A NOTE ON SOME PARAMETERS IN THE THEORY OF NUCLEATION ABOUT AN ION

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Abstract. The prefactor of the number density of ionic clusters and the radius of an ionic nucleus are discussed in the case of the hydration of ions within the classical liquid-drop model. The manner how to take these parameters is clarified for practical use.

1. Introduction

A comprehensive study of nucleation on gaseous ions was carried out by Russell(1969) at a rather early stage, which was afterwards applied to many works (Hamill *et al.* 1977) and presents us with the essence of procedure to calculate the rate of nucleation about an ion. However, as theory of nucleation in gaseous phase was developed at first in the homogeneous system with one component vapor and then directly extended to the case of heterogeneous system, the interpretation of the prefactor of the number density of ionic clusters is not so obvious.

The present objective is to argue, except a big problem of the limitation of classical theory, about some fundamental parameters of the prefactor of the number density of ionic clusters and the radius of an ionic nucleus. Since the problem of this prefactor is essentially related with the standard of free energy for nucleation and the strictly theoretical treatment exceeds this study, the problem is just practically cleared away.

2. Nucleation rate about an ion

We now consider a simple phenomenon of hydration of some stable ions. When the electric charge e is distributed uniformly over the surface of a spherical ionic nucleus, the ionic nucleus has the electro-static potential of

$$U_1 = \{e^2/(8\pi\epsilon_0)\}(1/r_i), \quad (1)$$

On the other hand, a spherical ionic cluster where a medium with a dielectric constant ϵ aggregates uniformly around the above ionic nucleus has the electro-static potential of

$$U_2 = \{e^2/(8\pi)\}\{(1/\epsilon)(1/r_i - 1/r) + (1/\epsilon_0)(1/r)\}, \quad (2)$$

where ϵ_0 is the dielectric constant of vacuum, and r_i and r are the radius of an ionic nucleus and cluster, respectively. The potential difference of

$$\Delta U_i(r) = U_2 - U_1 = \{e^2/(8\pi)\}\{(1/\epsilon_0 - 1/\epsilon)(1/r - 1/r_i)\}, \quad (3)$$

yields an additional term to Gibbs free energy $\Delta G_i(a)$ for the cluster formation such as,

$$\Delta G_i(a) = \Delta G(a) + \Delta U_i(r_a), \quad (4)$$

where

$$\Delta G(a) = -akT \ln(S) + 4\pi(r_a - r_i)^2\sigma, \quad (5)$$

a denotes the number of water molecules condensed to an ionic cluster, S is the saturation ratio, r_a and σ are the radius and surface energy of the cluster, respectively, k is Boltzmann's constant, and T the absolute temperature. According to the basic principle of detailed balance that the

frequency of coalescence of clusters is equal to that of their breaking up in the equilibrium state, the net rate of hydration of an ionic cluster $J_i(a)$ is

$$J_i(a) = \beta_{a-1} N_w N_i(a-1) \{ \phi_i(a-1) - \phi_i(a) \}, \quad (a=1, 2, 3, \dots) \quad (6)$$

where

$$\beta_a = \pi(r_w + r_a)^2 \sqrt{(8kT)(1/m_w + 1/m_a)}, \quad (7)$$

$$N_i(a) = N_t \exp\{-\Delta G_i(a)/kT\}, \quad (8)$$

$$\phi_i(a) = f_i(a)/N_i(a), \quad (9)$$

and N_w is the number density of water vapor molecules, r_w and m_w are the radius and mass of a water molecule respectively, m_a is the mass of the ionic cluster, $N_i(a)$ and $f_i(a)$ stand for the number density of ionic clusters of kind (a) in the equilibrium and steady state, respectively, N_t is considered afterwards, and a water molecule is assumed to be a sphere. The steady state is the state where the nucleation rate of J_i has one and the same value for all i and is nonzero, and therefore $f_i(a)$ does not change:

$$J_i = J(1) = J(2) = J(3) = \dots = J(a_{\max}), \quad (10)$$

where $a_{\max}$ is a sufficiently large value of a , while $J_i=0$ in the equilibrium state. Then the following boundary condition is quite reasonable:

$$\phi_i(a_{\max}) = 0, \quad (11)$$

From Eqs. (6), (10), and (11), we get

$$\phi_i(a) = J_i \sum_{b=a}^{a_{\max}-1} 1/\{\beta_b N_w N_i(b)\}, \quad (12)$$

(i) Model A

"Model A" is the usual one, where the following conditions are required:

$$\phi_i(0) = 1, \quad (13)$$

$$N_t = N_{ion}, \quad (14)$$

where N_{ion} is the number density of total ionic clusters. However, $N_t = N_i(0)$ in Eq. (8) is not the number density of total ionic clusters but $N_t \phi_i(0) = N_i(0) \phi_i(0) = f_i(0)$ is the number density of ionic nuclei. Only if $f_i(0) \gg f_i(a)$, $i(a>1)$, Eq. (14) may not be wrong. The condition of Eq. (13) may also be right on the same assumption. It seems that the assumption of $f_i(0) \gg f_i(a)$, $(a>1)$ comes from an analogy of the case of one component homogeneous nucleation. Putting $a=0$ in Eq. (12) and using Eqs. (13) and (14),

$$J_i = N_w / \sum_{b=0}^{a_{\max}-1} 1/\{\beta_b N_i(b)\}, \quad (15)$$

We will show some results calculated with Eq. (15) as "model A".

(ii) Model B

In "model B", in order to numerically evaluate the assumption in "model A", we follow the definition of N_{ion} strictly and then we get

$$\sum_{a=0}^{a_{\max}-1} f_i(a) = \sum_{a=0}^{a_{\max}-1} N_i(a) \phi_i(a) = N_{ion} \quad (16)$$

Eliminating $\phi_i(a)$ from Eqs. (12) and (16), we get

$$J_i = N_{ion} N_w / D, \quad (17)$$

$$D = \sum_{a=0}^{a_{\max}-1} N_i(a) \sum_{b=a}^{a_{\max}-1} 1/\{\beta_b N_i(b)\}, \quad (18)$$

Furthermore, from Eqs. (9), (12), and (17)

$$f_i(a) = N_i(a) \phi_i(a) = \{N_{ion} N_w / D\} \sum_{b=a}^{a_{\max}-1} N_i(b) / \{\beta_b N_w N_i(b)\}, \quad (19)$$

We will show some results calculated with Eqs. (17) and (19) as "model B". Finally, following the work of Russell(1969), we will show nucleation rates calculated on the basis of Lothe-Pound's correction such as:

$$\begin{aligned} \Delta G_{i,L-P}(a) &= \Delta G_i(a) - kT \ln\{q_t q_r / q_{rep}\} \bigg|_{r_i}^{r_a} \\ &= \Delta G_i(a) - 3kT \ln\{m_a r_a / m_i r_i\}, \end{aligned} \quad (20)$$

where

$$q_t = (2\pi mkT/h^2)^{3/2} (kT/p) \propto m^{3/2}, \quad (21)$$

$$q_r = \sqrt{\pi(8\pi^2 I kT/h^2)^{3/2}} \propto m^{3/2} r^3, \quad (22)$$

and r and m are the radius and mass of a cluster respectively, h is Plank's constant, I is the moment of inertia of the cluster, p is the partial pressure due to ionic nuclei which means: $p = f_i(0)kT$, the partition function corresponding to "replacement free energy" q_{rep} is assumed to be constant of the size of cluster, and the specific gravity of the ionic nucleus is assumed to be 1 in the calculation described in the next section. The second term of right hand side of Eq. (20) is the difference between the term due to an ionic cluster and that due to a nucleus, and then each complicated term from Eqs. (21) and (22) is cancelled out by the other.

3. Results of numerical calculation

The value of r_c which is the radius of a stable ionic nucleus is usually obtained as the smaller root of $\partial \Delta G_i(a) / \partial r_c = 0$ (which is denoted by r_c) and r_c is for an example 4.79^c angstrom {A.U.} for $S = 2.5971$ which is given later, where $a_{\max}$ is taken as more than 3 times of the value of a corresponding

Fig. 1. $\Delta G_i(a)$ in Eq. (4) with respect to r_c , where A, B, and C are for $r_c = 3, 4.79$, and 7 A.U., respectively, 0 is for $\Delta G(a)$, $S = 2.5971$, and $T = 293.15K$.

to the larger root, T is taken to be 293.15K, $1/\epsilon$ is considered to be negligibly smaller than $1/\epsilon_0$ in this study, and other physical parameters are from Heist *et al.* (1973). Since the reason why the value of r_i should be r_i^c in the above manner is not obvious, let us consider the cases of various values of the parameter r_i . In Fig. 1, we show $\Delta G_i(a)$ in Eq. (4) with respect to r_i for some cases where A, B, and C are for $r_i = 3, 4.79$, and 7 A.U., respectively, and 0 is for $\Delta G(a)$. The curve B corresponds to the case of $r_i = r_i^c$. The barrier of free energy for nucleation is much affected by the value of r_i . In Fig. 2, we show $f_i(a)$ in Eq. (19) with respect to r_i where physical parameters are as in Fig. 1, A, B, and C are also for $r_i = 3, 4.79$, and 7 A.U., respectively, and $N_{ion} = 1000 \text{ cm}^{-3}$. As shown in Fig. 2, the condition of $f_i(0) \gg f_i(a)$, ($a > 1$) does not hold for $r_i < r_i^c$. Shown in Fig. 3 are nucleation rates J_i of Eqs. (15) and (17) with respect to the radius of an ionic nucleus r_i where A is for model A (the usual one), B for model B (our model), and $S = 2.5971$ which gives $J_i = 1 \text{ cm}^{-3} \text{ s}^{-1}$ for the usual model with the usual selection of r_i (sign $\times$ in Fig. 3). It is observed how much the results of "model A" are apart from those of "model B". "Model A" is expected to give unreasonable results outside the region where the condition of $f_i(0) \gg f_i(a)$, ($a > 1$) holds and we see this fact for $r_i < r_i^c$. In Fig. 4, we show critical saturation ratio S which gives $J_i = 1 \text{ cm}^{-3} \text{ s}^{-1}$, with respect to r_i . As shown in Figs. 3 and 4, the values of nucleation rate are much affected by the value of r_i and much depend on the selection of models described in the former section. However, results from two models (or various values of r_i) are not

Fig. 2. $f_i(a)$ in Eq. (14) with respect to r_i , where A, B, C, and physical parameters are as Fig. 1.

Fig. 3. J_i with respect to r_i , where A is for "model A" [Eq. (15)], B for "model B" [Eq. (17)], and physical parameters are as Fig. 1.

so different on the value of critical saturation ratio. It is on this critical saturation ratio that theory is usually compared with experiment.

Finally, we show in Figs. 5 and 6 the nucleation rates and critical saturation ratios on the basis of Lothe-Pound's correction in Eq. (20), where physical parameters are as in Figs. 3 and 4, except for $S = 2.4540$ in Fig. 5 and sign $\times$ corresponds to $r_i^* = 5.12$ A.U. Critical saturation ratios in Fig. 6 are slightly lower than Fig. 4.

Fig. 4. Critical saturation ratios S with respect to r_i , where A and B are as Fig. 3.

Fig. 5. J_i with respect to r_i on the basis of Lothe-Pound's correction in Eq. (20), where A and B are as Fig. 3, $S = 2.4540$.

Fig. 6. Critical saturation ratios S with respect to r_i on the basis of Lothe-Pound's correction in Eq. (20), where A , B , and physical parameters are as Fig. 5.

4. Conclusions and discussion

The prefactor of the number density of ionic clusters and the radius of an ionic nucleus are important factors in the theory of nucleation about an ion. Although the treatment in this study is just practical, the effects of changing these parameters are numerically evaluated. We conclude that the value of nucleation rate much depends on these parameters but that the value of critical saturation ratio is insensitive to the change of these parameters. If theory is compared with experiment on this critical saturation ratio, the approximation of the usual model ("model A") is not observed easily.

References

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