TABLE 1. Characteristics of Synthesized Latexes

Polymeriza- tion system	R _H , Х	We 101	Δ, Α	W _n , kg H ₁ O/ kg NM	Kg ^{·10²} , kmoles/m	Electro lyte	kmoles/m ³
ST/R _s Mn _s OH	1290	1,36	272	1.03	14,62	Na, SO.	4,87
	1230	0.75	168	0.55	15,10		5,03
	1240	0,61	130	0,39	17,32	••	5,77
ST/R ₁₀ Mn ₂ OH	1200	1.63	241	0.96	17,28		5,76
	1380	0,55	109	0,28	19,99		6.66
	1110	0,47	57	0,17	28,13		9,38
ST, R ₁ Mn ₂ OH	1050	1.76	195	0,85	19,48	NaCl	9,74
						Na, SO,	6.49
						Na, PO,	4,87
	1200	0,71	100	0.30	22.27	Na, SO.	7,42
	1200	0.51	76	0,22	21.81		7,27
ST/R,,Mn,OH	1200	1,89	210	0.78	21,20	NaCl	10.60
						Na, SO,	7.07
						Na, PO,	5.30
	1420	0,76	114	0,28	23,75	Na, SO,	7,92
	1200	0.55	61	0.17	28.31		9.44
ST/R,,Mn,OH	1260	2,02	198	0.67	24,65		8,22
	1290	1.02	129	0.36	23,17	••	7,72
	1050	0.68	80	0.23	24.18		8.06
VA/R ₁₂ Mn ₂ OH	1460	18.27	432	1.86	17.60	••	5.87
	1460	13.46	403	1.64	14.84		4,95
47 PVA	1470	8.65	350	1,26	12.53	NaCl	6.27
						Na, SO,	4.18
						Na, PO	3.13
						BaCi,	4.18
						AICI,	3.13

n) ethoxy group; ST) styrene; VA) vinyl acetate; PVA) polyvinyl alcohol.

nonionogenic groups are stable. However, at distances greater than twice the thickness of the hydrate shells, the energy of attraction prevails (Fig. 3), as a result of which the particles can be fixed in the secondary potential minimum.

The introduction of comparatively small amounts of electrolytes (Fig. 2) somewhat lowers the potential energy of repulsion of the hydrate shells; however, it still exceeds the energy of attraction by three to four orders of magnitude, so that the dispersions remain in a stable state. Only under the action of heating or additions of large quantities of electrolytes is there an impairment of the stability and a coagulation of the dispersions stabilized by unsaturated noninongenic surfactants. From the condition that in the case of rapid coagulation $U_d = 0$, we can predict the critical concentration of the coagulant:

$$K_s = \frac{3.5 W_e}{M_e W_n} = i c_c \tag{6}$$

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where KS is the stability constant; c_c is the critical concentration of the coagulant.

The results of the calculation of the stability constants K_S of dispersions stabilized according to a solvate mechanism are presented in Table 1. The critical electrolyte concentration can be considered as the threshold of rapid coagulation for dispersions with this type of stabilization. We should mention that the coagulation thresholds found are many times (10-30) greater than the threshold of coagulation of colloidal systems stabilized by ionogenic surfactants in the presence of a significantly smaller content of the emulsifier [1].

As can be seen from the data presented in Table 1, the stability constant depends on the nature of the stabilizer, in particular, on the length of the hydrocarbon radical. The greatest stability is exhibited by dispersions stabilized by hexadecyl diethoxymaleate. A comparison of the data of viscosimetric measurements and investigations of the stability of latexes [5, 12] confirm these conclusions (Fig. 4). Comparing the stability constants for the latexes synthesized and those stabilized by OP-10 or PVA [12], widely used in industry, we can note that the attachment of nonionogenic groups to the surface of the particles by chemical localization increases the effectiveness of their stabilizing action.

LITERATURE CITED

- R. E. Neiman, Coagulation of Synthetic Latexes [in Russian], Izd. Voronezhsk. Univ., Voronezh (1967).
- 2. B. V. Deryagin, Theory of the Stability of Colloids and Thin Films [in Russian], Nauka, Moscow (1986).
- B. V. Deryagin, N. V. Churaev, F. D. Ovcharenko, et al., (eds.), Water in Dispersed Systems [in Russian], Khimiya, Moscow (1989).
- A. S. Gordeeva, N. M. Shevereva, R. V. Rodionova, and V. A. Volkov, Kolloidn. Zh., <u>52</u>, 574 (1990).
- N. M. Shevereva, R. V. Rodionova, and V. A. Volkov, Collection of Summaries of Reports at the Ninth International Conference on Surface Forces [in Russian], Moscow (1990), p. 97.
- 6. R. V. Rodionova, Synthesis and Investigation of the Colloidal Chemical Properties of a New Type of Nonionogenic Surfactant - Ethoxyalkylalkyl Maleates and Synthetic Latexes Based on Them: Dissertation for the Degree of Candidate of Chemical Sciences [in Russian], Moscow (1976).
- 7. I. F. Efremov, Periodic Colloidal Structures [in Russian], Khimiya, Moscow (1971).
- 8. R. V. Rodionova and V. A. Volkov, Kolloidn. Zh., 40, 508 (1978).
- 9. G. Zontag and K. Shtrenge, Coagulation and Stability of Dispersed Systems [in Russian], Khimiya, Leningrad (1973).
- E. M. Aleksandrova, A. S. Grodskii, N. A. Shabanova, and Z. M. Ustinova, Kolloidn. Zh., <u>37</u>, 537 (1975).
- V. A. Volkov, Surface-Active Substances in Detergents and Enhancers of Chemical Cleaning [in Russian], Legprombytizdat, Moscow (1985).
- 12. G. A. Denisova, N. M. Shevereva, R. V. Rodionova, and V. A. Volkov, Kolloidn. Zh., <u>52</u>, 960 (1990).

Colloid Journal of the Russian Academy of Sciences. 1991. V.53 (6), pp. 941-946.

ONE MECHANISM OF THE CHANGE IN THE CHARGE OF A DROP

IN AN ATMOSPHERE OF INERT GASES

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A theoretical model describing the loss of an electric charge by a charged drop evaporating in an inert-gas atmosphere is suggested. This model is characterized by a consideration of the presence of metastable atoms of the inert gas, upon collisions of which the vapor molecules may ionize (Penning ionization). Subsequent capture by the drop of ions primarily of opposite sign leads to discharge of the drop. Within the framework of the Fuchs method of joining ionic and molecular fluxes while taking into account the role of the image forces, the dependence of the rate of loss of charge by the drop and the rate of evaporation of the drop on the charge of the drop and gas pressure within the entire range of Knudsen numbers was investigated.

In experimental investigations of the processes of condensation of a super-saturated vapor onto a drop, usually inert gases are used as the passive noncondensing gas, in the atmosphere of which condensation or evaporation of the investigated substance occurs. This is a procedure used both in studying nucleation processes using a diffusion chamber or Wilson chamber and in observing individual drops in electrodynamic balance (current balance) setups. In this work we turn our attention to one circumstance characteristic of inert-gas atoms; the

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presence of long-lived metastable states with energies that take values from $\sim 10 \ to \ \sim 20$ eV for atoms of different inert gases. This characteristic of inert gases permits observation of the ionization of atoms or molecules of the investigated vapor during their collisions with an atom of an inert gas in a metastable state (Penning ionization [1, 2]). Since the energy of the metastable 2¹S and 2³S states of the helium atom is especially great and higher than the ionization potential of the overwhelming majority of substances (the singlet 2¹S possesses an energy of 20.61 eV and an average lifetime 0.03 sec; the triplet 2³S is characterized by an energy 19.82 eV and an average liftime 6·10⁵ sec), Penning ionization in helium can occur for virtually all the investigated vapors. The indicated property of helium is now finding use in ionization detectors in gas chromatography [3, 4].

Consideration of Penning ionization in the interpretation of the experimental data on nucleation on ions and data on the evaporation and condensation of surface-charged drops is essential if maintenance of a high concentration of inert gas atoms in a metastable state is possible under the experimental conditions. These metastable atoms, possessing high mobility and being electrically neutral, always prove to be in the active zone of nucleation in a diffusion chamber or in a Wilson chamber on account of thermal movement. Thus, despite the procedure providing for ions of only one sign in the nucleation zone, usually used in investigations of nucleation on ions, ions of both signs appear there as a result of collision of vapor molecules with metastable atoms. Under these conditions the charges of the ions, which apparently was also observed in the experiments of Rabeony and Mirabel [5] on the investigation of the "sign preference" of nucleation of vapors of polar liquids on ions.

For electrodynamic balance devices, Penning ionization can lead to the appearance of free ions around the evaporating drop, which may then be captured by the drop. Thus, the charge of the drop will decrease with the passage of time.

In this work we suggest a theoretical model describing the loss of electrical charge as a result of Penning ionization of a drop evaporating in an atmosphere of helium. It is suggested that the excitation of metastable states of helium atoms can occur either in the region of the electrodynamic balance setup near the electrode or uniformly through the entire volume of the working chamber under the influence of an external radioactive source, so that the concentration of metastable atoms close to the drop is kept constant.

For an analysis of the rate of change of the charge of the drop as a function of the gas pressure at arbitrary Knudsen numbers, let us use the well known method of N. A. Fuchs [6, 7]. Let us surround a drop of radius a with an imaginary sphere of radius a $+ \Delta$, where Δ is of the order of the length of the free path of the ions, which is a theoretical parameter. Henceforth we shall consider the problem of a spherically symmetrical drop with the origin of the coordinates in the center.

The number of ions entering a sphere of radius $a + \Delta$ in a unit time, assuming Maxwell distribution of the ions according to velocities, is equal to $\pi(a + \Delta)^2 c_i N(a + \Delta)$, where $\sqrt{a + T}$

 $c_i = \sqrt{\frac{8k_BT}{\pi m_i}}$ is the average Maxwell velocity of the ions; N(a + Δ) is the ion concentration

in the unit volume at a distance a + Δ from the center of the drop; m_i is the mass of the ions; T is the temperature of the gas; kg is Blotzmann's constant. However, only part of these ions will be captured by the drop. Introducing the coefficient of capture of ions α_i and considering the probability of escape of an ion from the surface of the drop as negligible, let us write an expression for the ion flux on the surface of the drop in the form

$$I = \alpha_i \pi (a + \Delta)^2 c_i N (a + \Delta)$$

The concentration N(r) of ions in a unit volume at a distance $r \ge a + \Delta$ can be found as the solution of a system of equations: the equation of steady-state diffusion of ions

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 D_1 \left(\frac{dN}{dr} + \frac{N}{k_{\rm B} T} \frac{d\varphi}{dr} \right) \right] + a \overline{c} n_m n = 0$$
⁽²⁾

and the equation of steady-state diffusion of vapor molecules

$$\frac{1}{r^2}\frac{d}{dr}(r^2D\frac{dn}{dr}) - \sigma\bar{c}n_m n = 0$$
(3)

Here D_1 and D are the diffusion coefficients of ions and vapor molecules; n and n_m are the concentrations of vapor molecules and metastable ions, respectively, in a unit volume; \overline{c} is the average relative velocity of vapor molecules and metastable atoms; σ is the cross-section of Penning ionization in the case of collision of vapor molecules with metastable atoms of the inert gas,

$$\varphi = \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{Ke^2 a^3}{8\pi\epsilon_0 r^2 (r^2 - a^2)}$$
(4)

is the potential of ion-drop interaction, in which the second term considers the presence of image forces in explicit form; Z is the charge of the nucleus in units of elementary

charge e;
$$\frac{1}{4\pi\epsilon_0}$$
 is a size coefficient in the SI system; $\kappa = \frac{\epsilon_L - 1}{\epsilon_L + 1}$, ϵ_L is the dielectric

permeability of the substance of the drop. The second terms in (2) and (3) describe the gain of ions at the expense of loss of vapor molecules as a result of Penning ionization.

Let us add to the system of (2) and (3) the boundary conditions at $r \rightarrow \infty$

$$N|_{r \to \infty} = 0, \quad n|_{r \to \infty} = 0 \tag{5}$$

and the conditions of joining of the fluxes at r = a + $\Delta,$ which, taking (1)-(3) into account, take the form

$$\kappa \pi a^2 c \left(n^{\rm S} - n \left(a + \Delta \right) \right) = -4\pi r^2 D \left. \frac{dn}{dr} \right|_{r=a+\Delta} \tag{6}$$

$$I = 4\pi D_i r^2 \left(\frac{dN}{dr} + \frac{N}{k_{\rm B} T} \frac{d\varphi}{dr} \right) \Big|_{r = q + \Delta}$$
⁽⁷⁾

Here α_K is the coefficient of condensation; n^S is the concentration of saturated vapor above the surface of the drop; c is the average Maxwell velocity of the vapor molecules.

Solving the system of Eqs. (2)-(3) with boundary conditions (5)-(7), we obtain

$$n(r) = \frac{J}{4\pi D} \frac{\exp[\nu(a+\Delta) - \nu r]}{[1 + \nu(a+\Delta)]r}$$
(8)

$$r_{T} = \frac{J - I}{4\pi D_{f}} \int_{r}^{\infty} \frac{dr'}{r^{2}} \frac{\varphi(r) - \varphi(r)}{k_{B}} \frac{J}{r} - \frac{J}{4\pi D_{f}} \frac{e^{\nu(a+\Delta)}}{1 + \nu(a+\Delta)} \int_{r}^{\infty} \frac{dr'}{r^{2}} \frac{\varphi(r)}{k_{B}} \frac{\varphi(r)}{r} \frac{r}{r(1 + \nu'r)},$$
(9)

where

(1)

v

$$\mathcal{Y} \equiv \alpha_K \pi a^2 c n^S \frac{1 + \nu (a + \Delta)}{1 + \nu (a + \Delta) + \frac{a^2 c \alpha_K}{4D (a + \Delta)}} \tag{10}$$

is the resultant flux of molecules evaporated from the drop at a set pressure of the inert gas v = $\sqrt{\sigma c} n_m/D$

$$\int_{1=\sqrt{2}}^{\infty} \frac{dr'}{r^{2}} \frac{\frac{\varphi(r') - \varphi(a + \Delta)}{kB}}{r^{2}} \left[1 - \frac{1 + \nu r'}{1 + \nu(a + \Delta)} e^{-\nu(r' - (a + \Delta))}\right]$$

$$- \frac{4D_{i}}{a_{i}(a + \Delta)^{2}c_{i}} + \int_{a + \Delta}^{\infty} \frac{dr'}{r^{\prime 2}} e^{\frac{\varphi(r') - \varphi(a + \Delta)}{kB^{2}}}$$
(11)

The expression for the ion flux I on the surface of the drop is most interesting for further analysis, since it determines the rate of loss of charge. Just as we should have expected, when $\Delta \gg a$ I \rightarrow 0, and when $\Delta \ll a$ we have from (11)

$$I = 4\pi a Dn^{S} \left[1 + va - e^{va} \frac{\varphi(r)}{\int dr e^{k_{B} \frac{r}{r}}} - \frac{vr}{(1 + vr)}\right]$$
(12)

Let the drop be negatively charged; then, for the rate of change of the charge of the drop we have

$$\frac{d\mathbf{Z}}{dt} = -(I^* - I^-) \tag{13}$$

where the superscripts + and - pertain to the fluxes of positive and negative ions, respectively; t is the time. Since for a negative charged drop $I^+ \gg I^-$, we shall henceforth be interested only in I^+ . It is convenient to change to new notations

$$z \equiv \frac{Ze^2}{4\pi\epsilon_0 k_B Ta}, \quad \tau = \frac{K}{2Z\epsilon}, \quad \delta \equiv \nu a\epsilon$$

$$z \equiv \frac{a^2 c \alpha_K}{4D(a+\Delta)}, \quad \beta_i \equiv \frac{\alpha_i (a+\Delta)^2 c_i}{4D_i a\epsilon}, \quad \mu \equiv \nu (a+\Delta)$$
(14)

Making the substitution of variable $\rho \neq \epsilon a/r'$ under the integral sign in (11) considering (4) and (14), we obtain

$$=\frac{\Im\beta_{\beta_{1}}}{\frac{\varphi(e+\Delta)}{b,\Phi(e,\Delta)+e}}\left\{\Phi(e,\Delta)-\frac{e^{\mu}}{1+\mu}\int_{0}^{e^{\frac{1}{\alpha+\Delta}}}d\rho e^{-\rho-\tau}\frac{\rho^{4}}{e^{2}-\rho^{2}}-\frac{\delta}{\rho}}{(1+\frac{\delta}{\rho})}\right\},$$
(15)

where

1*

$$\Phi(\epsilon, \Delta) \equiv \int d\rho e^{-\rho - \tau \frac{\rho^2}{(1-\rho)^2}}$$
(16)

is the standard integral, which arises in the N. A. Fucks method [7, formula (11)].

In general, integration in (15) can be performed only numerically; however, in the case of $\delta \ll 1$, corresponding to a low concentration of metastable atoms, the expression for I⁺ is substantially simplified. Let us rewrite the integral in brackets in (15) in the form

$$\int_{0}^{\frac{d}{1+\Delta}} \frac{d\rho}{d\rho} e^{-\rho - r} \frac{e^{\delta}}{e^{\delta}} = \frac{\delta}{\rho} \frac{1}{(\epsilon, \Delta)} + \int_{0}^{\frac{d}{1+\Delta}} \frac{d\rho}{d\rho} e^{-\rho - r} \frac{e^{\delta}}{(\epsilon^{\delta} - \rho^{\delta})} \left[e^{-\frac{\delta}{r}} \left(1 + \frac{\delta}{\rho} \right) - 1 \right]$$
(17)

Now let us note that when $\epsilon \frac{a}{a+\lambda} \gg \delta$, which is equivalent to the condition $\mu \ll 1$ and $\tau \leq 1$ according to (14), the following approximate equality exists:

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$$\int_{0}^{\frac{1}{\alpha+2}} d\rho e^{-\rho-\tau} \left[e^{-\frac{\delta}{\rho}} \right] \left[e^{-\frac{\delta}{\rho}} \right] \left[1 + \frac{\delta}{\rho} \right] = \left[1 + \frac{\delta}{\rho} \right] \left[1 + \frac{\delta}{\rho} \right] \left[1 + \frac{\delta}{\rho} \right]$$
(18)

It is not difficult to find the asymptote of the right-hand portion of (18) when $\delta \ll 1$, using the method of consolidatable aymptotic resolutions [8]. Breaking down the interval of integration in the right-hand portion of (18) (and, correspondingly, the integral itself) into two parts: $[0, \omega]$ and $[\omega, \infty]$, finding the asymptotes for each of the integrals at $\delta \ll \omega \ll 1$, as a result we find

$$\int_{0}^{\infty} d\rho e^{-\beta} \left[e^{-\frac{\delta}{\rho}} \left(1 + \frac{\delta}{\rho}\right) + 1 \right] \approx -\delta + \delta^{2} \left(\frac{3}{4} - \gamma\right) - \frac{1}{2} \delta^{2} \ln \delta + O(\delta^{3})$$
(19)

where γ = 0.5772 is Euler's constant. Then substituting (19) considering (17) and the strong inequality μ \ll 1 into (15), we obtain

$$I^{*} = \frac{\mathcal{I}_{\beta_{L}}}{\frac{\varphi(a+\Delta)}{\Phi(\epsilon,\Delta)\beta_{L} + e^{\frac{\varphi(a+\Delta)}{k_{B}T}}} \delta(1 + \frac{1}{2}\delta\ln\delta - 0.1728\delta)$$
(20)

Let us estimate the limits of applicability of the function obtained for I⁺. Let us note that the upper limit ∞ in (11), (12) and the lower limit 0 in (15)-(19) correspond to infinitely distant walls of the chamber in which the evaporating drop is investigated. Let R_0 be the effective finite size of the drop. Then the lower limit in (15)-(19) should be equal to c_a/R_0 . It is not difficult to note that replacement of $(c_a)/R_0$ by 0 at the lower limit of the integral in (19) does not lead to a large error only when the strong inequality $(c_a)/R_0 \ll \delta$ is fulfilled. Consequently, formulas (19) and (20) are correct under the condition

$$\frac{ea}{R_0} \leqslant \delta \leqslant \epsilon \frac{a}{a+\Delta} \tag{21}$$

or, considering (14)

$$\frac{1}{R_0} < \nu < \frac{1}{a+\Delta}$$
 (22)

The coefficient α_i of the capture of ions by the drop and the steady-state concentration of metastable particles n_m also make their own contribution to the complete dependence of I^+ on the gas pressure. Without discussing the details of the calculation, we should mention that for α_i^+ , considering the image forces at $Z \gg K$, we can obtain [9]

$$\alpha_{t} = 1 - \frac{(a+\Delta)^{2} - a^{2}}{(a+\Delta)^{2}} \left(1 - \frac{a^{2}}{(a+\Delta)^{2} - a^{2}} B^{V_{0}}\right) \exp\left(-\frac{mv_{m}^{2}}{2kBT}\right)$$
(23)

where

$$\equiv \frac{Ke^{2}}{8\pi\epsilon_{0}ak_{B}T} \frac{(a+\Delta)^{2}-a^{2}}{\frac{|Z|e^{2}}{8\pi\epsilon_{0}ak_{B}T}\left[(a+\Delta)^{2}+a^{2}\right] + \frac{\varphi(a+\Delta)}{k_{B}T}(a+\Delta)^{2}}$$
(24)

$$\frac{mv_m^2}{2k_{\rm B}T} \equiv \frac{a^2}{(a+\Delta)^2 - a^2} \left[\frac{|Z|e^2}{4\pi\epsilon_0 ak_{\rm B}T} + \frac{\varphi(a+\Delta)}{k_{\rm B}T} + \frac{Ke^2}{4\pi\epsilon_0 ak_{\rm B}T} B^{-\frac{1}{2}} \right]. \tag{25}$$

The steady-state concentration n_m of metastable atoms of the inert gas can be determined as the solution of the equation [10]:

$$D_m \nabla^2 n_m = -q_m + (\sigma_m c_m \bar{n} + b_m \bar{n}^2) n_m + \sigma \bar{c} n n_m$$
(26)

with arbitrary return of n_m to zero on the walls of the chamber. Here D_m is the diffusion coefficient for metastable atoms; c_m is the average velocity of metastable particles; \bar{n} is the concentration of inert gas atoms in a unit volume; the second term in the right-hand portion defines the rate of decrease in the concentration of metastable particles on account of double $(v_{\sigma m} c_m \bar{n})$ and triple $(vb_m n^2)$ collisions; q_m is the rate of production of metastable atoms in a unit volume. The solution of Eq. (26) is determined by the force function q_m and the concrete geometry of the working chamber and will not be discussed here. We should mention only that in the case when helium is taken as the inert gas, for the parameters entering into (26) at T = 300 K we have [10, 11] $D_m = 16.7 \cdot 10^{20} m^2/sec$, $\sigma_m = 9.8 \cdot 10^{-25} m^2$, $c_m = 1.8 \cdot 10^3 m/sec$, and $b_m = 2.5 \cdot 10^{-46} m^6/sec$.

In conclusion, as an example, let us estimate the rate of loss of charge (dZ)/(dt) by a drop of dioctyl phthalate at Z = 10 and a = 10^{-6} m in an atmosphere of helium at T = 300° K and a pressure P = 10^{5} N/m². Let us take the concentration of metastable particles as $n_m = 10^{6}$ m⁻³. For the case under consideration we have $n^{5} = 7 \cdot 10^{15}$ m⁻³, $\overline{c} = 1.8 \cdot 10^{3}$ m/sec, $c \simeq c_i = 1.3 \cdot 10^{2}$ m/sec, $D \simeq D_i = 1.34 \cdot 10^{-5}$ m²/sec, $\sigma = 3 \cdot 10^{-18}$ m², $\Delta \simeq 2.3 \cdot 10^{-8}$ m. From this, using (10), we find for the flux of molecules evaporating from the drop = $1.2 \cdot 10^{6}$ sec⁻¹, and for I⁺ from (20), considering (14) and (16) we obtain I⁺ = 0.02 sec⁻¹. Thus, in a minute the change $\Delta Z \simeq 1$, which can be detected experimentally under electrodynamic balance conditions.

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LITERATURE CITED

1. M. N. Zemansky, Phys. Rev., 34, 213 (1929).

R

 R. D. Rundel and R. F. Stebbings, The Role of Metastable Particles in Collision Processes. Case Studies in Atomic Physics, E. W. McDaniel and M. R. C. McDowell (eds.), Vol. 2 (1972), p. 547. 3. S. Lukač and J. Šačik, Chromatographia, 5, 258, 311 (1972).

- 4. F. Andrawes and A. Ramsey, J. Chrom. Sci., 24, No. 11, 513 (1986).
- 5. H. Rabeony and P. Mirabel, J. Phys. Chem., 91, 1815 (1987).
- N. A. Fuchs, Evaporation and the Growth of Drops in Gaseous Medium [in Russian], Izd. Akad. Nauk SSSR, Moscow (1958).
- 7. N. A. Fuchs, Geofis. Pura Appl., 56, 185 (1963).
- K. H. Hender and S. A. Orszag, Advanced Mathematical Methods for Scientists and Engineers, New York (1978), p. 593.
- 9. A. K. Shchekin, S. B. Leble, and D. A. Vereshchagin, Introduction to the Physical Kinetics of Rarefied Gases [in Russian], Izd. KGU, Kaliningrad (1990), p. 40.
- 10. H. S. W. Massey, Electronic and Ionic Impact Phenomena, Vol. 3, Clarendon Press, Oxford (1971), p. 1767.
- 11. W. P. Jesse and J. Sadauskin, Phys. Rev., 100, No. 6, 1755 (1955).

CRITERION FOR IDEAL POLARIZABILITY OF CONDUCTING PARTICLES

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We have obtained relations allowing us to estimate the value of the external electric field strength at which a conducting particle found in an electrolyte solution can be considered ideally polarizable, which corresponds to no electric current passing through it.

From the analysis presented in [1] of experimental work on measurement of the electrokinetic potential of conducting particles in aqueous electrolyte solutions, it follows that we can interpret the results obtained in these papers only within the framework of the theory of electrokinetic phenomena in nonconducting particles. According to [1], this is explained by the fact that under certain conditions the conducting particles should be considered as ideally polarizable, i.e., we can assume that there is no electric current passing through their surface. This question was first considered in detail in [2] for the special case when metal ion particles are present in the electrolyte. In this paper, we present a generalization of the ideas developed in [2] to the case of an arbitrary electrolyte, and we propose relations allowing us to estimate the conditions under which the metallic particles can be considered ideally polarizable.

Under the action of an external electric field, polarization charges are separated on the inner side of the surface of the conducting particle: negative charges where the force lines of the electric field enter the particle, positive charges where the force lines exit from it. As a result, the surface of the polarized particle can be considered as a system of two metallic electrodes immersed in the electrolyte solution. In this case, the part of the surface where separation of positive charge has been separated, will be the anode, and the remaining part, where the negative charge has been separated, will be the cathode. Such a model for a polarized conducting particle allows us to consider the process of passage of an electric current in the particle-electrolyte system as ordinary electrolysis.

Ions which approach each other under the action of an electric field from the volume of the electrolyte to the surface of the particle will be opposite in sign to the charges separated from the interior of the particle. For this discharge on the particle surface, i.e., for a current to be generated through the phase interface, the potential difference between the volume of electrolyte and the particle surface must be greater than the so called equilibrium potential, the magnitude of which is determined by the type of discharging ions [3]. As a result, passage of current is possible in a system of two electrodes only when

 $U_{\text{ext}} \succ \varphi_{\bullet}^{\circ} + \varphi_{c}^{\circ} \tag{1}$

where U_{ext} is the external potential difference applied to the system; φ_A^0 and φ_C^0 are the equilibrium potentials of the ions participating in the electrochemical reactions at the cathode respectively. the equilibrium potential difference $U_{eq} = \varphi_A^0 - \varphi_C^0$ is called the decomposition potential [3].

If inequality (1) is not satisfied, there is no electric current through the surface of the particle and such a conducting particle can be considered ideally polarizable.

The potential difference between two points found at opposite poles of the polarized spherical particle outside its electrical double layer, according to [1], is equal to

$$U_{ext} = 3 Ea$$
 (2)

(~)

where E is the external electric field strength; a is the radius of the particle. Taking into account (2), inequality (1) can be rewritten in the form

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