INFLUENCE OF THE DROPLET SIZE ON THE HEAT OF TRANSFER OF A VAPOR-PHASE MOLECULE INTO A DROPLET

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The dependence of the heat of transfer of a vapor-phase molecule into a droplet on the number of molecules in the droplet has been found for a homogeneous droplet and a droplet formed on a charged nucleus (or ion). Similar relations have been obtained for the increments of the total entropy and enthalpy of a droplet upon the additon of one molecule. These expressions for the thermal characteristics of the transfer of a vapor-phase molecule into a droplet were determined with consideration of corrections given by parameters of the curvature of the droplet, and in the case of a droplet on a charge nucleus, they describe the influence of the sign of the charge of the nucleus.

The important characteristics of small droplets include the thermodynamic quantities which define the thermal effects of the transfer of a vapor-phase molecule into a droplet. The present work is devoted to the investigation of the analytical dependence of the following three such quantities on the droplet size: the heat of condensation, the enthalpy, and the entropy per molecule in a droplet. Our purpose was to take into account the influence of the corrections for the droplet curvature appearing in the description of surface phenomenon by the Gibbs method of finding an expansion in a parameter of the curvature in the case of a homogeneous droplet [1] and a heterogeneous droplet formed in the strong electric field of a charged condensation nucleus [2]. The droplet size is understood to be the number of molecules found in it.

Homogeneous Droplet. Let us consider a spherical droplet containing ν molecules in equilibrium with a vapor at a certain temperature T. We shall define the heat of isothermal condensation q_ν of a molecule from the vapor in the droplet by the relation

$$q_v = T (s_v - s_v^\beta) \qquad (1)$$

where s_ν is the increment of the total entropy of a droplet of size ν upon the addition of one molecule, and s_ν^β is the entropy of a molecule in the vapor in equilibrium with a droplet of size ν (the superscript β will denote quantities referring to the vapor everywhere in the following).

Considering the vapor as an ideal gas, for s_ν^β we have

$$s_v^\beta = s_\infty^\beta - k_B \ln (p_v^\beta/p_\infty^\beta) \qquad (2)$$

where k_B is Boltzmann's constant, the infinity sign ∞ indicates that the respective quantity is determined for equilibrium between the liquid and gaseous phases at the assigned temperature T at the limit of a planar interface, and p_ν^β and p_∞^β are the vapor pressures at equilibrium with a drop of size ν and a planar surface of the liquid, respectively. The quantity $\ln (p_\nu^\beta/p_\infty^\beta)$ coincides with the shift of the chemical potential of the vapor expressed in unity of $k_B T$: $b \equiv (\mu_\nu - \mu_\infty)/k_B T$. According to [1], when the corrections for the curvature of the droplet are taken into account, the expression for $\ln (p_\nu^\beta/p_\infty^\beta)$ has the form

$$\ln (p_v^\beta/p_\infty^\beta) = b_v = \frac{2}{3} a v^{-1/3} \left[1 - \left(c_1 + \frac{1}{6} c_2 \right) v^{-1/3} \right] \qquad (3)$$

where

$$a \equiv \frac{4\pi \gamma_\infty}{k_B T} \left(\frac{3}{4\pi n_\infty^\alpha} \right)^{1/3} ; \quad c_1 \equiv \left(\frac{4\pi n_\infty^\alpha}{3} \right)^{1/3} \lambda_\infty \qquad (4)$$

$$c_2 \equiv 2\chi_\infty \gamma_\infty \left(\frac{4\pi n_\infty^\alpha}{3} \right)^{1/3} \tag{5}$$

γ is the surfce tension, n^α is the number of molecules in a unit of volume of the liquid phase (the superscript α will designate quantities referring to the liquid phase everywhere in the following), $\lambda = \Gamma/(n^\alpha - n^\beta)$, Γ is the Gibbs adsorption, and χ is the compressibility of the liquid. We note that it is assumed in (3) that one of the small parameters $c_1 v^{-1/3} \ll 1$ or $c_2 v^{-1/3} \ll 1$ is dominant over the other. It is seen that relations (2)-(5) completely define s_v^β.

Let us now find the dependence of s_v on v. According to [1], when $n^\alpha \gg n^\beta$, the number of molecules in a droplet is related to the radius of the tension surface of the droplet r by the equation

$$v = \frac{4\pi r^3}{3} n^\alpha + \Gamma_\infty 4\pi r^2 \tag{6}$$

A similar relation can also be written for the total entropy of a droplet S_v:

$$S_v = \frac{4\pi r^3}{3} n^\alpha s^\alpha + 4\pi r^2 \bar{s} \tag{7}$$

where $\bar{s}$ is the excess entropy per unit of the tension surface of the droplet. We note that the validity of (7) presupposes the fulfillment of the inequality

$$\bar{s} \gg \lambda n^\beta s^\beta \tag{8}$$

which allows us to consider the radius of the equimolecular surface of a droplet as its physical boundary.

The dependence of S_v on v is defined by the dependence of r, n^α, s^α, and $\bar{s}$ on v. According to [1], for n^α we have

$$n^\alpha = n_\infty^\alpha (1 + c_2 v^{-1/3}) \tag{9}$$

which is essentially on expansion of the density in a series with respect to the excess pressure within the droplet

$$\Delta p_r = 2\gamma/r \tag{10}$$

We can write a similar expansion for s^α:

$$s^\alpha = s_\infty^\alpha \left[1 + \frac{1}{s_\infty^\alpha} \left(\frac{\partial s_\infty^\alpha}{\partial p} \right)_T \Delta p_r + \frac{1}{2 s_\infty^\alpha} \left(\frac{\partial^2 s_\infty^\alpha}{\partial p^2} \right)_T (\Delta p_r)^2 \right] \tag{11}$$

The retention of two terms in the expansion will be substantiated below. We shall now take into account the following equalities

$$\left(\frac{\partial s_\infty^\alpha}{\partial p} \right)_T = -\frac{\alpha_p}{n_\infty^\alpha}, \quad \left(\frac{\partial^2 s_\infty^\alpha}{\partial p^2} \right)_T = \frac{\alpha_p \chi_\infty}{n_\infty^\alpha} \tag{12}$$

where $\alpha_p \equiv (-1/n_\infty^\alpha)(\partial n_\infty^\alpha/\partial T)_p$ is the coefficient of thermal expansion of the liquid (we shall neglect the weak dependence of α_p on the pressure). Using (4)-(6), (9), (10), (12), and Tolmen's relation for the surface tension γ

$$\gamma = \gamma_\infty (1 - 2\lambda_\infty/r) \tag{13}$$

we transform (11) into the equation

$$s^\alpha = s_\infty^\alpha \left[1 - 2\alpha_1 v^{-1/3} + 2\alpha_1 \left(c_1 + \frac{1}{6} c_2 \right) v^{-2/3} \right] \tag{14}$$

Here for the sake of convenience in writing the equation we used the notation

$$\alpha_1 \equiv \frac{1}{3} \frac{\alpha_p a k_B T}{s_\infty^\alpha} \tag{15}$$

The smallness of $\alpha_1 v^{-1/3}$ (the characteristic value of $\alpha_1 \lesssim 0.1$), as well as the smallness of the parameters of the curvature $c_1 v^{-1/3}$ and $c_2 v^{-1/3}$ allow us to terminate series (11) for s^α at the third term. It is clear that the third term in (14) has a first order of smallness with respect to the parameter of the curvature in comparison to the second term. In the

following we shall neglect the quantities of second order of smallness with respect to the parameter of the curvature everywhere.

In order to find $\bar{s}$, we shall utilize the system of equations of the thermodynamics of a surface layer [3]

$$d\gamma = -\Gamma d\mu - \bar{s}dT$$

$$dp^\alpha - dp^\beta = \frac{2d\gamma}{r} - \frac{2\gamma}{r^2}\,dr \tag{16}$$

$$dp^{\alpha,\beta} = n^{\alpha,\beta}d\mu + s^{\alpha,\beta}n^{\alpha,\beta}dT$$

Hence after some simple transformations we find the exact thermodynamic relation for $\bar{s}$

$$\bar{s} = -\left[1 + \frac{2\lambda}{r}\right]\left(\frac{\partial\gamma}{\partial T}\right)_r + (s^\alpha n^\alpha - s^\beta n^\beta)\lambda \tag{17}$$

Recalling inequality (8), we see that for $(\partial\gamma/\partial T)_r < 0$ inequality (8) holds when

$$s^\alpha n^\alpha \gg s^\beta n^\beta \tag{18}$$

In view of the fact that $s^\alpha \lesssim s^\beta$ (the characteristic value of s^β/s^α is ~1.5-2) and the fact that $n^\alpha \gg n^\beta$, strong inequality (18) and, therefore, (8) may be considered fulfilled. Then, taking into account (4)-(6), (9), (13), and (15), with the same accuracy as in (14) we find

$$\bar{s} = -\frac{\partial\gamma_\infty}{\partial T} + s_\infty^\alpha n_\infty^\alpha \lambda_\infty + 2\left(\gamma_\infty c_1\frac{d\ln\lambda_\infty}{dT} - \alpha_1 s_\infty^\alpha n_\infty^\alpha \lambda_\infty\right)v^{-1/3} \tag{19}$$

The last two terms in (19) should clearly be taken into account only at values of v at which

$$\frac{s_\infty^\beta n_\infty^\beta}{\gamma_\infty\left|\dfrac{d\ln\lambda_\infty}{dT}\right|n_\infty^{\alpha 1/3}}v^{1/3} \ll 1, \quad \frac{n_\infty^\beta s_\infty^\beta}{n_\infty^\alpha s_\infty^\alpha \alpha_1}v^{1/3} \ll 1 \tag{20}$$

In view of the absence of literature data on $d\ln\lambda_\infty/dT$, we shall only evaluate the second inequality in (20). Using the data from [4] for water, we find that this inequality will be violated only when $v > 10^8$, at which the last two terms in (19) may be totally neglected.

Now substituting (6), (9), (14), and (19) into expression (7) for the total entropy of a droplet S_v, we obtain

$$S_v = s_\infty^\alpha v + ak_\mathrm{B}v^{2/3}\left(\tilde{\gamma} - \frac{2}{3}\tilde{v}\right) - ak_\mathrm{B}v^{1/3}\left[2c_1\left(\tilde{\gamma} - \frac{1}{3}\tilde{v} + \tilde{\lambda}\right) + \frac{2}{3}c_2\left(\tilde{\gamma} - \frac{1}{6}\tilde{v}\right)\right] \tag{21}$$

Here we have introduced the new notation:

$$\tilde{\gamma} \equiv -\frac{d\ln\gamma_\infty}{d\ln T}, \quad \tilde{v} \equiv -\frac{d\ln n_\infty^\alpha}{d\ln T}, \quad \tilde{\lambda} \equiv -\frac{d\ln\lambda_\infty}{d\ln T} \tag{22}$$

The values of $\tilde{\gamma}$ and $\tilde{v}$ are positive, but there are no data on the magnitude or sign of $\tilde{\lambda}$ (the sign of $\tilde{\lambda}$ is presumably the reverse of the sign of λ_∞).

According to the previously given definition, s_v is equal to the derivative of the total entropy of the droplet S_v with respect to the number of molecules v at a fixed temperature. Therefore, differentiating (21) with respect to v, we obtain

$$s_v = s_\infty^\alpha + \frac{2}{3}ak_\mathrm{B}v^{-1/3}\left(\tilde{\gamma} - \frac{2}{3}\tilde{v}\right) - \frac{2}{3}ak_\mathrm{B}v^{-2/3}\left[c_1\left(\tilde{\gamma} - \frac{1}{3}\tilde{v} + \tilde{\lambda}\right) + \frac{1}{3}c_2\left(\tilde{\gamma} - \frac{1}{6}\tilde{v}\right)\right] \tag{23}$$

Next, substituting (2), (3), and (23) into (1), we arrive at the following expression for the heat of condensation

$$q_v/k_\mathrm{B}T \equiv \beta_v = \beta_\infty + \frac{2}{3}av^{-1/3}\left(1 + \tilde{\gamma} - \frac{2}{3}\tilde{v}\right) - \frac{2}{3}av^{-2/3}\left(\tilde{c}_1 + \frac{1}{6}\tilde{c}_2\right) \tag{24}$$

where

$$\tilde{c}_1 \equiv c_1\left(1 + \tilde{\gamma} - \frac{1}{3}\tilde{v} + \tilde{\lambda}\right), \quad \tilde{c}_2 \equiv c_2\left(1 + 2\tilde{\gamma} - \frac{1}{3}\tilde{v}\right) \tag{25}$$

TABLE 1. Heat of Condensation for a Planar Interface, Parameters of Eq. (26), and $(\Delta\beta_\nu^{(0)})_{hom}$ (the calculation was carried out for T = 298°K)

Liquid	β_∞	$\tilde{v}$	$\tilde{\gamma}$	a	$(\Delta\beta_\nu^{(0)})_{hom}, \nu = 10^2$
Water	—17,93	0,08	0,66	8,23	1,18
Methanol	—15,54	0,34	1,08	4,33	1,15
Ethanol	—17,25	0,32	1,07	5,55	1,48
Benzene	—13,77	0,36	1,48	9,29	2,99
Toluene	—15,46	0,31	1,30	10,37	3,12

and $\beta_\infty \equiv (s_\infty^\alpha - s_\infty^\beta)/k_B$. When the corrections given by the parameters of the curvature are neglected, expression (24) is transformed into Sreznevskii's formula [5]*

$$(\Delta\beta_\nu^{(0)})_{hom} \equiv \beta_\nu^{(0)} - \beta_\infty = \frac{2}{3} a\nu^{-1/3} \left[1 + \tilde{\gamma} - \frac{2}{3} \tilde{v} \right] \tag{26}$$

Since β_∞ is negative ($s_\infty^\alpha < s_\infty^\beta$, i.e., heat is evolved upon condensation), and since the sign of $(\Delta\beta_\nu^{(0)})_{hom}$ is positive, the absolute value of the heat of condensation β_ν also decreases with decreasing droplet size. For comparison Table 1 presents the values of β_∞, $\tilde{v}$, $\tilde{\gamma}$, and $(\Delta\beta_\nu^{(0)})_{hom}$ calculated from the data in [4, 8] at T = 298°K for water, methanol, ethanol, benzene, and toluene. The values of $(\Delta\beta_\nu^{(0)})_{hom}$ were found for $\nu = 10^2$; at such values of ν the corrections given by the parameters of the curvature also become significant.

The problem of the dependence of the heat of condensation of the droplet size in the case of small homogeneus droplets in equilibrium with a vapor was also solved in [9]. The result obtained here [Eqs. (14), (19), (21), (23), and (24)], is distinguished, first, by the fundamental consideration of the term $-(4/9)a\nu^{-1/3}\tilde{v}$, which is related to the coefficient of volumetric expansion of the liquid, second, by the explicit consideration of the corrections given by the parameters of the curvature, and, third, by the fact that all the final equations are written in the variable ν. This is considerably more convenient in evaluations and permits direct comparison with data from mass-spectrometric experiments.

Relation (24) can also be obtained from more general arguments. Let us consider a droplet which is not in chemical equilibrium with a vapor ($\mu_\nu \neq \mu^\beta$). We shall assume that the process of the transfer of a molecule from the vapor into the droplet takes place at constant values of p^β and T. The work for the transfer of a molecule from the vapor into the droplet is equal to $\mu_\nu - \mu^\beta$ in this case. In view of the general thermodynamic equality $s_\nu = -(\partial\mu_\nu/\partial T)_\nu$ {which can be substantiated in the framework of the quasi-chemical method of describing droplet—vapor systems [1] and is confirmed by Eqs. (3) and (23)} for the heat of condensation, we can write an analog of the van't Hoff equation:

$$q_\nu = -T^2 \left(\frac{\partial}{\partial T} \frac{(\mu_\nu - \mu^\beta)}{T} \right)_{p^\beta, \nu} = h_\nu - h^\beta \tag{27}$$

where $h_\nu \equiv \mu_\nu + Ts_\nu$ is the change in the total enthalphy of a droplet of size ν upon the addition of a molecule, and h^β is the enthalpy of a molecule in the vapor phase at the assigned pressure p^β. When $\mu_\nu = \mu^\beta$ and (3) is taken into account, relation (24) follows from (27). In the approximation of an ideal vapor, $h^\beta = h_\infty^\beta$ (the enthalpy of a molecule in the vapor phase is not dependent on the pressure at a fixed temperature). Since h_ν is not dependent on the state of the vapor, expressions (24) and (27) for the heat of condensation on a droplet of size ν remain valid as a whole for droplets not in equilibrium with the vapor phase.† In this case, the equality $h_\nu - h_\infty^\alpha = \Delta q_\nu$ holds. Making the transition to the dimensionless heat of condensation β_ν and the dimensionless chemical potential b_ν, we write the equality just indicated with the aid of (27) in the form

$$\Delta\beta_\nu = -T \left(\frac{\partial b_\nu}{\partial T} \right)_\nu \tag{28}$$

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*A relation for the variation of the heat of transfer at an assigned droplet radius was found in [5]. A similar equation, which, however, did not take into account the thermal expansion of the liquid, was obtained in [6, 7].

†Strictly speaking, only in the sense of analytical extrapolation at $b \neq b_\nu$.

Restricting ourselves to consideration of droplet—vapor equilibrium, from (28) and (3) we conclude that the Clausius—Clapeyron equation also remains valid in the case of a phase transition at a curved interface[*]:

$$\frac{1}{n_v^\beta} dp_v^\beta = -\frac{q_v}{T} dT \tag{29}$$

where n_v^β is the number density of the molecules in the vapor in equilibrium with a droplet of size v.

Heterogeneous Droplet. In order to find the dependence of the heat of condensation of a molecule on a droplet formed on a charged nucleus on the droplet size, we shall utilize general relation (28). According to [2, 10], in the case of a heterogeneous droplet, the chemical potential b_v of a droplet — vapor equilibrum is defined by the relation

$$b_v = \frac{2}{3} av^{-1/s} \left[1 - \left(c_1 + \frac{1}{6} c_2\right) v^{-1/s} + c_7 v^{-1} \right] -$$
$$- \frac{1}{3} a_q v^{-1/s} \left[1 + 2\left(c_1 + \frac{1}{3} c_2 + c_4 - c_6\right) v^{-1/s} - \frac{5}{6} (c_3 + 6c_5) v^{-1/s} + 4 \left(c_7 - \frac{2}{3} c_8\right) v^{-1} \right] \tag{30}$$

where

$$a_q \equiv (4\pi u_\infty q^2/k_B T)(4\pi n_\infty^\alpha/3)^{1/s}, \quad u_\infty \equiv \frac{1}{8\pi}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)$$
$$c_3 \equiv (4\pi n_\infty^\alpha/3)^{1/s} \chi_\infty u_\infty q^2, \quad c_4 \equiv (4\pi n_\infty^\alpha/3)^{-1/s} \theta_\infty \gamma_\infty/3u_\infty \varepsilon_\infty^\alpha \tag{31}$$
$$c_5 \equiv (4\pi n_\infty^\alpha/3)^{1/s} \theta_\infty q^2/6\varepsilon_\infty^\alpha, \quad c_6 \equiv (4\pi n_\infty^\alpha/3)^{1/s} k_1/2u_\infty$$
$$c_7 \equiv (4\pi q/3)(d\mathscr{P}_0/d\mu)_\infty, \quad c_8 \equiv 2\pi n_\infty^\alpha k_2 q/3u_\infty,$$

$\theta_\infty = (\partial \ln \varepsilon_\infty^\alpha/\partial\mu)_T$, q is the electric charge of the nucleus, ε is the dielectric constant, $\mathscr{P}_0$ is the spontaneous surface polarization, and k_1 and k_2 are the coefficients of the contributions which are linear and quadratic with respect to the induction to the induced surface polarization. Substituting (30) into (28), with consideration of (25) and definitions (22) and (26) we obtain

$$\Delta\beta_v = (\Delta\beta_v^{(0)})_{hom} - \frac{2}{3} av^{-1/s} \left(\tilde{c}_1 + \frac{1}{6}\tilde{c}_2\right) + \frac{2}{3} av^{-1/s}\tilde{c}_7 -$$
$$- \frac{1}{3} a_q v^{-1/s}\left(1 + \tilde{u} + \frac{1}{3}\tilde{v}\right) - \frac{2}{3} a_q v^{-1/s}\left(\tilde{\tilde{c}}_1 + \frac{1}{3}\tilde{\tilde{c}}_2 + \tilde{c}_4 - \tilde{c}_6\right) + \frac{5}{18} a_q v^{-1/s}(\tilde{c}_3 + 6\tilde{c}_5) - \frac{4}{3} a_q v^{-1/s}\left(\tilde{\tilde{c}}_7 - \frac{2}{3}\tilde{c}_8\right) \tag{32}$$

where we have used the notation

$$\tilde{\tilde{c}}_1 \equiv c_1(1 + \tilde{u} + 2/3\tilde{v} + \tilde{\lambda}), \quad \tilde{\tilde{c}}_2 \equiv c_2(1 + \tilde{u} + 2/3\tilde{v} + \tilde{\gamma})$$
$$\tilde{c}_3 \equiv c_3(1 + 2\tilde{u} + 5/3\tilde{v}), \quad \tilde{c}_4 \equiv c_4(1 - 1/3\tilde{v} + \tilde{\gamma} - \tilde{\varepsilon} + \tilde{\theta}),$$
$$\tilde{c}_5 \equiv c_5\left(1 + \tilde{u} + \frac{2}{3}\tilde{v} - \tilde{\varepsilon} + \tilde{\theta}\right), \quad \tilde{c}_6 \equiv c_6(1 + 2/3\tilde{v} + \tilde{k}_1) \tag{33}$$
$$\tilde{c}_7 \equiv c_7\left(1 + \tilde{\gamma} - \frac{2}{3}\tilde{v} + \tilde{\mathscr{P}}\right), \quad \tilde{\tilde{c}}_7 \equiv c_7(1 + \tilde{u} + 1/3\tilde{v} + \tilde{\mathscr{P}})$$
$$\tilde{c}_8 \equiv c_8(1 + 4/3\tilde{v} + \tilde{k}_2)$$

and

$$\tilde{u} \equiv -\frac{d \ln u_\infty}{d \ln T}, \quad \tilde{\varepsilon} \equiv -\frac{d \ln \varepsilon_\infty^\alpha}{d \ln T}, \quad \tilde{\mathscr{P}} \equiv -\frac{d \ln (\partial\mathscr{P}_0/\partial\mu)_\infty}{d \ln T}$$
$$\tilde{k}_1 \equiv -\frac{d \ln k_1}{d \ln T}, \quad \tilde{k}_2 \equiv -\frac{d \ln k_2}{d \ln T}, \quad \tilde{\theta} \equiv -\frac{d \ln \theta_\infty}{d \ln T} \tag{34}$$

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[*]In view of the fact that a quantity which is, in fact, equal to the heat of transfer of a molecule from the bulk of a vapor into the bulk of a droplet was called the heat of transfer of a molecule into a droplet in [9], the equations of the two-phase droplet—vapor equilibrium written in [9] do not reduce to the Clausius—Clapeyron equation.

Liquid	a_q	$\tilde{\varepsilon}$	$\tilde{u}$	$(\Delta\beta^{(o)})_{het}$
Water	145,1	1,4	0,02	2,32
Methanol	111,0	1,6	0,05	1,36
Ethanol	98,4	1,8	0,08	1,32
Benzene	47,9	0,3	0,2	5,70
Toluene	47,5	0,3	0,2	6,07

The values of $\tilde{u}$, $\tilde{\varepsilon}$, $\tilde{k}_1$, and $\tilde{\theta}$ are positive. The sign of $\mathscr{P}$ and $\tilde{k}_2$ are determined by the sign of the surface jump in the electric potential upon passage from the liquid into the vapor. As is seen from (31) and (33), $\tilde{c}_7$, $\tilde{\tilde{c}}_7$, and $\tilde{c}_8$ depend on the sign of the charge of the nucleus in (32). The contribution of the terms in (32) with these coefficients rapidly increases with decreasing droplet size. In the case of very small droplets, the dependence on the sign of the charge may be very significant and can be observed experimentally by comparing the heats of condensation in the case of droplets formed on oppositely charged ions.

As is seen from (32) and (26), the dependence of β_ν on the droplet size is basically defined by the relation

$$(\Delta\beta_\nu^{(0)})_{het} = \frac{2}{3} a\nu^{-1/_3} \left(1 - \frac{2}{3}\tilde{v} + \tilde{\gamma}\right) - \frac{1}{3} a_q\nu^{-1/_3}\left(1 + \tilde{u} + \frac{1}{3}\tilde{v}\right) \tag{35}$$

Table 2 presents values of the parameters $\tilde{u}$, a_q, and $\tilde{\varepsilon}$ calculated from the data in [4] for water, methanol, ethanol, benzene, and toluene at T = 298°K. The values of $(\Delta\beta^{(o)})_{het}$ presented in Table 2 correspond to the maximum value of the right-hand side of (35) for each substance and have an approximate character.

The values of β_ν for small clusters (ν = 1 to 10) of different substances were determined directly in mass-spectrometric experiments in [11]. Qualitative agreement with the fundamental formula for $(\Delta\beta_\nu^{(o)})_{het}$ was discovered in these experiments and that the nature of the condensation core (ion) becomes insignificant already when $\nu \geq 7$.

It is not difficult now to find the dependence of the increment of the total entropy of a droplet upon the addition of a single molecule on the sign of the charge and the size of the droplet with the use of the aforementioned equality $\Delta h/k_B T = \Delta\beta_\nu$ and the definition of the enthalpy

$$\frac{\Delta s_\nu}{k_B} \equiv \frac{s_\nu - s_\infty^\alpha}{k_B} = \Delta\beta_\nu - b_\nu \tag{36}$$

Substituting (30) and (32) into (36), we find

$$\frac{\Delta s_\nu}{k_B} = \left(\frac{\Delta s_\nu^0}{k_B}\right)_{het} - \frac{2}{3}a\nu^{-1/_3}\left[(\tilde{c}_1 - c_1) + \frac{1}{6}(\tilde{c}_2 - c_2)\right] + \frac{2}{3}a\nu^{-1/_3}(\tilde{c}_7 - c_7) - \frac{2}{3}a_q\nu^{-1/_3}\left|\left[\tilde{\tilde{c}}_1 - c_1 + \frac{1}{3}(\tilde{\tilde{c}}_2 - c_2) + \right.\right.$$
$$\left.\left. + \tilde{c}_4 - c_4 - \tilde{c}_6 + c_6\right] + \frac{5}{18}a_q\nu^{-1/_3}[\tilde{c}_3 - c_3 + 6(\tilde{c}_5 - c_5)] - \frac{4}{3}a_q\nu^{-1/_3}\left[\tilde{\tilde{c}}_7 - c_7 - \frac{2}{3}(\tilde{c}_8 - c_8)\right] \right. \tag{37}$$

where

$$\left(\frac{\Delta s_\nu^0}{k_B}\right)_{het} = \frac{2}{3}a\nu^{-1/_3}\left(\tilde{\gamma} - \frac{2}{3}\tilde{v}\right) - \frac{1}{3}a_q\nu^{-1/_3}\left(\tilde{u} + \frac{1}{3}\tilde{v}\right) \tag{38}$$

i.e., a relation which defines the principal dependence of s_ν on ν. From (37) and (38) it is seen that the relative role of the corrections given by the parameters of the curvature for Δs_ν is increased in comparison to the case of $\Delta\beta_\nu$. This occurs as a consequence of the partial compensation of the principal terms in (30) and (32) when they are substituted into (36). As the estimates of $\tilde{u}$, $\tilde{\varepsilon}$, $\tilde{\gamma}$, and $\tilde{v}$ presented in Tables 1 and 2 show, the contribution of the principal term to s_ν, which is proportional to the square of the charge of the nucleus, is small and comparable to the contribution of the corrections given by the parameters of the curvature [primarily of the corrections in (37) which are themselves proportional to the charge of the nucleus]. Since the magnitude of these corrections increases with decreasing droplet size, this accounts for the experimentally observed [11] significant difference in the behavior of Δs_ν for small clusters from that predicted by Eq. (38).

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MUTUAL POLARIZATION ON A DOUBLET OF PARTICLES WITH AN ARBITRARY
ORIENTATION RELATIVE TO THE FIELD VECTOR

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The problem of the mutual polarization of two spherical colloidal particles in an external electric field with an arbitrary orientation relative to the field vector has been considered in a general form. The mechanism of the polarization of the partial medium interface was not specified. The expression obtained permits the calculation of the binding energy of the particles in a doublet with any degree of accuracy *with consideration* of the multipole polarizabilities for arbitrary distances between the particles.

The investigation of the process of the coagulation of colloidal particles in an electrolyte under the influence of an electric field requires the correct description of the energy of the polarization interaction at distances commensurate with the thickness of the double layers of the particles. At just these distances the polarization forces (in the case of identical particles, they are forces of attraction) compete with the ionic electrostatic forces of repulsion. Until recently calculations of the polarization interaction of charged colloidal particles at small distances (or the multipole interaction) were carried out on the basis of the diagrammatic analytical method developed in [1, 2] only for the case in which the line of the centers of the particles is parallel to the vector of the external field. In contrast to the traditional methods [3-6], this method made it possible to solve the problem of the multipole interaction for an extensive class of models of the polarization of a particle—medium interface [1, 7, 8].

However, in real systems the particles are distributed arbitrarily relative to the field vector; therefore, the further generalization of the diagrammatic analytical method requires the solution of the analogous problem for just this case. This will make it possible to obtain the correct expression for the total energy of the interaction of colloidal particles in an electric field, which is needed, on the one hand, for the development of a systematic theory for nonequilibrium electrical surface phenomena in concentrated suspensions and, on the other hand, for the development of such a theory for the kinetics of electrocoagulation [9, 10].

The series of studies in [11-14] on the theory of nonequilibrium electrical surface phenomena in concentrated suspensions was carried out on the basis of the cell model, which