

6. BARRIERLESS NUCLEATION IN VAPORS OF ORGANIC LIQUIDS

A. K. Shchekin, A. I. Rusanov, and F. M. Kuni

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Values have been found for the chemical potential of the vapor corresponding to the threshold of barrierless nucleation on singly charged ions of opposite signs for methanol, ethanol, chloroform, chlorobenzene, benzene, and carbon tetrachloride. By comparison with experiment, values have been determined for the parameters describing the asymmetry of chemical potential with respect to the sign of the ionic charge. Corrections due to the dependence of the liquid permittivity on the chemical potential have been found in analytical form for the thermodynamic quantities of a small drop.

In [1-3], analytical expressions were derived for the thermodynamic quantities of a drop having spontaneous polarization in the surface layer and existing in a strong electric field of the nucleus. The formulas that were derived are asymptotic expansions of the corresponding quantities of the drop with respect to six small dimensionless parameters: $c_1 v^{-1/3}$, $c_2 v^{-1/3}$, $c_3 v^{-1/3}$, $c_4 v^{-1/3}$, $c_5 v^{-1}$, $c_6 v^{-1}$, where v is the number of molecules in the drop; the coefficients c_1, \dots, c_6 have the form [2], Eq. (10) :

$$\begin{aligned} c_1 &\equiv (4\pi\rho_\infty^\alpha/3)^{1/3}\lambda_\infty, & c_2 &\equiv 2(4\pi\rho_\infty^\alpha/3)^{1/3}\chi_\infty\gamma_\infty, & c_3 &\equiv (4\pi\rho_\infty^\alpha/3)^{1/3}\chi_\infty u_\infty q^2, \\ c_4 &\equiv (4\pi\rho_\infty^\alpha/3)^{1/3}k_1/2u_\infty, & c_5^\pm &\equiv \pm \frac{4\pi}{3}|q|\left(\frac{d\mathcal{P}_0}{d\mu}\right)_\infty, & c_6^\pm &\equiv \pm \frac{2\pi}{3}\rho_\infty^\alpha \frac{k_2|q|}{u_\infty} \end{aligned} \quad (1)$$

Here, ρ is the number of molecules in unit volume; λ_∞ is the difference between the radius of the equimolecular surface and the radius of the tension surface for a plane interface between liquid and gas phases; γ is the surface tension; χ is the compressibility of the liquid; q is the electric charge;

$$u \equiv (1/8\pi)(1/\epsilon^\beta - 1/\epsilon^\alpha) \quad (2)$$

ϵ is the permittivity; \mathcal{P}_0 is the spontaneous surface polarization; k_1 and k_2 are the coefficients in the expression for the induced surface polarization $\mathcal{P}_e: \mathcal{P}_e = k_1 q/r^2 + k_2 q^2/r^4$; r is the radius of the tension surface; μ is the chemical potential, measured from the value μ_∞ ; the superscripts α and β are used to denote the liquid and gas phases, respectively; the symbol $^\alpha$ denotes the case of a plane interface between the phases and the absence of a field; the plus sign or minus sign on a quantity indicates that it is determined with $q = +|q|$ or $q = -|q|$, respectively.

Of particular interest for comparison with experiment are the expressions for the chemical potential at the threshold of barrierless nucleation. Convenient characteristics of barrierless nucleation on positively and negatively charged nuclei are the half-sum (b^S) and difference (b^A) of the threshold values of the chemical potential, taken at the same temperature and expressed in heat units. For b^S and b^A and the ratio b^A/b^S , we have {[3], Eqs. (31) (33)}:

$$b^S = \frac{1}{2} a \left(\frac{2a_q}{a}\right)^{-1/3} \left[1 - 2\left(c_1 + \frac{3}{16}c_2 - \frac{1}{3}c_4\right)\left(\frac{2a_q}{a}\right)^{-1/3}\right] \quad (3)$$

$$b^A = \frac{8}{9} a \left(\frac{2a_q}{a}\right)^{-1/3} \left[1 - \frac{15}{4}\left(c_1 + \frac{1}{6}c_2 - \frac{5}{9}c_4\right)\left(\frac{2a_q}{a}\right)^{-1/3}\right] c_6^\pm \quad (4)$$

$$b^a/b^s = \frac{16}{9} \left(\frac{2a_q}{a}\right)^{-1} \left[1 - \frac{7}{4} \left(c_1 + \frac{1}{7} c_2 - \frac{17}{21} c_4\right) \left(\frac{2a_q}{a}\right)^{-1/3}\right] c_5^+ \quad (5)$$

In (4) and (5), it is assumed that $c_5^\pm = c_6^\pm$, and the coefficients α and α_q are determined as {[2], Eqs. (14) and (15)}:

$$a \equiv \frac{4\pi\gamma_\infty}{kT} \left(\frac{3}{4\pi\rho_\infty^\alpha}\right)^{2/3}, \quad a_q \equiv \frac{4\pi u_\infty}{kT} q^2 \left(\frac{4\pi\rho_\infty^\alpha}{3}\right)^{1/3} \quad (6)$$

where k is the Boltzmann constant and T is temperature. The value of q in Eqs. (3)–(5) is limited on the low side by the conditions of applicability of the theory. In [3], an estimate was obtained for the optimal value of the quantity $z \equiv q/q_0$ (q_0 is the elementary charge), which is also the smallest possible value {[3], Eq. (37)}:

$$z_{\min} \sim 5^{3/2} c_m^{3/2} (2a_{q_0}/a)^{-1/2} \quad (7)$$

Here, c_m is equal to the larger of the values of c_1 and c_2 (the curvature parameter $c_m v^{-1/3}$ is majorizing with respect to the other small parameters of the theory). As can be seen from (7), limitations imposed on the value of q are determined both by the characteristics of the surface layer and by the properties of the bulk part of the drop of the particular substance under investigation. If z_{\min} for some substance is substantially greater than unity, Eqs. (3)–(5) are insufficiently accurate for a description of nucleation in the vapor of such a substance on singly charged ions.

A number of experiments have been reported [4–9] on the determination of levels of limiting supersaturation ξ of vapor of one-component organic liquids above which the condensation process on ions begins to proceed rapidly. Being interested in the values of $b = \ln \xi$, we can consider that the values of b found in these experiments, in spite of different criteria for the start of condensation, lie close to the value corresponding to barrierless nucleation. For comparison, we will take the most detailed studies of Scharrer [8], on six organic substances: methanol, ethanol, chloroform, chlorobenzene, benzene, and carbon tetrachloride. Also of interest is a comparison of the properties of the substances with the properties of water.

We will first examine liquids with permittivities that are large in comparison with unity. Here we refer to the alcohols, chloroform, and chlorobenzene. In Table 1 we have listed values of the condensation temperature* and the limiting values of $b^{\text{S}_{\text{exp}}}$, $b^{\alpha_{\text{exp}}}$, and $b^{\alpha_{\text{exp}}}/b^{\text{S}_{\text{exp}}}$ corresponding to the appearance of several drops in a cubic centimeter of the vapor ("rain limit"). In the last column of Table 1 we show the results obtained in experiments performed by Frumkin [10, 11] on the surface potential $\Delta\varphi = 4\pi\mathcal{P}_0$ of these liquids (relative to the potential of water†). The values of $\Delta\varphi$ for water were taken from [12]. In Table 2, the values of a , α_{q_0} , and c_2 were determined from Eqs. (6) and (1) by means of the data of [13]. The coefficient c_1 (and correspondingly λ_∞) was found in accordance with the theory of isothermal homogeneous condensation [14] on the basis of the limiting supersaturations in the absence of ions that were measured by Scharrer [8]. Let us note that the values of λ_∞ thus determined for all of the substances are considerably smaller than the theoretical estimates made in [15]. For methanol, the values of c_1 , λ_∞ , and, correspondingly, $b^{\text{S}_{\text{theor}}}$ are not given in Table 1, in view of the ambiguity in the estimates obtained by working up the data of different investigators [6, 8, 9, 16].‡ The value of c_5^+ was obtained in the first approximation from (5) by means of the value of $b^{\alpha_{\text{exp}}}/b^{\text{S}_{\text{exp}}}$ from Table 1. The parameter κ was determined here in accordance with (1) and the relationship {[1], Eq. (44)}:

$$(d\mathcal{P}_0/d\mu)_\infty = -\kappa\mathcal{P}_{0\infty}/kT \quad (8)$$

Finally, the values of $b^{\text{S}_{\text{theor}}}$ were calculated by the use of Eq. (3) on the assumption that $c_1 = c_4$. It can be seen that for all of the substances other than methanol, as was expected,

*The condensation temperatures on ions differing in sign under the conditions of experiment [8] differed slightly, and this was taken into account in the indicated error in the values of T , a , and α_{q_0} .

†Directions from the center of the drop are positive.

‡From experiments with a Wilson chamber [6, 8], we find that $c_1 < 0$, whereas from the results of experiments with a diffusion chamber [9, 16], we find that $c_1 \approx 0$.

TABLE 1. Limiting Values of Chemical Potential of Vapor and Difference of Electric Potentials at Liquid-Vapor Interface

Substance	$T, ^\circ K$	b_{exp}^s	b_{exp}^a	b_{exp}^a/b_{exp}^s	$\Delta\phi, V$
Water	$265,8 \pm 1,3$	1,50	$\pm 0,16$	$+0,11$	$\sim -0,1$
Methanol	$265,8 \pm 1,5$	1,15	$-0,14$	$-0,12$	$\pm 0,378 \pm 0,003$
Ethanol	$276,3 \pm 0,7$	0,70	$-0,07$	$-0,10$	$\pm 0,378 \pm 0,003$
Chloroform	$257,1 \pm 0,4$	1,26	$-0,04$	$-0,03$	$-0,047 \pm 0,003$
Chlorobenzene	$249,7 \pm 1,3$	2,25	$+0,14$	$+0,06$	—
Benzene	255	1,60	0	0	$+0,01 \pm 0,003$
Carbon tetrachloride	$248 \pm 0,4$	1,79	$+0,10$	$+0,06$	0

TABLE 2. Coefficients in Expansion in Drop Curvature Parameter, and Threshold Value of Chemical Potential of Vapor

Substance	a	a_0	c_1	$\lambda_{\infty} \cdot 10^{10}, m$	c_2	c_3	κ	c_7	b_{theor}^s
Water	$9,75 \pm 0,07$	$163,1 \pm 0,7$	$0,00 \pm 0,08$	$0,0 \pm 0,2$	$0,31 \pm 0,02$	-2	$-1,4$	0	$1,47 \pm 0,08$
Methanol	$5,36 \pm 0,06$	$125,8 \pm 0,8$	—	—	$0,15 \pm 0,01$	-3	$-0,8$	0	—
Ethanol	$6,34 \pm 0,04$	$106,9 \pm 0,3$	$+0,16 \pm 0,08$	$+0,5 \pm 0,2$	$0,13 \pm 0,01$	-2	$+0,5$	0	$0,80 \pm 0,05$
Chloroform	$11,32 \pm 0,03$	$83,4 \pm 0,2$	$+0,55 \pm 0,06$	$+1,7 \pm 0,2$	$0,13 \pm 0,01$	$-0,3$	—	0	$1,57 \pm 0,16$
Chlorobenzene	$15,85 \pm 0,15$	$84,0 \pm 0,5$	$+0,44 \pm 0,06$	$+1,5 \pm 0,2$	$0,15 \pm 0,01$	$-0,4$	—	0	$2,55 \pm 0,24$
Benzene	$12,63 \pm 0,02$	$57,5 \pm 0,1$	$+0,43 \pm 0,06$	$+1,4 \pm 0,2$	$0,14 \pm 0,01$	0	—	$0,11 \pm 0,01$	$2,21 \pm 0,22$
Carbon tetrachloride	$13,25 \pm 0,04$	$56,7 \pm 0,3$	$+0,42 \pm 0,06$	$+1,4 \pm 0,2$	$0,13 \pm 0,01$	$-0,3$	—	$0,10 \pm 0,01$	$2,38 \pm 0,23$

these values lie close to the limiting values of b_{exp}^s . In the case of chloroform and chlorobenzene, the value of z_{min} determined in accordance with (7) proved to be slightly greater than unity, which can be explained by the large error in the corresponding values of b_{theor}^s .

In view of (1), (4), and (8), the sign of c_3^+ (and the sign of c_6^+), coinciding in our calculation with the sign of b_{exp}^a , are opposite to the sign of $\Delta\phi$. We can convince ourselves that, for the alcohols in the experiment, these signs are actually different. Since, in the case of the alcohols, the values of $\Delta\phi$ have been measured for the pure substances, we determined the parameter κ . The values found for κ proved to be positive and on the order of unity, which had been assumed previously in the theory [1].

In the case of chloroform with respect to the potential of water, we measured $\Delta\phi$ of a saturated solution of chloroform and water. In view of the low solubility of chloroform, the value listed for $\Delta\phi$ cannot be identified in absolute magnitude with the surface potential of pure chloroform; however, the sign indicated for $\Delta\phi$ should be correct. Since this sign is negative, it requires that b^a (and c_3^+) be positive, whereas, for chloroform, we have $b_{exp}^a < 0$. The reason for this discrepancy may be the substantial influence of nonisothermality of the condensation process on the limiting supersaturation of chloroform vapor.*

For chlorobenzene, no data are available on $\Delta\phi$. However, when we consider the empirical relationship noted in [10], that the presence of chlorine atoms in a molecule leads, in the case of a polar substance, to $\Delta\phi < 0$, we see the agreement between the signs of b^a and b_{exp}^a that is required by the theory.

For substances with low values of ϵ^α , there is a breakdown of the strong inequality $\epsilon^\alpha \gg 1$ that was used in [1-3], this inequality having made it possible to neglect the dependence of ϵ^α on μ . For low permittivities, the dependence $\epsilon^\alpha(\mu)$ becomes significant; and, in the case of a strong field of the nucleus, in view of $\mu = \mu(q)$, the dependence leads to nonlinearity of the electric properties of the liquid phase. This nonlinearity is unrelated to the phenomenon of dielectric saturation, i.e., to the explicit dependence of ϵ^α on the strength of the electric field E^α . With a fixed value of μ , the relationship between the field strength E^α and the induction $D = q/r^2$ remains linear: $D = \epsilon^\alpha(\mu)E^\alpha$.

*Let us note that chloroform has the highest vapor density of all of the substances examined; therefore, the thermalizing influence of a passive gas (air under the conditions of [8]) on the chloroform will be the least for any of the substances.

As substances with small values of ε^α for which experimental results have been reported on condensation on ions, we can name benzene [7, 8], carbon tetrachloride [8], toluene [7], and certain organic acids [5].

Let us examine successively what changes are introduced into the theory developed in [1-3] by accounting for the dependences $\varepsilon^\alpha = \varepsilon^\alpha(\mu)$. We will introduce the new quantity $\theta \equiv (1/\varepsilon^\alpha)(d\varepsilon^\alpha/d\mu)$. We can consider that it has a constant value $\theta = \theta_\infty$ in the region of chemical potentials of interest to us; in evaluating θ_∞ , we make use of the relationship

$$\theta_\infty \lesssim \rho_\infty^\alpha \chi_\infty \quad (9)$$

This estimate is supported by experiment [17], where, in the case of water at 0°C, the measured value of $(d \ln \varepsilon^\alpha/dp)_\infty$ (p is the pressure) proved to be equal to χ_∞ . According to (9), the corrections in the expressions for the thermodynamic quantities of a drop that are related to deviation of θ_∞ from zero are no greater than the correction for compressibility. Assuming that they are small, we can write for $u = u(\mu)$

$$u = u_\infty (1 + (1/u_\infty)(du/d\mu)\mu) \quad (10)$$

Taking the definition (2) into account, after expanding μ in (10) by means of the relationship {[1], Eq. (12)},

$$\mu = \mu^{(1)} = 2\gamma_\infty/\rho_\infty^\alpha r - u_\infty q^2/\rho_\infty^\alpha r^4 \quad (11)$$

we obtain

$$u = u_\infty (1 + \delta_7 - \delta_8) \quad (12)$$

Here,

$$\delta_7 \equiv \frac{\theta_\infty \gamma_\infty}{4\pi u_\infty \varepsilon_\infty^\alpha \rho_\infty^\alpha r}, \quad \delta_8 \equiv \frac{\theta_\infty q^2}{8\pi \varepsilon_\infty^\alpha \rho_\infty^\alpha r^4} \quad (13)$$

are new dimensionless parameters, supplemental to those introduced in [1]: $\delta_1 \equiv \lambda_\infty/r$,

$\delta_2 \equiv 2\chi_\infty \gamma_\infty/r$, $\delta_3 \equiv \chi_\infty u_\infty q^2/r^4$, $\delta_4 \equiv k_1/2u_\infty r$, $\delta_5 \equiv \frac{q}{\rho_\infty^\alpha r^3} \left(\frac{d\rho_0}{d\mu} \right)_\infty$, and $\delta_6 \equiv k_2 q/2u_\infty r^3$. Entering as the

majorizing parameter, as before, is the largest of the curvature parameters δ_1 and δ_2 . The same as in (12), we will always neglect in the future quantities of the second order of smallness with respect to the curvature parameter.

When an electric field is present, the dependence $\varepsilon^\alpha(\mu)$ leads to slight nonuniformity of the drop substance, and the density ρ^α begins to depend on the distance from the nucleus r' {[18], Eq. (19)}

$$\rho^\alpha(\mu, D) = \rho_0^\alpha(\mu) + \frac{q^2}{8\pi(\varepsilon^\alpha)^2 r'^4} \frac{d\varepsilon^\alpha}{d\mu} \quad (14)$$

Remembering the relationship for $\rho_0^\alpha(\mu)$ {[1], Eq. (28)} $\rho_0^\alpha(\mu) = \rho_\infty^\alpha(1 + \delta_2 - \delta_3)$, and also the definition of θ_∞ in (13), we write (14) in the form

$$\rho^\alpha(r') = \rho_\infty^\alpha (1 + \delta_2 - \delta_3 + \delta_8) \quad (15)$$

where, in contrast to δ_2 and δ_3 determined for the radius of the tension surface r , the parameter δ_8 is determined for an arbitrary point of observation r' ($r' \geq 10^{-9}$ m).

Examining the expressions for R (the radius of the equimolar surface), $\mathcal{P} = \mathcal{P}_0 + \mathcal{P}_e$ and γ , we are convinced that they remain unchanged {[1], Eqs. (38), (36), (40)}

$$R = r(1 + \delta_1 + \delta_5) \quad (16)$$

$$q\mathcal{P} = q\mathcal{P}_{0x} + 2\gamma_\infty r^2 \delta_5 + 2u_\infty (q^2/r) \left(\delta_4 - \frac{1}{2} \delta_5 + \delta_6 \right) \quad (17)$$

$$\gamma = \gamma_\infty (1 - 2\delta_1) + u_\infty (q^2/r^3) \left(\delta_1 + \delta_4 + \frac{4}{3} \delta_6 \right) \quad (18)$$

In order to find the relationship for μ in the second approximation with respect to the curvature parameter, let us return to the equations {[1], Eqs. (7) and (11)}:

$$\Delta\rho_0^\alpha(\mu) + u(\mu)q^2/r^2 = 2\gamma(\mu, D)/r \quad (19)$$

$$\Delta\rho_0^\alpha(\mu) = \rho_\infty^\alpha \cdot \mu \cdot \left(1 + \frac{1}{2} \rho_\infty^\alpha \chi_\infty \mu\right) \quad (20)$$

where $\Delta\rho_0$ is the deviation of the pressure (in the absence of a field) from its value with $r = \infty$. After substituting (18) into the right-hand side of (19) and using for the determination of the correction term in (20) the formula of the first approximation (11), and also taking into account (12) and the identity $2\gamma_\infty\delta_3 = (u_\infty q^2/r^3)\delta_2$, we arrive at the expression

$$\mu \equiv \mu^{(2)} = (2\gamma_\infty/\rho_\infty^\alpha r) \left(1 - 2\delta_1 - \frac{1}{2}\delta_2\right) - (u_\infty q^2/\rho_\infty^\alpha r^4) \left[1 - 2(\delta_1 + \delta_4) - \delta_2 + \frac{1}{2}\delta_3 - \frac{8}{3}\delta_5 + \delta_7 - \delta_8\right] \quad (21)$$

As would be expected, the expression found for $\mu^{(2)}$ satisfies the differential equation obtained from the equation of thermodynamic equilibrium of the drop-vapor system {[19], Eqs. (13) and (15)} with $\rho^\alpha \gg \rho^\beta$ and a fixed temperature

$$\rho^\alpha d\mu = d(2\gamma/r) - (1/4\pi)(E^\beta - E^\alpha)dD$$

where ρ^α is taken at a point on the tension surface.

The expression for the number of molecules in the drop is also changed by the presence in Eq. (15) for ρ^α of the term $\rho_\infty^\alpha \delta_8$, which depends on the distance to the nucleus. Let us examine a homogeneous liquid, in the absence of a charged nucleus, this liquid being included in a sphere with radius R_g (R_g may be as large as desired). When a nucleus is introduced into the liquid, the number of molecules in the liquid will change, both as a result of displacement of part of the liquid by the nucleus itself, and also as a consequence of the change in density of the liquid in the electric field. Designating as v_n the difference between the number of molecules of liquid without and with the field, we determine the total number of molecules in the drop v_t as

$$v_t = -v_n + 4\pi R_g^3 \rho_\infty^\alpha / 3 - 4\pi \int_R^{R_g} \rho^\alpha(r') r'^2 dr' \quad (22)$$

Using Eq. (15) with $r' \geq R$, from (22) with $R_g \gg R$, we find

$$v_t = -v_n + v$$

where

$$v \equiv (4\pi R^3/3) \rho_\infty^\alpha [1 + \delta_2(r) - \delta_3(r) - 3\delta_8(R)] \quad (23)$$

The conditions of applicability to the method of expansion with respect to the curvature parameter lead to $v_t \gg v_n$; thus, we can consider that v_n is independent of μ and constant.

Let us now pass on from a variable r to a variable v , which is more convenient in the theory of nucleation in view of the direct relationship between v and the number of molecules in the drop. After expressing, by means of the formulas of the first approximation $R = r$ and $v = (4\pi/3)R^3\rho_\infty^\alpha$, the parameters $\delta_1, \dots, \delta_8$ in terms of v , we find from (23), taking (16) into account,

$$r = (3/4\pi\rho_\infty^\alpha)^{1/3} v^{1/3} \left[1 - \left(c_1 + \frac{1}{3}c_2\right)v^{-1/3} - c_3 v^{-1} + \frac{1}{3}(c_3 + 3c_8)v^{-4/3}\right] \quad (24)$$

where c_1, \dots, c_6 are determined by equations (1), and

$$c_7 \equiv \frac{1}{3} \left(\frac{3}{4\pi\rho_\infty^\alpha}\right)^{1/3} \frac{\theta\gamma_\infty}{u_\infty \varepsilon_\infty^\alpha}, \quad c_8 \equiv \frac{1}{6} \left(\frac{4\pi\rho_\infty^\alpha}{3}\right)^{1/3} \frac{\theta_\infty q^2}{\varepsilon_\infty^\alpha} \quad (25)$$

For the dimensionless chemical potential $b_v \equiv \mu/kT$ as a function of v , on the basis of (21) and (24) and the identity

$$a_0/a \equiv 2c_3/c_2 \equiv 2c_8/c_7 \quad (26)$$

where $\bar{v} \equiv 2a_q/3a$ is the corresponding value of v at which b^1_v vanishes. Determining the point of the maximum $v = v_0$ of the part of (27) that is even in the sign of the charge, which we will designate as b^0_v , we find expressions for b^s and b^a {[3], Eqs. (27) and (30)}:

$$b^s = b^0_v \quad \text{and} \quad b^a = 2b^1_v \quad (33)$$

A direct calculation using the identity (26) shows that v_0 does not depend on c_7 and c_8 , and that it is determined by the relationship {[3], Eq. (17)}

$$v_0 = \frac{2a_q}{a} \left[1 + \frac{1}{2} \left(9c_1 + \frac{3}{2}c_2 - 5c_4 \right) \left(\frac{2a_q}{a} \right)^{-1/2} \right]; \quad (34)$$

correspondingly, for b^a , the previous expression (4) is retained. Only the formulas for b^s and b^a/b^s are changed:

$$b^s = \frac{a}{2} \left(\frac{2a_q}{a} \right)^{-1/2} \left[1 - 2 \left(c_1 + \frac{3}{16}c_2 - \frac{1}{3}c_4 + \frac{1}{8}c_7 \right) \left(\frac{2a_q}{a} \right)^{-1/2} \right] \quad (35)$$

$$b^a/b^s = \frac{16}{9} \left(\frac{2a_q}{a} \right)^{-1} \left[1 - \frac{7}{4} \left(c_1 + \frac{1}{7}c_2 - \frac{17}{21}c_4 - \frac{1}{7}c_7 \right) \left(\frac{2a_q}{a} \right)^{-1/2} \right] c_5^+ \quad (36)$$

We see that an accounting for the dependence of ϵ^α on the state of the drop leads to corrections that are similar in magnitude, with small ϵ^α , to the corrections for compressibility. Since the signs preceding the coefficients c_2 and c_7 in the expression for b^s coincide, the corresponding corrections have identical effects on the threshold value of the chemical potential, both lowering the potential. With coefficients c_2 and c_7 that are known in the case of small ϵ^α , an experimentally determined value of b^s offers a means for determining the parameters c_1 and c_4 , whereas an experimentally determined value of b^a makes it possible to find c_5^+ (i.e., c_6^+).

In Tables 1 and 2, data are given for benzene and carbon tetrachloride. The estimates of c_7 were made on the basis of (9) and (25); values of c_5^+ were found in the first approximation from Eq. (36) by means of the values of $b^a_{\text{exp}}/b^s_{\text{exp}}$ from Table 1; values of b^s_{theor} were calculated by the use of Eq. (35) in the approximation $c_1 = c_4$. The values of $\Delta\varphi$ that are listed in Table 1 were measured for saturated solutions of the substances in water. In view of the low solubilities of benzene and carbon tetrachloride, these values cannot be used for an unambiguous judgment of the order of magnitude of κ . Since both substances are non-polar, it should be expected that $\Delta\varphi$ would be equal to zero and, in accordance with (1) and (4), the values of c_5^+ and b^a would also be equal to zero. We can see that, for benzene, the values of $\Delta\varphi$, b^a_{exp} , and c_5^+ are actually on the order of zero, whereas, for carbon tetrachloride, b^a_{exp} and c_5^+ are nonzero.* The calculated threshold values of b^s_{theor} are considerably higher than the limiting values b^s_{exp} . Here it must be kept in mind that, for these substances, the value of z_{min} determined by Eq. (7) proves to be slightly greater than unity, and this leads to a large error in Eq. (35). An additional contribution to the error of computation of b^s_{theor} is made by the equality $c_1 = c_4$ that we have postulated, whereas, for these particular substances, only $c_1 \sim c_4$ can be fulfilled.

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