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Calculation of the Gibbs Energy of the Reaction $OH^- \cdot (H_2O)_{n-1}$ + H_2O = $OH^- \cdot (H_2O)_n$ by the Monte–Carlo Method

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Abstract—The energy and the Gibbs energy of the reaction $OH^- \cdot (H_2O)_{n-1} + H_2O = OH^- \cdot (H_2O)_n$ are calculated by the Monte–Carlo method with a large canonical ensemble for $n = 1, ..., 20$. The ion–water nonpair interaction potential was obtained by numerical fitting of calculated Gibbs energy and entropy of $(H_2O)_n$ clusters ($n = 1, ..., 5$) to experimental ones. A good fit to experiment both of the internal energy and the Gibbs energy can be obtained in terms of a model allowing for nonpair interaction. It is shown that constructing an ion–water interaction potential without allowance for the entropy factor can lead to considerable errors in the Gibbs energy of cluster formation and in the nucleation rate.

1. INTRODUCTION

Calculation of the Gibbs energies of cluster formation is an intricate computational problem. The free energy is expressed in terms of the statistical integral over all possible molecular configurations of the system, and, consequently, it is determined by the whole energy surface of the interacting particles. The most effective tool for solving multidimensional integration problem is the Monte–Carlo method on the basis of Markov's random processes. According to general principles of the Gibbs statistical mechanics, the probabilities of microstates in a molecular ensemble exponentially vary with their energies. With lowering temperature, this dependence sharpens. At low temperatures corresponding to the crystal state, the largest contribution is from immediate vicinity of the energy minimum; vice versa, in the gas phase, interactions of particles at large intermolecular distances are well described by higher members of the multipole series. The greatest difficulties are associated with medium temperatures corresponding to the liquid state. In constructing a model intermolecular potential for statistical-mechanical studies of molecular systems one has to look for a compromise between two alternative conditions. On the one hand, the potential should fairly reproduce interactions of real molecules. On the other hand, the functional dependence describing these interactions should be sufficiently simple, since a single computational experiment involves a multiply, up to hundred million times, repeated calculation of the system energy for different molecular configurations. Such a computational experiment takes several hours of a medium-throughput computer time. Unjustified complication of the functional dependence describing intermolecular interaction would inevitably cut down the resulting statistical database and, as a result, increase the statistical uncertainty in the resulting equilibrium averages.

From the very beginning of works on computer simulation of statistical-mechanical properties of water and water complexes, principally different approaches to constructing intermolecular potentials revealed thereselves. The research teams of Abraham, Mruzik, Schreiber, and Pound, as well as of Kistenmacher and Clementi [1], obtained the interaction potential by Hartree–Fock SCF computations. Tabulated results were approximated by several force centers fixed on the molecular frame, in terms of two multicenter models: Rowlinson five-center model (Rw) and Bernal–Fowler four-center potential (BF). The SSP method treats each electron as moving in an averaged field of rest electrons, and in its original version takes no account of electron correlation. Correlation effects, both exchange and Coulomb, are included as corrections [2]. This approach is exemplified by the CI method. Precise account for the permutational symmetry of the many-electron wave function of a system, with inclusion of its spin states, is a very intricate combinatorial problem and to tackle it requires invoking the theory of groups and Young's symmetry operators [3]. The energy of molecular interactions is obtained as a relatively small difference between the energies of isolated and interacting molecules. Approximations sufficient for describing the one-electron shell of a molecule as such may prove insufficient for calculating the relatively weak intermolecular forces of the van der Waals type, which are strongly contributed by electron correlations. Quantum-chemical calculations of water clusters [4, 5] show that nonpair interactions in water are considerable. The error in internal energy, associated with neglect for multiparticle interactions, may reach 30% [4]; at the same time, almost all (~99%) internal energy is exhausted by two- and three-particle terms. Three-particle interactions appreciably affect the structure [6] and energy [7] of ice. The role of electron correlations is especially pronounced in multiparticle interactions.

Whereas direct quantum-chemical calculation of intermolecular potentials is more attaractive methodically, the fact that precise calculations for medium intermolecular distances involve considerable difficulties makes researcher’s to look for altenative ways for constructing model dependences. The most promising approach is to determine the intermolecular potential from experimentally observed thermophysical and structural properties of real systems: liquid water, ice, and water clusters. After two-decade active investigations on aqueous systems, stochastic simulation has gained the greatest favor. Works in this fields has been initiated by Rahman and Stillinger [8–13]. They developed one of the best versions of multicenter potentials for water, an ST2 five-center potential, that includes electrostatic, exchange, and dispersion interactions. Parameters of the ST2 potential were set so as to fit, as close as possible, the binary correlation functions and internal energy of real water. While the hydrogen bond between real water molecules is not simply an electrostatic interaction (charge transfer and proton tunneling, too, contribute much), most model multicenter potentials, except for a numer of special versions, replace the hydrogen bond by some effective electrostatic interaction.

Over the last two decades, different authors have developed tens multicenter potentials for water. One of the best working is an SPC (Simple Point Charge) three-center potential with charges located in a common plane. While obviously simplified, the SPC model provided the best fit of the experimental dielectric constant of liquid water (ε_{H_2O} 78.0 at T 300 K; cf. ε_{SPC} 81.0) [14]. Presently, the SPC model is being most actively employed in the computer simulation of water by the Monte–Carlo and molecular dynamics methods [15–24]. Potentials of the TIPS (Transferable Intermolecular Potential Surface) family slightly differ from the SPC potential. The negative charge in TIPS models is displaced from the Lennard–Jones center along the bisector of the HOH angle at a certain distance varying with the TIPS model (TIP1, TIP2, TIP3, TIP4, and special Rw version). The HOH angle, distances to charges, and parameters of the Lennard–Jones part of the potential in latter models, too, slightly differ from respective SPS values [25]. The ST2 potential slightly overestimates the structuring degree of the liquid phase; vice versa, with TIPS potentials, underestimated degrees of molecular ordering in the second and further coordination layers are obtained. The ST2 model provides the best estimates for the self-diifusion coefficient.

Model potentials joined by a common name CFM (Central Force Model) treat water molecule not as a rigid species, but as three interacting ions, two positive and one negative. The molecule is assembled naturally, under the action of ion–ion forces, in the course of numerical simulation. Ion–ion potentials are written as a combination of exponentials, power dependences on distances and electrostatic interaction. The interaction parameters are set so that the geometry of the resulting conglomeration fits the molecular geometry of water, and the normal vibration frequencies and dissociation energy fit the corresponding experimental values for a real water molecule [26–29]. The ST2 model provides a slightly overestimated self-diffusion coefficient, while the CFM model, vice versa, tends to underestimate this value. The explanation is that in the formation of a real water molecule from oxygen and hydrogen ions involves partial filling of the outer electronic shell of the molecule, and intermolecular interaction proves weakened. The CFM model neglects this circumstance. An attractive feature of CFM potentials is that they operate with spherical particles. Sphericity strongly simplifies the calculation algorithm, especially in the case of the molecular dynamics method, since it makes unnecessary to solve equations for rotational degrees of freedom. Regardless of these advantages, the CFM method has been in disfavor for the last few years.

The SPC–FP (Simple Point Charge + Flexibility of Bonding + Polarization) model and its version MST–FP [30] are based on the concept of an integral but deformable water molecule. Exchange interaction is described by an exponential dependence on intermolecular distance, while dispersion, by the inverse sixth degree of distance. The MST–FP potential involves one additional term (as a Morze potential) responsible for hydrogen-bond formation. This additional term enables one to tackle the of overestimated self-diffusion coefficient in the liquid phase. The development of the ideas of the SPC–FP model can be found in the BJH [31] and DSFG models [32].

There is no a single universal thermodynamic property which might be relied on in judging about correctness of one or another model of intermolecular interaction. One should analyze a set of thermodynamic data. While internal energy is generally used as one of the main correctness indicators for model intermolecular potentials, the most informative is the Gibbs energy rather than internal energy of a system. According to general principles of Gibbs's statistical mechanics, the probability of any macroscopic event in a molecular ensemble are exponentially varies with Gibbs energy. The Gibbs energy $G = U - TS + pV$ (U is internal energy, T is temperature, S is entropy, p is pressure, and V is volume) includes an entropy term TS. Entropy, by definition, is directly related to the state density of the system [33]. In its turn, the state density is directly related to the shape of the energy surface determined by intermolecular potential. The Gibbs energy contains a more detailed information on the whole potential energy surface profile, whereas the internal energy is mainly determined by the depth of the potential well corresponding to the stable state of the system and, to a lesser extent, by the width of the well. Preliminary calculations show that if, for instance, fitting intermolecular potential to experimental data for internal energy only may result, in the typical case of ionic hydration, to an error in the Gibbs energy δG of several or, for relatively large clusters, several tens k_BT (k_B is Boltzmann's constant). This may result in errors in the probability and rate of clusterization $\sim\exp(-\delta G/k_BT)$ of about several orders of magnitude or even larger. Surely, the effect is weaker for the weaker interaction between electroneutral molecules, but here, because of the sharp, exponential dependence of principal microstructural characteristics on the Gibbs energy, the correctness of the description of molecular ordering in terms of the intermolecular potential obtained by fitting to experimental data for internal energy only still remains problematic. The calculated Gibbs energies of solvation of polar molecules in water [34] give a very good illustration for this fact. The Gibbs energy proves to be strongly dependent on the concrete model of intermolecular interaction. Ideally, the model potential should be constructed in such a way as to ensure reproduction of true values both for the Gibbs energies and of the internal energies of multiparticle conglomerations, which inevitably requires correctly accounting for nonpair terms in the system Hamiltonian. This procedure of constructing intermolecular potential may be based on experimental data on cluster formation. In the experiments on clusterization in adiabatically extending gas fluxes, Viisanen *et al.* [35] could, via variable-temperature mass spectral measurements of size distribution of clusters, fairly fit the entropy and Gibbs energy of cluster formation [35]. Two circumstances prevent utilization of this program for a broad range of molecular systems. The first consists in the lack of reliable experimental data on cluster formation for most systems interesting in terms of application. As a rule, relatively stable clusters are formed on ions. "Pure" clusters are usually less stable, and, therefore, reliable experimental data for such molecular complexes are more difficult to obtain. The second circumstance consists in that computer simulation of Gibbs energy involves greater computational difficulties, as compared with internal energy. The optimization of model intermolecular potential by successive approximations should be multiply repeated for various sets of numerical values of parameters. This program can be realized provided a sufficiently effective algorithm for calculating Gibbs energy is available. In the present work we demonstrate the practical possibility of constructing a correct model potential of intermolecular interaction between an OH^- ion with H_2O molecules, which ensures reproduction of known experimental Gibbs energy and entropy of the system. The neglect by entropy contributions into thermodynamic functions in fitting the model potential to the properties of the real system makes the model incorrect.

2. NONPAIRD INTERMOLECULAR POTENTIAL

The model of intermolecular interactions in the system comprising an OH^- ion and water molecules is based on the Rahman–Stillinger ST2 five-center potential [8–13] complemented by terms that take account of the deformation of the electronic shells of molecules in the electric field of ions. The deformation of electronic shells of molecules in the force field of ions is taken into account via dependence of parameters of the intermolecular potential on the ion–molecule distance. This additional, with respect to the original pair ST2 model, part of the Hamiltonian is nonpair in nature: the energy of interaction of two molecules in the field of an ion depends on the arrangement of other molecules, the effect being the stronger the shorter the distance to the ion. The main criterion for correct numerical values of the parameters is the fit of calculated to experimental Gibbs energies for different numbers of particles in the system, as well as the internal energy.

The continuous electron density distribution in the real water molecule is replaced, in the ST2 model, by four point charges placed on beams emerging from a common geometric center. The interbeam angle of 109.4712° corresponds to a regular tetrahedron. Two positive charges by q_+ 1.132062×10^{-10} CGSE are at the distance A 1.0 Å from the center (two negative charges $q_{-} = -q_{-}$, the same in absolute value as the positive charges, are fixed at the distance B 0.8 Å from the center). The geometric center accommodates a source of Lennard–Jones interaction with the potential depth ε_0^w 5.2605×10^{-15} erg and the interaction radius σ^w 3.1 Å. The special shielding function (1) depending on the distance r between the centers of two interacting molecules, smoothens the exaggeratedly nonuniform, compared with the real molecule, electric field of point charges with r_L 2.0160 and r_U 3.1287 Å [8–13].

$$s^w(r) = \begin{cases} 0, & 0 < r < r_\mathrm{L} \\ (r - r_\mathrm{L})^2(3r_\mathrm{U} - r_\mathrm{L} - 2r)/(r_\mathrm{U} - r_\mathrm{L})^3, & r_\mathrm{L} \le r \le r_\mathrm{U} \\ 1, & r_\mathrm{U} < r < \infty \end{cases} \tag{1}$$

Thus, the pair part of the interaction of water molecules is represented by Eq. (2):

$$U_\mathrm{pair}^{ww} = \sum_{i<j} u_\mathrm{pair}^{ij} = \sum_{i<j}\left\{4\varepsilon_0^w\left(\left[\frac{\sigma^w}{r_{ij}}\right]^{12} - \left[\frac{\sigma^w}{r_{ij}}\right]^{6}\right)\right. \\ \left. + s^w(r_{ij})\sum_{k=1}^{4}\sum_{l=1}^{4}\frac{q_k q_l}{\vec{r}_k^{\,i} - \vec{r}_l^{\,j}}\right\}. \tag{2}$$

Here $\vec{r}_k^{\,i}$ is the coordinate of the kth point charge of the ith molecule, r_{ij} is the distance between the sources of the Lennard–Jones fields of two molecules, while q_k and q_l take q_{+} and q_{-} values. The singularity points of potential (2) at $r_{ij} = 0$ and $|\vec{r}_k^{\,i} - \vec{r}_l^{\,j}| = 0$ are excludes from the range of acceptable molecular configurations via the introduction of solid spherical nuclei in all the five forces centers of the molecule, so that at $r_{ij} < d_0 = 1.55$ Å and $|\vec{r}_k^{\,i} - \vec{r}_l^{\,j}| < d_q = 0.1$ Å, by definition, $u_\mathrm{pair}^{ij} = \infty$.

In the absence of ions and sources of external electric field, all interactions in the system are exhausted by the term U_pair. In the electric field of ions and in the presence of additional point charges and external uniform field, direct Coulomb interaction of the field with undisplaced molecular charges (U_Coul^w) is taken into account, as well as the contribution into the energy of molecular polarization (U_pol^w). This part of the energy is nonpair in nature, since first the electric fieds from all the sources are vectorially added in the geometric center and then the polarization energy of the molecule is calculated by Eq. (3).

$$u_\mathrm{pol}^w(\vec{r}_0^{\,i}) = -\frac{1}{2}\alpha_w\left(\vec{E}(\vec{r}_0^{\,i}) + \sum \vec{E}_l^s(\vec{r}_0^{\,i}) + \vec{E}_0\right)^2. \tag{3}$$

Here $\alpha_w = 1.44$ Å^3 is the isotropic polarization coefficient of a free water molecule (experimental value); $\vec{r}_0^{\,i}$ is the coordinate of the geometric center of the ith water molecule; $\vec{E}(\vec{r})$ and $\vec{E}_l^s(\vec{r})$ are the electric fields of the ion and lth point source in the point $\vec{r}$; and $\vec{E}_0$ is the external uniform electric field whose inclusion is provided by the model. The intricate geometry of the electric field of molecular ions is simulated by point sources arranged in a certain manner. Each of the point sources is supplied by a solid spherical nucleus with the radius d_l^s, so that the singularity points of the electric field are excluded. The OH^- ion is supplied by two such sources to simulate the field produced by electron density displacement in the ion to the oxygen atom. The anisotropy of molecular polarizability tensor, interaction of induced dipole and higher multipole moments, as well as secondary polarization are considered as higher order effects and are neglected. Thus, the polarization energy of molecules in the electric field of the ion is given by Eq. (4).

$$U_\mathrm{pol}^w = \sum_i u_\mathrm{pol}^w(\vec{r}_0^{\,i}). \tag{4}$$

Apart from Coulomb and polarization, dispersion and exchange interactions of molecules with the ion are taken into account in the form of the Lennard–Jones potential (5).

$$U_\mathrm{LD} = \sum_i 4\varepsilon_0\left(\left[\frac{\sigma}{R_i}\right]^{12} - \left[\frac{\sigma}{R_i}\right]^{6}\right). \tag{5}$$

The potential singularity point $R_i = 0$ is excluded from the range of accessible molecular configurations be means of a solid spherical nucleus such that $U_\mathrm{LD} = \infty$ at $R_i < d_0$. The index i in Eq. (5) enumerates a water molecule and R_i is the distance from the center of the ion to the geometric center of the ith molecule.

The contribution into the energy, associated to the deformation of electronic shells at small ion–molecule distances, is the most complex part of the overall interaction. The pair part of this interaction at small distances is written in the form of the inclusion function (6) which is similar to $s^w(r)$ in Eq. (2).

$$u_D(R) = -U_0[1 - s(R)], \qquad (6)$$

Here

$$s(R) = \begin{cases} 0, & 0 < R < R_L \\ (R - R_L)^2(3R_U - R_L - 2R)/(R_U - R_L)^3, & R_L \le R \le R_U \\ 1, & R_U < R < \infty \end{cases} \qquad (7)$$

For a multimolecular system we obtain Eq. (8).

$$U_D^{IW} = \sum_i u_D(R_i). \qquad (8)$$

At small distances comparable with the radius of the outer electronic shell of the ion, the electric field of the latter deviates from the point charge field, while the interaction approaches chemical bonding with saturation at boundary values, characteristic of this type of interaction, like in dependences (6) and (7). This redistribution of the interaction energy between purely Coulomb and close-to-chemical is taken into account by smoothly shielding, at small distances, the point charge Q ascribed to the ion and simultaneously increasing the absolute value of $u_D(R)$. The shielding in accomplished using the inclusion functions $s(R)$. This weakening of the purely Coulomb part of the interaction shows up in weakened elecric field $\vec{E}_j(\vec{r})$ which enters the formulas for the polarization U^w_{pol} and Coulomb U^w_{Coul} energies. For example, the electric field in the $\vec{r}$ point of the ion with the coordinate $\vec{r}_I$ has Eq. (9).

$$\vec{E}_j(\vec{r}) = s(|\vec{r} - \vec{r}_I|)\, Q\, \frac{\vec{r} - \vec{r}_I}{|\vec{r} - \vec{r}_I|^3}. \qquad (9)$$

Interactions between the ion and water molecules at small ion–molecule distances are characterized by strong deformations of electronic shells and by the tendency to formation of chemical bonds. The system energy in such conditions loses its pair nature character. For molecules in the vicinity of the ion, the energy of nonpair interactions is given by Eq. (10).

$$U^{ww} = a_0 \{\sum_{i<j} [s(R_i)\, s(R_j) \exp(-r_{ij}/b_0)]^n\}^{1/n}. \qquad (10)$$

Here a_0 is amplitude, b_0 is the characteristic interaction radius, R_i is the distance to the ith molecule to the ion, and r_{ij} is the distance between the geometric centers of the ith and jth molecules.

The parameter n specifies the degree of nonlinearity $\tilde{\tilde{U}}^{ww}$ with respect to pair interaction (nonpair character of energy). The inclusion function $\tilde{s}(R)$ (11) takes account of the effect of spatial location of the ion on this part of intermolecular interactions.

$$\tilde{s}(R) = \begin{cases} 1, & 0 < R < \tilde{R}_L \\ 1 - (R - \tilde{R}_L)^2(3\tilde{R}_U - \tilde{R}_L - 2R)/(\tilde{R}_U - \tilde{R}_L)^3, & \tilde{R}_L \le R \le \tilde{R}_U \\ 0, & \tilde{R}_U < R < \infty \end{cases} \qquad (11)$$

All types of interactions are summated to obtain the total energy of interactions in the system [Eq. (12)].

$$U_{tot} = U^{ww}_{pair} + U^w_{Coul} + U^w_{pol} + U^{IW}_{LD} + U^{IW}_D + \tilde{\tilde{U}}^{ww}. \qquad (12)$$

3. RESULTS OF NUMERICAL EXPERIMENTS

The numerical values of parameters of the model intermolecular and ion-molecular interaction described in the preceding section were chosen so as to fit the internal and Gibbs energies of clusters $OH^- \cdot (H_2O)_n$ (n = 1, ..., 5), obtained in the experiments on cluster formation in the real system [36]. Optimal values of the parameters were determined by the following scheme. Firstly, geometric parameters were set, i.e. coordinates of point charges simulating the nonspherical part of the electric field of the ion; therewith, the coordinate of the positive charge was chosen as-close-as-possible to that obtained by quantum-chemical calculations for the OH^- ion. The radius and depth of the Lennard–Jones potential were set equal to the corresponding ST2 values for the water molecule. With these values, the internal and Gibbs energies of addition of one water molecule to the ion were calculated. First calculations already showed that, with such interaction potential, the reaction entropy is strongly underestimated compared to experimental, implying a too narrow potential well of the ion–water interaction. To change the shape of the potential well, we included a special interaction potential $u_D(R)$ [formulas (6) and (7)] and found values of its characteristic radii R_L and R_U. Simultaneously, parameters of the Lennard–Jones potential were varied to fit both the internal and Gibbs energies. The resulting parameters were used to calculate the internal and Gibbs energies of addition of a further water molecule. To fit experimental values for the latter reaction, we were to include the nonpair interaction potential [Eq. (10)] and find its parameters, except for n whose value affect the energy of a system comprising three or more molecules. In fact, the parameter n controls four-particle and higher contributions into cluster energie. The value of n was chosen so as to fit experimental internal and Gibbs energies of addition of a third water molecule. After that, check for fitting experimental values for additions of fourth and fifth water molecules was performed. Since at this point we revealed deviations larger than experimental errors, the whole procedure, beginning with the first molecule, was repeated with corrected geometric parameters of the ion. After several such iterations, the parameters presented in this publication. More than two hundreds calculations were performed, with various sets of parameters. Our experience in fitting the interaction curve in this way showed that the Lennard–Jones potential combined with electrostatic ion–molecule interaction leads to a too narrow potential well and a strongly underestimated entropy of the addition reaction. The pair interaction potential fails to reproduce the dependence of the energy of the addition reaction on the number of molecules in the cluster: nonpair interactions are of decisive importance. Not only three-particle, but also higher order multiparticle interactions contribute beyond experimental errors. The condition of fitting not only internal, but also Gibbs energy cardinally affects the interaction potential in the cluster. Neglecting this condition may result in a qualitatively incorrect statistical behavior of the cluster. The structure of the cluster at room temperatures may strongly differ from the configuration corresponding the interaction energy minimum: molecular motions may redistribute statistical weights in favor of weak but more favorable, in terms of entropy, bonds corresponding to wider local energy minima. Redistribution of statistical weights between statistically significant configurations may also result from strong nonpair interactions arising with growing hydration shell of the ion.

We could reproduce experimental data for clusters including up to five molecules but failed to check the validity of our model for larger clusters because of the lack of reliable experimental data on their Gibbs energies. Nevetheless, the developed model appears to be the most correct among those applied in statistical simulation, since other models have not been checked on the ability to reproduce Gibbs energies. There is no question that, as new experimental data for larger clusters will become available, the numerical values of interaction parameters will be refined, but the aim of the present work was to demostrate the possibility of determining the interparticle potential from experimental data on the Gibbs energies of cluster formation, rather then to finally formulate an interaction model which will be constantly refined.

Arshadi and Kebarle [36] reported values of the enthalpy $\Delta H_{n-1,n}$ of the reaction $\mathrm{OD}^-\cdot(\mathrm{D_2O})_{n-1}$ + $\mathrm{D_2O} \rightleftarrows \mathrm{OD}^-\cdot(\mathrm{D_2O})_n$, which is related to the reaction energy by the equation $\Delta U_{n-1,n} = \Delta H_{n-1,n} + k_\mathrm{B}T$. The summand $-k_\mathrm{B}T$ is equal to the change in the enthalpy of ideal gas for binding one molecule in a cluster. Since the mean kinetic energy of a molecule is not changed by its binding in a cluster, and, according to the theorem on equilibrium distribution of kinetic energy by degrees of freedom, remains equal to $(6/2)k_\mathrm{B}T$, the change in the internal energy $\Delta U_{n-1,n}$ amounts to a change in the mean interaction energy in the system, i.e. to the nonideal part of the energy, which is directly calculated by the Monte–Carlo method. The nonideal part of the internal energy of a cluster, which differs from the total energy by the summand $(6/2)nk_\mathrm{B}T + (3/2)k_\mathrm{B}T$ (n molecules + one ion) is related to $\Delta U_{n-1,n}$ by Eq. (13).

$$U_N = \sum_{n=1}^{N} \Delta U_{n-1,n}\,. \tag{13}$$

In essence, $\Delta G_{n-1,n}$, whose values were measured in [36], is a change in the Gibbs energy of the system on trasfer of one molecule from gas to cluster at given pressure p and temperature T, i.e. it is equal to the equilibrium work of addition of one molecule.

$$\Delta A_{n-1,n} = \Delta G_{n-1,n} = \Delta G^{\mathrm{cl}}_{n-1,n} - \mu_g(p,T). \tag{14}$$

Here $\Delta G^{\mathrm{cl}}_{n-1,n}$ is the change in the Gibbs energy of a cluster on addition of one molecule and $\mu_g(p, T)$ is the chemical potential of the ideal gas of water molecules.

$$\mu_g(p,T) = -k_\mathrm{B}T \ln\left(\Omega_\mathrm{tr}\,\Omega_\mathrm{rot}\,8\pi^2\,\frac{k_\mathrm{B}T}{p}\right), \tag{15}$$

$$\Omega_\mathrm{tr} = \left[\frac{h}{(2\pi m_0 k_\mathrm{B}T)^{1/2}}\right]^{-3}, \tag{16}$$

$$\Omega_\mathrm{rot} = \frac{(2\pi k_\mathrm{B}T)^{3/2}\,(I_1I_2I_3)^{1/2}}{h^3\,v}\,. \tag{17}$$

Here Ω_tr and Ω_rot the results of integration over translational and rotational impulses of molecules, respectively, in the statistical sum of the system; m_0

Internal energies U_n, formation works A_n from vapor under standard conditions [36], and Gibbs energies G_n^{cl} of water clusters on the OH⁻ ion, calculated by the Monte–Carlo method, and the corresponding experimental values U_n^{exp} and A_n^{exp} [36] (all values in eV).

n	$-U_n^{\mathrm{exp}}$	$-U_n$	$-A_n^{\mathrm{exp}}$	$-A_n$	$-G_n^{\mathrm{cl}}$
1	0.950	0.950	0.733	0.733	1.427
2	1.636	1.644	1.198	1.194	2.581
3	2.265	2.281	1.533	1.529	3.610
4	2.855	2.872	1.770	1.776	4.550
5	3.441	3.434	1.953	1.956	5.423
6		3.954		2.075	6.236
7		4.432		2.146	7.000
8		4.854		2.179	7.728
9		5.232		2.183	8.425
10		5.591		2.168	9.103
11		5.920		2.141	9.770
12		6.212		2.108	10.430
13		6.554		2.070	11.085
14		6.885		2.028	11.737
15		7.328		1.986	12.389
16		7.609			
17		7.908			
18		8.308			
19		8.689			
20		9.163			

3.0130×10^{-23} g is the weight of water molecules, I_1 1.024×10^{-40}, I_2 1.921×10^{-40}, and I_3 2.947×10^{-40} g cm^2 are the principal inertia moments of water molecules, ν is the spatial molecular symmetry parameter (2 for water molecules), h is Planck's constant, and $G(N, p, T)$ is the configurational part of the Gibbs energy. It is well known [37] that the equilibrium size distribution of clusters is expressed by the configurational integral of the system and is independent of dynamic characteristics of particles. According to this fundamental principle, the equilibrium concentrations of clusters and the steady-state nucleation rate are given by the differences $\Delta G_{n-1,n}^{\mathrm{cl}} - \mu_g(p, T)$ [38] which are independent of dymanic molecular characteristics m_0, I_1, I_2, and I_3. We give here the numerical values of A_N, obtained by summation of these differences.

$$A_N = \sum_{n=1}^{N} \Delta G_{n-1,n} \,. \tag{18}$$

Here A_N is the equilibrium work of cluster formation from vapor. The Gibbs energy of the cluster G_N^{cl} can be obtained from A_N using Eqs. (14)–(18).

Numerical values of parameters of intermolecular potentials were found by successive approximation. To this end, we performed, by the Monte–Carlo method [39], several hundreds of numerical experiments in the bicanonical statistical ensemble. In each of the experiments we calculated the Gibbs energies of water clusters $\mathrm{OH}^- \cdot (\mathrm{H_2O})_n$ with $n = 1, ..., 5$ by the previously developed method [40–44]. Then the calculations were repeated in the canonical statistical ensemble to obtain the internal energies of the clusters. The OH⁻ ion was fixed inside a void with the radius R 10 Å so that the oxygen ion is in the center with the coordinates x 0, y 0, and z 0. Calculation of the Gibbs energy takes, depending on allowable error, 5 to 60 min of an IBM PC Pentium-200 computer time. Final precision calculations of one point took 2 to 20 h, depending on the number of molecules in the cluster. By varying numerical values of parameters, we could, to a high accuracy ($\sim 0.1 k_{\mathrm{B}} T$), fit experimental Gibbs and internal energies [36]. The calculation results are listed in the table.

The following values of interaction parameters best fit experimental Gibbs and internal energies of cluster formation in the real system: charge of the oxygen ion Q -4.80298×10^{-10} CGSE; Lennard–Jones potential depth ε_0 3.10×10^{-12} erg, radius σ_0 2.87 Å, solid nucleus radius d_0 1 Å; amplitude of pair ion–water interaction U_0 1.465×10^{-12} erg; parameters of the inclusion function R_{L} 4.94 and R_{U} 7.02 Å; amplitude of nonpair interactions of molecules in the ion field a_0 0.833×10^{-12} erg, interaction radius b_0 11.25 Å, energy nonpairity index n 1.118, parameters of the inclusion function of nonpair interactions R_{L} 4.23 and $\tilde{R}_{\mathrm{U}}$ 7.49 Å. The number of additional point sources of electric field, simulating the charge distribution in the OH⁻ ion, is two: one is fixed in the center of the oxygen ion with the coordinates x 0, y 0, and z 0 and bears the charge q_1^{s} -1.758×10^{-10} CGSE, and the other is at a distance of 0.5 Å (x 0, y 0, and z 0.5 Å) and bears the charge q_2^{s} $+1.758 \times 10^{-10}$ CGSE. The solid nucleus radii for each of these sources are $d_1^{\mathrm{s}} = d_2^{\mathrm{s}}$ 0.1 Å. With these parameters, by the Monte–Carlo method, we obtained the values listed in the table (T 300 K). The length of Markov's process for one point was 50 million steps, the step frequencies for varying the number of molecules in the system and for spatial shifting molecules were related as 5 : 1. To avoid rounding-off errors, all the acquired sums were saved with double accuracy.

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