the shifts of b relative to b_0 due to the corrections for the curvature parameter, for a given value of N. We will consider that with the values of v_{e0} and v_{c0} corresponding to b_0, the following inequalities are valid:

$$| F^1_{v_{c0,c0}} / F_{v_{c0,c0}} | \lesssim c_m v_{c0,c0}^{-1/3}, \quad |v_{t,c} - v_{t0,c0}|/v_{e0,c0} \lesssim c_m v_{c0,c0}^{-1/3} \tag{10}$$

$$c_m v_{c0}^{-1/3} \ll 1 \tag{11}$$

The first of the inequalities (10) is a consequence of the remarks made above relative to the order of magnitude of F_v^1. The justification for the second inequality will be given below. The inequality (11), ensuring applicability of the method of expansion with respect to the curvature parameter, imposes a bottom limit on the possible values of v_{e0}, and hence on the number of drops.

Solving the equation

$$F_{v_c} - F_{v_e} = F^0_{v_{c0}} - F^0_{v_{c0}}$$

by expanding F_{vc} and F_{vc} in Taylor series in the vicinities of the points v_{c0} and v_{e0} respectively, using Eqs. (1) and (2), and neglecting, in accordance with (10), values of the second order of smallness with respect to the curvature parameter $c_m v^{-1/3}$ ($v = v_{e0,c0}$), and converting to the universal variables u_c and u_e and the chemical potential in units of unperturbed threshold values $\beta \equiv 2a^{-1} v_0^{1/3} b$, we obtain the sought relationship for the perturbed chemical potential,

$$\beta = \beta_0 [1 - (c_1 C_1(\beta_0) + c_2 C_2(\beta_0) - c_4 C_4(\beta_0) + c_7 C_7(\beta_0)) v_0^{-1/3} + c_6 C_6(\beta_0) v_0^{-1}] \tag{12}$$

where

$$C_1(\beta_0) \equiv 3 \frac{u_{c0}^{2/3} - u_{c0}^{2/3}}{u_{c0} - u_{c0}}, \quad C_2(\beta_0) \equiv \frac{3}{8}\beta_0, \quad C_4(\beta_0) \equiv \beta_0^{-1} \frac{u_{c0}^{-2/3} - u_{c0}^{-2/3}}{u_{c0} - u_{e0}}$$

$$C_6(\beta_0) \equiv \frac{2}{3}\beta_0^{-1} \frac{u_{c0}^{-4/3} - u_{c0}^{-4/3}}{u_{c0} - u_{c0}}, \quad C_7(\beta_0) \equiv \frac{3}{4} \frac{u_{c0}^{-1/3} - u_{c0}^{-1/3}}{u_{c0} - u_{c0}} \tag{13}$$

Values of C_1, ..., C_7 as functions of β_0 are listed in Table 1. With decreasing supersaturation, in view of the rapid increase in the difference $u_{c0} - u_{e0}$, the values of C_1, ..., C_7 also decrease. Therefore, the relationship N(ζ) can be found with good accuracy all the way down to rather low supersaturations. However, the application of (12) for the determination of the coefficients c_1, ..., c_7 is justified only with supersaturations down to the lower limit imposed by condition (11).

By means of (12), (1), and (2), it is not difficult to show that the second of the inequalities (10), if the first of the inequalities (11) is fulfilled, will be valid, both in the subthreshold region of supersaturations and at the threshold point itself.

Because of the lack of any reliable experimental or theoretical data on λ_∞, $\varkappa$, k_1, and k_2, it is impossible to use (9) to find c_1, c_4, $c_5(q)$, and $c_6(q)$. A possibility of determining the corresponding coefficients, and along with them the characteristic electrical and nonelectrical parameters of the surface layer, is offered by a combined analysis of experiments on homogeneous and heterogeneous nucleation.

---

*The sign of approximate equality in (9) ensures logarithmic accuracy [3, Eq. (46)]; the indexes K and D refer to free-molecule and diffusional regimes, respectively; η is the number of ions in unit volume; τ_K and τ_D are quantities with the dimensionality of time, determined for the free-molecular made by the use of [1, Eq. (19)], and for the diffusional mode as indicated in [2].

TABLE 1. Values of Functions C_1, C_2, C_4, C_6, and C_7 in the Sub-threshold Region of Supersaturations

β	$C_1(\beta)$	$C_2(\beta)$	$C_4(\beta)$	$C_6(\beta)$	$C_7(\beta)$
0.96	1.932	0.360	0.627	0.842	0.227
0.94	1.898	0.353	0.607	0.818	0.216
0.92	1.864	0.345	0.587	0.794	0.205
0.90	1.830	0.338	0.568	0.771	0.195
0.88	1.795	0.330	0.548	0.747	0.185
0.86	1.760	0.323	0.529	0.723	0.175
0.84	1.725	0.315	0.510	0.699	0.165
0.82	1.689	0.308	0.491	0.675	0.156
0.80	1.653	0.300	0.472	0.651	0.147
0.78	1.617	0.293	0.453	0.628	0.138
0.76	1.581	0.285	0.435	0.605	0.129
0.74	1.544	0.278	0.416	0.582	0.121
0.72	1.507	0.270	0.398	0.558	0.113
0.70	1.470	0.263	0.380	0.535	0.105
0.68	1.432	0.255	0.362	0.512	0.098
0.66	1.394	0.248	0.345	0.489	0.091
0.64	1.356	0.240	0.328	0.467	0.084
0.62	1.318	0.233	0.311	0.444	0.078
0.60	1.279	0.225	0.294	0.422	0.071

Note. For each substance, it is convenient to convert from the variable β to the supersaturation ζ by means of the formula $\zeta = \exp(\alpha\beta/2v_0^{1/3}) - 1$.

Let ζ_n and $\overline{\zeta_{\overline{n}}}$ be the experimentally determined values of the supersaturation at which n and $\overline{n}$ drops are formed in 1 cm³ as a result of heterogeneous and homogeneous condensation, respectively (the values of $\overline{n}$ may lie in the range from 10^{-1} to 10^4; the values of n are limited by the condition $n \ll \eta$, taking as η the number of ions in 1 cm³). Selecting 1 cm³ as the unit volume, we have

$$\ln N|_{\zeta = \zeta_n} = \ln n, \quad \ln \overline{N}|_{\zeta = \overline{\zeta}_{\overline{n}}} = \ln \overline{n} \tag{14}$$

By a method that was developed in [1-3] and also in [14, 15], it can be shown that with the same accuracy as in (9), the following is valid:

$$\overline{F}(\zeta^K) \simeq \frac{4}{3} \ln\left[\frac{n_\infty}{n}\right], \quad F(\zeta^D) \simeq \frac{5}{3} \ln\left[\frac{n_\infty^\beta}{n}\left(\frac{\tau_D}{\tau_K}\right)^{3/4}\right] \tag{15}$$

where $\overline{F}(\zeta)$ is the height of the barrier to nucleation, which in the case of homogeneous nucleation coincides with the work of formation of a critical drop. Neglecting the corrections for curvature parameter, we have

$$\overline{F}_0 = \frac{1}{3} a\overline{v}_{c0}^{-1/3}, \quad \overline{v}_{c0} = [2a/3 \ln(1 + \overline{\zeta}_{\overline{n}0})]^3 \tag{16}$$

The influence of the corrections for curvature parameters on the characteristics of homogeneous condensation is not difficult to take into account within the framework of the above-described approach to heterogeneous condensation. In (12), we equate to zero the quantities v_{e0}, c_u, c_6, and c_7, which have an electrical nature, and we find

$$\overline{b} = \overline{b}_0\left(1 - 3c_1\overline{v}_{c0}^{-1/3} - \frac{3c_2\overline{b}_0}{4a}\right) \tag{17}$$

Here, $\overline{b}_0 = \ln(1 + \overline{\zeta}_0)$ is the unperturbed value of the chemical potential. By means of (15) and (16), we find for this unperturbed chemical potential

$$\overline{b}_0^K \simeq [a^3 9 \ln(n_\infty^\beta/n)]^{1/3}, \quad \overline{b}_0^D \simeq \left[4a^3 45 \ln\left\{\left(\frac{\tau_D}{\tau_K}\right)^{3/4}\left(\frac{n_\infty^\beta}{n}\right)\right\}\right]^{1/3} \tag{18}$$

Now taking (16) into account, we rewrite (17) in the form of a relationship for c_1,

$$c_1 = \frac{2}{9} a \frac{\overline{b}_0 - \overline{b}}{\overline{b}_0^2} - \frac{1}{6} c_2 \tag{19}$$

TABLE 2. Values of Parameters of Surface Layer for Water, Ethanol, and Benzene, Based on Data of [16]

Substance	$\bar{T}$	$\bar{\zeta}_n$	T	ζ_n^+	ζ_n^-	c_1	c_3	c_4	c_6^+	c_7
Water	265	3,91	266	3,87	3,14	0,0±0,1	0,31	2,5±0,3	3,4±0,4	0
Ethanol	275	1,13	276	0,94	1,08	0,1±0,1	0,13	0,8±0,1	−2,8±0,4	0
Benzene	253	4,32	255	3,94	3,94	0,3±0,1	0,14	0,2±0,1	0,0±0,4	0,1

Thus, if an experimental value is known for $\bar{\zeta}_n$, we can then use (19) to find the coefficients c_1. If the value of c_1 is determined, then (12), with $q = \pm|q|$,* gives two equations for c_4 and $c_6(q)$. We now add and subtract these equations, term by term, considering that $\beta^\pm$ are determined for an identical number of drops. We obtain

$$\beta^s \equiv \frac{1}{2}(\beta^+ + \beta^-) = \beta_0 [1 - (c_1 C_1(\beta_0) + c_3 C_3(\beta_0) - c_4 C_4(\beta_0) + c_7 C_7(\beta_0)) v_0^{-1/3}] \tag{20}$$

$$\beta^a \equiv \beta^+ - \beta^- = 2c_6^+ v_0^{-1} \beta_0 C_6(\beta_0) \tag{21}$$

where the superscripts "+" and "−" indicate that the quantity is determined with $q = +|q|$ and $q = -|q|$, respectively. Equation (20) determines c_4, and Eq. (21) determines c_6^+. Naturally, more nearly complete information on c_1, c_4, and c_6^+, including their temperature dependences, can be obtained if the supersaturations ζ_n (with each sign of the charge) and $\bar{\zeta}_n$ are known for several values of n and $\bar{n}$ at various temperatures. Let us note that Eqs. (19)-(21) are valid regardless of the mode of mass transfer between supercritical drops and vapor (only the unperturbed values ζ_0 themselves depend on the condensation mode).

Let us examine the results obtained by working up data from the experiments of Scharrer [16] on homogeneous and heterogeneous nucleation of water, ethanol, and benzene; the data of Shmitt, Adams, and Zalabsky [6] and Hagen, Kassner, and Miller [7] on homogeneous nucleation of ethanol and water vapor; and the data of White and Kassner [5] on heterogeneous nucleation of water. In Table 2, the values of $\bar{\zeta}_n$, ζ_n^+, and ζ_n^- were taken from [16];[†] the corresponding values of the temperature $\bar{T}$ and T were found on the assumption of adiabatic expansion of volume in the central part of a Wilson chamber, using data on the coefficients of expansion (the initial temperature before expansion, for all of the experimental points, was approximately 290°K. The values of $\bar{n}$ and n coincide for all of the substances and are approximately equal to 5 cm^{-3}. The number density of ions was estimated, following [17], as ~10^4 cm^{-3}. Values of c_6 and c_7 were calculated by the use of Eq. (3). The coefficients c_1, c_4, and $c_6^+ = c_6^+ \cdot$ (q_0), where q_0 is the elementary charge, were found by means of (19)-(21) on the assumption of isothermal condensation and a diffusion regime of supercritical drop growth. In the case of water in the experiment of [16], isothermal conditions were ensured by a hundredfold predominance of the gas (air) density over the water vapor density; in the case of ethanol and benzene, the predominance was tenfold. By means of [3, Eqs. (42) and (45)], it is not difficult to be convinced that with a value of the condensation coefficient $\alpha_c = 1$ (found for water and a number of organic liquids in [18, 19]), the drop size at the end of the condensation process is considerably greater than the length of the free path of a vapor molecule, so that the mode of supercritical drop growth could be considered as diffusional.

As can be seen from Table 2, in the case of ethanol and benzene, the parameter c_4 has the same sign and order of magnitude as c_1, which confirms the estimate of these parameters given in [3, 4]. For water, however, c_4 proves to be very large, whereas c_1 is close to zero.

In addition to the data of [16], we worked up the data of [5-8]. In Fig. 1 we show the experimentally determined relationships for the number of observed drops in homogeneous nucleation of water and ethanol [6-8] and heterogeneous nucleation of water on positive and negative ions [5]. Since the time of artificial cutoff of the nucleation process t_{cut} that was used in [5-8] was much shorter than the time t_i ($t_{cut} \sim 0.01$ sec [6, 7], $t_{cut} \sim 0.001$ sec [8]; with diffusional growth of supercritical drops, $\bar{t}_i \sim$ 1-5 sec and $t_i \sim$ 1-5 sec, $\bar{t}_2 \sim 10^3$ sec and $t_2 \sim 10^3$ sec), the number of drops formed is determined as $\bar{n} = \bar{I} t_{cut}$ and $n = I t_{cut}$. Here $\bar{I} \sim n_\infty^\beta / \tau_K (1 + \bar{\zeta})^2 e^{-\bar{F}(\zeta)}$ and $I \sim (n/\tau_K) e^{-\Delta F(\zeta)}$ are the stationary rates of homogeneous

*The nature of the nuclei (ions) with opposite signs of the charges is not important for the characteristics of the condensation process that are under consideration.
[†]Let us remember that the supersaturation that we are using is obtained by subtracting 1 from the ratio of densities of supersaturated and saturated vapor.
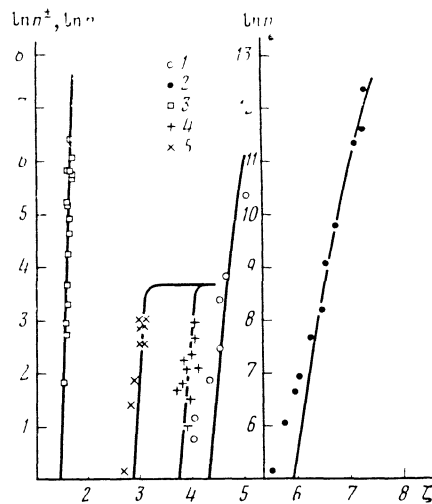
Fig. 1. Experimental and theoretical dependences of $\ln n^{\pm}$ and $\ln n$ on vapor supersaturation. 1) Homogeneous nucleation of water at $\bar{T} = 272°K$ [7] ($c_1 = -0.2 \pm 0.1$); 2) homogeneous nucleation of water at $\bar{T} = 266°K$ [8] ($c_1 = 0.2 \pm 0.1$); 3) homogeneous nucleation of ethanol at $\bar{T} = 262°K$ [6] ($c_1 = 0.10 \pm 0.05$); 4, 5) heterogeneous nucleation of water on positive and negative ions, respectively, at $T = 275°K$ [5] ($c_1 = 0.0 \pm 0.1$, $c_4 = 1.6 \pm 0.3$, $c_6^+ = 3.7 \pm 0.4$).

and heterogeneous nucleation, written with logarithmic accuracy. In the end, in finding values of $\bar{s}_0$ and β_0 corresponding to the experimental points in Fig. 1, into Eq. (8), in place of (15) we should substitute the formula $\bar{F}(\zeta) \simeq \ln (n_\infty^\rho (1 + \bar{\zeta})^2 t_{cut}/\bar{n}\tau_K)$, and in place of (9) the formula $\Delta F(\zeta) \simeq \ln(n t_{cut}(n\tau_K)$. The density of the passive gas (argon) in the experiments of [5-8] was more than two orders of magnitude greater than the density of the vapor, thus justifying the use of the isothermal condensation approximation. The value of c_1 for homogeneous nucleation was determined by means of (19) to be $c_1 = -0.2 \pm 0.1$ [7, 8] for water, and $c_1 = 0.15 \pm 0.05$ at $T = 252°K$ [6] for ethanol. The values of c_4 and c_6^+ for heterogeneous nucleation of water were determined by means of (20) and (21) to be $c_4 = 1.6 \pm 0.3$ and $c_6^+ = 3.7 \pm 0.4$ [5]. The calculated errors include contributions from inaccuracies in measuring the supersaturation, the number of observed drops, and the temperature, as well as error arising from the use of the mean temperature $T = (T^+ + T^-)/2$ in working up the experimental data of [5, 16]. Also included in calculating the error Δc_1 was the contribution due to discarding terms of higher order of smallness in comparison with $c_1 \bar{c_0}^{-1/3}$ in Eqs. (17), (20), and (21). In Fig. 1, in addition to the experimental relationships, we show the theoretical relationships $\ln n^{\pm}(\zeta)$ and $\ln \bar{n}(\zeta)$ corresponding to the mean values found for c_1, c_4, and c_6^+.

Let us note that, in spite of the substantial differences in design of the Wilson chamber, in the nature of the carrier gas, and in the number density of ions in [16] and [5-8], the values calculated for c_1, c_4, and c_6^+ for water on the basis of [16] are close, within the limits of indicated errors, to the results obtained from [5, 7, 8]. This is also the case with the values of c_1 for ethanol calculated on the basis of the data of [16] and [6]. In the interval of temperature T from 245 to 266°K, the temperature does not influence the coefficient c_1 for water, according to a calculation based on the data of [8]. The negative value obtained for c_1 for water may be due to a significant influence in (17), with $c_1 \sim 0$, of the subsequent terms in the expansion in drop curvature parameter (it is not difficult to show that the sign of the second correlation is opposite to the sign of c_1). For ethanol, from [6] in the region of T from 251 to 272°K, it was found that c_1 increases with decreasing temperature, approximately as $dc_1/dT \simeq 0.005°K^{-1}$.

In Table 3, the values of $\mathscr{P}_{0\infty}$ were taken from [11], where they were calculated from data on the electric surface potential of the liquid/vapor boundary. The values of γ_∞ and $\varkappa$ were calculated by means of (3) and (4) with the values of c_1 and c_6^+ from Table 2 and Fig. 1 on the assumption that $c_5^+ = c_6^+$, which was justified in [3, 4]. It can be seen that $\varkappa$ for

TABLE 3. Values of Difference between Radii of Equimolecular Surface and Tension Surface, and Spontaneous Surface Polarization, in the Limit of a Plane Interface, for Water, Ethanol, and Benzene according to Data of [5-8, 16]

Substance	$\lambda_\infty \cdot 10^{-10}$, m	$\varkappa'_{0\infty}$, V	$\varkappa$
Water [17]*	$0,0\pm0,2$	$-0,008$	2,3
Water [5, 7, 8]	$-0,4\pm0,2$	$-0,008$	2,6
Ethanol [17]*	$0,3\pm0,3$	$0,022$	0,7
Ethanol [6]	$0,28\pm0,14$	—	—
Benzene [17]*	$1,0\pm0,3$	0	—

*As in Russian original; possibly in error — Translator.

water and ethanol is positive and is on the order of magnitude of unity, which confirms the estimate given in (4).

LITERATURE CITED

1. F. M. Kuni, Kolloidn. Zh., 46, No. 4, 674 (1984).
2. F. M. Kuni, Kolloidn. Zh., 46, No. 5, 902 (1984).
3. F. M. Kuni, Kolloidn. Zh., 46, No. 6, 1120 (1984).
4. I. M. Lifshits and V. V. Slëzov, Zh. Eksp. Teor. Fiz., No. 2 (8), 480 (1958).
5. D. R. White and J. L. Kassner, jr., J. Aerosol Sci., 2, No. 2, 201 (1971).
6. J. L. Shmitt, G. W. Adams, and R. A. Zalabsky, J. Chem. Phys., 77, No. 4, 2089 (1982).
7. D. E. Hagen, J. L. Kassner, Jr., and R. C. Miller, J. Atmos. Sci., 39, No. 5, 1115 (1982).
8. P. E. Wagner and R. J. Strey, J. Phys. Chem., 85, No. 18, 2694 (1981).
9. F. M. Kuni, A. K. Shchëkin, and A. I. Rusanov, Kolloidn. Zh., 45, No. 4, 682 (1983).
10. F. M. Kuni, A. K. Shchëkin, and A. I. Rusanov, Kolloidn. Zh., 45, No. 5, 901 (1983).
11. F. M. Kuni, A. K. Shchëkin, and A. I. Rusanov, Kolloidn. Zh., 45, No. 6, 1083 (1983).
12. A. K. Shchëkin, A. I. Rusanov, and F. M. Kuni, Kolloidn. Zh., 45, No. 3, 535 (1983).
13. A. W. Castleman, jr. Adv. Colloid Interface Sci., 10, (special issue), 73 (1979).
14. N. N. Tunitskii, Zh. Fiz. Khim., 15, No. 10, 1061 (1941).
15. O. M. Todes, Probl. Kinet. Katal., No. 7, 91 (1949).
16. L. Scharrer, Ann. Phys., 35, No. 7, 619 (1939).
17. T. Glosios, Kolloid-Z., 80, No. 3, 269 (1937).
18. A. I. Neizvestnyi, Results from Experimental Determination of Condensation Coefficient of Water [in Russian], Izd. VNIIGMI—MTsD, Obninsk (1976), p. 50.
19. H. K. Cammenga, in: Current Topics in Material Science, E. Kaldis (ed.), Amsterdam (1980), Vol. 5, p. 335.