

THEORY OF NUCLEATION ON CHARGED CORES.

2. THERMODYNAMIC PARAMETERS OF AN EQUILIBRIUM NUCLEUS

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The dependence of the surface tension, the radius of the tension surface, the radius of the equimolecular surface, the absolute specific adsorption, the specific surface entropy, the surface polarization, the excess large thermodynamic potential, and the work for the formation of a nucleus on the magnitude and sign of its charge has been determined for a critical nucleus with an electric charge at its center.

The fundamental equations of the thermodynamics of nucleation on charged cores established in [1] make it possible to determine the dependence of the fundamental thermodynamic parameters of the nucleus on the magnitude and sign of the charge located at its center. A nucleus of an α phase formed on a spherical solid or liquid core (γ phase) from a β phase is understood to be a spherical layer of the α phase together with the excesses of the surface layers on the $\alpha\gamma$ and $\alpha\beta$ boundaries, which are assigned, respectively, to the boundary surface of the core and to a selected separating surface between the α and β phases. Considering the core to be insoluble, we shall assume that the $\alpha\gamma$ and $\alpha\beta$ surface layers do not overlap. We shall assume that the substances in the α and β phases have dielectric properties, and that the core is a conductor, which carries an electric charge q .

Surface Polarization. Allowing the existence of spontaneous polarization (P_0) in the surface layer of the nucleus for the sake of generality, we write the local relations for the electric field strength E and the induction:

$$E = -4\pi P_0 + D/\epsilon, \quad E^{\alpha, \beta} = D/\epsilon^{\alpha, \beta}, \quad D = q/r^2, \quad (1)$$

where P is the dipole moment of a unit volume, ϵ is the dielectric constant, r is the distance to the center of the nucleus, the subscript 0 characterizes the quantities in the absence of the field of the core, and the indices α and β refer to the phase (which are homogeneous in the absence of the field).

The excess surface polarization \mathcal{P} [1, 2] is represented as

$$\mathcal{P} = \frac{1}{4\pi} \int_{r_1}^r (E^\alpha - E) dr' + \frac{1}{4\pi} \int_r^{r_2} (E^\beta - E) dr', \quad (2)$$

where the radii r_1 and r_2 have been selected somewhat in the bulk portions of the α and β phases, and r is the radius of a certain separating surface. We shall subsequently assume that r_1 and r_2 are fixed.

Using (1), we write (2) in the form

$$\mathcal{P} = \mathcal{P}_0 + 2aq, \quad (3)$$

where the coefficient

$$a \equiv \frac{1}{8\pi} \left[\int_{r_1}^r \left(\frac{1}{\epsilon^\alpha} - \frac{1}{\epsilon} \right) \frac{dr'}{r'^2} + \int_r^{r_2} \left(\frac{1}{\epsilon^\beta} - \frac{1}{\epsilon} \right) \frac{dr'}{r'^2} \right] \quad (4)$$

is determined, on the one hand, by the shape of the profile of the dielectric constant $\epsilon(r')$ in the surface layer and, on the other hand, by the position of the separating surface. As was previously shown [2, p. 913], at assigned temperatures and chemical potentials the dielectric constant of a bulk phase may be assumed constant with accuracy to terms which are quadratic with respect to the field. Similarly, it may be assumed that the profile of the dielectric constant is defined (with the same accuracy) by assigning only the temperature T and the chemical potentials $\{\mu_i\}$, and thus $a \equiv a(T, \{\mu_i\}, r)$. Then (4) yields the expression (which does not depend on the selection of r and r_0 between r_1 and r_2)

$$a = a_0 - b(1/r - 1/r_0), \quad (5)$$

where $a_0 = a(T, \{\mu_i\}, r_0)$ and the quantity

$$b \equiv \frac{1}{8\pi} \left(\frac{1}{\epsilon^\alpha} - \frac{1}{\epsilon} \right) \quad (6)$$

is also assumed to be a function of the temperature and the chemical potentials: $b_x \equiv b(T, \{\mu_i\})$.

The dependence of the coefficient α on the position of the separating surface is defined, as is seen from (4), by the relation

$$\left(\frac{\partial a}{\partial r} \right)_{T, \{\mu_i\}} = \frac{b}{r^2}. \quad (7)$$

We note that this relation is also applicable to the case of the displacement of the separating surface (with an assigned way of defining it) under the effects of an electric field.

Substituting (5) into (3), we obtain the expression

$$\mathcal{P} = \mathcal{P}_0(T, \{\mu_i\}) + 2 \left[a_0 - b \left(\frac{1}{r} - \frac{1}{r_0} \right) \right], \quad (8)$$

in which the contribution introduced by the existence of a charge to the surface polarization has been explicitly singled out.

Specific Adsorption and Surface Entropy. We shall start out from the fundamental equations for the normal (p_N) and tangential (p_T) components of the pressure tensor in the system under consideration. According to [1, Eq. (13)], we have

$$\delta p_N^{\alpha, \beta} = s_v^{\alpha, \beta} \delta T + \sum_i \rho_i^{\alpha, \beta} \delta \mu_i - (E^{\alpha, \beta} / 4\pi) \delta D, \quad (9)$$

where s_v is the entropy per unit volume, and ρ_i is the density of the mass of the i -th component. Next we write the Gibbs-Duhem relation [1, Eq. (8)] for the part of the system between spherical surfaces of radii r_1 and r_2 in the form

$$4\pi \delta \int_{r_1}^{r_2} p_T r^2 dr = S \delta T + \sum_i m_i \delta \mu_i + \int_{r_1}^{r_2} D (\delta E) r^2 dr, \quad (10)$$

where S and m_i are the entropy and mass of the i -th component of the part of the system under consideration. Under the assumption made regarding the separation of the $\alpha\gamma$ and $\alpha\beta$ surface layers, the part of the system under consideration (r_1 and r_2 are fixed) may be understood to be autonomous.

Taking into account (1) and integrating relations (9) and (10) with respect to q at constant T and $\{\mu_i\}$, we find

$$p_N^{\alpha, \beta} = p_{N_0}^{\alpha, \beta}(T, \{\mu_i\}) - \frac{q^2}{8\pi \epsilon^{\alpha, \beta} r^4}, \quad (11)$$

$$\int_{r_1}^{r_2} p_T r^2 dr = \int_{r_1}^{r_2} \left[p_{T_0}(T, \{\mu_i\}) + \frac{q^2}{8\pi \epsilon r^4} \right] r^2 dr. \quad (12)$$

In the case of bulk phases, relation (12) may be written in the local form

$$\rho_T^{\alpha,\beta} = \rho_{T_0}^{\alpha,\beta}(T, \{\mu_i\}) + \frac{q^2}{8\pi e^{\alpha,\beta} r^4}. \quad (13)$$

Using (1) again and considering (10) at constant T , $\{\mu_j \neq i\}$, and q , we arrive at the relation

$$\int_{r_1}^{r_2} \left(\frac{\partial p_T}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}, q} r^2 dr = \frac{m_i}{4\pi} - \int_{r_1}^{r_2} \left[\left(\frac{\partial P_0}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} q + \frac{1}{4\pi e^2} \left(\frac{\partial e}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} \frac{q^2}{r^2} \right] dr. \quad (14)$$

In the case of bulk phases, relation (14) may also be written in the local form

$$\left(\frac{\partial p_T}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}, q}^{\alpha,\beta} = \rho_i^{\alpha,\beta} - \frac{1}{4\pi (e^{\alpha,\beta})^2} \left(\frac{\partial e^{\alpha,\beta}}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} \frac{q^2}{r^4}. \quad (15)$$

Differentiating (12) and (13) with respect to μ_i at constant T , $\{\mu_j \neq i\}$, and q and taking into account (14) and (15) with $q = 0$, we obtain

$$\int_{r_1}^{r_2} \left(\frac{\partial p_T}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}, q} r^2 dr = \frac{m_{i0}(T, \{\mu_i\})}{4\pi} - \int_{r_1}^{r_2} \frac{1}{8\pi e^2} \left(\frac{\partial e}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} \frac{q^2}{r^2} dr, \quad (16)$$

$$\left(\frac{\partial p_T^{\alpha,\beta}}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}, q} = \rho_{i0}^{\alpha,\beta}(T, \{\mu_i\}) - \frac{1}{8\pi (e^{\alpha,\beta})^2} \left(\frac{\partial e^{\alpha,\beta}}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} \frac{q^2}{r^4}. \quad (17)$$

Comparing (14) with (16) and (15) with (17), we find

$$\frac{m_i}{4\pi} = \frac{m_{i0}(T, \{\mu_i\})}{4\pi} + \int_{r_1}^{r_2} \left[\left(\frac{\partial P_0}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} q + \frac{1}{8\pi e^2} \left(\frac{\partial e}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} \frac{q^2}{r^2} \right] dr, \quad (18)$$

$$\rho_i^{\alpha,\beta} = \rho_{i0}^{\alpha,\beta}(T, \{\mu_i\}) + \frac{1}{8\pi (e^{\alpha,\beta})^2} \left(\frac{\partial e^{\alpha,\beta}}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} \frac{q^2}{r^4}. \quad (19)$$

Directly from the definition of the absolute specific adsorption Γ_i as an excess parameter we have

$$\Gamma_i r^2 \equiv \frac{m_i}{4\pi} - \int_{r_1}^r \rho_i^{\alpha,\beta} r'^2 dr' - \int_r^{r_2} \rho_i^{\beta,\alpha} r'^2 dr' \quad (20)$$

(r is the radius of a certain separating surface). From (20), (18), and (19) with consideration of (3) we find

$$\Gamma_i r^2 = \Gamma_{i0}(T, \{\mu_i\}, r) r^2 + \left(\frac{\partial P_0}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} q + \left(\frac{\partial a}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}, r} q^2, \quad (21)$$

where the quantities $\Gamma_{i0}(T, \{\mu_i\}, r)$ and $\left(\frac{\partial a}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}, r}$ are assigned for the position of the separating surface r in the presence of a field. According to (5) we can write

$$\left(\frac{\partial a}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}, r} = \left(\frac{\partial a_0}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}, r_0} - \left(\frac{\partial b}{\partial \mu_i} \right)_{T, \{\mu_j \neq i\}} \left(\frac{1}{r} - \frac{1}{r_0} \right) \quad (22)$$

Taking into account (22) and the relation between $\Gamma_{i0}(T, \{\mu_i\}, r)$ and $\Gamma_{i0}(T, \{\mu_i\}, r_0)$ following from (20) with $q = 0$, we transform (21) into the final formula for the specific adsorption

$$\Gamma_i = \Gamma_{i0}(T, \{\mu_i\}, r_0) \frac{r_0^3}{r^3} - (\rho_{i0}^\alpha - \rho_{i0}^\beta) \frac{r^3 - r_0^3}{3r^3} + \left(\frac{\partial \mathcal{F}_0}{\partial \mu_i} \right)_{T, \{\mu_{j \neq i}\}} \frac{q}{r^3} + \left(\frac{\partial a_0}{\partial \mu_i} \right)_{T, \{\mu_{j \neq i}\}, r_0} \frac{q^3}{r^3} + \left(\frac{1}{r} - \frac{1}{r_0} \right) \left(\frac{\partial b}{\partial \mu_i} \right)_{T, \{\mu_{j \neq i}\}} \frac{q^3}{r^3}, \quad (23)$$

in which the contribution due to the charge of the core has been explicitly singled out.

The equation obtained (23) for the absolute specific adsorption also makes it possible to find an expression for the parameter

$$\lambda_i \equiv \Gamma_i / (\rho_i^\alpha - \rho_i^\beta), \quad (24)$$

which plays a significant role in the determination of the dependence of the surface tension and other parameters of the nucleus on its diameter. For its part, the expression found in this manner for λ_i makes it possible to find the radius R_i of the equimolecular surface, which is related to r , λ_i , and q by the equation

$$R_i^3 = r^3 + 3\lambda_i r^3 + 3 \left(\frac{1}{r} - \frac{1}{R_i} - \frac{\lambda_i}{r^3} \right) \left(\frac{\partial b}{\partial \mu_i} \right)_{T, \{\mu_{j \neq i}\}} \frac{q^3}{(\rho_{i0}^\alpha - \rho_{i0}^\beta)}, \quad (25)$$

which follows from (20) and (24) with consideration of (6) and (19).

Replacing the differentiation with respect to μ_i at constant T , $\{\mu_{j \neq i}\}$, and q by differentiation with respect to T at constant $\{\mu_i\}$ and q in (14)-(19) and, accordingly, replacing m_i by S and ρ_i by s_V , instead of (23) we obtain an expression for the specific surface entropy $\bar{s} \equiv \bar{S}/4\pi r^2$:

$$\bar{s} = \bar{s}_0(T, \{\mu_i\}, r_0) \frac{r_0^3}{r^3} - (s_{v0}^\alpha - s_{v0}^\beta) \frac{r^3 - r_0^3}{3r^3} + \left(\frac{\partial \mathcal{F}_0}{\partial T} \right)_{\{\mu_i\}} \frac{q}{r^3} + \left(\frac{\partial a_0}{\partial T} \right)_{\{\mu_i\}, r_0} \frac{q^3}{r^3} - \left(\frac{1}{r} - \frac{1}{r_0} \right) \left(\frac{\partial b}{\partial T} \right)_{\{\mu_i\}} \frac{q^3}{r^3}, \quad (26)$$

in which the contribution due to the charge of the core has also been isolated.

Surface Tension and Radius of the Tension Surface. Up to this point our arguments have referred to any, arbitrarily selected position of the separating surface. We shall now select a tension surface as such a surface. We shall use r and γ to denote its radius and the mechanical surface tension belonging to it. As we know [2, 3], γ and r are determined by the conditions

$$\frac{2\gamma}{r} = p_N^\alpha - p_N^\beta \quad (27)$$

$$\gamma r^3 = \int_{r_0}^r (p_T^\alpha - p_T) r'^3 dr' + \int_r^{r_0} (p_T^\beta - p_T) r'^3 dr'. \quad (28)$$

From (27) and (28) and the analogous conditions for $q = 0$, with consideration (11)-(13), (4), and (6) we have

$$\frac{2\gamma}{r} = \frac{2\gamma_0(T, \{\mu_i\})}{r_0} - \frac{bq^3}{r^4} \quad (29)$$

$$\gamma r^3 = \gamma_0(T, \{\mu_i\}) r_0^3 + \frac{2\gamma_0}{3r_0} (r^3 - r_0^3) + aq^3 \quad (30)$$

(r_0 and γ_0 are the values of r and γ for $q = 0$). Substituting (5) into (30), we obtain

$$\gamma r^3 = \gamma_0 r_0^3 + \frac{2\gamma_0}{3r_0} (r^3 - r_0^3) + a_0 q^3 - b \left(\frac{1}{r} - \frac{1}{r_0} \right) q^3. \quad (31)$$

Eliminating γ from relations (29) and (31), we arrive at the equation

$$\frac{\gamma_0}{3r_0}(r^3 - r_0^3) + \frac{b}{2r}q^2 - \left(a_0 + \frac{b}{r_0}\right)q^2 = 0, \quad (32)$$

which defines the dependence of the radius of the tension surface on the charge of the core: $r = r(q)$. Varying (32) at constant T and $\{\mu_i\}$, we can write the relationship between r and q in differential form:

$$\left(\frac{\partial r}{\partial q}\right)_{T, \{\mu_i\}} = \left(2a_0q - \frac{bq}{r} + \frac{2bq}{r_0}\right) / \left(\frac{\gamma_0}{r_0}r^2 - \frac{bq^2}{2r^2}\right). \quad (33)$$

We note that the expressions obtained for the surface tension, the radius of the tension surface, the surface polarization, the specific adsorption, and the specific surface entropy, as expected, satisfy the generalized equation of the specific adsorption [1, Eq. (27)].

Excess Large Thermodynamic Potential and Work for the Formation of a Nucleus. Let us now use the expression for the excess large thermodynamic potential [1, Eq. (22)]:

$$\bar{\Omega} = \gamma A - 4\pi\mathcal{P}q = 4\pi(\gamma r^2 - \mathcal{P}q). \quad (34)$$

Substituting (8) and (31) into this equation and taking into account (32), we obtain

$$\bar{\Omega} = \bar{\Omega}_0(T, \{\mu_i\}) - 4\pi\mathcal{P}_0q + 4\pi\left(a_0 + \frac{b}{r_0}\right)q^2, \quad (35)$$

where

$$\bar{\Omega}_0 \equiv 4\pi r_0^2 \gamma_0.$$

Equation (35) rigorously defines the dependence of $\bar{\Omega}$ on q . Knowing the dependence of r , \mathcal{P} , and γ on the charge, according to [1, Eq. (50)] we can also find the dependence of the work for the formation of a critical nucleus on q

$$\Delta\Omega = \frac{4\pi}{3}\gamma r^2 - 4\pi\mathcal{P}q - \frac{16\pi b q^3}{3r} + \Delta\Omega_n, \quad (36)$$

where $\Delta\Omega_n$ is the work needed to bring the charged core from the vapor into the liquid. As follows from [1, Eq. (51)], in the general case, the value of $\Delta\Omega_n$ depends on the charge on the surface of the core. In cases in which the nucleation cores are ions, experimental estimates are known for $\Delta\Omega_n$ (solvation or hydration energies) [4].

Substituting relations (31) and (8) into (36), we obtain

$$\begin{aligned} \Delta\Omega = \Delta\Omega_0(T, \{\mu_i\}) + \frac{8\pi\gamma_0}{9r_0}(r^3 - r_0^3) - 4\pi\mathcal{P}_0q - \\ - \frac{20\pi}{3}\left(a_0 + \frac{b}{r_0}\right)q^2 + \frac{4\pi}{3}\frac{bq^2}{r} + \Delta\Omega_n. \end{aligned} \quad (37)$$

where $\Delta\Omega_0 \equiv \frac{4\pi}{3}\gamma_0 r_0^3$ and the contribution due to the charge of the core has been explicitly singled out.

Influence of Fields on the Parameters of Critical Nuclei. The expressions obtained in the preceding sections for the parameters of an equilibrium nucleus in the presence of an electric field still do not provide an answer to the question of the dependence of the parameters on the magnitude and sign of the charge of the core [with the exception of Eq. (35) for the excess large thermodynamic potential]. According to Eqs. (8), (23)-(26), (29), and (37), the determination of the dependence of \mathcal{P} , Γ_1 , λ_1 , R_1 , \bar{s} , γ , and $\Delta\Omega$ on the field reduces to the determination of the dependence of r on q from Eq. (32). The fact that the charge q appears in Eq. (32) only in the form of q^2 means that r is not dependent on the sign of the charge. Accordingly, Eq. (29) leads to independence of the surface tension with respect to the sign of the charge. Equations (8), (23)-(26), (35), and (37) demonstrate the dependence of \mathcal{P} , Γ_1 , λ_1 , R_1 , \bar{s} , $\bar{\Omega}$, and $\Delta\Omega$ on the sign of the charge.

Let us find the value of the root r of Eq. (32) corresponding to an unstable equilibrium of the nucleus with the β phase (the critical nucleus). In this case, we can solve Eq. (32)

in the approximation of a small value of q . Assuming that the deviation $\Delta r \equiv r - r_0$ is accordingly small, we linearize (32) with respect to Δr and q^2 . As a result we arrive at

$$r = r_0(T, \{\mu_i\}) + \left(a_0 + \frac{b}{2r_0}\right) \frac{q^2}{\gamma_0 r_0}. \quad (38)$$

From (38) it is seen that the conditions for the applicability of the approximation made are

$$bq^2/\gamma_0 r_0^3 \ll 1, \quad a_0 q^2/\gamma_0 r_0^2 \ll 1. \quad (39)$$

When the charge has a minimal value (equal to an elementary charge), conditions (39) actually restrict the dimensions of the nuclei accessible to consideration from below. For example, in the case of the condensation of water vapor near 0°C , $r_0 \gg 5 \text{ \AA}$ is required. In the following we shall restrict ourselves, as in (38), to the approximation indicated.

From (29) and (38) we have

$$\gamma = \gamma_0(T, \{\mu_i\}) + \frac{a_0 q^2}{r_0^2}. \quad (40)$$

Then from (8) and (38) we obtain

$$\mathcal{P} = \mathcal{P}_0(T, \{\mu_i\}) + 2a_0 q + \left(a_0 + \frac{b}{2r_0}\right) \frac{2bq^3}{\gamma_0 r_0^3}. \quad (41)$$

and from (23)-(25) and (38) we find

$$\Gamma_i = \Gamma_{i0}(T, \{\mu_i\}) - \left(a_0 + \frac{b}{2r_0}\right) (\rho_{i0}^\alpha - \rho_{i0}^\beta + \frac{2\Gamma_{i0}}{r_0}) \frac{q^2}{\gamma_0 r_0} + \left(\frac{\partial \mathcal{P}_0}{\partial \mu_i}\right)_{T, \{\mu_j \neq i\}} \frac{q}{r_0^2} + \left(\frac{\partial a_0}{\partial \mu_i}\right)_{T, \{\mu_j \neq i\}, r_0} \frac{q^2}{r_0^2}, \quad (42)$$

$$\lambda_i = \lambda_{i0}(T, \{\mu_i\}) - \left(a_0 + \frac{b}{2r_0}\right) \left(1 + \frac{2\lambda_{i0}}{r_0}\right) \frac{q^2}{\gamma_0 r_0} + \left[\left(\frac{\partial \mathcal{P}_0}{\partial \mu_i}\right)_{T, \{\mu_j \neq i\}} \frac{q}{r_0^2} + \left(\frac{\partial a_0}{\partial \mu_i}\right)_{T, \{\mu_j \neq i\}, r_0} \frac{q^2}{r_0^2} + \lambda_{i0} \left(\frac{\partial b}{\partial \mu_i}\right)_{T, \{\mu_j \neq i\}} \frac{q^2}{r_0^4}\right] / (\rho_{i0}^\alpha - \rho_{i0}^\beta), \quad (43)$$

$$R_i^2 = R_{i0}^2(T, \{\mu_i\}) + 3 \left[\left(\frac{\partial \mathcal{P}_0}{\partial \mu_i}\right)_{T, \{\mu_j \neq i\}} q + \left(\frac{\partial a_0}{\partial \mu_i}\right)_{T, \{\mu_j \neq i\}, r_0} \cdot q^2\right] / (\rho_{i0}^\alpha - \rho_{i0}^\beta) + 3 \left(\frac{1}{r_0} - \frac{1}{R_{i0}}\right) \left(\frac{\partial b}{\partial \mu_i}\right)_{T, \{\mu_j \neq i\}} \cdot q^2 / (\rho_{i0}^\alpha - \rho_{i0}^\beta), \quad (44)$$

where $\lambda_{i0} \equiv \Gamma_{i0} / (\rho_{i0}^\alpha - \rho_{i0}^\beta)$, $R_{i0}^2 = r_0^2 + 3\lambda_{i0} r_0^2$.

Similarly, from (26) and (38) we have

$$\bar{s} = \bar{s}_0(T, \{\mu_i\}) - \left(a_0 + \frac{b}{2r_0}\right) (s_{00}^\alpha - s_{00}^\beta + \frac{2\bar{s}_0}{r_0}) \frac{q^2}{\gamma_0 r_0} + \left(\frac{\partial \mathcal{P}_0}{\partial T}\right)_{\{\mu_i\}} \frac{q}{r_0^2} + \left(\frac{\partial a_0}{\partial T}\right)_{\{\mu_i\}, r_0} \frac{q^2}{r_0^2}. \quad (45)$$

Finally, from (37) with the aid of (38) we obtain

$$\Delta\Omega = \Delta\Omega_0(T, \{\mu_i\}) - 4\pi \mathcal{P}_0 q - 4\pi \left(a_0 + \frac{b}{r_0}\right) q^2 + \Delta\Omega_n. \quad (46)$$

Equations (38) and (40)-(46) define the dependence of r , γ , \mathcal{P} , Γ_i , λ_i , R_i , \bar{s} , and $\Delta\Omega$ on q in approximation (39).

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INFLUENCE OF DIFFUSION OF ELECTROPHORETIC DEPOSITION
IN A UNIFORM ELECTRIC FIELD

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An equation for calculating the weight of an electrophoretic deposit with consideration of the thermal motion of the particles has been obtained. The diffusion flows of the particles accompanying electrophoretic deposition in a uniform electric field influence the laws of deposition when $v^2t/4D \approx 5$, where v is the electrophoresis rate, D is the diffusion coefficient of the particles, and t is the time of action of the field.

The analysis of the experimental data obtained from the investigation of electrophoretic deposition is usually based on the theory in [1-3], in which it is assumed that the changes in the concentration of the dispersed system caused by the action of the electric field are completely determined by the electrophoresis rate and their thermal motion is not taken into account. For example, in the calculation of the weight of an electrophoretic deposit in [3] it was assumed that the concentration of the disperse system in the electrode gap remains constant under the action of the electric field and varies abruptly at the electrode surface. The neglect of diffusion in the investigation of electrophoretic deposition is justified in the case of coarsely dispersed systems and should result in some errors in the case of highly dispersed systems.

A theoretical investigation of electrophoretic deposition with consideration of diffusion was carried out in [4-6]. However, Us'yarov et al. [4] restricted themselves to consideration of the initial stage of electrophoretic deposition, in [5] a numerical method was used to solve one specific problem in electrophoretic deposition, and in [6] the flow of particles caused by the action of the electric field on them was not taken into account in the determination of the concentration profile of the electrode gap.

In this communication we present the results of an investigation of electrophoretic deposition in a uniform field with consideration of the diffusion of the particles. Our attention was focused on electrophoretic deposition with deposition parameters above the critical parameters [2, 3].

The concentration of a disperse system C at any point in an electrophoretic bath with different times of action t of an electric field is determined from the equation

$$\frac{\partial C}{\partial t} = -\operatorname{div} j, \quad (1)$$

in which $j = j_1 + j_2$, $j_1 = vC$ is the electromigrational flow (which is determined by the electrophoresis of the particles), v is the electrophoresis rate, $j_2 = -D \operatorname{grad} C$ is the diffusional flux, and D is the diffusion coefficient.

Electrophoretic deposition was investigated in a uniform electric field, for which Eq. (1) has the following form

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