FROM THE CURRENT LITERATURE

Bubston structure of water and electrolyte aqueous solutions*

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Abstract. This paper develops the theoretical concept of a bubston, a stable gas bubble that exists in pure water and in electrolyte water solutions in equilibrium with their gaseous environment. A theoretical model of ion adsorption on a water surface is constructed and used to quantitatively describe the double electric layer that forms. These results also enable a thermodynamic description of a bubston structure in the water-gaseous environment system to be performed. It is shown that for certain temperatures and certain concentrations of dissolved impurity ions the emergence of such a structure is a first-order phase transition. The unique role of helium as a gaseous environment in the context under study is established: in this case, a bubston structure does not appear whatever the initial ion concentration, and the solubility of helium itself increases with increasing temperature. The mechanism of formation of experimentally observed bubston clusters is discussed.

Keywords: stable gas bubbles, thermodynamically equilibrium systems, ionic adsorption at the water surface, double electric layer, first-order phase transition

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1. Introduction

When studying cavitation phenomena, there long posed the problem of explaining the existence of stable gas bubblescavitation nuclei-in pure water containing no foreign microparticles (or any cracks in the walls of the cuvette in which the water is held). The necessity of existing such species follows from the fact that, as was shown in numerous studies devoted to this phenomenon, the threshold of the mechanical strength of water (i.e., the magnitude of the negative pressure p that leads to the formation of a cavitation pocket) is always substantially lower (by at least an order of magnitude), in spite of the careful purification of the water, than the molecular strength of water $p^* \sim \sigma n^{1/3} \approx 3 \times 10^3$ atm $(\sigma \sim 10^2 \text{ erg cm}^{-2} \text{ is the coefficient of surface tension, and}$ $n = 3.3 \times 10^{22}$ cm⁻³ is the number density of water molecules). The only factor that can be responsible for such a decrease in the threshold of strength may be the existence in water (as well as in some other liquids) of stable gas bubbles (cavities) in a sufficiently high concentration. This point of view became generally accepted long ago; however, for many years it has not been theoretically or experimentally substantiated. An important circumstance that attracted wider interest in this problem was the fact that a similar situation was observed in recent years in the case of the phenomenon of

* In this issue of the journal, we publish the last article by F V Bunkin written (together with his younger son N F Bunkin) shortly before his death. This article, in fact, represents a survey of Fedor Vasil'evich's work concerning the thermodynamics of stable gas bubbles in liquids and the novel ideas on this problem resulting from his many years of reflection. This material may seem strange and even debatable for this journal; however, the publication of this article is not only a tribute to the memory of an outstanding scientist, but also a suggestion for experimentalists to check the theoretical predictions contained in the article. The obituary devoted to F V Bunkin was published in the July issue of *Physics–Uspekhi* **59** 722 (2016). (*Note from the Editorial Board.*)

optical (laser) breakdown of water: the threshold for the breakdown of carefully purified water is always substantially lower than the values that correspond to the threshold of ionization of the molecular structure of the liquid water itself. And here, also, as was shown for the first time in paper [1], the physical reason lies in the existence of stable gas bubbles that fall into the focal region of the laser beam. In them, as in free gas, a breakdown occurs due to the development of an electron avalanche.

Two principal questions remained unsolved: first, how can gas bubbles arise in a continuous medium (water) that is in equilibrium with an external gaseous medium (e.g., with ambient air);¹ and, second, why do such bubbles become stable after they appear?

The first question arises, strictly speaking, only if the liquid is not near the boiling temperature or in a superheated state. Otherwise, vapor bubbles - nuclei of the new phasecan arise in it with a noticeable probability as a result of thermal fluctuations; these bubbles, in turn, can serve as nuclei of cavitation and optical breakdown. However, far from the boiling point the probability of the formation of vapor nuclei is extremely small; therefore, their role in the problem considered is ruled out. As to the second question, it is *a priori* obvious that the stability of a gas bubble cannot be ensured only due to the mechanism of surface tension. In this case, the necessary condition for the stability of the bubble would be as follows: $p_{\rm b} = p + 2\sigma/R$ (where $p_{\rm b}$ is the gas pressure inside the bubble, p is the external pressure, and Ris the bubble radius). However, this condition simultaneously indicates that relative to the gas inside the bubble the solution itself is unsaturated; therefore, a diffusive escape of gas particles should occur from the bubble into the liquid, i.e., the bubble should become dissolved. At the same time, as long ago as the first quarter of the 20th century, experiments [2] were performed that showed that on the water surface (in particular, on the surface of an air bubble in water) there are electric charges. Alty [2] reported that their presence could be qualitatively explained by a selective (with respect to the charge sign) adsorption of ions, which are always present in water, on the surface. However, this idea of the selective adsorption of ions was not developed further for a long time. The first attempt to take into account the role of adsorbed ions in the stability of gas bubbles was presumably undertaken in paper [3]. However, the concept of the selective adsorption of ions was not developed in that study; therefore, the problem of the stability of bubbles with allowance for the adsorption of ions proved to be only posed, but not completely solved. The next attempt to solve the problem of the stability of a bubble was undertaken in paper [4], where the term *bubston* itself (an abbreviation of 'bubble stabilized by ions') was introduced. However, the results obtained in Ref. [4], just as in the subsequent study [5], proved to be insufficient for the establishment of an unambiguous dependence of the parameters of stable bubbles—bubstons—on the properties of the solution itself.

The failure of the above-mentioned and other attempts to completely solve the problem of the stability of gas bubbles in liquid ionic solutions (in particular, in water) was eventually due to a lack of theoretical concepts concerning the mechanism of selective adsorption of ions on the surface of an

aqueous ionic solution. Such a problem has recently been solved in Ref. [6]. The present publication, which has the character of a monograph, is devoted to a description of the theoretical aspects of the appearance of stable mesoscopic cavities - bubstons - in aqueous solutions of strong electrolytes that are in equilibrium with an external gaseous medium far from the boiling temperature. As a result of this theoretical work, the foundations were laid for the experimental study of various properties of the bubston structure arising in such a medium depending on the parameters of the problem: the concentration of ions, temperature, and pressure. Numerous experimental data concerning these problems, which were obtained by one of the authors of this paper, N F Bunkin, and his colleagues, are presented in the Conclusion, but only in the form of references to published works. In this case, we mean only solutions of strong electrolytes, i.e., those with given concentrations of impurity ions independent of temperature. It is important to note that the intrinsic aqueous ions H⁺ and OH⁻ that arise as a result of the thermal electrolytic dissociation of water molecules are not dissolved ions in the commonly accepted understanding of the dissolution phenomenon, since their concentration is unambiguously determined by the water temperature and is independent of the presence of any ionic sorbents in water. This constitutes the essential distinction from the solutions with a given amount of a strong electrolyte, in which the total number of ions, including adsorbed ones, is retained, whereas the number of truly solved (free) ions (their concentration) is not retained in the presence of sorbents. It is obvious already from the above that the presence in the liquid (in particular, in water) of only intrinsic ions cannot, in general, lead to the formation of bubstons, since this would mean an increase in the free energy of the liquid only due to the absorption of heat. The free energy could increase in this case due to the emergence of the surface of bubstons and their electric fields, whereas the absorption of heat could occur as a result of the dissociation of the molecules of the liquid itself. But such a process, as is known from thermodynamics, is impossible.

Further, we will theoretically consider mainly 'canonical' ionic solutions, by which we mean the aqueous solutions of Na⁺ and Cl⁻ ions (i.e., of the NaCl salt) that have been thoroughly purified of any colloid particles. It is precisely such solutions that, on the one hand, permit one to advance sufficiently far in the physical understanding of the appearance of a bubston structure in them, and, on the other hand, are the direct products of various technologies of the water purification. There are grounds to assume that in ultimately purified water the ions of Na⁺ and Cl⁻ always exist in concentrations exceeding those of other impurity ions. The dominating role of such ions first of all follows from the composition of salts dissolved in the world reserves of water. The solid residue of sea water, which is almost the same for both oceans and open seas, has, as is known [7], the following composition: NaCl, 78.32%; MgCl₂, 9.44%; KCl, 1.69%; MgSO₄, 6.4%, and CaSO₄, 3.9%. After the first stage of purification (distillation, ion-exchange sorption), only inorganic ions are retained in the water, irrespective of the type and geographic location of the source of water on Earth. At the second stage of purification, the separation of the retained ions is carried out by filtration through a porous wall (technology of back osmosis, or Milli-Q technology). As a result, the ions with the smallest radii remain. In particular, Na⁺ ions (their radius is $\delta_i = 0.98 \text{ Å}$) and Cl⁻ ions

¹ It is certainly assumed that the liquid is under stationary conditions and a constant active source of gas that is introduced into it (generator of bubbles) is absent.

 $(\delta_i = 1.81 \text{ Å})$ fall into this category and, therefore, should represent the dominant component of impurity ions in such a purified water.

Water is perceived as being extremely pure if its electrical resistivity λ at room temperature $t = 25 \,^{\circ}\text{C}$ is close to $\lambda = 1.8 \times 10^7 \,\Omega$ cm. This value of λ is mainly determined by the intrinsic ions H⁺ and OH⁻ at this temperature, i.e., in fact it is the 'intrinsic resistivity' of water. Indeed, the total resistivity (measured in the process of the purification) is defined as

$$\lambda = \frac{\lambda_{\rm w}\lambda_1}{\lambda_{\rm w} + \lambda_1} = \frac{\lambda_{\rm w}}{1 + \lambda_{\rm w}/\lambda_1} \,, \tag{1.1}$$

where λ_w is the intrinsic water resistivity, and λ_1 is the 'impurity' water resistivity (i.e., caused only by impurity ions). While the water is purified of impurity ions, its resistivity λ_1 increases, and the measured resistivity λ tends to a maximum value λ_w . Independent experimental data [8] on measured mobilities of H⁺ and OH⁻ ions at $t = 25 \,^{\circ}\text{C}$, according to the Nernst relationships, give the following values of the diffusion coefficients of these ions: $D_{\text{H}^+} = 9.27 \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1}$, and $D_{\text{OH}^-} = 5.07 \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1}$. Since at such a temperature the number density of the ions in pure water is $n_{\text{iw}} = 6 \times 10^{13} \, \text{cm}^{-3} \, (\text{pH} = 7)$, for the intrinsic resistivity of water we have

$$\lambda_{\rm w} = \frac{T}{e^2 n_{\rm iw} (D_{\rm H^+} + D_{\rm OH^-})} = 2.1 \text{ CGSE} = 1.9 \times 10^7 \ \Omega \text{ cm} \,.$$
(1.2)

Hereinafter, *T* is the temperature in energy units (at $t = 25 \,^{\circ}$ C, $T = 4.1 \times 10^{-14}$ erg). The thus obtained value λ_w of resistivity is only 5% higher than the extreme value $1.8 \times 10^7 \,\Omega$ cm. Such a divergence may, of course, be due to the errors in measuring both the mobilities of H⁺ and OH⁻ ions and the extreme value of the resistivity itself. However, if we assume that the true value of the intrinsic resistivity of water λ_w is equal to precisely $1.9 \times 10^7 \,\Omega$ cm, then the lower value of the measured extreme resistivity $\lambda = 1.8 \times 10^7 \,\Omega$ cm should be referred to the small contribution (which is not removed by the purification) of impurity ions to λ . Assuming that these impurity ions are Na⁺ and Cl⁻, let us determine their number density n_i at which the total resistivity is $\lambda < \lambda_w$. According to (1.1) and (1.2) and to the following formula

$$\lambda_1 = \frac{1}{e^2 n_{\rm i} (D_{\rm Na^+} + D_{\rm Cl^-})} , \qquad (1.2a)$$

we obtain

$$n_{\rm i} = n_{\rm iw} \, \frac{D_{\rm H^+} + D_{\rm OH^-}}{D_{\rm Na^+} + D_{\rm Cl^-}} \left(\frac{\lambda_{\rm w}}{\lambda} - 1\right). \tag{1.3}$$

The diffusion coefficients of the Na⁺ and Cl⁻ ions in water at room temperature are well known, being equal to $D_{\text{Na}^+} = 1.36 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{Cl}^-} = 2.03 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; therefore, according to the above values of D_{H^+} and D_{OH^-} , the second multiplier in expression (1.3) is equal to 4.2. Correspondingly, we obtain

$$n_{\rm i} = 2.52 \times 10^{14} \left(\frac{\lambda_{\rm w}}{\lambda} - 1 \right) \,{\rm cm}^{-3} \,.$$
 (1.4)

Table 1

Hence it follows that at $\lambda = 1.8 \times 10^7 \Omega$ cm, when $\lambda_w/\lambda - 1 = 5.55 \times 10^{-2}$, the number density of impurity ions is $n_i = 1.4 \times 10^{13}$ cm⁻³. This value should be considered the minimum number density of the Na⁺ and Cl⁻ impurity ions reached as a result of the purification of water using Milli-Q technology at temperature t = 25 °C.

It is important to note that formula (1.4) determines the number density of properly dissolved (free) Na⁺ and Cl⁻ ions in water with an arbitrary resistivity $\lambda < \lambda_w$. Hereinafter, we will denote this density as n_i^s . In the case of the existence of a bubston structure in the ionic solution, some of the dissolved impurity ions prove to be not free (they are adsorbed on the surface of gas bubbles), and enter into the composition of the ionic shells that surround the bubbles, forming so-called double electric layers. In this case, the number density of the properly dissolved ions is $n_i^s = sn_i^0$, where n_i^0 is the total number density of the dissolved ions, and the quantity s determines the fraction of free ions (its values lie in the range of $0 < s \le 1$). We will see below that the quantity *s* enters into a number of parameters that determine, at given values of the temperature and the number density of ions n_i^0 , the characteristics of the bubston structure of the solution.

Table 1 lists the values [calculated from formula (1.4)] of the number density n_i^s of the properly dissolved Na⁺ and Cl⁻ ions in water at $t = 25 \,^{\circ}$ C, which correspond to seven values of the solution resistivity.

It can be seen from the data given in the table that the water purified in this or another way—according to the Milli-Q technology ($\lambda = 1.8 \times 10^7 \ \Omega$ cm) or double distillation ($\lambda \simeq 10^6 \ \Omega$ cm)—represents a solution of Na⁺ and Cl⁻ ions with the number density of ions falling in the range $1.4 \times 10^{13} \ \text{cm}^{-3} < n_i^s < 4.5 \times 10^{15} \ \text{cm}^{-3}$. Solutions with larger values of n_i^s should be considered as specially prepared solutions of the NaCl salt in carefully purified water. This refines the concept of a canonical ionic solution we introduced above. All numerical estimates given in this paper refer to the ion number densities $n_i^s > 10^{14} \ \text{cm}^{-3}$.

A quantitative consideration of the problems that are touched in this paper is carried out in terms of the Gaussian absolute system of units (CGSE). The dielectric constant ε of water is assumed to be equal to 80; the Bjerrum length $l_{\rm B} = e^2/\varepsilon T$ that is frequently encountered in formulas is assumed to be equal to 7.0×10^{-8} cm; the specific energy of the surface tension is $\sigma = 73$ erg cm⁻²; the radius of the water molecule is $\delta_1 = 1.38$ Å, and, finally, the radii of the Na⁺ and Cl⁻ ions are 0.98 and 1.81 Å, respectively.

2. Model of the adsorption of ions dissolved in water on its surface — a boundary with gas

Let us consider an impurity ion with a charge *e* that is located in water at a depth *z* from its surface serving as a flat boundary with a gas medium. In a wide range of *z* values, when $n^{-1/3} \ll z \ll a_D$, where $n = 3.3 \times 10^{22}$ cm⁻³ is the volume number density of water molecules $(n^{-1/3} = 3.2 \text{ Å})$, $a_D = (8\pi I_B n_i^s)^{-1/2}$ is the Debye radius $(n_i^s$ is the number density of impurity ions in water far from its surface; at $n_i^s \approx$ 3×10^{15} cm⁻³, the magnitude of $a_D \sim 0.1 \ \mu\text{m}$), the force effect of the surface on the ion under consideration can be

 1.8×10^{7} 2×10^{6} 10^{6} 3×10^5 10^{5} 3×10^4 $\lambda, \Omega \, \mathrm{cm}$ 6×10^{6} $1.4 imes 10^{13}$ 5.4×10^{14} $2.1 imes 10^{15}$ 1.6×10^{17} 4.5×10^{15} 1.6×10^{16} 4.8×10^{16} $n_{\rm i}^{s}, {\rm cm}^{-3}$

described in terms of macroscopic electrostatics: the ion as a separate charge *e* is repulsed from the surface with an 'image force' whereto a potential energy corresponds [9]:

$$W_0 = \frac{e^2(\varepsilon - 1)}{4z(\varepsilon + 1)\varepsilon} \approx \frac{e^2}{4\varepsilon z}$$
(2.1)

(for water, $\varepsilon = 80 \ge 1$). The physical meaning of the conditions indicated for the depth z is as follows: as $z \ll a_{\rm D}$, the Debye screening of the ion can be ignored, the ion can be considered a separate charge, and the inequality $z \ge n^{-1/3}$ points out the applicability condition of the macroscopic electrostatics, i.e., the validity of formula (2.1) itself. It can be assumed that at small z the potential is approximately written out as formula (2.1) up to z values that are no less than $3n^{-1/3} = 9.6$ Å. At the same time, it is obvious that with a further decrease in z from the level of $3n^{-1/3}$, when the macroscopic description stops being valid, the repulsion force acting on the ion should first decrease and then pass into the attraction force to individual surface water molecules. This means that the maximum energy W^{max} of the repulsion of an ion from the surface is approximately $W_0(z = 3n^{-1/3}) \approx 4.7 \times 10^{-3}$ eV. It is just such a potential barrier that separates the ions dissolved in water from its surface. However, at room temperatures $W_0^{\text{max}}/T \approx 0.2$; therefore, in the process of their thermal motion, the ions are capable of reaching the surface of the water. The minimum possible value of z in this case should be scaled as $\delta_0 = (\delta_1 + \delta_i)$, where $\delta_1 = 1.38$ Å is the radius of the water molecule, and δ_i is the ion radius. This corresponds to the representation of the surface monomolecular layer of water as the plane z = 0, on which the centers of molecules—'hard spheres' with radii $\delta_1 = 1.38$ Å—are located. The specific number density (per unit area) of water molecules in such a layer has a random nature; its average values γ_1 are estimated as $\gamma_1 = n^{2/3} = 10^{15} \text{ cm}^{-2}$, where $n = 3.3 \times 10^{22} \text{ cm}^{-3}$ is the average volume number density of water molecules. Simultaneously, the average spacing between the molecules in the surface layer is $(\gamma_1/2)^{-1/2} = 1.58$ Å. All the distances in such a model are the spacings between the centers of the corresponding 'spheres'. For the Na⁺ ions ($\delta_i = 0.98$ Å), the scale $\delta_0 = 2.36 \text{ Å}$; for the Cl⁻ ions ($\delta_i = 1.81 \text{ Å}$), we obtain $\delta_0 = 3.19$ Å.

It is obvious that at $z \sim \delta_0$ the dominating role belongs to the interaction of the ion with separate surface water molecules; the energy of this interaction, as is well known, is written out as $-\beta e^2/2r^4$, where $\beta = 1.47 \times 10^{-24}$ cm³ is the average polarizability of water molecules, and r is the distance between the molecule and the ion. For the Na⁺ ions at $z = r = \delta_0 = 2.36$ Å, the attraction energy of the ion to the molecule ('ion affinity') is 0.34 eV; for the Cl- ions at $z = \delta_0 = 3.19$ Å, this energy equals 0.10 eV. Since this energy is proportional to $1/r^4$, it can be assumed that the ion sticks only to one water surface molecule, transforming into an adsorbed ion with a certain lifetime. The surface density of adsorbed ions γ in this case is determined by the concentration of the dissolved ions, and the above given ion affinity energies for the Na⁺ and Cl⁻ ions coincide with the values of the adsorption energy U_{AD} of these ions: $U_{AD}^{Na^+} = 0.34$ eV, and $U_{\rm AD}^{\rm Cl^-} = 0.10$ eV. It follows from the above that the maximum possible surface number density γ of adsorbed ions is $\gamma_{max}=\gamma_l=10^{15}\ cm^{-2}.$

The above picture exposing the interaction of an ion with surface molecules of water is described by the potential $W_1(z)$, which is written out as

$$W_1(z) = \frac{\lambda}{z^n} - \frac{1}{2} \frac{\beta e^2}{z^4} \,. \tag{2.2}$$

Here, the first term defines the repulsion energy $(\lambda > 0)$ caused by the impossibility of overlapping the electron shells of the ions and water molecules. In the adopted 'hard-sphere' model, the exponent *n* should be sufficiently large (see below). The energy $W_1(z)$ passes through minimum at the point $z = z_0$, at which $W'(z_0) = 0$ and $W''(z_0) > 0$. Simple calculations show that

$$W_1(z_0) = W_1^{\min} = -\frac{1}{2} \frac{\beta e^2}{z_0^2} \left(1 - \frac{4}{n}\right)$$
$$W_1''(z_0) = \frac{10\beta e^2}{z_0^6} \left(\frac{n+1}{5} - 1\right).$$

Hence, it can be seen that in our model we should assume that $n \ge 4$ and $z_0 = z_{\min} = \delta_0$. At n = 40, we obtain

$$W_1^{\min} = -\frac{1}{2} \frac{\beta e^2}{\delta_0^4}, \qquad W_1''(z_0) = \frac{70\beta e^2}{\delta_0^6}.$$
 (2.3)

Thus, the total potential $W_1(z)$ of the ion interaction with the water surface in the entire range of z values, $z_{\min} = \delta_0 < z < \infty$, looks like what is plotted in Fig. 1. When in an electric field with such a potential, the ions can reach the surface of the solution and be adsorbed on it. According to the above, the adsorption energy of the ions is given by

$$U_{\rm AD} = -W_1^{\rm min} = \frac{\beta e^2}{2\delta_0^4} \,. \tag{2.3a}$$

For the Na⁺ ions, this energy is 0.34 eV \approx 33 kJ mol⁻¹; for the Cl⁻ ions, it is 0.10 eV \approx 9.7 kJ mol⁻¹. The second formula in Eqn (2.3) makes it possible to determine the frequency *v* of ion vibrations in an adsorbed state:

$$v = \frac{1}{2\pi} \sqrt{\frac{W''(z_0)}{m}},$$
 (2.3b)



Figure 1. Dependence of the potential energy of an ion in water at a distance z from the surface; $z_1 \cong 3n^{-1/3} = 9.6$ Å, $z_{\min} = \delta_0$, $W^{\max} = W_0(z_1) \cong 4.7 \times 10^{-3}$ eV, and $W^{\min} = -\beta e^2/2\delta_0^4$. For the Na⁺ ions, $\delta_0 = 2.36$ Å, and $W^{\min} = 0.34$ eV. For the Cl⁻ ions, $\delta_0 = 3.19$ Å, and $W^{\min} = 0.1$ eV.

where *m* is the ion mass. For the Na⁺ ions, this frequency is $v = 9.5 \times 10^{12} \text{ s}^{-1}$; for the Cl⁻ ions, $v = 3.1 \times 10^{12} \text{ s}^{-1}$.

To establish the adsorption equilibrium, it is necessary that the desorption energy $U_{\rm D} = (W^{\rm max} + U_{\rm AD} - U_{\rm a})$ be sufficiently large compared to *T* (in order for there to be a significant potential barrier preventing the thermodesorption process). Here, $W^{\rm max} = 4.7 \times 10^{-3}$ eV for ions of both signs, and $U_{\rm a}$ is the activation energy of adsorption, i.e., in our case, the repulsion energy of the probe adsorbed ion from the water surface layer due to the lateral Coulomb interaction of this ion with all other adsorbed ions.

The maximum value of the energy U_a corresponds to meeting the following conditions: (1) the surface number density γ of adsorbed ions passes through maximum, i.e., it is equal to $\gamma_1 = 10^{15} \text{ cm}^{-2}$; (2) the *z* coordinate of only one probe ion exceeds its minimum value δ_0 and is equal to $z = \delta_0 + z_1$, where $z_1 > 0$, and (3) the sign of all adsorbed ions coincides with the sign of the probe ion. To determine this energy, we take advantage of one particular result² which follows from the Gauss electrostatic theorem. In our problem, the infinite medium is formed from a gas ($\varepsilon_2 = 1$), the insulator evolves from a water solution ($\varepsilon_1 = \varepsilon = 80$), and the solid angle is $\Delta \Omega = 2\pi$. The formula for **E**(*r*) that is given in footnote 2 defines the strength of the field created at the point of the location of the probe ion by adsorbed ions taking up positions far from the probe ion. Let us consider the surface of the solution as a plane in the polar coordinate system (ρ, φ, z) with the polar z-axis passing through the probe ion. Then, the elementary surface charge dq = $e\gamma_1 \rho \, d\varphi \, d\rho$ under the condition of $(z_1/\rho)^2 \ll 1$ creates, according to the general formula at the point of the location of the probe ion, a field of strength $d\mathbf{E} = (2 dq/\epsilon \rho^2) \mathbf{r}/r$, with the projection of this strength onto the normal (z-axis) being $(2 dq/\epsilon \rho^2) z_1/\rho = 2e\gamma_1 z_1 d\varphi d\rho/\epsilon \rho^2$. The total force $F(z_1)$ acting on the probe charge is thus determined through the multiplication by the probe charge e and integrating with respect to φ in the interval $(0, 2\pi)$, and with respect to ρ in the interval (ρ_0, ∞) . Here, ρ_0 is the average distance between the adsorbed ions. As a result, we arrive at

$$F(z_1) = \frac{4\pi e^2 \gamma_1 z_1}{\varepsilon \rho_0} \,,$$

and the maximum activation energy U_a of adsorption corresponding to this force is equal to

$$U_{\rm a} = \int_0^{z_1} F(z_1) \, \mathrm{d}z_1 = \frac{2\pi e^2 \gamma_1 z_1^2}{\epsilon \rho_0} \tag{2.4}$$

 $(\gamma_1 = 10^{15} \text{ cm}^{-2}, \text{ and } \rho_0 = 1.58 \text{ Å})$. Under equilibrium conditions, the quantity z_1^2 should be set equal to the average square of thermal fluctuations of the oscillator coordinate, i.e., equal to $\overline{z^2} = (T/m)/(2\pi v)^2$, where *m* is the ion mass, and *v* is the frequency of ion oscillations in the adsorbed state. For the Na⁺ and Cl⁻ ions, these values are equal to 3.83×10^{-23} g and $v = 9.5 \times 10^{12} \text{ s}^{-1}$, and 5.92×10^{-23} g and $v = 3.1 \times 10^{12} \text{ s}^{-1}$, respectively (see above). Based on formula

(2.4), we obtain for the activation energies $U_a^{\text{Na}^+} = 4.2 \times 10^{-4} \text{ eV}$, and $U_a^{\text{Cl}^-} = 6.1 U_a^{\text{Na}^+} = 2.6 \times 10^{-3} \text{ eV}$. Given the energies U_D and U_a and the frequencies v of the

Given the energies U_D and U_a and the frequencies v of the ion oscillations in the adsorbed state, we can consider the problem of the selective character of the process of the ion adsorption. The lifetime of an ion in the adsorbed state is $\tau = v^{-1} \exp(U_D/T)$. Therefore, the ratio between the Na⁺ and Cl⁻ ion lifetimes in these states is given by

$$\frac{\tau^{\mathrm{Na}^{+}}}{\tau^{\mathrm{Cl}^{-}}} = \frac{\nu^{\mathrm{Cl}^{-}}}{\nu^{\mathrm{Na}^{+}}} \exp\left(\frac{U_{\mathrm{AD}}^{\mathrm{Na}^{+}} - U_{\mathrm{AD}}^{\mathrm{Cl}^{-}} + U_{\mathrm{a}}^{\mathrm{Cl}^{-}} - U_{\mathrm{a}}^{\mathrm{Na}^{+}}}{T}\right). \quad (2.5)$$

According to the above-made quantitative estimates, $v^{Cl^-}/v^{Na^+} \approx 0.33$, and

$$U_{\rm AD}^{\rm Na^+} - U_{\rm AD}^{\rm Cl^-} + U_{\rm a}^{\rm Cl^-} - U_{\rm a}^{\rm Na^+} = (0.24 + 2.2 \times 10^{-3}) \text{ eV};$$

therefore, $\tau^{Na^+}/\tau^{Cl^-} \approx 4 \times 10^3$. Hence it follows that the Cl⁻ ions cannot compete with the Na⁺ ions from the viewpoint of adsorption. Note that the lifetime itself of the Na⁺ ion in the adsorbed state, τ^{Na^+} , according to our estimates equals 7×10^{-8} s. This result can be considered as one more reason indicating the impossibility of the formation of bubstons via the adsorption of the intrinsic ions of water on its surface: the adsorption of the H⁺ and OH⁻ ions would lead to the formation of the H₃O⁺ and H₃O⁻₂ ions, whose lifetime, as is well known, is several orders of magnitude less than the value of τ^{Na^+} obtained above.

3. Appearance of bubston nuclei in aqueous ionic solutions

From the physical viewpoint, it is of interest to consider the following question: how can cavities of a mesoscopic size arise in water in a state far from the boiling point? We will, as before, proceed from the assumption that even the most purified water represents a solution of Na⁺ and Cl⁻ ions and of particles of a neutral gas with which the solution is in equilibrium. The mesocavities arising in such solutions will be called bubston nuclei. The process of the formation of such nuclei is identical to the process of the nucleation of ionic crystals of the NaCl salt in the Na⁺ and Cl⁻ aqueous solutions. The crystallization process itself begins from the formation of droplets of an ionic condensate, i.e., of ionic NaCl crystallites of mesoscopic dimensions. Having arisen with some probability, such a droplet can remain quasistable only if the concentration of dissolved Na⁺ and Cl⁻ ions in it is sufficiently large. In supersaturated solutions such a droplet will continue growing (with a probability close to unity) with the formation of macroscopic NaCl crystals. In the solutions far from saturation, the mesodroplets cannot retain their stability; their decomposition occurs, which has the character of a 'Coulomb explosion', which leads to the formation of mesocavities in the solution.

The mechanism of the formation of bubston nuclei outlined above requires greater detail and, first of all, poses the question of growth of ionic droplets: how they arise and how they grow? It is assumed that there are no stable inhomogeneities (e.g., in the form of foreign condensed particles) in the solution and, thus, the only 'defects' of the structure of the aqueous ionic solution comprise neutral particles of a gas that are contained in the solution. It is precisely on such defects, in our opinion, that the growth of ionic droplets begins as a result of dissolved ion diffusion

² The field strength at an arbitrary point of space at a distance *r* from a point charge *q* located at the vertex of an infinite cone (or pyramid) with a solid angle $\Delta\Omega$, which is uniformly filled with an insulator with a dielectric constant ε_1 and is embedded into an infinite uniform medium with a dielectric constant ε_2 , is equal to $\mathbf{E}(r) = (e/r^2)(\mathbf{r}/r)[\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)\Delta\Omega/4\pi]^{-1}$.

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towards them. The primary step is the formation of 'gas particle + ion' ionic complexes — 'ionic dimers', which arise via the attachment of ions to neutral particles. The ion affinity (attachment) energy of dissolved gas particles is of an electrostatic nature (see Section 2) and is defined by the formula $U = \beta e^2 / 2(\delta_g + \delta_i)^4$, where β is the electron polarizability of the gas particles, δ_g is their radius, and δ_i is the ion radius. If the lifetime τ_d of such dimers is sufficiently large, then, as a result of diffusion of surrounding ions towards the 'surface' of a dimer, a condensation of ions can occur and, with a certain probability, droplets with a spatial arrangement of ions in the form of a simple cubic lattice are produced, where the spacing between the nearest ions of different signs is $a = (\delta_{Na^+} + \delta_{Cl^-}) = 2.8$ Å, i.e., it is equal to half the lattice parameter. Due to such an arrangement of the ions, the Coulomb attraction between ions with opposite signs of the charges becomes stronger than the repulsion between ions of the same sign. In other words, all the ions in the droplet are located in sufficiently deep potential wells and the droplet becomes mechanically stable. The direct calculation of the Coulomb interaction of a single ion from a droplet with all other ions shows that the smallest number of condensed ions of both signs, at which mechanical stability is attained, reaches 27. In this case, 14 ions of one sign occupy 6 vacancies of the first coordination shell (with a radius of a) and 8 vacancies of the third coordination shell (with a radius of $\sqrt{3}a$; the other 13 ions of the opposite sign occupy 12 vacancies of the second coordination shell (with a radius of $\sqrt{2a}$ and one site of the original dimer. With such a 'trilayer' structure of the droplet, the interaction energy of one ion with 26 other ions of the droplet proves to be equal to $w_1 = -1.3e^2/a$ on the first shell, to $w_2 = -2.0e^2/a$ on the second shell, to $w_3 = -1.0e^2/a$ on the third shell, and to $w_0 = -2.1e^2/a$ at the site of the original dimer. The droplet takes the form of a cube with the lengths of edges 2a = 5.6 Å. Such a droplet, consisting of 27 ions, can be called a 'dry droplet' to emphasize that its absolutely stable state is observed only outside the solution, i.e., when the interaction of its ions with water molecules is absent. As to the solution, in it, owing to the polarization of the water that surrounds the droplet, under the action of the Coulomb field of the composing ions, a significant decrease (in absolute magnitude) occurs in the binding energy between the ions themselves, i.e., of the depths of the potential wells (in which they are located). The most significant decrease in the binding energy is characteristic of the ions that occupy the third coordination shell. A simple estimate based on the electrostatic Gauss theorem (see Footnote 2) shows that the binding energy $|w_3|$ for these ions decreases by a factor of $\epsilon \Delta \Omega/4\pi$ (here, $\varepsilon = 80$ is the dielectric constant of water, and $\Delta \Omega = 4\pi - \pi/2 = 7\pi/2$ is the solid angle at which the water is viewed from the point where the ion is located on the third coordination shell), i.e., by a factor of almost 70, and becomes equal to $|w'_3| = e^2/70a = 0.073$ eV; in this case, one finds $|w'_3|/T = 2.8$. A significant decrease is also observed for the binding energies of other ions that compose the droplet. As a result, the ionic bond in the droplet becomes unstable because of thermal processes, which leads to the droplet decomposition (Coulomb explosion) and thereby to the formation of a mesocavity with radius $R_n \approx a \approx 3$ Å.

As was already noted, one of the necessary conditions for the realization of the above formation mechanism of mesocavities is that the lifetime τ_d of the ionic dimers arising in the solution be sufficiently large, and during this time they can grow (with a finite probability) to an ionic droplet with radius a = 2.8 Å. Let us give some quantitative estimates referring to this problem. The time $\tau_d = v_d^{-1} \exp(U/T)$, where v_d is the frequency of the dimer vibrations, and U is the energy of ion affinity of the gas particles introduced above. According to the well-known formula of classical mechanics, the respective relation for the frequency is $v_d = (1/2\pi)\sqrt{w''(0)/\mu}$, where $w(x) = \beta e^2/2(\delta_0 + x)^4$, $\delta_0 = \delta_g + \delta_i$, μ is the reduced mass of a gas particle and an ion, $w''(0) = 10\beta e^2/\delta_0^6$, $w(0) = U = \beta e^2/2\delta_0^4$, and the lifetime is then given by

$$\tau_{\rm d} = \sqrt{\frac{4\mu\delta_0^6}{\beta e^2}} \exp\left(\frac{\beta e^2}{2\delta_0^4 T}\right). \tag{3.1}$$

It is of interest to determine the time τ_d for four types of dimers: (N_2+Na^+) , (N_2+Cl^-) , $(He+Na^+)$, and $(He+Cl^-)$, which correspond to two cases where the aqueous solution resides in equilibrium with (1) nitrogen (air), and (2) a helium external medium. For the dimer $(N_2 + Na^+)$, we have $\beta = 1.76 \times 10^{-24}$ cm⁻³, $\delta_0 = 1.58 + 0.98 = 2.56$ Å, $\mu = 2.1 \times 10^{-23}$ g, and formula (3.1) gives $\tau_d = 2.4 \times 10^{-8}$ s. For the dimer (N_2+Cl^-) , $\delta_0 = 1.58 + 1.81 = 3.39$ Å, $\mu = 2.6 \times 10^{-23}$ g, and $\tau_d = 2.6 \times 10^{-11}$ s. For the dimer $(He+Na^+)$, $\beta = 2.0 \times 10^{-25}$ cm⁻³, $\delta_0 = 1.22 + 0.98 = 2.2$ Å, $\mu = 0.57 \times 10^{-23}$ g, and $\tau_d = 2.6 \times 10^{-12}$ s. For the dimer $(He+Cl^-)$, $\delta_0 = 3.03$ Å, $\mu = 0.6 \times 10^{-23}$ g, and $\tau_d = 1.2 \times 10^{-12}$ s. It can be seen that the lifetime of the dimer $(N_2 + Na^+)$ is four orders of magnitude greater than that of the dimer $(He + Na^+)$, which indicates the extremely important role of helium in the problem under consideration.

The characteristic time of a droplet formation via diffusion towards an ionic dimer of the surrounding ions is $\tau_{\rm dr} = a^2/D_{\rm i}^{\rm eff}$, where $D_{\rm i}^{\rm eff}$ is the effective diffusion coefficient, which substantially differs from the diffusion coefficients of Na⁺ and Cl⁻ ions (which at $t = 25 \,^{\circ}\text{C}$ are equal to 1.36×10^{-5} cm² s⁻¹ and 2.0×10^{-5} cm² s⁻¹, respectively). The physical meaning of this coefficient is that it defines only those diffusion flux $D_i^{\text{eff}} \nabla n_i$ of the Na⁺ and Cl⁻ ions towards the surface of the growing ionic droplet that remains stable, i.e., when the Na⁺ and Cl⁻ ions that come onto each droplet are arranged into a simple cubic lattice. Fluxes that do not satisfy this condition are excluded, since they lead to a premature decomposition of the droplet. We assume that the diffusion coefficient D_i^{eff} is equal to $\alpha (D_{\text{Na}^+} + D_{\text{Cl}^-})/2$, where $\alpha \ll 1$, and has the sense of the growth probability of the droplet to a size a, remaining stable. In this case, $\tau_{\rm dr} = a^2 / \alpha (D_{\rm Na^+} + D_{\rm Cl^-}) \approx (5 \times 10^{-11} / \alpha) \, {\rm s} \quad (a = 2.8 \, {\rm \AA}),$ and, correspondingly, the necessary condition for the formation of a mesocavity takes the form $\tau_d > \tau_{dr} = (5 \times 10^{-11}/\alpha) \, s.$ But since $\alpha \ll 1$, the lifetime of the dimers should satisfy the condition $\tau_d \ge 5 \times 10^{-11}$ s. These estimates of the lifetime τ_d give evidence that the last condition can be fulfilled only if the growth of the droplet occurs on the dimer $(N_2 + Na^+)$, for which $\tau_d = 2.4 \times 10^{-8}$ s. The probability α in this case should exceed 2×10^{-3} ; this means that at least two dimers $(N_2 + Na^+)$ from a thousand dimers should grow to the dimensions of a droplet with radius a. The question of whether such values of α can be realized remains open and, therefore, it cannot be considered that the formation of mesocavities precisely occurs according to the above mechanism. At the same time, the above consideration leads to an important conclusion: the presented mechanism of the bubston nucleation is a fortiori ruled out in the case of a helium ambient medium (for which $\tau_d \sim 10^{-12}$ s). This, in turn, makes it possible to suppose that in the last case the bubston structures in aqueous NaCl solutions (canonical solutions) are completely impossible. In the next sections of this paper, this supposition will be confirmed based on a thermodynamic consideration of the problem.

4. Double electric layer on the surface of a gas bubble located in an aqueous ionic solution

Let us consider an aqueous solution of NaCl salt in which there exists a gas bubble of radius $R \ge 10$ nm. Such a radius significantly exceeds the average spacing between the water molecules in the surface layer, which, according to our estimates, is 1.58 Å (see above). Therefore, we can assume that the adsorption of ions on the surface of such a bubble occurs in the same manner as on the free surface of the solution.

Owing to the adsorption of Na⁺ ions with an average number density γ , the unit area of the bubble acquires a *positive* charge $e\gamma$; the entire adsorbed charge is $Q_1 = 4\pi R^2 e\gamma$. As a result, an electric field is induced in the solution with a close-to-spherical symmetry, whose strength differs from zero only for $r \ge R(r)$ is the distance from the center of the bubble). Thus, the arising electric field with a potential $\varphi(r)$ and a strength $E(r) = -d\varphi/dr$ creates a so-called double electric layer (DEL). Around a positively charged bubble carrying a charge Q_1 , a negatively charged shell is formed with a density of the electric charge $\rho(r)$, which is pressed to the surface of the bubble due to the electrostriction pressure $p_{str}(r) = (\epsilon/8\pi)E^2(r)$ (where ε is the dielectric constant of water).

The potential $\varphi(r)$ is determined from the Poisson–Boltzmann equation

$$\frac{(r\varphi)''}{r} = -\frac{4\pi}{\varepsilon} \rho(r) \tag{4.1}$$

with the boundary conditions $\varphi(\infty) = 0$, and $-\varphi'(R) = E(R) = Q_1/\varepsilon R^2$. The charge density is then given by

$$\rho(r) = e \left[n_i^s \exp\left(-\frac{e\varphi(r)}{T}\right) - n_i^s \exp\left(\frac{e\varphi(r)}{T}\right) \right], \qquad (4.2)$$

where n_i^s is the number density of the dissolved (free) impurity ions far from the bubble surface. Let us first consider the case where $F \equiv e\varphi(R)/T \ll 1$ and, therefore, according to formula (4.2), $\rho(r) = -2n_i^s e^2 \varphi(r)/T$. Substituting this expression into Eqn (4.1) and solving the obtained equation gives the following result:

$$\varphi(r) = \frac{Q_1}{\varepsilon(1+\kappa R)} \frac{\exp\left(-\kappa(r-R)\right)}{r}, \qquad (4.3)$$
$$E(r) = \frac{Q_1(1+\kappa r)}{\varepsilon(1+\kappa R)} \frac{\exp\left(-\kappa(r-R)\right)}{r^2},$$

where $\kappa = (8\pi l_B n_i^s)^{1/2}$, and $l_B = e^2/\varepsilon T = 7 \times 10^{-8}$ cm. In this case, the density of the electric charge in the DEL, $\rho(r) = -2n_i^s e^2 \varphi(r)/T$, is written out as

$$\rho(r) = \rho(R) \frac{R}{r} \exp\left(-\kappa(r-R)\right), \quad \rho(R) = -\frac{Q_1 \kappa^2}{4\pi R(1+\kappa R)}.$$
(4.3a)

The total electric charge of the bubble (together with the charge of the DEL) in the (R, r) layer is equal, according to

Eqn (4.3a), to

$$Q(r) = Q_1 + 4\pi \int_R^r r^2 \rho(r) \, \mathrm{d}r = Q_1 \, \frac{1 + \kappa r}{1 + \kappa R} \exp\left(-\kappa(r - R)\right).$$
(4.4)

It can be seen that for all $r \ge R$ the total charge of the bubble is positive and, upon moving from the surface of the bubble (i.e., with increasing *r*), its gradual neutralization comes into play, causing $Q(\infty) = 0$. According to formulas (4.3) and (4.4), the strength $E(r) = Q(r)/\varepsilon r^2$, i.e., it corresponds to the Gauss electrostatic theorem. The electric energy related to the bubble is then takes the form

$$W_E = \frac{\varepsilon}{2} \int_R^\infty r^2 E^2(r) \,\mathrm{d}r = \frac{Q_1^2}{4R\varepsilon} \frac{2+\kappa R}{\left(1+\kappa R\right)^2} \,. \tag{4.4a}$$

All the quantitative characteristics of the DEL obtained above depend, according to Eqns (4.3)–(4.4a), on the specified values of the parameters for the problem: bubble radius, number density of dissolved ions, and temperature. However, the surface density γ of adsorbed ions (or the charge $Q_1 = 4\pi R^2 e \gamma$) remains uncertain. The dependence of γ on the specified parameters under equilibrium conditions is determined from the condition of the minimum of the total free energy of the DEL per adsorbed ion, i.e., according to formula (4.4a), of the minimum of the quantity

$$f = \frac{4\pi R^2 \sigma + W_E}{4\pi R^2 \gamma} = \frac{\sigma}{\gamma} + \frac{\pi R e^2 \gamma (2 + \kappa R)}{\varepsilon (1 + \kappa R)^2} .$$
(4.5)

The equilibrium value of γ is the root of the equation df/dr = 0 [at a constant value of κ , i.e., at the unaltered distribution of the charge density $\rho(r)$]. This root is written out as follows:

$$\gamma = \left(\frac{\varepsilon\sigma}{\pi R e^2 (2+\kappa R)}\right)^{1/2} (1+\kappa R) = \begin{cases} \left(\frac{\varepsilon\sigma}{2\pi R e^2}\right)^{1/2}, & \kappa R \leqslant 1, \\ \left(\frac{\varepsilon\sigma\kappa}{\pi e^2}\right)^{1/2}, & \kappa R \geqslant 1. \end{cases}$$
(4.6)

All the above results were obtained under the condition of $F = e\varphi(R)/T \ll 1$ (Debye approximation). Now, we should check whether the results obtained satisfy this condition. According to Eqns (4.3) and (4.6), we have

$$F = \begin{cases} \left(\frac{8\pi\sigma l_{\rm B}R}{T}\right)^{1/2}, & \kappa R \ll 1, \\ \left(\frac{16\pi\sigma l_{\rm B}}{\kappa T}\right)^{1/2}, & \kappa R \gg 1. \end{cases}$$
(4.7)

The first variant of this formula gives $F \approx 18R^{1/2}$ [nm]; the second variant yields $F \approx 2.2 \times 10^6 / (n_i^s [au^{-3}])^{1/4}$. Since $R \ge 10$ nm and $n_i^s \le 10^{20}$ cm⁻³ (i.e., the number density of the ions in the NaCl solution is close to saturation), for both limiting values of κR we have $F \ge 1$. This means that the Debye approximation used above for the description of a DEL arising around the bubble in an aqueous ionic solution is inapplicable, in principle.

Below, we give a description of the DEL on a bubble based on the condition $F = e\varphi(R)/T \ge 1$. In this case, the distribution of the charge density $\rho(r)$ is presented in the form analogous to formula (4.3a):

$$\rho(r) = \rho(R) \frac{R}{r} \exp\left(-b(r-R)\right), \qquad (4.8)$$

where $\rho(R)$ and b are to be determined. In this case, the total electric charge in the (R, r) layer is defined as

$$Q(r) = Q_1 + \frac{4\pi R \rho(R)}{b^2} \left[(1 + bR) - (1 + br) \exp\left(-b(r - R)\right) \right]$$
(4.8a)

Since $Q(\infty) = 0$, we obtain

$$\rho(R) = -\frac{Q_1 b^2}{4\pi R(1+bR)},$$

$$Q(r) = Q_1 \frac{1+br}{1+bR} \exp\left(-b(r-R)\right), \quad r \ge R,$$
(4.8b)

i.e., formulas (4.3a) and (4.4) upon the substitution $\kappa \rightarrow b$. The electric energy associated with the bubble is equal, according to formula (4.4a), to

$$W_E = \frac{Q_1^2}{4R\epsilon} \frac{2+bR}{(1+bR)^2}, \quad Q_1 = 4\pi R^2 e\gamma.$$
 (4.8c)

The potential $\varphi(r)$ under the condition $\varphi(\infty) = 0$ is calculated from the equation $\varphi'(r) = -Q(r)/\varepsilon r^2$, where Q(r) is defined by formula (4.8b). Thus, we obtain

$$\varphi(r) = \frac{Q_1 \exp\left(-b(r-R)\right)}{\varepsilon(1+bR)r}, \quad r \ge R,$$
(4.9)

which also coincides with formula (4.3) upon the substitution $\kappa \rightarrow b$.

It will be seen from the further description that in the case under consideration, where $F \ge 1$ and $R \ge 10$ nm, the parameter bR is always more than unity and, based on Eqns (4.2), (4.8b), and (4.9), we obtain two independent equations

$$\gamma b = n_{\rm i}^s e^F, \tag{4.9a}$$

$$\frac{\gamma}{b} = \frac{F}{4\pi l_{\rm B}} \,. \tag{4.9b}$$

The magnitude of F in these equations remains uncertain (with the only condition that $F \ge 1$) and these equations should be supplemented with a third independent equation. This equation, just as in the Debye approximation, follows from the condition of the minimum of the total free energy of the DEL per adsorbed ion, i.e., from the minimum of the quantity f determined by Eqn (4.5) with the substitution $\kappa \rightarrow b$ under the condition of $bR \ge 1$. Correspondingly, according to Eqn (4.6), we obtain the sought-after third equation as

$$\gamma = \left(\frac{\varepsilon \sigma b}{\pi e^2}\right)^{1/2}.$$
(4.9c)

The simultaneous solution of equations (4.9a)-(4.9c) gives

$$\gamma = \frac{\gamma_0}{F}, \qquad b = \frac{b_0}{F^2}, \tag{4.10}$$

where $\gamma_0 = 4\sigma/T = 7.1 \times 10^{15} \text{ cm}^{-2}$, $b_0 = 16\pi e^2 \sigma/\varepsilon T^2 = 6.3 \times 10^9 \text{ cm}^{-2}$ (t = 25 °C), and the magnitude of *F* satisfies the equation

$$F^3 e^F = \frac{n^*}{n_i^s} \,, \tag{4.10a}$$

where $n^* = \gamma_0 b_0 = 64\pi e^2 \sigma^2 / \varepsilon T^3 = 4.5 \times 10^{25} \text{ cm}^{-3}$. Formulas (4.10) and (4.10a) represent the dependences of γ , b, and F on the ion number density n_i^s at a given temperature. The first formula in (4.10) defines the adsorption isotherm. The logarithmic derivatives with respect to n_i^s are written out as

$$\frac{n_i^s}{\gamma} \frac{\mathrm{d}\gamma}{\mathrm{d}n_i^s} = \frac{1}{F+3} , \qquad \frac{n_i^s}{b} \frac{\mathrm{d}b}{\mathrm{d}n_i^s} = \frac{2}{F+3} , \qquad \frac{n_i^s}{F} \frac{\mathrm{d}F}{\mathrm{d}n_i^s} = -\frac{1}{F+3} .$$
(4.10b)

Since $F \ge 1$, all these derivatives are small in absolute magnitude compared to unity. With increasing volume number density n_i^s of ions, the surface density γ of adsorbed ions increases slowly, and the 'thickness' (b^{-1}) of the DEL decreases. It is also seen from these formulas that the parameters γ , b, and f are independent of the adsorption energy U_{AD} of the ions. Only the lifetime of ions in the adsorbed state depends on the latter energy (exponentially, see Section 2), whereas the structure of the DEL itself is unambiguously determined by the parameters n_i^s , σ , and T of the solution. This circumstance indicates that results (4.8c), (4.9), and (4.10a) obtained for the canonical solution are in fact applicable also to other aqueous solutions of univalent ions (e.g., for the LiCl and KCl solutions). This, however, does not mean that the threshold for the formation of a bubston structure in aqueous solutions of univalent ions is also independent of the type of these ions (for more detail, see the discussion below).

As was noted above, the intrinsic ions of water, i.e., H⁺ and OH⁻, cannot lead to the formation of stable gas bubbles (bubstons), but these ions can affect the structure of the DEL of the bubbles arising due to the adsorption of impurity ions (in the canonical solution under consideration, Na⁺ ions). In the solutions based on pure water, for which the hydrogen index is pH = 7 (neutral solutions), the number densities of the H⁺ and OH⁻ ions are identical ($n_{iw} = 6 \times 10^{13} \text{ cm}^{-3}$). In this case, according to formula (4.2), the charge density in the DEL is $\rho(R) = -e(n_i^s + n_{iw})e^F$ and, correspondingly, Eqn (4.10a) is transformed into $F^3e^F = n^*/(n_i^s + n_{iw})$ (formulas (4.10) remain unaltered in this case). Hence, for $n^s > 10^{14} \text{ cm}^{-3}$ in neutral aqueous solutions, the H⁺ and OH- ions do not produce any effect on the DEL structure. At the same time, in the aqueous solution of the NaCl salt with the addition of, for example, hydrochloric acid (acidic solutions, pH < 7), the number density of H^+ ions is $10^{-pH} \times 6 \times 10^{20}$ cm⁻³ (and can significantly exceed the impurity ion density n_i^s), while with the addition of an alkali (alkaline solution, pH > 7), the density of OH^- ions is $10^{\text{pH}-14} \times 6 \times 10^{20} \text{ cm}^{-3}$ (and can also exceed the impurity ion density n_i^s). In these cases, the effect of the H⁺ and OH⁻ ions on the DEL structure can become quite significant.

5. Thermodynamics of a bubston structure of aqueous solutions of electrolytes

The results considered in the previous sections concerning with the problems of the ion adsorption on the surface of water and the formation of a double electric layer on it, were obtained based on model concepts. These results form the initial data for the elaboration of a thermodynamic approach to the problem of the appearance of a stable structure of gaseous bubbles in aqueous ionic solutions being in equilibrium with an external gaseous medium. We shall call it as the *bubston structure of aqueous solutions of electrolytes*. The system that will be considered below consists of two subsystems interacting between themselves: an aqueous ionic solution with a sufficiently large volume V (the necessity to impose a restriction on V will be seen from the discussion presented below), and an external gaseous medium with a volume $V_0 \gg V$. In the state of thermodynamic equilibrium, the parameters of the bubston structure, i.e., the radius R of the bubstons, their density $n_{\rm b}$ (number of bubstons per unit volume of the solution), and the specific volume content of the free gas contained inside the bubstons, $K_v = (4\pi/3)R^3n_b$, should be defined by three parameters of the system: temperature T, pressure p, and the total number density n_i^0 of the dissolved ions (for canonical solutions, of Na⁺ and Cl⁻ ions). The thermodynamic results have a general phenomenological character; therefore, the extent of the quantitative correspondence between these results and the experimental data on the observation of bubston structures may serve as a criterion of the validity of the model concepts assumed to provide the basis as concern the adsorption of ions and the formation of a double electric layer.

The system under consideration has a substantial feature: one of its components, namely, the gas bubbles that arise in the presence of a gas dissolved in water, tend to float up and to exhibit Brownian movement. Therefore, the description of a bubston structure is, in general, a kinetic problem. A thermodynamic description is possible only under certain restrictions put on the parameters of the system itself. The most obvious restriction follows from the requirement that the arising structure be stationary and homogeneous over the volume of the solution, i.e., its parameters, such as the radius R of the bubstons and their density $n_{\rm b}$ must be independent of the time and of the site of observation inside the solution. This requirement, in fact, means that the equilibrium bubston structure corresponds to the case of Archimedes' buoyancy and the Brownian movement of already equilibrium bubstons that are nucleated in all points of the volume V on dissolved gas particles and ions. A characteristic time of the transformation of a bubston nucleus into an equilibrium bubston of radius R is determined by the rate of diffusion of ions and gas particles towards its surface; i.e., it is on the order of $R^2/D_{i,g}$, where $D_{i,g}$ are the diffusion coefficients of ions and gas particles in water, which by order of magnitude coincide with one another and are $\sim 10^{-5}$ cm² s⁻¹. This time should be small compared to the characteristic time R/u_A of the Archimedes' buoyancy of a separate bubston and of the Brownian movement of a separate bubston, $R^2/D_{\rm b}$. Here, the quantities that follow

$$u_{\rm A} = \frac{4}{15} \frac{gR^2}{v} , \qquad D_{\rm b} = \frac{T}{5\pi\rho vR}$$
 (5.1)

are, correspondingly, the rate of the Archimedes' floating up of bubstons and their diffusion coefficient.³ The two above conditions for the time $R^2/D_{i,g}$ lead to the following restrictions on the bubston radius (the numerical estimates

refer to room temperatures):

$$R^3 \ll \frac{15}{4} \frac{\nu D_{i,g}}{g}$$
, or $R < 3 \,\mu m$, (5.2)

$$R \gg \frac{T}{5\pi\rho v D_{i,g}}$$
, or $R > 3 \text{ nm}$. (5.2a)

Apart from this restriction on the bubston radius R, we will also impose a limitation on the density of bubstons n_b , assuming that it is so small that the processes of the Brownian movement of separate bubstons occur independently of one another. Such a 'Brownian independence' is realized when the time between the 'collisions' (time of the Brownian approach) of two bubstons, $n_b^{-2/3}/(2D_b)$, is large compared to the time R^2/D_b of the Brownian displacement of a bubston over a distance equal to its radius, i.e., when $R^2 n_b^{2/3} < 1/20$, or

$$n_{\rm b} < \frac{1}{90R^3} = \frac{1.1 \times 10^{19}}{(R \ [{\rm nm}])^3} \ [{\rm cm}^{-3}] \,.$$
 (5.2b)

This poses, in fact, a limitation on the value of the parameter $K_v = (4\pi/3)R^3n_b$; upon fulfillment of inequality (5.2b), we have

$$K_v < \frac{4.2}{90} = 4.7 \times 10^{-2}$$
 (5.2c)

Thus, we will be interested only in such solutions to the problem of the determination of the bubston structure parameters which satisfy conditions (5.2)–(5.2c).

The discussed feature of the system under consideration also manifests itself in its thermodynamic description implying the allowance for boundary conditions on the free solution-gas surface. Owing to the Archimedes' buoyancy and to the Brownian movement, the bubstons reach the surface of the solution, where they disappear (are destroyed). The related ions entering the DEL (both basic ions and counterions) pass into the solution (become free), and the free gas contained in the bubstons passes into the external gaseous medium. As a result, an excessive density n_i^s of free ions arises at the interface and is permanently maintained, which leads to the appearance of a permanent diffusion flux of these ions into the solution, thereby ensuring their uniform distribution over the entire volume. The escape into the external medium of the gas contained inside the bubstons that reach the solution surface is compensated for under stationary conditions by the thermal flux of gaseous particles from the external medium onto the interface. This boundary condition, which specifies a certain quantitative linkage among the parameters of the bubston structure, complements the condition of thermodynamic equilibrium.

5.1 Thermodynamic potential of an ionic solution and of an external gaseous medium

According to the above concepts explaining the formation of bubston nuclei (see Section 3), no nuclei arise in the ionic solution (first subsystem) isolated from the external gaseous medium (second subsystem) because of the absence of dissolved gas particles in it, and the bubston structure is absent. The thermodynamic potential (Gibbs free energy) of these two subsystems at a temperature T and a pressure p is

³ In deriving these formulas for u_A and D_b in the equality of the Archimedes' force $(4\pi/3)R^3\rho g$ to the Stokes force F_{ST} the latter is assumed to be equal to $5\pi\rho\nu Ru$ (where *u* is the velocity of a bubston; ν is the kinematic viscosity of water; ρ is the water density, and *g* is the acceleration of gravity). This corresponds to taking into account the fact that the bubston is surrounded by a layer of water that is 'frozen-in' to the DEL. In this case, the mobility is defined as $\mu = u/F_{ST} = 1/5\pi\rho\nu R$, and the diffusion coefficient is $D_b = \mu T = T/5\pi\rho\nu R$.

written out as [10]

$$\Phi_{1} = N\mu_{0} + \left\{ I_{0} \left(T \ln \frac{I_{0}}{2.72N} + \psi_{i} \right) + I_{0} \left(T \ln \frac{I_{0}}{2.72N} + \bar{\psi}_{i} \right) - \frac{2}{3} \frac{e^{3}}{\varepsilon^{3/2}} \left(\frac{\pi n}{T} \right)^{1/2} N \left(\frac{2I_{0}}{N} \right)^{3/2} \right\},$$
(5.3)

$$\Phi_2 = G_0 T \ln \frac{p}{p_0}, \quad p_0 = T \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}.$$
(5.3a)

In formula (5.3), the following quantities are specified: N is the total number of molecules of the solvent (water), μ_0 is the chemical potential of the solvent, and I_0 is the total number of dissolved ions (for the canonical solution, the number of basic Na⁺ ions and of Cl⁻ counterions). The first term in curly brackets in formula (5.3) refers to the basic ions; the second term refers to the counterions; the magnitudes of ψ_i and $\bar{\psi}_i$ for both types of ions (they are determined below) depend on temperature (and, in general, on pressure). Notice that each of these two terms coincides in the general form with the thermodynamic potential of the neutral dissolved particle with the number I_0 [cf. with the last term in formula (5.4) below], with the substantial difference that, in the case of ions, the magnitudes of ψ_i and ψ_i depend not only on T and p but also on the charge of the ions. The third term in the curly brackets is the so-called correlation correction, which takes into account the Coulomb interaction between the ions; $n = 3.3 \times 10^{22} \text{ cm}^{-3}$ is the number density of water molecules; $\varepsilon = 80$ is the dielectric constant of water, and e is the elementary charge. In formula (5.3a), G_0 is the total number of gas particles in the external medium, which is a specified number; $T \ln (p/p_0)$ is the chemical potential of an ideal gas; *m* is the mass of a gas particle, and $\hbar = h/2\pi$ (*h* is the Planck constant).

After the establishment of thermal and mechanical contacts between the subsystems considered, their thermodynamic potentials become

$$\begin{split} \Phi_{1}' &= N\mu_{0} + \left\{ I_{s} \left(T \ln \frac{I_{s}}{2.72N} + \psi_{i} \right) + \bar{I}_{s} \left(T \ln \frac{\bar{I}_{s}}{2.72N} + \bar{\psi}_{i} \right) \right. \\ &\left. - \frac{2}{3} \frac{e^{3}}{\epsilon^{3/2}} \left(\frac{\pi n}{T} \right)^{1/2} N \left(\frac{I_{s} + \bar{I}_{s}}{N} \right)^{3/2} \right\} \\ &\left. + B \left[G_{1} T \ln \frac{p_{1}}{p_{0}} + 4\pi R^{2} \sigma + W_{E} + \frac{4\pi}{3} R^{3} (p - p_{1}) \right] \right. \\ &\left. + G_{2} \left(T \ln \frac{G_{2}}{2.72N} + \psi_{g} \right), \end{split}$$
(5.4)

$$\Phi_2' = (G_0 - BG_1 - G_2) T \ln \frac{p}{p_0}.$$
(5.4a)

Here, *B* is the total number of gas bubbles with a radius *R* that arise in the solution; G_1 is the number of gas particles inside one bubble; G_2 is the total number of gas particles dissolved in the liquid; I_s and \bar{I}_s are the total numbers of properly dissolved (free) basic ions and of counterions, respectively; the magnitude of ψ_g for the dissolved gas particles depends on temperature (and, generally speaking, on pressure); σ is the coefficient of surface tension at the water–gas interface; W_E is the energy of the electric field of a single bubble, which is created by the ions adsorbed on its surface and by the ionic shell (i.e., by the DEL), and p_1 is the gas pressure inside the bubbles, which is related to the radius *R* and to the number of

particles G_1 via the Clapeyron equation:

$$p_1 = \frac{G_1 T}{(4\pi/3)R^3} \,. \tag{5.4b}$$

In the representation of Φ'_2 by formula (5.4a), it is assumed that the dissolution of gas particles in the liquid does not lead to a decrease in the number density of gas particles n_g in the external medium; consequently, the external pressure $p = n_g T$ remains unaltered. To ensure this condition, it is sufficient that the volume of the external gaseous medium be significantly larger than the volume of the liquid.

The change in the thermodynamic potential of the entire system after the establishment of contact, $\Delta \Phi = (\Phi'_1 + \Phi'_2) - (\Phi_1 + \Phi_2)$, is written out as

$$\Delta \Phi = -(BG_1 + G_2) T \ln \frac{p}{p_0} + G_2 \left(T \ln \frac{G_2}{2.72N} + \psi_g \right) + B \left[G_1 T \ln \frac{p_1}{p_0} + 4\pi R^2 \sigma + W_E + \frac{4\pi}{3} R^3 (p - p_1) \right] + \left\{ I_s \left(T \ln \frac{I_s}{2.72N} + \psi_i \right) + \bar{I}_s \left(T \ln \frac{\bar{I}_s}{2.72N} + \bar{\psi}_i \right) - \frac{2}{3} \frac{e^3}{\varepsilon^{3/2}} \left(\frac{\pi n}{T} \right)^{1/2} N \left(\frac{I_s + \bar{I}_s}{N} \right)^{3/2} \right\} + \text{const}, \qquad (5.5)$$

where the last term (const) is equal to the term in curly brackets if the quantities I_s and \overline{I}_s are replaced by a given number I_0 taken with the opposite sign.

According to what was said at the beginning of this section, the parameters of the solution in the equilibrium state, such as the number density n_i^s of the properly dissolved ions, the number density n_g^s of dissolved gas particles, and the radius R and the number density n_b of gas bubbles, are established as identical over the entire volume of the solution. Our task is to determine the equilibrium values of these parameters depending on temperature T, pressure p, and total number density of the dissolved ions, $n_i^0 = I_0/V$ (V is the volume of the solution). This task is reduced to finding the values of these parameters that correspond to a minimum change $\Delta \Phi$ in the potential.

Further, we will use the results obtained in Section 4 for the structure of the DEL on the surface of a gas bubble; namely, we assume that the energy W_E is determined by formula (4.8c), while the surface density γ of the adsorbed ions and the thickness b^{-1} of the double layer are determined by formulas (4.10), and (4.10a). In addition, it should be taken into account that the solution on the whole remains electrically neutral; therefore, $I_s = I_0 - B(I_1 + I^*) = \bar{I}_s =$ $I_0 - B\bar{I}^*$. Here, I_1 is the number of basic ions adsorbed on the surface of a single bubston; I^* and \bar{I}^* are the numbers of basic ions and counterions located inside the screening ionic shell of one bubston. Since $I^* \approx (4\pi R^2/b)n_i^s e^{-F}$ and $\bar{I}^* \approx$ $(4\pi R^2/b)n_i^s e^F$, we have $\bar{I}^*/I^* = e^{2F} \ge 1$; hence, it follows that $I_1 \approx \bar{I}^*$ and

$$I_s = \bar{I}_s = I_0 - BI_1 \,, \tag{5.5a}$$

$$n_{\rm i}^{s} = \bar{n}_{\rm i}^{s} = n_{\rm i}^{0} - n_{\rm b}I_{\rm I},$$
 (5.5b)

where $n_i^0 = I_0/V$ is the total number density of dissolved ions, and $n_b = B/V$ is the number density of bubstons.

One of the independent parameters of the system under consideration, apart from G_1 , G_2 , and R, is the above-

mentioned (in Section 1) quantity $s = I_s/I_0 = n_i^s/n_i^0$, which defines the fraction of the properly dissolved ions; its values lie in the range 0 < s < 1. At s = 1, the equality $n_i^s = n_i^0$ is fulfilled; consequently, adsorption is absent, as is the bubston structure $(n_b = 0)$; at s = 0, all the dissolved ions are adsorbed, i.e., they are located inside the double layers, and $n_b = n_i^0/I_1$.

By rewriting Eqn (5.5) taking into account that $I_s = \overline{I}_s = sI_0$ and that the energy W_E is determined by formula (4.8c), we obtain

$$\begin{split} \Delta \Phi &= -(BG_1 + G_2)T\ln\frac{p}{p_0} + G_2\left(T\ln\frac{G_2}{2.72N} + \psi_g\right) \\ &+ B\left[G_1T\ln\frac{p_1}{p_0} + 4\pi R^2\sigma + \frac{4\pi}{3}R^3(p-p_1) + \frac{e^2I_1^2(x+2)}{4\epsilon R(x+1)^2}\right] \\ &+ 2TI_0s\left\{\frac{\psi_i + \bar{\psi}_i}{2T} - 1 - \ln\frac{n}{sn_i^0} - \frac{4}{3}\left(\frac{sn_i^0\pi I_B^3}{2}\right)^{1/2}\right\} + \text{const}\,, \end{split}$$

where x = bR, $l_B = e^2/\epsilon T$, and the last term (const) is equal to the penultimate term with the opposite sign at s = 1.

5.2 Equations defining the stationary point of the system under consideration

The bubston structure of the system under consideration corresponds to its thermodynamically equilibrium state, when the potential difference $\Delta \Phi$ has a minimum value. This is achieved at the stationary point of expression (5.6) as a function of the variables G_1, G_2, R , and *s* with allowance made for Eqns (5.4b) and (5.5a), which can be represented more conveniently as

$$I_1 = \frac{I_0(1-s)}{B} \,. \tag{5.6a}$$

The stationary point itself is determined from the condition of vanishing the derivatives $(\Delta \Phi)'_{G_1}, (\Delta \Phi)'_{G_2}, (\Delta \Phi)'_R$, and $(\Delta \Phi)'_s$. These derivatives correspond to the minimum of $\Delta \Phi$, when Sylvester's criteria are fulfilled (see below).

Based on expression (5.6) and with allowance for expressions (5.4b) and (5.6a), we find

$$(\Delta \Phi)'_{G_1} = -BT \ln \frac{p}{p_0} + BT \ln \frac{p_1}{p_0} = BT \ln \frac{p}{p_1}, \qquad (5.6b)$$

$$(\Delta \Phi)'_{G_2} = T \ln \frac{G_2}{N} + \psi_g - T \ln \frac{p}{p_0},$$
 (5.6c)

$$(\Delta \Phi)'_R = B \left[4\pi R^2 (p - p_1) + \frac{\partial}{\partial R} \left(4\pi R^2 \sigma + \frac{e^2 I_1^2 (x + 2)}{4\epsilon R (x + 1)^2} \right) \right],$$
(5.6d)

$$(\Delta \Phi)'_{s} = 2T I_{0} \left\{ \frac{\psi_{i} + \bar{\psi}_{i}}{2T} - f - \frac{e^{2} I_{1}(x+2)}{4\varepsilon R T(x+1)^{2}} \times \left[1 + \frac{x(x+3)}{(x+1)(x+2)} \frac{1-s}{2s} \left(\frac{s}{b} \frac{\partial b}{\partial s} \right) \right] \right\}.$$
 (5.6e)

When obtaining Eqn (5.6e), we used the formulas $B(\partial I_1^2/\partial s) = -2I_0I_1$, $BI_1^2 = I_0I_1(1-s)$ [see Eqn (5.6a)], and $\partial x/\partial s = (x/s)(s/b)\partial b/\partial s$. The quantity f in formula (5.6e) is written out as

$$f = \ln \frac{n}{sn_{\rm i}^0} + 2.5(sn_{\rm i}^0 l_{\rm B}^3)^{1/2} \,. \tag{5.6f}$$

Formulas (5.6c) and (5.6e) contain yet undetermined quantities ψ_g , ψ_i , $\overline{\psi}_i$, and $(s/b)\partial b/\partial s$. As to the quantity $(s/b)\partial b/\partial s$, it is equal, according to formula (4.10b), to 2/(F+3).

Let us now turn to the determination of the energies ψ_g , ψ_i , and $\bar{\psi}_i$. As was already noted, the above expressions for the potentials of dissolved ions and counterions (in the absence of bubbles) [see Eqn (5.3)] coincide, to an accuracy of a correlation correction, with the potential of the solution of neutral gases [see Eqn (5.4)] with the replacements $I_0 \rightarrow G_2$ and $\psi_i, \bar{\psi}_i \rightarrow \psi_g$. It is well known (see, e.g., book [11], Section 81) that all these energies have the same physical nature and are determined by the energy U of dissolved particles in the force field created by the molecules of the solvent (of water in our case) as follows:

$$\psi = U + T \ln\left[n\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}\right],\tag{5.7}$$

where *m* is the mass of the dissolved particles, and *n* is the number density of the water molecules. The second term on the right-hand side of Eqn (5.7) formally coincides with the chemical potential of an ideal gas with a number density *n* of particles (Ref. [10], Section 45). The energy *U* is equal to the minimum work which should be spent to introduce into water an ion (in the case of ionic solutions) or a neutral particle (in the case of a dissolved gas). In the latter case, the energy *U* is determined by the minimum work of the formation in the water of a cavity necessary for the introduction of a neutral particle with radius δ_g . This energy is calculated in Appendix A and is defined by the expression

$$U_{\rm g} = u_{\rm s}^2 \rho^2 \frac{N_{\rm A}}{M} \frac{2^9 \delta_{\rm l}^6}{3^5} (\alpha^3 - 2^{3/2})^2 = 6.7 \times 10^{-3} (\alpha^3 - 2^{3/2})^2 \text{ eV},$$
(5.7a)

where u_s is the sound velocity in water, ρ is the mass density of water, M = 18 is the molecular mass of water, $N_A = 6 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant, δ_1 is the radius of the water molecule, and $\alpha \equiv \alpha_g = 1 + \delta_g/\delta_1$. The last variant of formula (5.7a) corresponds to the certain values of $u_s = 1.49 \times 10^5$ cm s⁻¹, $\rho = 1$ g cm⁻³, and $\delta_1 = 1.38$ Å. The dependence of U_g on T and p is determined by the dependence of the sound velocity u_s and density ρ on the same quantities.

In the case of an ionic solution, the energy U is defined by formula (5.7a) at $\alpha \equiv \alpha_i = 1 + \delta_i/\delta_1$ with an addition of the energy of electrostatic interaction of the introduced ion with the water molecules. As a result, the total energy for the Na⁺ ions is $U_i = 0.834$ eV, and $\overline{U}_i = 0.870$ eV for the Cl⁻ ions.

5.3 Equilibrium parameters

of the system under consideration

The equilibrium parameters of the 'ionic aqueous solution + external gaseous medium' system under consideration are determined by solving four equations— $(\Delta \Phi)'_{G_1} = 0$, $(\Delta \Phi)'_{G_2} = 0$, $(\Delta \Phi)'_R = 0$, and $(\Delta \Phi)'_s = 0$ —subject to Sylvester's criteria. According to formula (5.6b), it follows from the condition $(\Delta \Phi)'_{G_1} = 0$ that, if $B \neq 0$ (i.e., if bubstons exist), then

$$p_1 = p , \qquad (5.8)$$

i.e., the gas pressure inside the bubstons in equilibrium is equal to the external pressure *p*.

The condition $(\Delta \Phi)'_{G_2} = 0$, according to formula (5.6c), gives

$$\frac{G_2}{N} \equiv \frac{n_{\rm g}^s}{n} = \frac{p}{p_0} \exp\left(-\frac{\psi_{\rm g}}{T}\right),\,$$

where $n_g^s = G_2/V$ is the number density of the properly dissolved gas particles, and p_0 is determined by formula (5.3a). The substitution into the right-hand side of the last formula, according to formula (5.7), of the expression

$$\psi_{\rm g} = U_{\rm g} + T \ln \left[n \left(\frac{2\pi\hbar^2}{mT} \right)^{3/2} \right]$$

leads to the following dependence of the number density n_g^s of the properly dissolved gas on its number density $n_g = p/T$ in the external gaseous medium:

$$n_{\rm g}^s = H_0 n_{\rm g} = \frac{H_0}{T} p \,,$$
 (5.8a)

$$H_0 = \exp\left(-\frac{U_g}{T}\right). \tag{5.8b}$$

In Appendix A, the values of the energy U_g for nitrogen (0.332 eV) and helium (0.10 eV) have been obtained. At T = 298 K, we obtain $H_0^{N_2} = 2 \times 10^{-6}$ in the first case, and $H_0^{\text{He}} = 0.019$ in the second case, i.e., $H_0^{\text{He}}/H_0^{N_2} = 10^4$.

Dependence (5.8a) formally reflects the content of the Henry law: the number density n_g^s is proportional to the number density n_g or, at a given temperature, to the pressure $p = n_g T$. However, the temperature dependence of the coefficient H_0/T in equality (5.8a) contradicts the experimental data, according to which the solubility of gases at a constant pressure decreases with increasing temperature or passes through an extremum, whereas $\partial(H_0/T)/\partial T > 0$ (since $U_g/T > 1$). A principal exception to the above-established dependence is helium, for which the solubility in water at a constant pressure indeed increases with increasing temperature. This contradictory situation is resolved if we take into account that the Henry law defines the dependence of the total content of gas in a unit volume on the pressure p, i.e., the number density is given by

$$n_{\rm g}^0 = n_{\rm g}^s + \frac{4\pi}{3} R^3 n_{\rm b} n_{\rm g} = (H_0 + K_v) n_{\rm g} \equiv H_1 p \,. \tag{5.8c}$$

Here, $H_1 = (H_0 + K_v)/T$ is the true Henry coefficient, and $K_v = (4\pi/3)R^3n_b$. We will see below that in the case of a helium external medium the bubston structure is absent, i.e., $K_v = 0$; therefore, the solubility of helium should indeed increase with increasing *T*. The problem of the temperature dependence of the coefficient H_1 for other gases requires a separate consideration with allowance for the temperature dependences of the bubston parameters *R* and n_b .

At $p = p_1$ and $B \neq 0$, the condition $(\Delta \Phi)'_R$, according to formula (5.6d), leads to the equation

$$\frac{\partial}{\partial R} \left(4\pi R^2 \sigma + \frac{e^2 I_1^2 (x+2)}{4\varepsilon R (x+1)^2} \right) = 0, \qquad x = bR.$$
(5.9)

Notice that the differentiation of the second term in this equation with respect to R should be carried out at constant values of b and $I_1 = Q_1/e$, since the changes to these quantities caused by the processes of the ion diffusion occur significantly more slowly than the process of the change in the

pressure due to the mechanical change in the magnitude of *R*. Equation (5.9) determines the condition of the mechanical equilibrium of a bubston. Indeed, the pressure exerted on the surface of a bubble in the direction of the external normal to its surface, which is related to the surface tension energy $W_{\sigma} = 4\pi R^2 \sigma$, has the form

$$p_{\sigma} = -\frac{1}{4\pi R^2} \frac{\partial W_{\sigma}}{\partial R} = -\frac{2\sigma}{R} , \qquad (5.9a)$$

whereas the ponderomotive pressure on the bubble surface in the same direction, which is related to the electric field energy W_E , is given by

$$p_E = -\frac{1}{4\pi R^2} \frac{\partial}{\partial R} \left(\frac{e^2 I_1^2}{4\varepsilon R} \frac{x+2}{(x+1)^2} \right) = \frac{e^2 I_1^2 (x^2 + 3x + 1)}{8\pi \varepsilon R^4 (x+1)^3} .$$
(5.9b)

The minus sign in formula (5.9a) indicates that the pressure p_{σ} is directed inward toward the bubble and is determined by the Laplace formula. According to formulas (5.9a) and (5.9b), equation (5.9) takes on the form

$$\frac{2\sigma}{R} = p_E = \frac{e^2 I_1^2}{8\pi\varepsilon R^4} \frac{x^2 + 3x + 1}{(x+1)^3}$$
(5.10)

and represents the condition of the mechanical equilibrium for a bubston. Notice that the external pressure p of the gas does not enter into this condition, since it, according to formula (5.8), is balanced by the pressure p_1 of the gas that is inside the bubstons.

In the entire range of ion number densities being considered (see Table 2 below) and for $R \ge 10$ nm, the values of the parameter F are such that the magnitude of $x = bR = b_0 R/F^2$, in agreement with formulas (4.10) and (4.19a), turns out to be large compared with unity. In this case, equation (5.10), taking into account that $I_1 = 4\pi R^2 \gamma$, takes on a form that is independent of R:

$$b^{-1} = \frac{\varepsilon\sigma}{\pi (e\gamma)^2} \,, \tag{5.11}$$

which coincides with formula (4.9c) obtained from the condition of the equilibrium for the DEL of the bubbles. Hence, we arrive at the conclusion that all bubbles with radii that satisfy the condition

$$R \gg b^{-1} = \frac{\varepsilon \sigma}{\pi (e\gamma)^2} \tag{5.11a}$$

are mechanically stable, i.e., they constitute bubstons. It follows from formulas (4.10) that for $n_s^s > 10^{14}$ cm⁻³ the number density γ is greater than 4×10^{14} cm⁻². In this case, condition (5.11a) means that $R \ge 5$ Å, or R > 5 nm, i.e., the radii of bubstons in canonical solutions always exceed 5 nm. Notice that this restriction imposed on the size of bubstons formally coincides with condition (5.2a), which has quite a different physical meaning. The sense of the new restriction on *R* in formula (4.11a) can be easily understood if we write it down as

$$\frac{2\sigma}{R} \ll \frac{2\pi (e\gamma)^2}{\varepsilon}$$
 (5.11b)

A bubston can be represented as a virtual spherical capacitor filled with water. The inner electrode in such a capacitor

coincides with the surface of the bubble, i.e., its radius is $R_1 = R$. The effective radius of the outer electrode is $R_2 = R_1 + 1/2b$, and the electric capacitance is defined as $C = R_1 R_2 \varepsilon / (R_2 - R_1) = 2\varepsilon b R^2$ (since $bR \ge 1$). In this case, the energy stored in the capacitor is $W_E = Q_1^2/2C = Q_1^2/4\varepsilon b R^2$ and it coincides with expression (4.8c) (for $bR \ge 1$). Under equilibrium conditions, the electrodes have specific charges $(\pm e\gamma)$ (per unit area). According to formula (5.11b), the equilibrium between bubstons is ensured, since for all R > 5 nm the pressure due to the surface tension that compresses the bubble (the inner electrode) is small

We now turn to the last equation of system (5.6b)–(5.6e). Substituting into it, according to formula (5.7), the relation

compared to the pressure due to the mutual attraction of the

charges of the 'capacitor-bubston'.

$$\frac{\psi_{\rm i} + \psi_{\rm i}}{2T} = \frac{W_{\rm i}}{T} - \ln \frac{v_0}{n} \,, \tag{5.12}$$

where

Table 2

$$W_{\rm i} = \frac{U_{\rm i} + \bar{U}_{\rm i}}{2}, \quad v_0 = \left(\frac{\sqrt{m\bar{m}}T}{2\pi\hbar^2}\right)^{3/2}.$$
 (5.12a)

Here, U_i and \overline{U}_i are the energies introduced in Section 4, which are equal to 0.834 eV for Na⁺ ions and 0.870 eV for Cl⁻ ions, *m* and \overline{m} are the masses of these ions, and $v_0 = 1.5 \times 10^{26}$ cm⁻³. Taking into account that $x \ge 1$, $I_1 = 4\pi R^2 \gamma$, and with allowance made for formulas (4.9b), (5.6f), and

$$\frac{s}{b}\frac{\partial b}{\partial s} = \frac{2}{F+3}$$

equation (5.6e) takes on the following form:

$$(\Delta \Phi)'_{s} = 2T I_{0} \left[\frac{W_{i}}{T} + \ln \frac{sn_{i}^{0}}{v_{0}} - \frac{F}{4} \left(1 + \frac{1-s}{s} \frac{1}{F+3} \right) - 2.5 (sn_{i}^{0} l_{B}^{3})^{1/2} \right].$$
(5.13)

The quantity *F* satisfies equation (4.10a) at $n_i^s = sn_i^0$ (the aqueous solution is assumed to be neutral, pH = 7) and, therefore, $e^{F/4} = (n^*/sn_i^0)^{1/4}/F^{3/4}$ ($n^* = 4.5 \times 10^{25}$ cm⁻³). As a result, the equation $(\Delta \Phi)'_s = 0$ after some transformations can be represented as

$$n_{i}^{0} = n_{1} \exp\left[-\frac{4W_{i}}{5}\left(\frac{1}{T} - \frac{1}{T_{0}}\right)\right] \frac{1}{sF^{3/5}} \exp\left(\frac{1-s}{s}\frac{F/5}{F+3}\right) \\ \times \exp\left[2(sn_{i}^{0}l_{B}^{3})^{1/2}\right], \qquad (5.13a)$$

where

$$n_{\rm i} = \left[v_0(n^*)^{1/4}\right]^{4/5} \exp\left(-\frac{4W_{\rm i}}{5T_0}\right),\tag{5.13b}$$

and $T_0 = 4.1 \times 10^{14}$ erg (at $t = 25 \,^{\circ}$ C). In this case, $[v_0(n^*)^{1/4}]^{4/5} = 1.3 \times 10^{26}$ cm⁻³, and $n_1 = 4.1 \times 10^{14}$ cm⁻³. The last term in formula (5.13a) for all $n_i^0 \leq 10^{20}$ cm⁻³ is close to unity and is disregarded below (it is due to the introduction of the correlation correction in formulas (5.3), (5.4), and (5.5). In equation (5.13a), it is only the third multiplier that depends on *s*; as *s* increases from 0 to 1, it decreases monotonically and at s = 1 has a minimum value $1/F_1^{3/5}$. Hence, for s < 1 (the necessary condition for the existence of bubstons), equation (5.13a) has a solution $s = s(n_i^0)$ only if the total number density n_i^0 of the dissolved ions satisfies the inequality

$$n_{\rm i}^0 > \frac{n_1}{F_1^{3/5}} \exp\left[-\frac{4W_{\rm i}}{5}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \equiv (n_{\rm i}^0)_{\rm th} \,.$$
 (5.14)

This means that some temperature-dependent threshold number density $(n_i^0)_{\text{th}}$ exists for the formation of bubstons. At $T = T_0$, we have $(n_i^0)_{\text{th}} = 4.1 \times 10^{14} \text{ cm}^{-3} / F_1^{3/5}$, where $F_1 = 18.5$ is the root of the equation $F_1^{3} e^{F_1} = n^* / (n_i^0)_{\text{th}} = (4.5 \times 10^{25} / 4.1 \times 10^{14}) F_1^{3/5} = 1.1 \times 10^{11} F_1^{3/5}$. The threshold ion number density in this case is

$$(n_i^0)_{\rm th} = 7.1 \times 10^{13} \,{\rm cm}^{-3}, \quad t = 25 \,{}^{\circ}{\rm C}.$$
 (5.14a)

The dependence of *s* on the values of $n_i^0 > (n_i^0)_{\text{th}}$ at $t = 25 \,^{\circ}\text{C}$ is determined from equation (5.13a), which can be represented as follows:

$$\ln \frac{z}{y} = (y-1) \frac{F/5}{F+3} + \frac{3}{5} \ln \frac{18.5}{F}, \qquad (5.15)$$

where y = 1/s, and $z = n_i^0/(n_i^0)_{\text{th}}$ is the overshoot of the threshold. This equation should be supplemented by equation (4.10a):

$$F^{3}e^{F} = y \frac{n^{*}}{n_{i}^{0}} = \frac{y}{z} \frac{n^{*}}{(n_{i}^{0})_{th}} = 6.4 \times 10^{11} \frac{y}{z}.$$

As a result, we obtain

$$\ln\frac{z}{y} + F + 3\ln F = 27.2.$$
 (5.15a)

The simultaneous solution to equations (5.15) and (5.15a) determines the dependence of y on z, i.e., of s on n_i^0 , and the dependence of F on y, i.e., of F on n_i^0 . The numerical values of these solutions are given in Table 2.

$n_{\rm i}^0, {\rm cm}^{-3}$ M, mol l ⁻¹	$\frac{10^{15}}{1.7\times10^{-6}}$	$\begin{array}{c} 3\times10^{15} \\ 5\times10^{-6} \end{array}$	$\frac{10^{16}}{1.7\times10^{-5}}$	$\begin{array}{c} 3\times10^{16} \\ 5\times10^{-5} \end{array}$	$\frac{10^{17}}{1.7\times10^{-4}}$	$\begin{array}{c} 3 \times 10^{17} \\ 5 \times 10^{-4} \end{array}$	$\frac{10^{18}}{1.7\times10^{-3}}$	$\begin{array}{c} 3\times10^{18} \\ 5\times10^{-3} \end{array}$	$\frac{10^{19}}{1.7\times10^{-2}}$	$\begin{array}{c} 3 \times 10^{19} \\ 5 \times 10^{-2} \end{array}$
s = 1/y	0.17	0.10	$7.0 imes 10^{-2}$	$5.3 imes 10^{-2}$	$4.1 imes 10^{-2}$	$3.3 imes 10^{-2}$	$2.8 imes 10^{-2}$	$2.4 imes 10^{-2}$	$2.0 imes 10^{-2}$	$1.8 imes 10^{-2}$
$n_{\rm i}^{\rm s}=sn_{\rm i}^0,{\rm cm}^{-3}$	$1.7 imes 10^{14}$	$3.0 imes 10^{14}$	$7.0 imes 10^{14}$	$1.6 imes 10^{15}$	4.1×10^{15}	$1.0 imes 10^{16}$	$2.8 imes 10^{16}$	$7.2 imes 10^{16}$	$2.0 imes 10^{17}$	$5.4 imes 10^{17}$
F	17.7	17.2	16.5	15.8	15.0	14.3	13.4	12.7	11.8	11.1
$10^{-14}\gamma$, cm ⁻²	4.0	4.1	4.3	4.5	4.7	5.0	5.3	5.6	6.0	6.4
K_v	$0.86 imes 10^{-7}$	$2.0 imes 10^{-7}$	5.9×10^{-7}	1.4×10^{-6}	3.5×10^{-6}	8.0×10^{-6}	2.0×10^{-5}	$4.5 imes 10^{-5}$	1.1×10^{-4}	2.1×10^{-4}
$\eta_2 = (1/K_v)^{3/7}$	$1.0 imes 10^3$	730	460	320	220	150	102.0	73.7	49.4	37.7

The above-found solutions to equations $(\Delta \Phi)'_{G_1} = 0$, $(\Delta \Phi)'_{G_2} = 0$, $(\Delta \Phi)'_R = 0$, and $(\Delta \Phi)'_s = 0$, which determine the stationary point of the potential $\Delta \Phi = 0$, are written in the explicit form by formulas (5.8) and (5.8a), and in the implicit form by equations (5.10) and (5.13a). Now, we should show that this point corresponds to the minimum of the potential $\Delta \Phi$, i.e., that these equations determine the equilibrium parameters of the system under consideration.

A necessary and sufficient condition for this is Sylvester's criterion. In our case, it requires that all four determinants of the symmetrical matrix a_{ik} composed of the values of the second derivatives of $\Delta \Phi$ with respect to the parameters G_1 , G_2 , R, and s at the stationary point be positive (the first of these determinants is simply $a_{11} = (\Delta \Phi)''_{G_1G_2}$). According to formulas (5.6b)–(5.6e) with allowance for (5.4b) and (5.6a) and taking into account that $x \ge 1$, we obtain for the diagonal terms of this matrix:

$$a_{11} = (\Delta \Phi)''_{G_1G_1} = \frac{BT}{G_1}, \qquad a_{22} = (\Delta \Phi)''_{G_2G_2} = \frac{T}{G_2},$$

$$a_{33} = (\Delta \Phi)''_{RR} = B(12\pi Rp + 32\pi\sigma),$$

$$a_{44} = (\Delta \Phi)''_{ss} = \frac{2TI_0}{s} \left(1 + \frac{I_0I_{\rm B}}{4RBx} \frac{1+s^2}{2s}\right).$$

The nonzero off-diagonal matrix elements have the form

$$a_{13} = (\Delta \Phi)''_{G_1R} = a_{31} = (\Delta \Phi)''_{RG_1} = -\frac{3BT}{R},$$

$$a_{34} = (\Delta \Phi)''_{Rs} = a_{43} = (\Delta \Phi)''_{sR} = \frac{l_{\rm B}TI_0}{BR^2x} \frac{1-s^2}{2s}.$$

The determinants corresponding to this matrix are (to an accuracy of terms of order 1/x) given by

$$\begin{split} & \Delta_1 = a_{11} = \frac{BT}{G_1} , \qquad \Delta_2 = \begin{vmatrix} a_{11} & 0 \\ 0 & a_{22} \end{vmatrix} = \frac{BT^2}{G_1G_2} , \\ & \Delta_3 = \begin{vmatrix} a_{11} & 0 & a_{13} \\ 0 & a_{22} & 0 \\ a_{31} & 0 & a_{33} \end{vmatrix} = \frac{BT^2}{G_1G_2} \, 32\pi\sigma , \\ & \Delta_4 = \begin{vmatrix} a_{11} & 0 & a_{13} & 0 \\ 0 & a_{22} & 0 & 0 \\ a_{31} & 0 & a_{33} & a_{34} \\ 0 & 0 & a_{43} & a_{44} \end{vmatrix} = \frac{16\pi\sigma I_0 B^2 T^3}{G_1G_2 s} . \end{split}$$

All these quantities are positive, i.e., Sylvester's criterion is fulfilled.

6. Radius and density of bubstons

As was shown in Section 5, the condition of the mechanical equilibrium (5.10) that follows from the equation $(\Delta \Phi)'_R = 0$ for R > 5 nm degenerates into an independent-of-R equality (5.11). Therefore, to determine the radius R of bubstons and their number density n_b depending on the concentration n_i^0 of ions, two additional independent equations should be invoked. They follow, first, from the yet unused condition of the conservation of the total number of ions in the solution—both adsorbed (i.e., bound in the DEL) and the properly dissolved (i.e., free) ions. This condition can be represented, according to expression (5.5a), as follows:

$$n_{\rm b} = \frac{n_{\rm i}^0 (1-s)}{4\pi\gamma R^2} \,, \tag{6.1}$$

where n_i^0 is the total number density of dissolved ions (a specified quantity). The dependence on n_i^0 of the quantities *s* and γ that enter into formula (6.1) is determined by the equations (4.10), (4.10a), and (5.13a) (see Table 2). The second additional equation follows from the condition of the conservation of the number of neutral particles in the entire system. This condition is derived in Appendix B and is written out as follows:

$$\frac{(K_v/w_1)T(1+R^4/S_1)}{5\pi\rho v(D_g/\delta_g)R^2H_0} = 1,$$
(6.2)

where $K_v = (4\pi/3)R^3n_b$, $w_1 = \pi R^2 n_b^{2/3}$, $H_0 = \exp(-U_g/T)$, D_g is the diffusion coefficient of gas particles in water, δ_g is the radius of these particles, $S_1 = 3T/4\pi\rho g \approx 10^{-17}$ cm⁴, $v = 10^{-2}$ cm² s⁻¹ is the kinematic viscosity of water, ρ is its density, and g is the acceleration of gravity. The dependence of the left-hand part of formula (6.2) on the parameter H_0 is quite significant: $H_0^{\text{He}}/H_0^{\text{N}_2} = 10^4$.

Let us first consider the case where the aqueous solution is in equilibrium with a helium external medium. Here, $D_g =$ 6.8×10^{-5} cm² s⁻¹, $\delta_g = 1.22$ Å, $D_g/\delta_g = 5.6 \times 10^3$ cm s⁻¹, $U_g = 0.1$ eV, $H_0 = \exp(-U_g/T) = 2.0 \times 10^{-2}$, and equation (6.2) can be represented as follows:

$$0.2K_v^{1/3} \frac{1+10^{-11}(R \text{ [nm]})^4}{(R \text{ [nm]})^2} = 1.$$
(6.3)

It can be seen that for $R \ge 3$ nm and for $R \le 3 \mu m =$ 3×10^3 nm, we have $K_v < 4.7 \times 10^{-2}$ ($K_v^{1/3} < 0.36$), i.e., in the range of parameters that corresponds to the realized bubston structures [see formulas (5.2)-(5.2c)], the value of the left-hand part in formula (6.3) is much less than unity. This is equivalent to the situation where the first term in equation (B.7) is negligibly small compared to the other two terms of the equation, i.e., the flux of the bubston-induced ejection of gas particles from the aqueous ionic solution is absent. Thus, in the case under consideration, there are no bubston structures which could contribute to gas equilibrium at the interface. In this case, equation (B.7) is satisfied at $n_b = 0$, $w_1 = \pi R^2 n_b^{2/3} = 0$, and it corresponds to the condition of gas equilibrium for the 'bubstonless' solution. Thus, we can conclude that in water with an arbitrary concentration of ions that resides in equilibrium with a helium medium, the bubston structure is absent.

This result reveals a unique new property of helium. First, it removes the above-noted contradiction with the experimental data concerning the temperature dependence of the helium solubility in water. Since $K_v = 0$ in the case of helium, the true Henry coefficient is $H_1 = H_0 = \exp(-U_g/T)$; hence, the solubility of helium at constant pressure should increase with increasing temperature [since $\partial(H_0/T)/\partial T > 0$] rather than decrease, as is observed for other gases. Another new property of water being in equilibrium with helium ('helium water') is that such water allows quite significant overheatings: at a helium pressure of 1 atm, overheatings to 200 °C are observed. The very fact that such overheatings exist indicates that the nuclei responsible for the bubble-like boiling of usual pure water residing in equilibrium with air are bubstons existing in it rather than vapor bubbles spontaneously arising in it with increasing temperature (as is usually assumed).

Quite a different situation is observed in the case of a nitrogen external medium. In this case, equation (6.2) also takes on the form of expression (6.3), but its right-hand part is

$n_{\rm i}^0, {\rm cm}^{-3}$	10^{15}	3×10^{15}	10^{16}	3×10^{16}	10^{17}	3×10^{17}	10^{18}	$\begin{array}{c} 3\times10^{18}\\ 5\times10^{-3}\end{array}$	10^{19}	3×10^{19}
M, mol l ⁻¹	1.7×10^{-6}	5×10^{-6}	1.7×10^{-5}	5×10^{-5}	1.7×10^{-4}	5×10^{-4}	1.7×10^{-3}		1.7×10^{-2}	5×10^{-2}
$R^{(1)}, nm$	9.6	12.1	15.5	19.2	24.1	28.8	37.2	46.3	57.8	72.2
$R^{(2)}, \mu m$	9.6	8.8	7.1	6.15	5.2	4.3	3.7	3.4	2.9	2.6
$n_{\rm b}^{(1)}, {\rm cm}^{-3}$ $n_{\rm b}^{(2)}, {\rm cm}^{-3}$	$\begin{array}{c} 1.8\times10^{11}\\ 1.8\times10^5\end{array}$	$\begin{array}{c} 3.6\times10^{11}\\ 4.8\times10^5\end{array}$	7.7×10^{11} 3.7×10^{6}	$\begin{array}{c} 1.45\times10^{12}\\ 1.4\times10^{7}\end{array}$	$\begin{array}{c} 2.9\times10^{12}\\ 6.0\times10^{7}\end{array}$	$\begin{array}{c} 5.8\times10^{12}\\ 2.6\times10^{8}\end{array}$	1.1×10^{13} 1.1×10^{9}	$\begin{array}{c} 2.0\times10^{13}\\ 3.9\times10^{9} \end{array}$	$\begin{array}{l} 4.0 \times 10^{13} \\ 1.6 \times 10^{10} \end{array}$	7.2×10^{13} 5.0×10^{10}
$K_v^{(1)} \ K_v^{(2)}$	$6.6 imes 10^{-8}$ $6.6 imes 10^{-4}$	$2.6 imes 10^{-6}$ $1.9 imes 10^{-3}$	1.2×10^{-5} 5.6×10^{-3}	$\begin{array}{c} 4.3 \times 10^{-5} \\ 1.4 \times 10^{-2} \end{array}$	1.7×10^{-4} 3.7×10^{-2}	$5.8 imes 10^{-4}$ $8.7 imes 10^{-2}$	2.4×10^{-3} 0.24	$8.3 imes 10^{-3}$ 0.61	3.3×10^{-2} > 1	> 0.1 > 1

replaced by the expression

$$a \equiv \frac{(D_{\rm g}/\delta_{\rm g})^{\rm N_2}}{(D_{\rm g}/\delta_{\rm g})^{\rm He}} \frac{H_0^{\rm N_2}}{H_0^{\rm He}} = 1.95 \times 10^{-5} \,, \tag{6.3a}$$

where $D_g^{N_2} = 1.63 \times 10^{-5}$ cm² s⁻¹, $\delta_g^{N_2} = 1.56$ Å, and $H_0^{N_2} = 2 \times 10^{-6}$. Notice that the transformation of equation (6.2) to the form (6.3) with the replacement of the unity on the right-hand side by a quantity $a \ll 1$ relates not only to nitrogen but also to other gases (except for atomic hydrogen). For the nitrogen external medium, equation (6.2) takes on the following form:

$$R = Sn_b^{1/3} \left(1 + \frac{R^4}{S_1} \right), \qquad S_1 = 10^{-17} \text{ cm}^4, \tag{6.4}$$

$$S = \frac{4T}{(D_g/\delta_g)H_0^{N_2} 15\pi\rho\nu} \,. \tag{6.4a}$$

At $t = 25 \,^{\circ}$ C, we have $S = 1.7 \times 10^{-10} \text{ cm}^2$.

Thus, to determine R and n_b in the case of the nitrogen external medium, we should solve the system of equations (6.1) and (6.4). Eliminating the variable n_b from these equations, we obtain

$$R = \frac{S^{3/5} (n_{\rm i}^0)^{1/5}}{(4\pi\gamma)^{1/5}} (1-s)^{1/5} \left(1 + \frac{R^4}{S_{\rm i}}\right)^{3/5},\tag{6.5}$$

or, in the dimensionless form:

$$\eta^{5/3} = 1 + \kappa \eta^4 \,. \tag{6.5a}$$

Here, the notion was used as follows

$$\eta = R \frac{(4\pi\gamma)^{1/5}}{S^{3/5} (n_i^0)^{1/5}} \frac{1}{(1-s)^{1/5}}, \quad \kappa = \frac{S^{12/5} (n_i^0)^{4/5}}{(4\pi\gamma)^{4/5}} (1-s)^{4/5} \frac{1}{S_1}$$
(6.5b)

where $S = 1.7 \times 10^{-10}$ cm², and $S_1 = 10^{-17}$ cm⁴. For the ten values of the total number density n_i^0 of dissolved ions and corresponding values of γ and *s* represented in Table 2, Eqn (6.5a) has two roots: $\eta_1 = 1$ and $\eta_2 = (1/\kappa)^{3/7}$. According to formulas (6.5b) and (6.1), two branches of solutions correspond to each of these roots:

$$R^{(1)} = S^{3/5} \left(\frac{n_{i}^{0}(1-s)}{4\pi\gamma} \right)^{1/5}, \quad n_{b}^{(1)} = \frac{n_{i}^{0}(1-s)}{4\pi\gamma(R^{(1)})^{2}}, \quad (6.6)$$
$$K_{v}^{(1)} = \frac{4\pi}{3} (R^{(1)})^{3} n_{b}^{(1)}, \quad R^{(2)} = \eta_{2} R^{(1)}, \quad n_{b}^{(2)} = \frac{n_{b}^{(1)}}{\eta_{2}^{2}}, \quad K_{v}^{(2)} = \eta_{2} K_{v}^{(1)}. \quad (6.6a)$$

The numerical results for these solutions at $t = 25 \,^{\circ}\text{C}$ are listed in Table 3. It can be seen from this table that the first branch of the solutions in the entire range of the ion concentrations considered $(1.7 \times 10^{-6} \le M \le 1.7 \times 10^{-2})$ satisfies all three conditions (5.2), (5.2a), and (5.2c) of the applicability of our thermodynamic description of the bubston structure, whereas the second branch does not satisfy these conditions. Therefore, only those solutions that refer to the first branch should be assumed the physically realizable solutions. At the same time, at enhanced ion concentrations $(M > 1.7 \times 10^{-2})$ solutions characteristic of the first branch do not satisfy the condition (5.2c); therefore, they cannot be considered as physically realizable either. This conclusion about the physical realizability of the solutions obtained does not naturally mean that for $M > 10^{-2}$ the bubston structure in canonical ionic solutions is completely absent. The mechanism of the spontaneous formation of bubston nuclei that has been considered in Section 4 exists at all concentrations of Na⁺ and Cl⁻ ions; therefore, the nonrealizability of the obtained solutions at enhanced ion concentrations means only that in these cases a kinetic (rather than thermodynamic) description of the phenomenon under consideration is required.

It can be seen from expression (6.5) that owing to a very weak dependence of γ and s on the ion number density n_i^0 (it can be seen from Table 2) the main dependence of the parameters R, n_b , and K_v of the bubston structure on n_i^0 takes the following form

$$R \sim (n_i^0)^{1/5}, \quad n_b \sim (n_i^0)^{3/5}, \quad K_v \sim (n_i^0)^{6/5}.$$
 (6.7)

The above bubston structure allows, in general, the formation of bubston clusters. This problem is considered in the following section.

7. Formation of bubston clusters

At sufficiently large ion number densities and, consequently, at large number densities of bubstons, the possibility of their mutual interaction should be taken into account. This can manifest itself in sticking bubstons together and, correspondingly, in the formation of bubston clusters. The reason for the possibility of such sticking together is that in the process of movement of bubstons (Archimedes' buoyancy and Brownian motion) their DEL (a screening negative ion shell) can be distorted, as opposed to the equilibrium shell which is determined by the distribution of the charge density $\rho(r)$ according to formulas (4.8) and (4.8b). As a result of such distortions, the negative charge of the ion shell can randomly and equiprobably both decrease and increase (in absolute magnitude), unlike the equilibrium adsorbed positive charge

Table 3

 $4\pi R^2 \gamma e$. In the first case, the bubston becomes positively charged; in the second case, it becomes negatively charged. The positive bubstons thus arising prove to be mechanically unstable and rapidly annihilate (are dissolved), since in this case the pressure due to the mutual attraction of the electrodes of the spherical 'capacitor-bubston' decreases [right-hand side of condition (5.11b)]; this especially concerns bubstons with small radii R. Negative bubstons, on the contrary, acquire additional stability due to an increase in the right-hand part of formula (5.11b), and their lifetime significantly exceeds that of positive bubstons. Thus, there is all the reason to assume that under stationary conditions at each value of the ion concentration the bubstons of three types appear in the solution: neutral, positively charged, and negatively charged. The radii R of all these types are identical and are determined by formula (6.5), but the number densities $n_{\rm b}^{(+)}$ and $n_{\rm b}^{(-)}$ of the positively and negatively charged bubstons are always small compared to the number density $n_{\rm b}$ of neutral bubstons given by formula (6.6), and the number density $n_{\rm b}^{(+)}$ of positive bubstons, in turn, is small as compared to the number density $n_{\rm b}^{(-)}$ of negative bubstons: $n_{\rm b} \ge n_{\rm b}^{(-)} \ge n_{\rm b}^{(+)}$.

The existence of both neutral and charged bubstons in the solutions gives rise to an electrostatic attraction between the neutral and charged bubstons, as well as between the negative and positive bubstons; upon their sufficiently close approaching, the formation of bubston clusters occurs, i.e., aggregates consisting of stuck together bubstons, which have a certain fractal dimensionality, gyration radius R_{cl} , mass N_{cl} , and number density n_{cl} . Here, R_{cl} is the radius of the sphere which includes mainly all bubstons of the cluster, N_{cl} is the number of bubstons in this sphere, and n_{cl} is the number of clusters in a unit volume. According to the above concepts, such clusters are homogeneous in composition, i.e., at a given number density of dissolved ions, all bubstons that enter into a cluster have the same radius R. The mechanism of the formation of clusters themselves has a diffusion character: a diffusion flux of both neutral and charged bubstons, which stick to the nucleus and to each other, is directed onto a nucleus of a cluster (this can be a single bubston or a group of already stuck together bubstons). In this process, a charged sticky bubston does not lose its charge and the neutral bubston remains neutral. This ensures the stability of the cluster, which on the whole becomes negatively charged, since

Which on the matrix $n_b^{(-)} \ge n_b^{(+)}$. The mass $N_{\rm cl}$ of the arising cluster is determined by the total number of bubstons coming as a result of diffusion towards the growing cluster nucleus during a characteristic time of its Archimedes' floating-up, i.e., in a time $\tau_{\rm cl}^{\rm A} = R_{\rm cl}/u_{\rm cl}^{\rm A}$, where $u_{\rm cl}^{\rm A} = (4/15)gR^3N_{\rm cl}/vR_{\rm cl}$ is the velocity of the cluster floating-up. Thus, the mass $N_{\rm cl}$ should satisfy the equation $N_{\rm cl} = 4\pi R_{\rm cl}^2(D_{\rm b}/R)n_{\rm b}\tau_{\rm cl}^{\rm A}$, where $D_{\rm b} = T/5\pi\rho vR$

Table 4

is the diffusion coefficient of bubstons. Hence, we obtain

$$N_{\rm cl} = \sqrt{\frac{3Tn_{\rm b}R_{\rm cl}^4}{\rho g R^5}}.$$
 (7.1)

Since $N_{\rm cl} \propto R_{\rm cl}^2$, in the considered model of the formation of bubston clusters their fractal dimensionality is equal to two. Let us determine their number density $n_{\rm cl}$. If all free bubstons passed into the clusters, then, from the condition of the conservation of the total number of bubstons (both free and bound in the clusters) in the solution, their number density $n_{\rm cl}$ would equal to $n_{\rm b}/N_{\rm cl}$. But it is well-known that only part of the bubstons equal to $(R/R_{\rm cl})^3$ passes into the clusters, which corresponds to the probability that in the solution there is at least one bubston locating in the center of a sphere of radius $R_{\rm cl}$, which, due to the diffusion of surrounding bubstons towards this bubston, will transform into a cluster with a gyration radius $R_{\rm cl}$. Thus, one has

$$n_{\rm cl} = \frac{n_{\rm b}}{N_{\rm cl}} \left(\frac{R}{R_{\rm cl}}\right)^3. \tag{7.2}$$

Substituting formula (7.1) into formula (7.2), we obtain

$$n_{\rm cl} = \sqrt{\frac{\rho g n_{\rm b} R^{11}}{3 T R_{\rm cl}^{10}}} = \sqrt{\frac{\rho g R^8 K_v}{12.6 T R_{\rm cl}^{10}}}, \qquad K_v = \frac{4\pi}{3} R^3 n_{\rm b} \,. \tag{7.3}$$

The gyration radius $R_{\rm cl}$ is determined from the condition that the characteristic time $R_{\rm cl}^2/D_{\rm b}$ of the formation of clusters be small compared to the time $\tau_{\rm cl}^{\rm A}$. Assuming that $R_{\rm cl}^2/D_{\rm b} = 0.1\tau_{\rm cl}^{\rm A}$, we find

$$N_{\rm cl} = 0.1 \, \frac{3}{4\pi} \frac{T}{\rho g R^4} \,. \tag{7.4}$$

The substitution of the last formula into Eqn (7.1) gives

$$R_{\rm cl}^4 = 8 \times 10^{-4} \, \frac{T}{\rho g K_v} \,. \tag{7.5}$$

At T = 293 K, the radius is $R_{cl} \text{ [nm]} = 1.3 \times 10^2 / K_v^{1/4}$. From equations (7.1)–(7.3), we obtain

$$n_{\rm cl} \, [{\rm cm}^{-3}] = 2 \times 10^3 \left(\frac{\rho g K_v}{T}\right)^{1/4} R^4 = 10^4 (R \, [{\rm nm}])^4 K_v^{7/4} \,,$$
 (7.6)

$$N_{\rm cl} = 0.1 \, \frac{n_{\rm b} T}{\rho g R K_v} = \frac{4 \times 10^{-11} n_{\rm b} \, [\rm cm^{-3}]}{R \, [\rm nm] \, K_v} \,. \tag{7.7}$$

The values of the cluster parameters R_{cl} , n_{cl} , and N_{cl} at $t = 25 \,^{\circ}\text{C}$, which are determined according to formulas (7.5)–(7.7), are given in Table 4 along with the values of the parameters R and n_b of the free bubstons that coexist with the clusters (at a given number density n_i^0 of ions).

$n_{\rm i}^0, {\rm cm}^{-3}$ $M, { m mol} { m l}^{-1}$	$\frac{10^{15}}{1.7\times10^{-6}}$	$\begin{array}{c} 3\times10^{15}\\ 5\times10^{-6}\end{array}$	$\frac{10^{16}}{1.7\times 10^{-5}}$	$\begin{array}{c} 3\times10^{16} \\ 5\times10^{-5} \end{array}$	$\frac{10^{17}}{1.7\times10^{-4}}$	$\begin{array}{c} 3\times10^{17}\\ 5\times10^{-4}\end{array}$	$\frac{10^{18}}{1.7\times10^{-3}}$	$\begin{array}{c} 3\times10^{18}\\ 5\times10^{-3}\end{array}$	$\frac{10^{19}}{1.7\times10^{-2}}$
$R_{\rm cl},\mu{ m m}$	4.6	3.2	2.2	1.6	1.1	0.84	0.60	0.42	0.31
$n_{\rm cl},{\rm cm}^{-3}$	$1.5 imes 10^{-3}$	$3.6 imes 10^{-2}$	1.4	31.0	$8.6 imes 10^2$	$1.5 imes 10^4$	$5.0 imes 10^5$	$1.3 imes 10^7$	$2.9 imes 10^8$
$N_{\rm cl}$	$1.1 imes 10^6$	$4.6 imes 10^5$	$1.7 imes 10^5$	$6.8 imes10^4$	$2.8 imes 10^4$	$1.4 imes 10^4$	$4.9 imes 10^3$	$2.1 imes 10^3$	$8.4 imes 10^2$
<i>R</i> , nm	9.6	12.1	15.5	19.2	24.1	28.8	37.2	46.3	57.8
$n_{\rm b},{\rm cm}^{-3}$	$1.8 imes 10^{11}$	$3.6 imes10^{11}$	$7.7 imes 10^{11}$	$1.4 imes 10^{12}$	$2.9 imes 10^{12}$	$5.8 imes 10^{12}$	$1.1 imes 10^{13}$	$2.0 imes 10^{13}$	$4.0 imes10^{13}$

The formation of clusters, generally, should lead to a decrease in the number density of free bubstons; this density $n'_{\rm b}$ is determined from the condition of the conservation of the total number of bubstons in the solution: $n_{\rm b} = n_{\rm cl}N_{\rm cl} + n'_{\rm b}$. According to formulas (7.2), we arrive at

$$n_{\rm b}' = n_{\rm b} \left[1 - \left(\frac{R}{R_{\rm cl}} \right)^3 \right], \tag{7.8}$$

and from expression (5.2d), we have

$$\left(\frac{R}{R_{\rm cl}}\right)^3 = 4.2 \times 10^{-7} (R \ [\rm nm])^3 K_v^{3/4} \,.$$
 (7.8a)

It can be seen from Tables 3 and 4 that the value of $(R/R_{cl})^3$ is maximum at $n_i^0 = 10^{19}$ cm⁻³, when R = 57.8 nm and $K_v = 3.3 \times 10^{-2}$. In this case, $(R/R_{\rm cl})^3 \sim 10^{-2}$. Thus, upon forming a bubston-cluster structure, the number density of free bubstons $n'_{\rm b}$ at all the densities of ions under consideration remains close to n_b , i.e., the value of the number density of bubstons in the absence of clusters. This is connected with one more, no less important, result: the number density of clusters n_{cl} , according to formula (7.6) and Table 4, is also maximum at $n_i^0 = 10^{19} \text{ cm}^{-3}$ and amounts to around 3×10^8 cm⁻³, which is several orders of magnitude less than the number density n'_b of free bubstons. A similar relationship between n_{cl} and n'_b is also retained at other ion densities. In turn, as a consequence of these two results, the flux of the free gas that comes onto the surface of the solution due to the escape of clusters onto the surface proves to be negligibly small compared to the flux that is determined by the emergence of free bubstons onto the surface. Thus, the formation of clusters does not change the condition of gas equilibrium on the solution-gas interface that was represented in the form (6.2).

The above-considered model describes the formation of compositionally homogeneous clusters. At the same time, the electrostatic character of the interaction between bubstons supposed in the model indicates the possibility of the formation of a more complex type of clusters in the solution, namely, of aggregates consisting of clusters of the above type with random gyration radii. It is obvious that the average density of such clusters of the 'second order' should be small compared to the average number density n_{cl} of clusters of the 'first order'.

8. Formation of a bubston structure as a first-order phase transition

It has been shown in Section 5 that the necessary condition s < 1 for the existence of bubstons is fulfilled if the total number density of dissolved impurity ions is $n_i^0 > (n_i^0)_{\text{th}}$, where $(n_i^0)_{\text{th}}$ stands for a temperature-dependent threshold density:

$$(n_{i}^{0})_{th} = (n_{i}^{0})_{th}(T_{0}) \exp\left[-W_{b}\left(\frac{1}{T} - \frac{1}{T_{0}}\right)\right],$$
 (8.1)

 $(n_i^0)_{th}(T_0) = 7.1 \times 10^{13} \text{ cm}^{-3}$ $(T_0 = 298 \text{ K} = 4.1 \times 10^{-14} \text{ erg} = 25 \text{ °C})$, and $W_b = 0.8(U_i + \bar{U}_i)/2 = 0.682 \text{ eV}$. On the (n_i^0, T) plane, the dependence of $(n_i^0)_{th}$ on the temperature is represented by a curve that increases slowly with temperature (Fig. 2). At a given value of T, the points $n_i^0 > (n_i^0)_{th}$ correspond on this plane to values of s < 1, which means the

existence of a 'bubston phase' in the solution; the points $n_i^0 < (n_i^0)_{\text{th}}$ are associated with a 'homogeneous (bubstonless) phase' of the solution. Such a transition at a given temperature of the aqueous ionic solution from a homogeneous phase into a bubston phase should be considered a first-order phase transition. The order parameter in this case is the quantity $K_v = (4\pi/3)R^3n_b$, which changes jumpwise (from zero to some finite value) and characterizes the relative fraction of the volume free of liquid, which is filled with gas. It follows directly from the Le Chatelier–Brown principle that the heat of the transition from the homogeneous phase into the bubston phase is negative, i.e., heat is released (similar to how this occurs in the transition of liquid water into ice).

The general conclusion about the existence of a phase transition in the 'aqueous ionic solution + external gaseous medium' system does not agree with the previous conclusions that in the case of an external helium medium the bubble structure is impossible at any concentration of ions. This contradiction is solved as follows. The inference about the existence of a phase transition was made based only on one necessary condition for the existence of bubstons, namely, s < 1. But this condition is insufficient for the formation of a bubston phase. It is necessary, in addition, as was shown in previous sections, that in the presence of bubstons a condition (6.2) of the gaseous equilibrium be also fulfilled. In the case of a nitrogen or some other (except for helium) gaseous medium, this condition is fulfilled, whereas in the case of helium this condition can be fulfilled only in the absence of the bubston phase. Thus, the 'aqueous ionic solution + external helium medium' system differs from other similar systems in the absence in it of the phase transition under consideration. It should be said that the existence of such 'exclusiveness' is not somewhat new in the physics of phase transitions; as an example, we may mention glasses which remain amorphous in all their condensed states irrespective of temperature (the physics of the phenomenon here is, naturally, different).

Above-obtained result (8.1) refers to the aqueous solution of NaCl salt. But the energy $W_b = 0.8(U_i + \bar{U}_i)/2$ and, consequently, according to formulas (5.13a) and (5.13b), the preexponential factor depend on the type of dissolved impurity ions (see Appendix A). For univalent ions (e.g., in LiCl or KCl solutions), the energy W_b can easily be determined via the same formulas given in Appendix A that



Figure 2. Curve of the 'bubston phase-homogeneous phase' equilibrium for an NaCl solution. In the equilibrium curve, one has s = 1, $K_v = 0$, $W_b = 0.6282$ eV, and $T_0 = 298$ K (t = 25 °C).

were obtained for an NaCl solution with the corresponding replacement of the values of the ionic radii: $\delta_{Na^+} = 0.98 \text{ Å} \rightarrow \delta_{Li^+} = 0.68 \text{ Å}$ or $\delta_{Na^+} = 0.98 \text{ Å} \rightarrow \delta_{K^+} = 1.33 \text{ Å}$.

It is also important to note that the above value of the threshold density $(n_i^0)_{\rm th} = 7.1 \times 10^{13} {\rm cm}^{-3}$ at $T = 298 {\rm K}$ proves to be on the order of magnitude close to the value of the minimum number density (at this temperature) of impurity ions in water, $n_i^s = 1.4 \times 10^{13} {\rm cm}^{-3}$ (when its resistivity is $\lambda = 1.8 \times 10^7 {\rm \Omega}$ cm, see Table 1), which is achieved with modern technologies of the water deionization. This circumstance makes it possible to assume that the mechanism of the deionization itself in such technologies lies in the elimination from the water (by filtration) of bubstons (which accumulate impurity ions): the deionization stops when all bubstons prove to be filtered away. Hence, it follows that the employed technologies of the deionization do not, in principle, allow us to reduce at a given temperature the ion concentration to below $(n_i^0)_{\rm th}(T)$.

9. Conclusion

The above theoretical aspects of the existence of stable gas bubbles — bubstons — in the aqueous solutions of electrolytes residing in equilibrium with an external gaseous medium, as was said in the Introduction, have led to numerous experimental investigations in this field. The results of this work, given, for instance, in Refs [12–24], make it possible to estimate the degree of the completeness of current investigations into this phenomenon in the physics of water.

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Appendix A

To determine the energy U(T,p), we will proceed from modern concepts of the structure of water as a (locally) tetrahedral network of H₂O molecules interacting via hydrogen bonds. The coordination polyhedron — a regular tetrahedron — has edges of length $a_0 = (4/\sqrt{6})l_0$, where $l_0 = k2\delta_1$ is the distance to the four nearest neighbors, which is equal to the radius of the circumscribed sphere of the tetrahedron, and $\delta_1 = 1.38$ Å is the radius of the water molecule. The coefficient k determines the degree of packing ('looseness') of the water structure. The volume of such a tetrahedron, which coincides with the specific (per molecule) volume of water, is given by

$$v_0 = \frac{\sqrt{2}}{12} a_0^3 = \frac{\sqrt{2}}{12} \left(\frac{4}{\sqrt{6}}\right)^3 k^3 (2\delta_l)^3 = \frac{2^6 \delta_l^3 k^3}{3^{5/2}} .$$
(A.1)

Under normal conditions, $v_0 = 1/n = 3.04 \times 10^{-23}$ cm³ $(n = \rho N_A/M = 3.3 \times 10^{22}$ cm⁻³ is the number density of water molecules, ρ is the mass density of water, N_A is the Avogadro constant, and M = 18 is the molecular weight of water). By substituting this value of v_0 into (A.1), we conclude, taking into account that $\delta_1^3 = 2.63 \times 10^{-24}$ cm³, that $k = \sqrt{2}$ under normal conditions.

For neutral dissolved gas particles, the sought-after energy U is equal to one-fourth of the minimum work that should be expended to produce a uniform extension of water and, consequently, of its coordination tetrahedron in such a manner that four cavities are formed with dimensions sufficient for the location of particles with a radius δ in them. The requirement for the minimum work appears to reduce to the necessity that in the extended state the spacing l_1 between the nearest water molecules be equal to $2\delta_1 + 2\delta_i$; in other words, the structure of 'extended water' — water with vacant cavities — should have the maximum packing density (k = 1). The length of the edges of the extended tetrahedron is $a_1 = (4/\sqrt{6})l_1 = (8/\sqrt{6})\delta_1\alpha$, where $\alpha = 1 + \delta/\delta_1$, and the volume of the tetrahedron is equal to

$$v_1 = \frac{\sqrt{2}}{12} a_1^3 = \frac{2^6 \delta_1^3 \alpha^3}{3^{5/2}} .$$
 (A.2)

Thus, the specific volume of water at $k = \sqrt{2}$, according to formulas (A.2) and (A.1), should be increased by

$$\Delta v = (v_1 - v_0) = \frac{2^6 \delta_1^3}{3^{5/2}} (\alpha^3 - 2^{3/2})$$
(A.3)

for the formation of four required cavities. The sought-after energy U can be represented in the following form

$$U = \frac{1}{4} \left[E(V) - E(V_1) \right] = \frac{1}{8} \left(\frac{d^2 E}{dV^2} \right)_{V=V_0} (\Delta V)^2 \frac{M}{N_A}$$
$$= \frac{1}{8} \left| \frac{dp}{dV} \right|_{V=V_0} (\Delta V)^2 \frac{M}{N_A} .$$
(A.4)

Here, E(V) is the specific (per unit mass) internal energy of the liquid (water) related exclusively to the forces of the interaction between the molecules (elastic energy), $V_0 = v_0 N_A/M = 1/\rho$ is the equilibrium specific volume of water, and $\Delta V = \Delta v N_A/M$. The pressure inside the liquid is P = -dE/dV; at $V = V_0$, the pressure comes to nought: P = 0, dP/dV < 0, and $|dP/dV|_{V=V_0} = 1/\beta V_0 = u_s^2 \rho^2$, where u_s is the velocity of sound in water (β is the isothermal compressibility of water). Taking these formulas into account, the substitution of formula (A.3) into (A.4) gives

$$U = u_{\rm s}^2 \rho^2 \frac{N_{\rm A}}{M} \frac{2^9 \delta_{\rm l}^6}{3^5} (\alpha^3 - 2^{3/2})^2 = 6.70 \times 10^{-3} (\alpha^3 - 2^{3/2})^2 \text{ eV}.$$
(A.5)

The last formula was obtained at $u_s = 1.49 \times 10^5$ cm s⁻¹, $\rho = 1$ g cm⁻³ (t = 20 °C), and $\delta_1 = 1.38$ Å. The dependence of U on T and ρ is determined by the dependences of the sound velocity u_s and density ρ on these quantities.

For nitrogen molecules, $\delta \equiv \delta_g = 1.58$ Å, the parameter $\alpha = 1 + \delta_g/\delta_1 = 2.143$, and, according to formula (A.5), $U_g = 0.332$ eV. For helium atoms, $\delta \equiv \delta_g = 1.22$ Å, $\alpha = 1.884$, and, according to formula (A.5), the energy takes the value of $U_g = 0.10$ eV.

When the dissolved particles are ions, the sought-after energy U_i is summed from the elastic energy, which is defined by formula (A.5) at $\delta = \delta_i$ (ion radius), and the energy of the electrostatic interaction of the incorporated ion, first with five molecules of water entering into the tetrahedron (four molecules in its vertices and one in its center), and, second, with all other molecules of water, i.e., the energy $e^2/2\delta_i\varepsilon$ (ε is the dielectric constant of water). The first of these energies is equal to $2\beta e^2/2x_1^4 + 3\beta e^2/2x_2^4$, where $x_1 = \delta_1 + \delta_i$, and $x_2 = x_1\sqrt{57/9}$. For Na⁺ ions, this energy is equal to 0.707 eV; for Cl⁻ ions, this energy is 0.214 eV. The energy $e^2/2\delta_i \varepsilon$ for the Na⁺ ions is 0.0915 eV; for the Cl⁻ ions it equals 0.0675 eV. Thus, the full electrostatic energy for Na⁺ ions is equal to 0.802 eV; for Cl⁻ ions, it is 0.264 eV. The elastic energy for the Na⁺ ions, according to formula (A.5), is 0.032 eV; for the Cl⁻ ions, $\bar{U}_i = 0.605$ eV. As a result, the total energy U_i for the Na⁺ ions is 0.830 eV; for the Cl⁻ ions, $\bar{U}_i = 0.870$ eV. Finally, the energy $W_i = (U_i + \bar{U}_i)/2 = 0.852$ eV.

Appendix **B**

In equilibrium, the flux j_1 (per unit area) of gas particles that escape from the solution into the external gaseous medium is compensated for by the flux j_2 of such particles that come onto the interface from the external medium and penetrate into the solution. If the bubstons are absent ($n_b = 0$), the flux j_1 is of a purely diffusive character and is determined by the diffusion coefficient D_g of the gas dissolved in the liquid, by the radius δ_g of gas particles, and by the number density $n_g^s = H_0 n_g$, where $n_g = p/T$ is the density of the gas in the external medium, and $H_0 = \exp(-U_g/T)$ [see formulas (5.8a) and (5.8b)]. The dimensional method yields

$$j_1 = (j)_{D_g} = Cn_g^s \left(\frac{D_g}{\delta_g}\right) = Cn_g \left(\frac{D_g}{\delta_g}\right) H_0.$$
 (B.1)

The dimensionless constant *C* is the probability that the dissolved gas particles that fall onto the interface as a result of their diffusive escape from the solution (pass into the external medium). In the case of the absence of bubstons that we consider here, we assume that C = 1. The compensating flux j_2 from the external medium is defined as (see monograph [10])

$$j_2 = n_{\rm g} \bar{v} w_0 \,, \tag{B.2}$$

where $\bar{v} = \sqrt{T/2\pi m}$ is the average value of the normal (relative to the interface) component of the thermal velocity of gaseous particles that fall onto the boundary, *m* is their mass, and w_0 is the probability of the penetration of such particles into the solution. From the equality $(j_1)_{D_g} = j_2$, it follows, according to formulas (B.1) (at C = 1) and (5.7), that

$$w_0 = \frac{D_{\rm g}/\delta_{\rm g}}{\bar{v}} H_0. \tag{B.3}$$

In the case of the existence of bubstons in the solution, the flux j_1 is composed of three parts. The first is the diffusion flux of the dissolved gas $(j_1)_{D_g}$, which is determined from the formula (B.1), but in this case the constant *C* is equal to $1 - w_1$ rather than to unity, where w_1 is the probability that the gas particle reaching the interface due to diffusion proves to be captured by a surface bubston. The *stationary surface density* of such bubstons⁴ can be assumed to be equal to $n_b^{2/3}$ and, correspondingly, the probability is $w_1 = \pi R^2 / n_b^{-2/3}$. Add to this that all bubstons in the solution, including surface bubstons, can be considered to be traps exchangers of dissolved gas particles. When having collided with a bubston, a gas particle is trapped, but under equilibrium conditions (when $N_g = (4\pi/3)R^3n_g = \text{const}$) an exchange occurs between the trapped particles and other identical particles that escape from the bubston into the surrounding solution. Thus, the surface bubstons serve as a screen for gas particles, preventing their escape from the solution. Notice that the probability $w_1 = \pi R^2 n_b^{2/3}$ can be related to the parameter $K_v = (4\pi/3)R^3n_b$, so that $w_1 = 1.21K_e^{2/3}$.

Thus, in the presence of bubstons, the diffusion flux of the dissolved gas that escapes the solution is described, according to expression (B.1), by the formula

$$(j_1)_{D_g} = n_g \left(\frac{D_g}{\delta_g}\right) H_0(1 - w_1), \qquad (B.4)$$

where $w_1 = \pi R^2 n_b^{2/3}$. Along with the flux $(j_1)_{D_a}$, there come contributions to the gas flux j_1 from the processes of the transfer onto the interface of the free gas containing inside the bubstons that are lost at the interface; the gas contained in them passes (is thrown out) into the external medium. Such processes, as was said at the beginning of Section 5, are the Archimedean buoyancy and Brownian motion. The first process makes a contribution equal to $(j_1)_A = N_g(j_b)_A$, where $N_{\rm g} = (4\pi/3)R^3 n_{\rm g}$, $(j_{\rm b})_{\rm A} = n_{\rm b}u_{\rm A}$ is the Archimedean flux of bubstons, where $u_{\rm A} = (4/15)gR^2/v$ is the rate of their floating up [see Eqn (5.1)]. The contribution to the gas flux j_1 from the Brownian motion of bubstons is determined by their diffusion flux $(j_b)_{D_b} = n_b(D_b/R)$ towards the interface and is given by $(j_1)_{D_b} = N_g(j_b)_{D_b} = N_g n_b(D_b/R)$, where $D_b = T/5\pi\rho v R$ [see Eqn (5.1)]. When using these formulas for the fluxes $(j_1)_A$ and $(j_1)_{D_b}$, it is assumed that after the moment of bubston reaching the interface, they are lost with a probability of 1, with the escape of $N_g = (4\pi R^3/3)n_g$ gas particles into the external medium (a similar assumption was made when using formula (B.1), in which we assumed that C = 1 at $n_{\rm b} = 0$). Thus, the contribution to the flux j_1 from the total flux of the free gas takes the form

$$(j_1)_{\rm A} + (j_1)_{D_{\rm b}} = N_{\rm g} n_{\rm b} \, \frac{D_{\rm b}}{R} \left(1 + \frac{R^4}{S_1} \right),$$
 (B.5)

where

$$N_{\rm g} = \frac{4\pi}{3} R^3 n_{\rm g} , \qquad S_1 = \frac{3T}{4\pi\rho g} .$$
 (B.5a)

Under terrestrial conditions, the parameter S_1 is approximately equal to 10^{-17} cm⁴. Under microgravity conditions (on board a space vehicle), the second term in parentheses on the right-hand side of formula (B.5) is always small. Under equilibrium, the flux (B.5) of the free gas and the diffusion flux (B.4) are compensated for by the flux j_2 of gas from the external medium, which in the absence of bubstons is determined, according to relations (B.2) and (B.3), by the formula

$$j_2 = n_{\rm g} \, \frac{D_{\rm g}}{\delta_{\rm g}} \, H_0 \,. \tag{B.6}$$

A substantial circumstance is that the presence of a bubston structure in the solution $(n_b \neq 0)$ does not exert an effect on the flux of gas that penetrates into the solution, i.e., this flux,

⁴ This quantity determines the number of bubstons that at each time moment reside inside an element of a plane layer of a solution of thickness $n_b^{1/3}$ with a unit area that adjoins the interface. Each surface bubston disappears, but due to the constant flux of bubstons coming onto the surface, it is replaced by another bubston. As a result, the surface density of the permanently renewed bubstons remains stationary.

as before, is determined by the formula (B.6). Indeed, in this case j_2 can be represented as

$$\dot{v}_2 = n_{\rm g} \bar{v} w_0' w_1' + n_{\rm g} \bar{v} w_0 (1 - w_1'),$$
 (B.6a)

where w'_1 is the probability that a gas particle falling normally onto the interface from the external medium collides with the 'shadow' of the surface bubston (i.e., with its projection onto the interface). It is obvious that this probability coincides with $w_1 = \pi R^2 n_b^{2/3}$. In the last expression, w'_0 is the probability of penetrating such a particle with a thermal velocity \bar{v} into the solution. This probability, since the particle trapped by a surface bubston is replaced by another particle which comes out into the solution, proves to coincide with w_0 . Assuming that $w'_1 = w_1$ and $w'_0 = w_0$ in formula (B.6a) and taking into account formula (B.3), we obtain formula (B.6). As a result, according to relations (B.4), (B.5), and (B.6), the condition of equilibrium at the interface takes on the following form:

$$\frac{4\pi}{3} R^3 n_b \left(\frac{D_b}{R}\right) \left(1 + \frac{R^4}{S_1}\right) + \frac{D_g}{\delta_g} H_0(1 - w_1) = \frac{D_g}{\delta_g} H_0. \quad (B.7)$$

By substituting $D_b = T/5\pi\rho vR$ and $K_v = (4\pi/3)R^3n_b$ into this equation, we arrive at

$$\frac{(K_v/w_1)T(1+R^4/S_1)}{5\pi\rho v(D_g/\delta_g)R^2H_0} = 1, \qquad (B.8)$$

where $K_v/w_1 = 0.83 K_v^{1/3}$.

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