

NONLINEARITY OF ELECTRICAL PROPERTIES OF LIQUIDS
IN THERMODYNAMICS OF DROPLETS FORMED ON CHARGED NUCLEI

A. K. Shchekin and T. V. Sasim

UDC 536.421.3:537

The contributions to the work of formation of droplets which are in equilibrium and not in equilibrium with the vapor, as well as the chemical potential, enthalpy, and entropy of the molecules in a droplet, due to dielectric saturation and the electrostriction of the droplet liquid in the strong field of a charged nucleus have been found. The role of these contributions, as well as the dimensions of the ions, in the thermodynamics of condensation on ions, has been investigated. The parameters of a droplet which determine the effects of electrostriction and dielectric saturation have been evaluated by means of comparison with experimental data on the dielectric constants of liquids in strong electric fields.

The problems in the theory of heterogeneous nucleation include the further development of the thermodynamic description of a small droplet formed on a charged nucleus and the investigation of the dependence of the work of formation of a droplet and other thermodynamic characteristics of a droplet on its size, charge, and the magnitude of the charge of the nucleus.

Kaliningrad University. Translated from *Kolloidnyi Zhurnal*, Vol. 50, No. 4, pp. 782-789, July-August, 1988. Original article submitted June 16, 1986.

It would be of interest to take into account the nonlinear electrical effects in the thermodynamics of droplets, whose influence should increase as the size of the droplet decreases. The role of the nonlinear electrical properties of the surface layer of a droplet and of electrostriction in the bulk of a droplet in the theory of nucleation on ions was previously examined in [1-4]. The contribution of dielectric saturation to the dielectric constants of many liquids is comparable to the contribution of electrostriction [5]. Therefore, in the present work we shall supplement the investigations carried out in [1-4] by taking into account the effect of dielectric saturation in the bulk of a droplet.

In a number of studies concerning the theory of nucleation on ions [6-9], values for the dielectric constants of the liquids which were strongly underestimated in comparison to the tabulated values were used for comparisons with experiment. The basis for this was the assumption that the field of the ion has a strong effect on the liquid in a droplet. Systematic consideration of the nonlinear electric contributions to the dielectric constant of the liquid makes it possible to establish the limits for the applicability of the relations of linear electrostatics in the thermodynamics of droplets and to test the assumption just indicated.

Let us select the chemical potential μ , the temperature T , and the induction of the field D as the independent thermodynamic parameters for a one-component liquid dielectric in an electric field. In a strong field the relationship between the field strength E^* and the induction in a dielectric becomes nonlinear. We shall take this into account in a first approximation with the aid of the relation

$$\left(\frac{\partial E}{\partial D}\right)_{\mu, T} = \frac{1}{\epsilon(\mu, T)} + a_2 D^2 \quad (1)$$

where ϵ is the dielectric constant defined as a function of the chemical potential and the temperature; the dependence of the coefficient a_2 on μ at an assigned value of T will be neglected. If the chemical potential μ is not fixed, the value of ϵ is implicitly dependent on D in an electric field $\mu = \mu(D)$: $\epsilon(\mu, T) = \epsilon(\mu(D), T)$. We shall refer to this dependence as the electrostriction effect. The term $a_2 D^2$, in turn, determines the effect of dielectric saturation.

Let us consider a droplet at whose center there is a spherically symmetric insoluble nucleus bearing a charge q . The dimensions of the droplet are assumed to be such that the spherical nucleus-liquid and liquid-vapor surface layers do not intersect. As was shown in [1], the main equations of the thermodynamics of a droplet on a charged nucleus have the form

$$dp_N^{\alpha, \beta} = s^{\alpha, \beta} dT + n^{\alpha, \beta} d\mu - \frac{1}{4\pi} E^{\alpha, \beta} dD \quad (2)$$

$$p_N^{\alpha}(r) - p_N^{\beta}(r) = 2\gamma/r \quad (3)$$

$$d\gamma = -\bar{s}dT - \Gamma d\mu - Dd\mathcal{P} \quad (4)$$

where p_N is the normal component of the pressure tensor in the polarized medium; s is the entropy per molecule; n , the number density of the molecules; γ , the surface tension; r , the radius of the tension surface of the droplet; Γ , the adsorption; \mathcal{P} , the surface polarization; \bar{s} , the surface entropy; the superscript α refers to quantities of the liquid phase; the superscript β refers to quantities of the gaseous phase. The induction D for a spherical dielectric in a central electrostatic field is determined by the ratio $D = q/r'$, where r' is the radius of the point of observation. Taking this into account and using relation (1) we find an expression for $p_N^{\alpha, \beta}$ and n^{α} at $r' = r$ with the aid of (2):

$$p_N^{\alpha}(r) = p_0^{\alpha}(\mu, T) - \frac{q^2}{8\pi\epsilon^{\alpha}(\mu, T)r^4} - \frac{a_2^{\alpha}q^4}{48\pi r^6} \quad p_N^{\beta}(r) = p_0^{\beta}(\mu, T) - \frac{q^2}{8\pi\epsilon^{\beta}(\mu, T)r^4} \quad (5)$$

$$n^{\alpha}(r) = n_0^{\alpha}(\mu, T) + \frac{q^2}{8\pi(\epsilon^{\alpha})^2 r^4} \left(\frac{\partial \epsilon^{\alpha}}{\partial \mu}\right)_T \quad (6)$$

We note that the effects of dielectric saturation in vapors are negligible. This allows us to neglect the term with the coefficient a_2^{β} for p_N^{β} .

Using the method developed in [2] for expansion in a parameter of the curvature of a droplet, we can calculate the correction to any thermodynamic quantity of a droplet for di-

*We are interested in the case of a spherically symmetric field, for which the directions of the vectors E and D coincide; therefore, the sign of the vector will not be indicated for E and D .

electric saturation with the aid of (5) and (6) and Eqs. (2)-(4). In particular, it is not difficult to obtain an expression for the correction μ^{ad} to the value of the chemical potential of a molecule in a droplet of radius r for electrostriction and dielectric saturation

$$\mu^{ad} = -\frac{u_{\infty} q^2}{n_{\infty}^{\alpha} r^4} (\delta_4 - \delta_5 - \delta_6) \quad (7)$$

Here the infinity sign (∞) is used to indicate quantities determined for liquid-vapor equilibrium at an assigned temperature T and a planar phase boundary:

$$\delta_4 = \frac{\theta_{\infty}^{\alpha} v_{\infty}}{4\pi u_{\infty} \epsilon_{\infty}^{\alpha} n_{\infty}^{\alpha} r}, \quad \delta_5 = \frac{\theta_{\infty}^{\alpha} q^2}{8\pi \epsilon_{\infty}^{\alpha} n_{\infty}^{\alpha} r^4}, \quad \delta_6 = \frac{a_2^{\alpha} q^2}{48\pi u_{\infty} r^4} \quad (8)$$

$$u = \frac{1}{8\pi} \left(\frac{1}{\epsilon^{\beta}} - \frac{1}{\epsilon^{\alpha}} \right), \quad \theta^{\alpha} = \left(\frac{\partial \ln \epsilon^{\alpha}}{\partial \mu} \right)_T \quad (9)$$

Expression (7) is valid under the condition that all the dimensionless parameters δ_4 , δ_5 , and δ_6 are small in comparison to unity. This restricts the minimal size of the droplets under consideration, but only to a slight extent, as is clear from numerical evaluations of δ_4 , δ_5 , and δ_6 . We note that the numbering of the parameters here and in the following corresponds to the order in [10].

In view of the fact that our purpose is to apply the results to the theory of nucleation, it is convenient to express the thermodynamic parameters of a droplet as functions of the number of molecules in it v . We find the relationship between v and r with the aid of the relation [3, Eq. (22)]

$$v = n_0^{\alpha}(T, \mu) \frac{4\pi R_g^3}{3} - 4\pi \int_{R(r)}^{R_g} n^{\alpha}(T, \mu, D) r'^2 dr' - v_n \quad (10)$$

Here $n_0^{\alpha}(T, \mu)$ is the number density of the molecules in a macroscopic volume of liquid with a spherical boundary of radius R_g in the absence of a charged nucleus at assigned values of μ and T ; $n^{\alpha}(T, \mu, D)$ is the density of the liquid at the same values of μ and T , but in the presence of the nucleus; $R(r)$ is the radius of the equimolecular surface of the droplet, which is related to the radius of the tension surface r by the expression

$$R = r(1 + \delta_1 + \delta_7) \quad (11)$$

where the small parameters δ_1 and δ_7 have the forms

$$\delta_1 = \lambda_{\infty}/r, \quad \delta_7 = (q/n_{\infty}^{\alpha} r^3) \left(\frac{\partial \mathcal{P}_0}{\partial \mu} \right)_T \quad (12)$$

λ_{∞} is the distance between the equimolecular surface and the tension surface for a planar surface layer between the liquid and the vapor, and \mathcal{P}_0 is the spontaneous surface polarization. The difference between the number of liquid molecules at given T and μ within a sphere of radius R_g in the absence of a nucleus and in its presence is denoted by means of v_n .

The convenience of Eq. (10) is due to the fact that knowledge of the density $n^{\alpha}(T, \mu, D)$ only at $r' \geq R$ is required for the determination of v . This eliminates the problem of determining the density of the liquid in the immediate vicinity of the nucleus, where the nonlinear electrical effects are known to be strong and relation (1) becomes inapplicable. In the case of droplets with values of r for which (1) is valid, the quantity $n^{\alpha}(T, \mu, D)$ in (10) can be determined with the aid of (6) for $r = r'$. Hence it follows that condensation of the dielectric saturation has no effect on the number of molecules in a droplet when the radius of the tension surface is assigned. Next, reasoning precisely as in [3], from (10) with consideration of (6), (8), (9), (11), and (12), we find

$$r(v) = \left(\frac{3}{4\pi n_{\infty}^{\alpha}} \right)^{1/3} v^{1/3} \left[1 - \left(c_1 + \frac{1}{3} c_2 \right) v^{-1/3} + \left(\frac{1}{3} c_3 + c_5 \right) v^{-2/3} - \left(c_7 - \frac{1}{3} v_n \right) v^{-1} \right] \quad (13)$$

Here we have used the following notation:

$$c_1 = (4\pi n_\infty^\alpha/3)^{1/2} \lambda_\infty, \quad c_2 = 2(4\pi n_\infty^\alpha/3)^{1/2} \chi_\infty^\alpha \gamma_\infty$$

$$c_3 = (4\pi n_\infty^\alpha/3)^{1/2} \chi_\infty^\alpha u_\infty q^2, \quad c_5 = \frac{1}{6} (4\pi n_\infty^\alpha/3)^{1/2} \theta_\infty^\alpha q^2 / \varepsilon_\infty^\alpha \quad (14)$$

$$c_7 = \frac{4\pi q}{3} \left(\frac{\partial \mathcal{P}_0}{\partial \mu} \right)_{T, \infty}$$

In addition, $\chi^\alpha = (\partial \ln n^\alpha / \partial p)_T$ is the isothermal compressibility of the liquid. The term with the coefficient v_n in (13) takes into account the finite nature of the dimensions of the nucleus in a first approximation with respect to the small parameter $v_n v^{-1} \ll 1$. Although data on the absolute values of v_n in the case of condensation on ions were not encountered in the literature, the value of v_n may be appreciably greater than unity, since the density of the liquid in the immediate vicinity of the nucleus varies significantly. The value of v_n should obviously be dependent on the values of the charge and radius of the ion and, in the case of polar liquids, on the sign of the charge of the ion.

Substituting $r = r(v)$ in form (13) into Thomson's relation [3, Eq. (11)] for the chemical potential of a molecule in a droplet in the absence of corrections for the curvature and into expression (7) with maintenance of all the terms associated with consideration of dielectric saturation, electrostriction, and the finite nature of the dimensions of the nucleus, in a first approximation with respect to the curvature parameter we find

$$b_v^{ad} \equiv \frac{\mu^{ad}}{kT} = -\frac{2}{9} a v_n v^{-1/2} - \frac{1}{3} a_q v^{-1/2} \left[2c_4 v^{-1/2} - (5c_3 + c_5) v^{-1/2} - \frac{4}{3} v_n v^{-1} \right] \quad (15)$$

Here k is Boltzmann's constant;

$$a = \frac{4\pi \gamma_\infty}{kT} \left(\frac{3}{4\pi n_\infty^\alpha} \right)^{1/2}, \quad a_q = \frac{4\pi u_\infty q^2}{kT} \left(\frac{4\pi n_\infty^\alpha}{3} \right)^{1/2}$$

$$c_4 = \frac{1}{3} \left(\frac{4}{3} \pi n_\infty^\alpha \right)^{-1/2} \theta_\infty^\alpha \gamma_\infty / u_\infty \varepsilon_\infty^\alpha, \quad c_5 = \frac{a_q^2 q^2}{48\pi u_\infty} \left(\frac{4\pi n_\infty^\alpha}{3} \right)^{1/2} \quad (16)$$

Relation (15) can be used to determine the corrections to the values of the enthalpy β_v and the entropy σ_v of the transfer of a molecule from the vapor into a droplet of size v expressed in thermal units and to the value of the work of formation of the droplet F_v . Using the general thermodynamic relations

$$\beta_v = -T \left(\frac{\partial b_v}{\partial T} \right)_v, \quad \sigma_v = \beta_v - b_v, \quad \frac{dF_v}{dv} = b_v - \beta_v \quad (17)$$

we find

$$\beta_v^{ad} = -\frac{2}{9} a v_n v^{-1/2} \left(1 + \tilde{\gamma} - \frac{2}{3} \tilde{n}^\alpha + \tilde{v}_n \right) -$$

$$-\frac{2}{3} a_q c_4 v^{-1/2} \left(1 - \frac{1}{3} \tilde{n}^\alpha + \tilde{\theta}^\alpha + \tilde{\gamma} - \tilde{\varepsilon}^\alpha \right) +$$

$$+\frac{5}{3} a_q c_5 v^{-1/2} \left(1 + \tilde{u} + \frac{2}{3} \tilde{n}^\alpha + \tilde{\theta}^\alpha - \tilde{\varepsilon}^\alpha \right) +$$

$$+\frac{1}{3} a_q c_3 v^{-1/2} \left(1 + \frac{5}{3} \tilde{n}^\alpha + \tilde{a}_2^\alpha \right) + \frac{4}{9} a_q v_n v^{-1/2} \left(1 + \tilde{u} + \frac{1}{3} \tilde{n}^\alpha + \tilde{v}_n \right) \quad (18)$$

$$\sigma_v^{ad} = -\frac{2}{9} a v_n v^{-1/2} \left(\tilde{\gamma} - \frac{2}{3} \tilde{n}^\alpha + \tilde{v}_n \right) - \frac{2}{3} a_q c_4 v^{-1/2} \left(\tilde{\theta}^\alpha - \frac{1}{3} \tilde{n}^\alpha + \tilde{\gamma} - \tilde{\varepsilon}^\alpha \right) +$$

$$+\frac{5}{3} a_q c_5 v^{-1/2} \left(\tilde{u} + \frac{2}{3} \tilde{n}^\alpha + \tilde{\theta}^\alpha - \tilde{\varepsilon}^\alpha \right) + \frac{1}{3} a_q c_3 v^{-1/2} \left(\frac{5}{3} \tilde{n}^\alpha + \tilde{a}_2^\alpha \right) +$$

$$+\frac{4}{9} a_q v_n v^{-1/2} \left(\tilde{u} + \frac{1}{3} \tilde{n}^\alpha + \tilde{v}_n \right) \quad (19)$$

$$F_v^{ad} = \frac{2}{3} a v_n v^{-1/2} + a_q c_4 v^{-1/2} - a_q \left(c_3 + \frac{1}{5} c_5 \right) v^{-1/2} - \frac{1}{3} a_q v_n v^{-1/2} \quad (20)$$

where any quantity x marked with a tilde has the form $\tilde{x} \equiv -d \ln x_\infty / d \ln T$.

The expression for the work of formation F_v of a droplet makes it possible to find the height of the activation barrier for nucleation $\Delta F = F_{v_c} - F_{v_e}$, where v_c and v_e are roots of the equation $dF_v/dv = 0$ ($v_c > v_e$). The influence of the corrections associated with dielectric saturation, electrostriction, and the finite nature of the dimension of an ion investigated on the intensity of the formation of droplets on ions under the conditions of a Wilson cloud chamber can thereby be evaluated.

We shall use N to denote the number of droplets observed at the end of the condensation process. In experiments of various types performed with a Wilson cloud chamber, the value of N and the height of the activation barrier ΔF at the maximum degree of supersaturation of the vapor ζ are related by the expression

$$N = Ae^{-B\Delta F} \quad (21)$$

The explicit form of the parameters A and B is determined by the conditions of the experiment. For example, in cases in which the process of the formation of new droplets ceases as a result of the exhaustion of the vapor by droplets growing under free-molecule condition, the parameters A and B have the forms [11, Eqs. (36) and (37)]

$$A = \eta \left(\frac{n_{\infty}^0}{\eta} \right)^{1/4}, \quad B = \frac{3}{4}$$

(η is the number density of the ions in the vapor).

Using the method developed in [4], we shall find the dependence of the chemical potential of the vapor b corresponding to the maximum degree of supersaturation of the vapor ζ on the number N of droplets formed. This can be done with any accuracy with respect to the small parameters $c_4 v^{-1/3}$, $c_5 v^{-4/3}$, $c_9 v^{-4/3}$, and $v_n v^{-1}$ with the aid of relation (21). We write the expression for the height of the activation barrier for nucleation without consideration of the corrections with respect to the curvature parameter in the form $\Delta F^{(0)} = F_{v_{c0}}^{(0)} - F_{v_{e0}}^{(0)}$, where

$$F_v^{(0)} = -bv + \alpha v^{1/2} + a_q v^{-1/2}, \quad \left. \frac{dF_v^{(0)}}{dv} \right|_{v=v_{c0}}^{v=v_{e0}} = 0 \quad (22)$$

The latter of relations (22) defines the relationship between $b = b^{(0)}$, on the one hand, and v_{c0} and v_{e0} , on the other hand. With the aid of the expression for $F_v^{(0)}$, it is then not difficult to establish the relation between $\Delta F^{(0)}$ and $b^{(0)}$. Since the values of $\Delta F^{(0)}$ and N for assigned experimental conditions are related by Eqs. (21), a unique correspondence between N and $b^{(0)}$ can be established.

We shall now consider how $b^{(0)}$ varies for an assigned value of N , if the corrections for electrostriction, dielectric saturation, and the finite nature of the dimensions of the nucleus are taken into account in the height of the activation barrier. At an assigned value of N , with the aid of (21) we set

$$\Delta F^{(0)}(b^{(0)}) = \Delta F(b)$$

or

$$F_{v_{c0}}^{(0)} - F_{v_{e0}}^{(0)} = F_{v_c}^{(0)} - F_{v_e}^{(0)} + F_{v_c}^{ad} - F_{v_e}^{ad} \quad (23)$$

where b , v_c , and v_e are determined from the equation $d(F_v^{(0)} + F_v^{ad})/dv = 0$. Using (20) and (22) and expanding the right-hand side of (23) in a Taylor series relative to v_{c0} and v_{e0} according to the largest of the small parameters $c_4 v^{-1/3}$, $c_5 v^{-4/3}$, $c_9 v^{-4/3}$, and $v_n v^{-1}$, in a first approximation we find

$$\begin{aligned} \frac{b - b^{(0)}}{b^{(0)}} &= \frac{2}{3} \alpha v_n b^{(0)-1} \frac{v_{c0}^{-1/2} - v_{e0}^{-1/2}}{v_{c0} - v_{e0}} - \frac{1}{3} a_q v_n b^{(0)-1} \frac{v_{c0}^{-3/2} - v_{e0}^{-3/2}}{v_{c0} - v_{e0}} \\ &- a_q c_4 b^{(0)-1} \frac{v_{e0}^{-1/2} - v_{c0}^{-1/2}}{v_{c0} - v_{e0}} + a_q \left(c_5 + \frac{1}{5} c_9 \right) b^{(0)-1} \frac{v_{e0}^{-5/2} - v_{c0}^{-5/2}}{v_{c0} - v_{e0}} \end{aligned} \quad (24)$$

According to the latter of relations (22), the first and second terms on the right-hand side of (24) compensate one another. Thus b is not dependent on v_n . As the degree of supersaturation of the vapor is increased, the values of v_{e0} and v_{c0} tend to $v_0 = 2a_q/a$, and the value of $b^{(0)}$ tends to its threshold value $b_{\max}^{(0)} = (1/2)av_0^{-1/3}$, which corresponds to barrier-free nucleation on the ions. It can be shown that the multipliers in front of c_4 , c_5 , and c_9 in (24) increase with increasing degrees of supersaturation. Performing the limiting transition at $v_{e0} \rightarrow v_{c0} \rightarrow v_0$ in (24) and taking into account the equality $c_5 = (1/4)v_0c_4$, which follows from (14) and (16), we find that the maximum relative contribution of electrostriction and the dielectric saturation of the liquid to expression (24) for the chemical potential of the vapor is defined as

$$b_{\max}^{ad} = \left(\frac{b - b^{(0)}}{b^{(0)}} \right)_{\max} = -\frac{1}{4}c_4v_0^{-1/3} + \frac{1}{3}c_9v_0^{-1/3} \quad (25)$$

With the aid of (25) it is easy to evaluate the role of the corrections investigated in the calculations of the initial supersaturation of the vapor for an assigned number of droplets formed in a Wilson cloud chamber. The absence of a correction with v_n in (24) and (25) indicates that the rate of the condensation process on ions in a Wilson cloud chamber does not depend on the size of the ions. Hence it follows that the asymmetry of the rate of nucleation on ions of different signs cannot be attributed to the difference between the sizes of positive ions (which are usually ions of alkali metals) and negative ions (which are usually halide ions).

Table 1 presents the values of the parameters ϵ_∞^α , n_∞^α , v_0 , a_2^α , $\bar{\epsilon}^\alpha$, \bar{n}^α , c_4 , c_5 , and c_9 for carbon tetrachloride, benzene, chloroform, water, methanol, and ethanol. The values of a_2^α were calculated from the experimental values of $(\epsilon^\alpha - \epsilon_\infty^\alpha)/E^2$ presented in [5, 12, 13] for a liquid placed in a strong homogeneous electric field of strength E . When the data from these experiments were treated in the original works, the contribution of electrostriction to the measured values of $(\epsilon^\alpha - \epsilon_\infty^\alpha)/E^2$ were excluded. Therefore, we may set

$$a_1^\alpha = -\frac{\epsilon^\alpha - \epsilon_\infty^\alpha}{E^2 (\epsilon_\infty^\alpha)^2}$$

The values of θ_∞^α were found with the use of the formula $\theta_\infty^\alpha = n_\infty^\alpha \lambda_\infty^\alpha \bar{\epsilon}^\alpha / \bar{n}^\alpha$. This relation for θ_∞^α follows from the definition of θ in (9) under the condition that

$$\left(\frac{\partial \epsilon^\alpha}{\partial T} \right)_n \ll \left(\frac{\partial \epsilon^\alpha}{\partial T} \right)_p$$

As was shown in [14], this condition is, in fact, fulfilled for the liquids under consideration. The substances in Table 1 were selected according to the following criteria. Water, ethanol, and methanol, which are liquids with high dielectric constants, large values of $(\epsilon^\alpha - \epsilon_\infty^\alpha)/E^2$, and relatively small molecular weights, are traditional objects of nucleation theory. Carbon tetrachloride and benzene are nonpolar compounds with small dielectric constants and large values of a_2^α , and chloroform is a polar compound with a relatively small dielectric constant and a relatively high value of a_2^α .

We see that the value of c_9 for water is very small, while the values of c_4 and c_5 are comparatively large. The values of c_9 for the alcohols are an order of magnitude greater

TABLE 1. Values of the Principal Parameters Appearing in the Relations for the Correction due to Electrostriction and Dielectric Saturation ($T = 293$ K, $q = 1.6 \cdot 10^{-19}$ C)

Substance	ϵ_∞^α	$n_\infty^\alpha, \text{m}^{-3}$	v_0	$a_2^\alpha \cdot 10^{10} \text{m}^2 / \text{V}^2$	$\bar{\epsilon}^\alpha$	\bar{n}^α	c_4	c_5	c_9
CCl_4	2,24	$6,2 \cdot 10^{27}$	9,83	-1,9	0,22	0,36	0,09	0,21	-0,90
Benzene	2,28	$6,8 \cdot 10^{27}$	10,09	-2,3	0,25	0,36	0,09	0,23	-1,25
Chloroform	4,80	$7,5 \cdot 10^{27}$	16,57	$+6,6 \cdot 10^{-1}$	0,35	0,38	0,04	0,15	+0,28
Water	80,08	$3,3 \cdot 10^{28}$	35,15	$+2,4 \cdot 10^{-3}$	1,46	0,08	0,08	0,68	+0,01
Methanol	32,35	$1,5 \cdot 10^{28}$	50,61	$+6,2 \cdot 10^{-3}$	1,54	0,34	0,02	0,27	+0,06
Ethanol	25,00	$1,0 \cdot 10^{28}$	35,62	$+1,2 \cdot 10^{-1}$	1,76	0,32	0,03	0,22	+0,07

than the value for water, but they are appreciably smaller than the values for the other substances listed in Table 1. The values of c_4 and c_5 for the alcohols are close to the corresponding values for benzene, carbon tetrachloride, and chloroform. The largest values of c_9 are observed for benzene and carbon tetrachloride.

Thus, the results of the thermodynamic investigation carried out here of the combined effects of dielectric saturation and electrostriction in the theory of nucleation on charged nuclei are as follows. In calculations of the thermodynamic quantities of a droplet, these effects result in the appearance of corrections with the coefficients c_5 and c_9 . It is seen with the aid of the values presented in Table 1 that in the case of a unit charge on the nucleus, the relative role of these corrections in the expressions for the chemical potential and the work of formation of a droplet is small, but their role in the expression for the enthalpy and especially for the entropy per molecule in a droplet may be significantly greater. As the charge of the droplet nucleus is increased, the values of c_5 and c_9 increase as z^2 , where z is the multiplicity of the charge of the nucleus. The contribution of the corrections with these coefficients for the thermodynamic quantities of small droplets will increase accordingly. With respect to the consideration of electrostriction and dielectric saturation in the kinetics of the condensation of droplets under the conditions of a Wilson cloud chamber, as is seen from Table 1 and relation (25), the value of the maximum correction b_{\max}^{ad} for the effects under consideration in the dependence of the chemical potential of the vapor on the number of droplets formed is small. When the charge of the nucleus is increased by a factor of z , the terms $(1/4)c_4v_0^{-1/3}$ and $(1/3)c_9v_0^{-4/3}$ in (25) decrease by a factor of $z^{2/3}$. Therefore, at any value of z the value of $(b - b^{(0)})/b^{(0)}$, which is determined according to (24), will certainly be small. This allows us, in general, to neglect the corrections for dielectric saturation and electrostriction in calculations of the rate of the nucleation of droplets in a Wilson cloud chamber and to use the tabulated values of the dielectric constant of the liquid. We should also mention the additional finding that in the first approximation with respect to the curvature parameter of a droplet used everywhere in this work, the rate of the nucleation process on ions does not depend on the size of the ions.

LITERATURE CITED

1. A. I. Rusanov and F. M. Kuni, *Kolloidn. Zh.*, 44, No. 5, 934 (1982).
2. F. M. Kuni, A. K. Shchekin, and A. I. Rusanov, *Kolloidn. Zh.*, 45, No. 4, 682 (1983).
3. A. K. Shchekin, A. I. Rusanov, and F. M. Kuni, *Kolloidn. Zh.*, 46, No. 3, 535 (1984).
4. F. M. Kuni, A. K. Shchekin, and K. V. Kopeikin, *Kolloidn. Zh.*, 47, No. 2, 295 (1985).
5. C. J. F. Bottcher, *Theory of Electric Polarization*, Elsevier, Amsterdam (1973), p. 377.
6. D. R. White and J. L. Kassner, Jr., *J. Aerosol Sci.*, 2, No. 2, 201 (1971).
7. L. J. Chan and V. A. Mohnen, *J. Atmos. Sci.*, 37, No. 10, 2323 (1980).
8. S. H. Suck, *J. Chem. Phys.*, 75, No. 10, 5090 (1981).
9. S. H. Suck, D. E. Hagen, J. L. Kassner, Jr., and L. E. Stoddard, *J. Chem. Phys.*, 79, No. 9, 4502 (1983).
10. A. K. Shchekin, *Kolloidn. Zh.*, 48, No. 5, 980 (1986).
11. F. M. Kuni, *Kolloidn. Zh.*, 46, No. 5, 902 (1984).
12. S. Kielich, *Dielectric and Related Molecular Processes*, Vol. 1, London (1972), p. 192.
13. G. P. Jones, *Dielectric and Related Molecular Processes*, Vol. 2, London (1975), p. 198.
14. I. L. Fabelinskii, *Molecular Scattering of Light* [in Russian], Nauka, Moscow (1965), p. 42.