

Modified Classical Homogeneous Nucleation Theory and a New Minimum in Free Energy Change

(2) Behavior of Free Energy Change with a Minimum Calculated for Various Systems

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Abstract:

In the previous study, modified classical homogeneous nucleation theory considering the free energy change in parent phase was developed, which revealed the presence of a minimum in nucleation curve (the curve of total free energy change vs. nuclear radius) of binary solution. In the present study, using the modified theory, numerical calculations were performed for other various systems; liquid and solid solution systems with compound nuclei and mixed gas systems with liquid nuclei. The calculated results proved the presence of a minimum in each nucleation curve of these various systems. The minimum in nucleation curves has been passed unnoticed by many researchers in various fields. Therefore, Kelvin equation is misunderstood as it describes the maximum state. However, it should be the minimum state that Kelvin equation describes. The large difference between the critical radius size of water droplet calculated at the maximum point (17\AA at 200% humidity) and the observed micron order size of water droplet in cloud and fog can be explained through considering that the micron order droplet should be in the minimum state. The contradiction comes from the misunderstanding that a nucleation curve has only a maximum. Therefore, it is essential to review the various nucleation phenomena on the standpoint of the presence of a minimum. The influence of the change of initial content, initial pressure, interfacial tension, and number of nuclei in 1 mol system to the behavior of nucleation curve was discussed.

Keywords: classical homogeneous nucleation theory, minimum of free energy, critical nucleus, cloud, fog

1. Introduction.

A curve of free energy change with respect to nuclear radius (nucleation curve), in the process of classical homogeneous nucleation, has a maximum, as is well known [1-10]. However, the classical homogeneous nucleation theory ignores the free energy change of parent phase. In the previous reports [1], we proposed a modified equation of the theory in which the free energy change of the parent phase was considered. The modified equation revealed the presence of a minimum in nucleation curve for the formation of pure solid nuclei from the binary dilute solution. Further, it was proved that the minimum state was in the equilibrium state with the surrounding parent phase and could be described by Kelvin equation.

There is only a few report concerning the minimum, that is, the minimum in free energy change for metal-hydrogen system calculated by P.S.Popel et al. [11], that for closed one-component vapor system under isochoric-isothermal conditions reported by J. Schmeltzer et al. [12], and that for Fe-Al-O liquid ternary alloy system reported by some of the present authors [13]. Therefore, the survey for the minimum on nucleation curve in many systems in various fields should be necessary. In the present study, the numerical calculation of the nucleation curves for compound nuclei in solution system and liquid water nuclei in mixed gas system was performed by using the modified equation. The calculated nucleation curve in each system proved the presence of a minimum, and thus, that Kelvin equation, in principle, corresponds to the minimum state. Further, the behavior of the nucleation curve accompanied by the change of initial content, initial pressure, interfacial tension and number of nuclei in 1 mol of the system was investigated. On the basis of the obtained results, the contradiction between the critical radius of water droplet calculated at the maximum point (17\AA at 200% humidity) [8] and the observed micron order size of water droplet in cloud and fog [14] was discussed.

2. Free Energy Change during Nucleation.

As shown in the previous reports[1], nucleation under a constant temperature in a closed system is considered; the system includes m components and is composed of the spherical liquid or solid nuclei with radius r , a parent phase and interfaces between nuclei and the parent phase;

each nucleus includes c components and assumed to be entirely homogeneous; the m and c are integers and $m \geq c$.

The following equations can be written:

$$\Delta V = V^n + V^* - V. \quad (2.1)$$

$$n_i = n_i^n + n_i^* + n_i^l, \quad \sum_{i=1}^c n_i = \sum_{i=1}^c n_i^n + \sum_{i=1}^c n_i^* + \sum_{i=1}^c n_i^l, \quad \sum_{i=c+1}^m n_i = \sum_{i=c+1}^m n_i^* + \sum_{i=c+1}^m n_i^l. \quad (2.2)$$

The superscript, n , $*$ and l show nucleus phase, parent phase and interfacial phase, respectively. The subscript i shows the quantity of component i . The parameters without superscripts show the initial state before nucleation. In Eq. (2.1) and (2.2), n_i is the mole number of component i and V shows the volume. Then, the following equations for the free energy change during nucleation can be written [1]:

$$\begin{aligned} \Delta F &= \sum_{i=1}^c \{n_i^n (\mu_i^n - \mu_i^*)\} + \sum_i \{n_i (\mu_i^* - \mu_i)\} + \sum_i \{n_i^l (\mu_i^l - \mu_i^*)\} + \sigma A + K \\ &= -\left(\sum_{i=1}^c n_i^n\right) RT \ln S + \sum_i \{n_i (\mu_i^* - \mu_i)\} + \sum_i \{n_i^l (\mu_i^l - \mu_i^*)\} + \sigma A + K, \end{aligned} \quad (2.3)$$

$$K = -(P_0 - P)V^n - (P^* - P)V^*, \quad (2.4)$$

$$\Delta G = -\sum_{i=1}^c \{n_i^n (\mu_i^n - \mu_i^*)\} + \sum_i \{n_i (\mu_i^* - \mu_i)\} + \sum_i \{n_i^l (\mu_i^l - \mu_i^*)\} + \sigma A,$$

where ΔF and ΔG show the Helmholtz free energy change under constant volume condition and Gibbs free energy change under constant pressure condition, respectively, P the pressure of the system, μ_i the chemical potential of component i , σ and A are the interfacial tension and total area of the interface between nuclei and parent phase, respectively, and S is the supersaturation degree. When the initial system is the liquid or solid phase, μ_i , μ_i^* and μ_i^n can be written as:

$$\mu_i = \mu_i^\circ + RT \ln a_i, \quad \mu_i^* = \mu_i^\circ + RT \ln a_i^*, \quad \mu_i^n = \mu_i^\circ + RT \ln a_i^{sat}. \quad (2-5)$$

When the initial system is the gas phase:

$$\mu_i = \mu_i^+ + RT \ln P_i, \quad \mu_i^* = \mu_i^+ + RT \ln P_i^*, \quad \mu_i^n = \mu_i^+ + RT \ln P_i^{sat}, \quad (2-6)$$

where μ_i° and μ_i^+ are the standard chemical potentials, and a_i and P_i or a_i^* and P_i^* are the activity and partial pressure of component i before nucleation or in the parent phase, respectively. The superscript sat shows the saturated value, thus, a_i^{sat} and P_i^{sat} are the values over the flat nucleus ($1/r \approx 0$). Here, when considering ΔF under constant volume condition, μ_i^n , a_i^{sat} and P_i^{sat} should be the values under a total pressure P_0 , the value of which we can select arbitrarily, but when considering Kelvin equation it should be the final pressure of nucleation over the flat nucleus. Under constant pressure condition, P_0 equals P .

When the initial system is the liquid or solid phase, S equals $\prod_{i=1}^c (a_i^*)^{x_i^n} / \prod_{i=1}^c (a_i^{sat})^{x_i^n}$, and when

it is the gas phase, S equals $\prod_{i=1}^c (P_i^*)^{x_i^n} / \prod_{i=1}^c (P_i^{sat})^{x_i^n}$, where x_i is the molar fraction of component i and the molar fraction in nucleus x_i^n is constant because of the assumption of homogeneous nucleus.

When nucleus is a compound [1]:

$$\Delta F = -n^n RT \ln S + \sum_i \{n_i(\mu_i^* - \mu_i)\} + \sum_i \{n_i^l(\mu_i^l - \mu_i^*)\} + \sigma A + K, \quad (2.3.a)$$

$$\Delta G = -n^n RT \ln S + \sum_i \{n_i(\mu_i^* - \mu_i)\} + \sum_i \{n_i^l(\mu_i^l - \mu_i^*)\} + \sigma A, \quad (2.5.a)$$

where n^n is the mole number of the compound. For the liquid or solid system, S equals $\prod_{i=1}^c (a_i^*)^{q_i} / \prod_{i=1}^c (a_i^{sat})^{q_i}$, and for the gas system, S equals $\prod_{i=1}^c (P_i^*)^{q_i} / \prod_{i=1}^c (P_i^{sat})^{q_i}$, where $q_1, q_2, q_3, \dots, q_c$ are integers and show the stoichiometric ratio of the compound. For instance, the compound is expressed as $A_{q_1}B_{q_2}$ when it is composed of A and B components.

3. Nucleation Curves Calculated Numerically for Various Systems.

The interfacial term expressed as $\sum_i \{n_i^l(\mu_i^l - \mu_i^*)\}$ in Eqs. (2.3), (2.5), (2.3.a), (2.5.a) was

neglected for performing the following numerical calculation. The term might have influence to a nucleation curve in a small radius region, but it would have no influence for the region with larger radius, especially the region around the minimum of the curve.

3.1 Nucleation of AB Compound from A-B-C Ternary Solution.

From Eq. (2-3a), ΔG for the nucleation of AB compound in 1 mole of an A-B-C ternary solution system is written as:

$$\Delta G = -n_A^n RT \ln \{a_A^* a_B^* / (a_A^{sat} a_B^{sat})\} + n_A RT \ln(a_A^* / a_A) + n_B RT \ln(a_B^* / a_B) + n_C RT \ln(a_C^* / a_C) + \sigma A \quad (3.1)$$

The subscripts A, B and AB show the value of A and B components and AB compound. The following equations are given when the solution is ideal with equal value of mole fraction of A and B (x_A, x_B):

$$a_A = n_A = x_A, \quad a_B = n_B = x_B = x_A, \quad a_C = x_C = 1 - 2x_A, \quad (3.2)$$

$$a_A^* = x_A^* = \frac{x_A - n_{AB}^n}{1 - 2n_{AB}^n}, \quad a_B^* = x_B^* = x_A^* = \frac{x_A - n_{AB}^n}{1 - 2n_{AB}^n}, \quad a_C^* = x_C^* = \frac{1 - 2x_A}{1 - 2n_{AB}^n}, \quad (3.3)$$

$$n_{AB}^n = n_A^n = n_B^n, \quad n_{AB}^n = \frac{4\pi r^3 N}{3v^n}, \quad A = 4\pi r^2 N, \quad (3.4)$$

$$\mu_{AB}^{on} - \mu_A^\circ - \mu_B^\circ = RT \ln(a_A^{sat} a_B^{sat}), \quad (3.5)$$

where N is the total number of nucleus formed in 1 mole of the system and v^n and μ_{AB}^{on} are the molar volume and chemical potential of the compound AB, respectively.

The calculated ΔG for the ideal solution system with various initial mole fraction of A and B ($x_A = x_B = 2.5 \cdot 10^{-3}, 2 \cdot 10^{-3}, 1.5 \cdot 10^{-3}$) are shown in Fig. 1. Calculation was performed under the following condition; $a_A^{sat} = x_A^{sat} = a_B^{sat} = x_B^{sat} = 10^{-3}$, $v^n = 2 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, $\sigma = 0.8 \text{ Nm}^{-1}$, $N = 10^{16}$ and $T = 1000 \text{ K}$; the unknown n_{AB}^n and A in Eq. (3.1) can be expressed by r as Eq. (3.4). Thus, the calculation started from a near-zero value of r and was proceeded through increasing r step by step and finished just when a_A^* reached a_A^{sat} .

In Fig. 1, the calculated nucleation curve is shown, in which a minimum is clearly observed. Accompanied the change of x_A , N and σ , the ΔG curves vary as shown in Figs. 1-3; the value of ΔG decreases with N and σ , in contrast that ΔG increases with decrease of x_A .

3.2 Nucleation in the Gas Phase.

3.2.1 Nucleation in Ideal Mixed Gas Phase under the Condition of 1 atm Pressure.

When water nucleates from 1 mole of an ideal mixed gas phase of water and air at 1 atm total pressure, Gibbs free energy change is written as follows:

$$\Delta G = -n_{H_2O}^n RT \ln(P_{H_2O}^* / P_{H_2O}^{sat}) + n_{H_2O} RT \ln(P_{H_2O}^* / P_{H_2O}) + n_{air} RT \ln(P_{air}^* / P_{air}) + \sigma A \quad (3.6)$$

The subscript H₂O and air show the value of water and air component. Since air can be assumed as an ideal mixed gas, we can treat the system as two components gas system. In Eq. (3.6), P_{H_2O} , P_{air} and those with superscript show the partial pressure of water vapor and air in atm unit respectively, thus, the followings can be written:

$$P_{H_2O} = n_{H_2O} = x_{H_2O}, \quad P_{air} = n_{air} = x_{air}, \quad (3.7)$$

$$P_{H_2O} + P_{air} = n_{H_2O} + n_{air} = 1. \quad (3.8)$$

Further, following equations can be written:

$$P_{H_2O}^* = \frac{n_{H_2O} - n_{H_2O}^n}{1 - n_{H_2O}^n}, \quad P_{air}^* = \frac{(1 - n_{H_2O})}{1 - n_{H_2O}^n}, \quad (3.9)$$

$$n_{H_2O}^n = \frac{4\pi r^3 N}{3v^n}, \quad A = 4\pi r^2 N, \quad (3.10)$$

$$\mu_{H_2O}^{\circ,n} = \mu_{H_2O}^+ + RT \ln P_{H_2O}^{sat}. \quad (3.11)$$

Here, $P_{H_2O}^{sat}$ is the vapor pressure of flat water in atm unit under 1 atm pressure and $\mu_{H_2O}^{\circ,n}$ and v^n are the chemical potential and molar volume of liquid water, respectively. In Fig. 4, solid curves of ΔG calculated for various initial vapor pressures of water ($P_{H_2O} = 0.026, 0.028, 0.030$ atm) are shown. The numerical calculation was performed under the following condition using that; $p_{H_2O}^{sat} = 2.3 \cdot 10^{-2}$ atm, $v^n = 1.8 \cdot 10^{-5}$ m³, $\sigma = 7.3 \cdot 10^{-2}$ Nm⁻¹, $N = 10^{16}$ and $T = 298.15$ K. Thus, ΔG is a function of r and the calculation started by making r increase step by step and finished just when $P_{H_2O}^*$ reached $P_{H_2O}^{sat}$.

In each curve of 0.030atm and 0.028atm of P_{H_2O} , a minimum and a maximum are observed. In Fig. 5, solid curves of ΔG calculated for 0.03 atm of P_{H_2O} and various N ($10^{16}, 3 \cdot 10^{16}, 10^{17}$) are shown.

3.2.2 Nucleation in an Ideal Mixed Gas under Constant Volume Condition.

When water nucleates under constant volume condition from 1 mole of an ideal mixed gas of water gas and air with 1 atm initial pressure P , ΔF can be expressed as follows:

$$\Delta F = n_{H_2O}^n RT \ln(P_{H_2O}^* / P_{H_2O}^{sat}) + n_{H_2O} RT \ln(P_{H_2O}^* / P_{H_2O}) + n_{air} RT \ln(P_{air}^* / P_{air}) + \sigma A - (P^* - P)V^*. \quad (3.12)$$

Here, P_0 is equal to P because $P_{H_2O}^{sat}$ is taken as the value under 1 atm pressure. Eqs. (3.7), (3.8), (3.10), and (3.11) are also applicable in this system, and the following equations can be written:

$$P_{H_2O}^* = (n_{H_2O} - n_{H_2O}^n) RT / (V - V^n), \quad (3.13)$$

$$P_{air}^* = (1 - n_{H_2O})RT / (V - V^n). \quad (3.14)$$

Here, P^* and P are in Nm^{-2} units but other partial pressure in Eqs. (3.12) in logarithm (P_{H_2O} , P_{air} , $P_{H_2O}^*$ and P_{air}^*) are in atm units. The value of P is $1.013 \cdot 10^5 Nm^{-2}$ and that of P^* is equal to $(P_{H_2O}^* + P_{air}^*) \cdot 1.013 \cdot 10^5 Nm^{-2}$. The total volume of nucleus phase V^n can be written as:

$$V^n = n_{H_2O}^n \cdot v^n = \frac{4\pi r^3 N}{3}. \quad (3.15)$$

Helmholtz free energy ΔF expressed by Eq. (3.12) is also a function of r if P_{H_2O} is determined and under the following condition; $p_{H_2O}^{sat} = 2.3 \cdot 10^{-2} atm$, $v^n = 1.8 \cdot 10^{-5} m^3$, $\sigma = 7.3 \cdot 10^{-2} Nm^{-1}$, $N = 10^{16}$, $T = 298.15 K$, and $V = 2.446 \cdot 10^{-2} m^3$. Thus ΔF was calculated similarly as performed in the previous section for various P_{H_2O} (0.026, 0.028, 0.030 atm). The calculated results are shown in Fig. 4 by broken curves. In Fig. 5, the nucleation curves calculated for various N (10^{16} , $3 \cdot 10^{16}$, 10^{17}) and 0.030 atm of P_{H_2O} are also shown by broken curves, respectively. In Figs. 4 and 5, the broken curves are slightly larger than the solid curves. It is clear that a minimum is observed in each curve, which establishes Kelvin equation at the minimum.

3.3 Behavior of Free Energy Change for Various N , Initial Content, Initial Pressure, and σ .

3.3.1 Free Energy Change for Various Values of N .

The variation of nucleation curve with the change of N can be obtained only when the change of parent phase are taken into consideration. In contrast, the classical homogeneous nucleation theory can derive only one curve with a maximum for a given initial supersaturation degree. The nucleation curve for large N shows positive value and does not show extrema as shown in Figs. 2 and 5. It indicates that the change of parent phase proceeds even in the earlier stage of nucleation because of the formation of numerous nuclei. However, through repeating collision and coalescence, the curve transforms to new one with smaller N and smaller free energy. In accordance with it, a maximum and a minimum come to appear. The stirring accelerates collision and coalescence in case of liquid solution or gas phase, which reduces N step by step, losing the speed of nucleation because of the decrease of collision chance; the distance between the minimum and the final end point (the saturated point) of nucleation curve becomes shorter, if possible, until both the points meet, which is the final goal in stable saturated equilibrium. In case of fairly low saturation value of concentration in parent phase, reach to the saturated state would be difficult because of low probability of collision. Thus even repeated stirring would not have effect to reach it and the system remains to stay at the minimum.

3.3.2 Free Energy Change for Various Initial Contents and Pressures.

The nucleation curve shows more positive value of the free energy change as the initial content or pressure decreases. Consequently, nucleation is difficult when initial content or pressure is low. However, the change of free energy decreases with decrease of N . Therefore stirring would effective for promotion of nucleation if the collision and coalescence is possible. Thus, critical supersaturation degree, in which actually no collision and coalescence are occurred, would depend on initial content or pressure and N values. The increasing behavior of nucleation curve without extremum at lowest initial content or pressure shown in Figs. 1, 4, 6 is obtained only when the change of the parent phase are taken into consideration. The calculation from the classical homogeneous nucleation theory for the same condition shows a

curve with a maximum. Thus, it indicates the large positive free energy change of the parent phase compensates the negative free energy change of nuclei in the given condition.

3.3.3 Free Energy Change for Various σ .

The free energy change with small values of σ does not show a minimum, but a sufficient large value of σ gives a deep valley at a minimum. Therefore, for a system with large value of σ , the valley would be deep yet even after repeated decrease of N and, thus, the system could not get out of the valley. Further, it is shown from Kelvin equation, the larger value of σ causes the larger S . It means that the system with large σ shows the large S at the minimum of nucleation curve.

It should be noted that dependence of σ on r is not taken into account in calculation of the curves in the present work. However, σ should depend on curvature of a droplet, namely on nuclear radius. Defay and Prigogine [10] derived the following equation:

$$\frac{\sigma}{\sigma_0} = \frac{1/v}{2\Gamma/r + 1/v}, \quad (3.16)$$

where σ_0 , σ are the interfacial tension of flat interface with zero curvature, and that of a spherical droplet with radius r , respectively, v is the molar volume of the droplet and Γ is the surface excess. Using Eq. (3.16) regarding the dependence of σ on nuclear radius, free energy change on nucleation of water from mixed gas containing air and water vapor under 1 atm pressure was calculated. In the calculation, $\Gamma = 9 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$ was used [10]. Other condition of the calculation is the same as in Fig. 4 except σ . The results are shown in Fig. 6. Strictly speaking, Eq. (3.16) can be applied only to the system in equilibrium condition between droplet and parent phase, thus, it describes the interfacial tension on a locus of a minimum or a maximum in free energy change for various N . However, the estimation using Eq. (3.16) was used for the calculation of Fig. 6 assuming that nucleation occurs in a condition close to equilibrium. Yet, in the case of smaller nucleus than a few ten Å, Eq. (3.16) would not show an appropriate estimate. Even so, the curves in Fig. 6 are similar to those shown in Fig. 4, showing a little lower ΔG value than the curves in Fig. 4.

Further investigation of the calculated results in Fig. 6, made clear the following; at the final saturated edge point of the nucleation curve with 0.03 atm initial vapor pressure in Fig. 6, σ value shows 0.071 Nm^{-1} although the water vapor pressure is the saturated one ($p_{H_2O}^{sat} = 2.3 \cdot 10^{-2}$ atm); the σ value does not reach yet the value of zero curvature ($0.073 \text{ N} \cdot \text{m}^{-1}$), indicating that the edge point does not show a stable equilibrium state between the flat water and the gas phase, which is also clear from that the point is not an extremum. However, if N decreases to a value that the minimum corresponds to the saturated point, the σ reaches the near value of zero curvature of the water.

3.3.4 Kelvin Equation and the Minimum Described by N , Initial Content, Initial Pressure and σ .

From the above results, the behavior of the nucleation curve for the change of N , initial content, initial pressure and σ can be clarified. Consequently, the minimum state that corresponds to Kelvin equation could be described clearly by the change of N , initial content, initial pressure and σ . The minimum state, we think, would have appeared in many places of nucleation, but it has been remained unnoticed as well as the following cases of cloud and fog.

3.4 Droplets in Cloud and Fog.

The above mentioned results in this chapter confirmed the presence of a minimum in each nucleation curve for many systems. Therefore, it is necessary to review the various nucleation phenomena in light of the presence of a minimum and the possible stability of nano or micron-sized nuclei should be discussed.

For instance, fine water droplets in cloud and fog often remain stable for a long time. The

long-time stability of cloud and fog shows the droplets to be in an equilibrium state and in a state corresponds to Kelvin equation. F.F.Abraham [8] reported that the critical radius of water droplet in water vapor calculated from classical homogeneous nucleation theory ignoring the free energy change in parent phase is 17\AA when S_{ini} equals 2, which corresponds to 200% humidity. However, the size of droplets observed in cloud or fog are not so small but in micron order [14]. Therefore, we consider that the long-time stability of cloud and fog with droplets of micron order should be in a minimum state. The numerical calculation when N decreases down to 10^{13} in Fig. 5, the nuclear radius at the minimum reaches to the micron order. Therefore, the size observed in nature would correspond to the calculated size at the minimum. Generally, the cloud and fog are said to be the aggregation of water droplets which nucleate heterogeneously on fine dust floating in air. However, the vapor pressure around the droplets should be described by Kelvin equation, no matter how the dust may exist at the center of the droplet, and the better stability at a minimum state than a maximum state should be occurred even though the system experiences an initial heterogeneous nucleation process. The clouds and fog would be a familiar example for indicating the necessity of re-examination of nucleation process from the standpoint of presence of a minimum.

3.5 Consideration for the Present Model.

The parabolic increasing behavior of nucleation curve with no maximum for the large N in Figs. 2 and 5 and for the lowest supersaturated content or pressure in Figs. 1,4 and 6 shows that the change of parent phase has influence in the curves even in the small radius region. In the previous reports [1], we introduced the argument on the standpoint of molecular dynamics against classical homogeneous nucleation theory for the small radius region [7,15,16]. Surely the present model might have a vague point for the very small radius region viewing from a molecular dynamic point and it ignored the interfacial term for performing the numerical calculations. But it can predict the influence of the free energy change of parent phase even in the small radius region with large N and low supersaturated content or pressure as mention above. Thus, the consideration of the parent phase also should be important even for the molecular dynamic procedure for small radius region. The comparison of the results of different procedure by taking into account the parent phase would be desirable.

We believe that the behavior of nucleation curve described in the present study would be helpful in analyzing the nucleation phenomena in various fields. Especially, the formation of bulk glassy and bulk nanostructured alloy, which is now being investigated extensively, might be related to the behavior of nucleation curve with a minimum or with a large N value or low supersaturated content, although it also relates to the stability of the liquid alloy state. The process of formation of bulk glassy and bulk nanostructured alloy is not isothermal one, but, by assuming a supercooled liquid alloy, a simulation is expected.

4. Conclusion.

The liquid and solid solution and mixed gas phase were considered by modified classical homogeneous nucleation theory and the nucleation curves were calculated numerically. The results proved the presence of a minimum in addition to a maximum in each nucleation curve in the systems. The minimum in the nucleation curve has been unnoticed. Therefore, Kelvin equation not only at the maximum but also at the minimum was established by the present model. The stability of the micron order size of droplets in clouds and fog indicates that the system is in a minimum state which is corresponding to the state that Kelvin equation describes. Therefore, real systems should be reinvestigated through new eyes on the standpoint of the presence of a minimum in nucleation curve. Numerical calculation made clear that the nucleation curve depends on the total number of nucleus (N), initial contents and pressures of components, and interfacial tension between nucleus and parent phase (σ);

- (1) In case of large N value, the free energy change shows positive value and increases with

nuclear radius. With decrease of N , each curve of free energy with different N shifts to the lower value direction. The collision and coalescence of nuclei brings the decrease of N finally to result in arrival to the saturated equilibrium of the system. However, if the probability of collision is scarce even by the repeated stirring, the system would remain to stay at a minimum for a long time.

(2) With decrease of initial content or pressure, nucleation curve goes to the positive direction. Therefore, lower initial content or pressure causes the lower possibility of nucleation.

(3) With the decrease of σ , each curve with different σ shifts to the negative direction and shows a deep minimum valley. Kelvin equation indicates that the larger value of σ causes the larger supersaturation degree at the minimum. In real systems, σ should change with nuclear radius. Yet, taking the dependence of σ on nuclear radius into account also leads to the similar behavior of the curves in free energy change.

(4) The parabolic increasing behavior of nucleation curve for the large N and for the low supersaturated content or pressure was observed, which shows that the change of parent phase has influence in the curves even in the small radius region.

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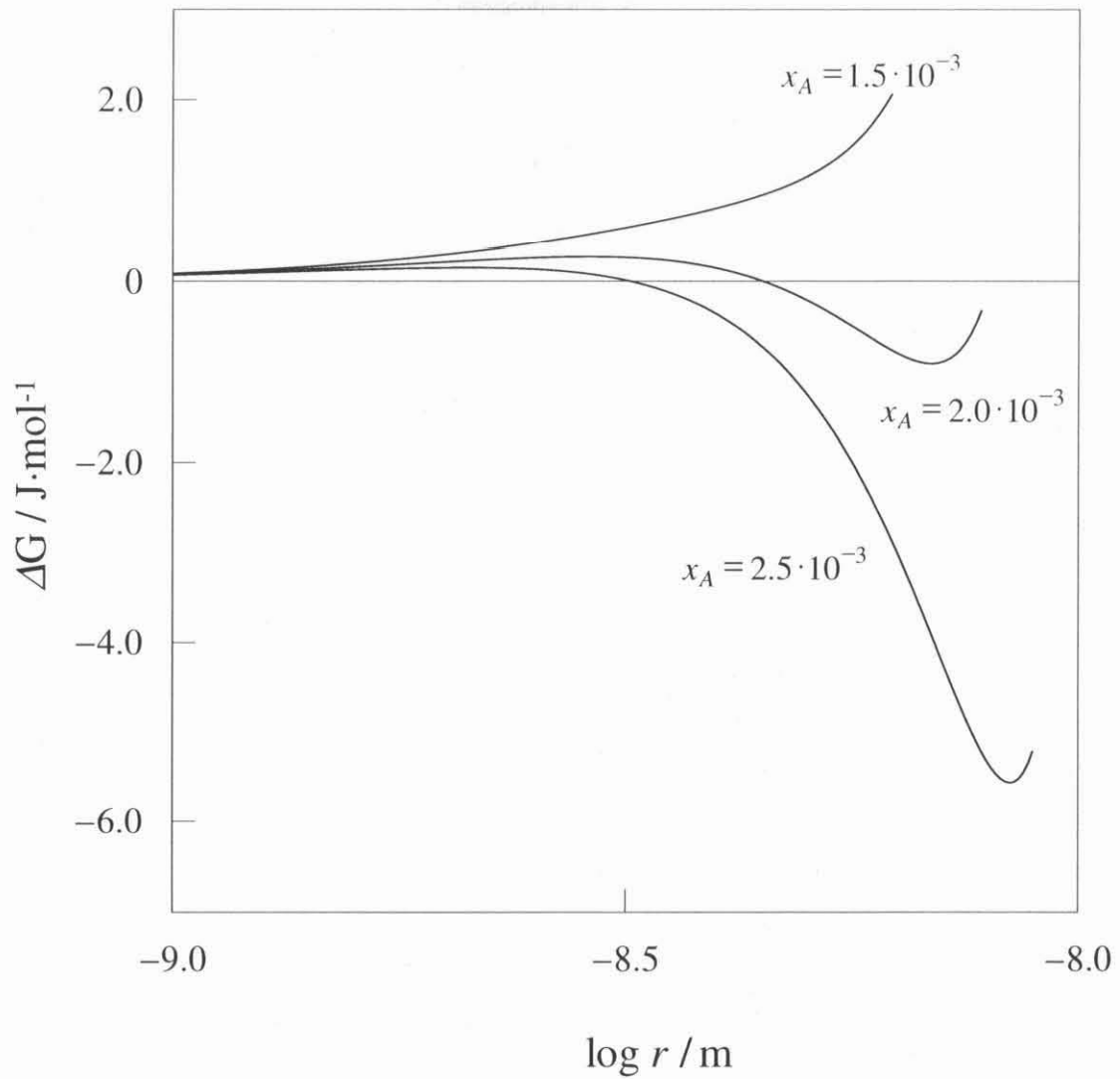


Fig.1 Gibbs free-energy change (ΔG) during nucleation of AB compound from A-B-C ternary solution calculated for various initial mole fractions of A (x_A). Calculation was performed under the following condition; $x_A = x_B$, $a_A^{sat} = x_A^{sat} = a_B^{sat} = x_B^{sat} = 10^{-3}$, $v^n = 2 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$, $\sigma = 0.8 \text{ N}\cdot\text{m}^{-1}$, $N = 10^{16}$ and $T = 1000 \text{ K}$.

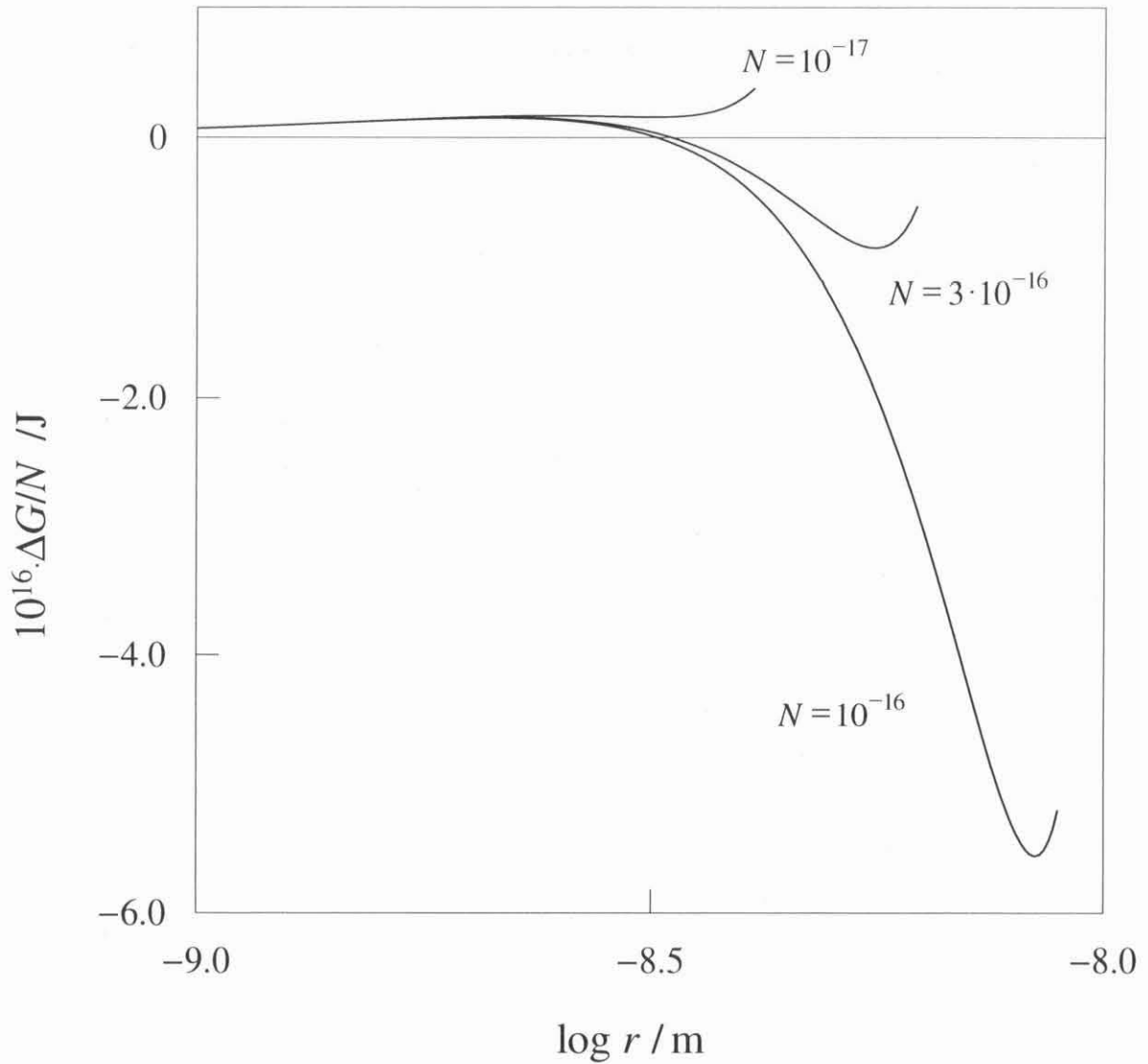


Fig.2 Gibbs free-energy change per one nucleus ($\Delta G / N$) during nucleation of AB compound from A-B-C ternary solution calculated for various total number of nuclei per one mole of the system (N). Calculation was performed under the following condition;

$$x_A = x_B = 2.5 \cdot 10^{-3}, \quad a_A^{sat} = x_A^{sat} = a_B^{sat} = x_B^{sat} = 10^{-3}, \quad v^n = 2 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1},$$

$$\sigma = 0.8 \text{ N m}^{-1} \text{ and } T = 1000 \text{ K}.$$

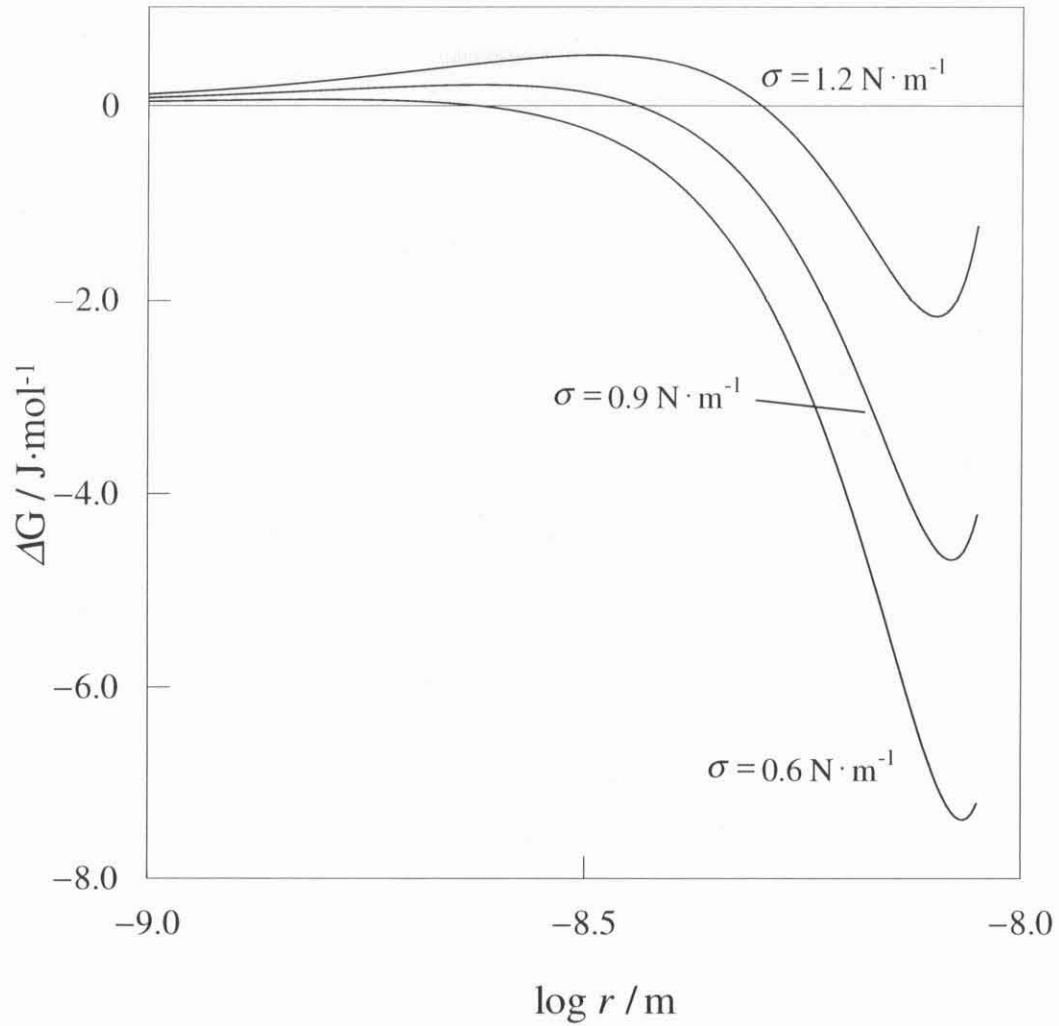


Fig.3 Gibbs free-energy change (ΔG) during nucleation of AB compound from A-B-C ternary solution calculated for various interfacial tension values (σ). Calculation was performed under the following condition; $x_A = x_B = 2.5 \cdot 10^{-3}$, $a_A^{sat} = x_A^{sat} = a_B^{sat} = x_B^{sat} = 10^{-3}$, $v^n = 2 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$, $N = 10^{16}$ and $T = 1000 \text{ K}$.

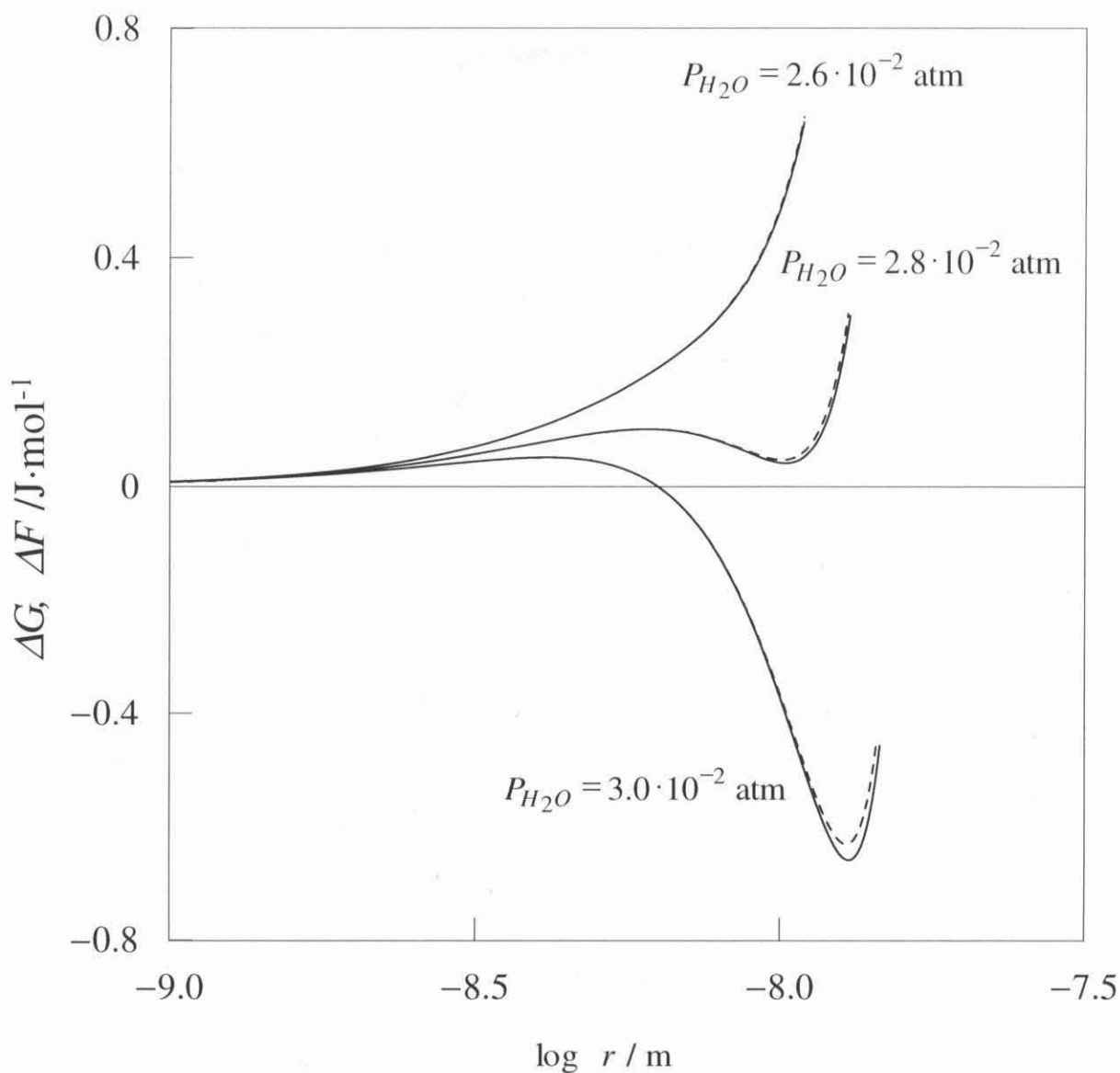


Fig.4 Gibbs free-energy change (ΔG) and Helmholtz free-energy change (ΔF) during nucleation of water from water-air pseudo-binary mixed gas system calculated for various initial vapor pressures of water (P_{H_2O}). Each solid curve shows ΔG under the condition of $p_{H_2O}^{sat} = 2.3 \cdot 10^{-2} \text{ atm}$, $v^n = 1.8 \cdot 10^{-5} \text{ m}^3$, $\sigma = 7.3 \cdot 10^{-2} \text{ Nm}^{-1}$, $N_0 = 10^{16}$ and $T = 298.15 \text{ K}$. Each broken curve shows ΔF under the same condition as in the ΔG and $V = 2.446 \cdot 10^{-2} \text{ m}^3$.

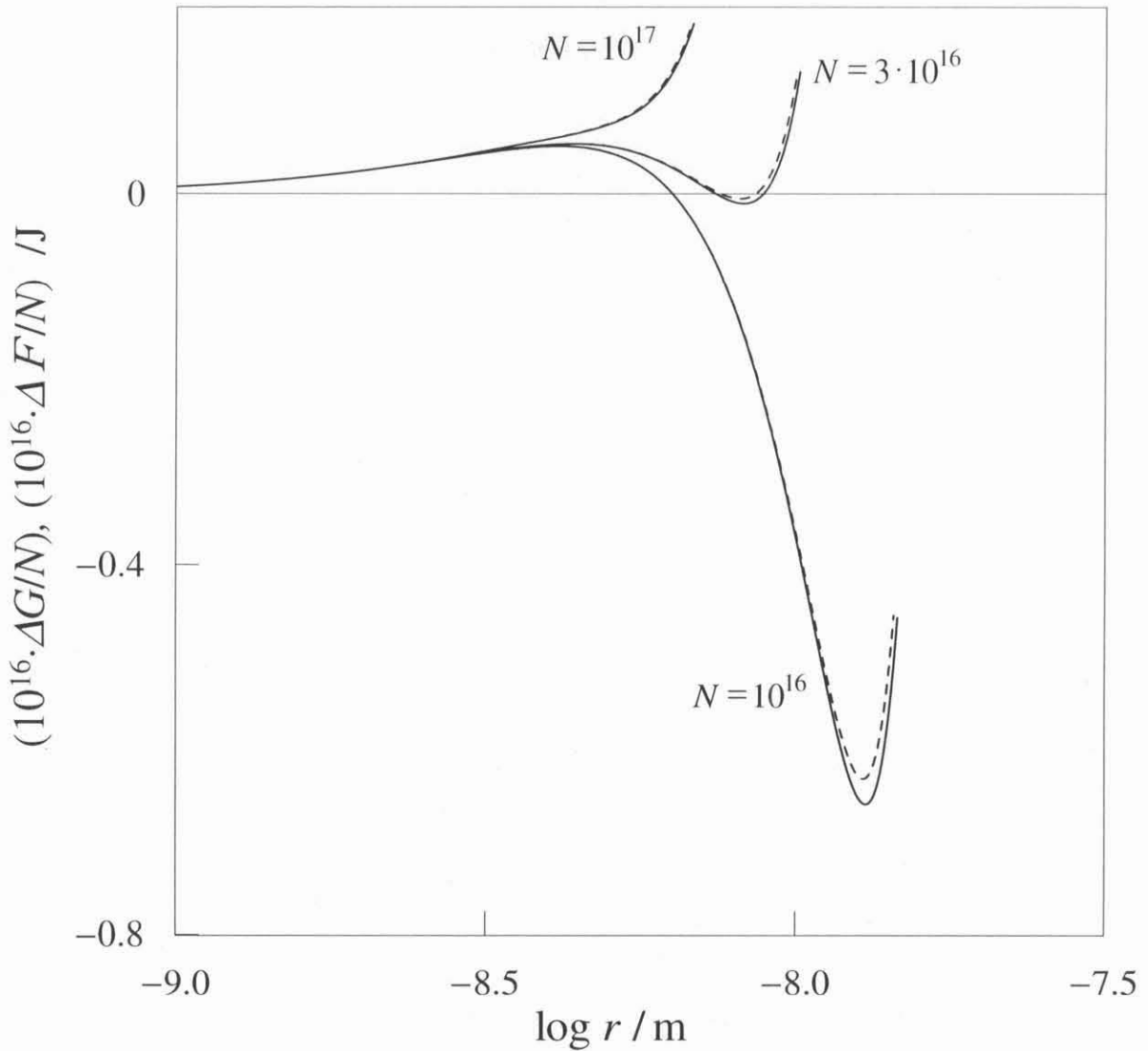


Fig.5 Gibbs free-energy change per one nucleus ($\Delta G / N$) and Helmholtz free-energy change per one nucleus ($\Delta F / N$) during nucleation of water from water-air pseudo-binary mixed gas system calculated for various total number of nuclei per one mole of the system (N). Each solid curve shows $\Delta G / N$ under the condition of $p_{H_2O} = 3.0 \cdot 10^{-2}$ atm, $p_{H_2O}^{sat} = 2.3 \cdot 10^{-2}$ atm, $v^n = 1.8 \cdot 10^{-5}$ m³, $\sigma = 7.3 \cdot 10^{-2}$ Nm⁻¹ and $T = 298.15$ K. Each broken curve shows $\Delta F / N$ under the same condition as in the $\Delta G / N$ and $V = 2.446 \cdot 10^{-2}$ m³.

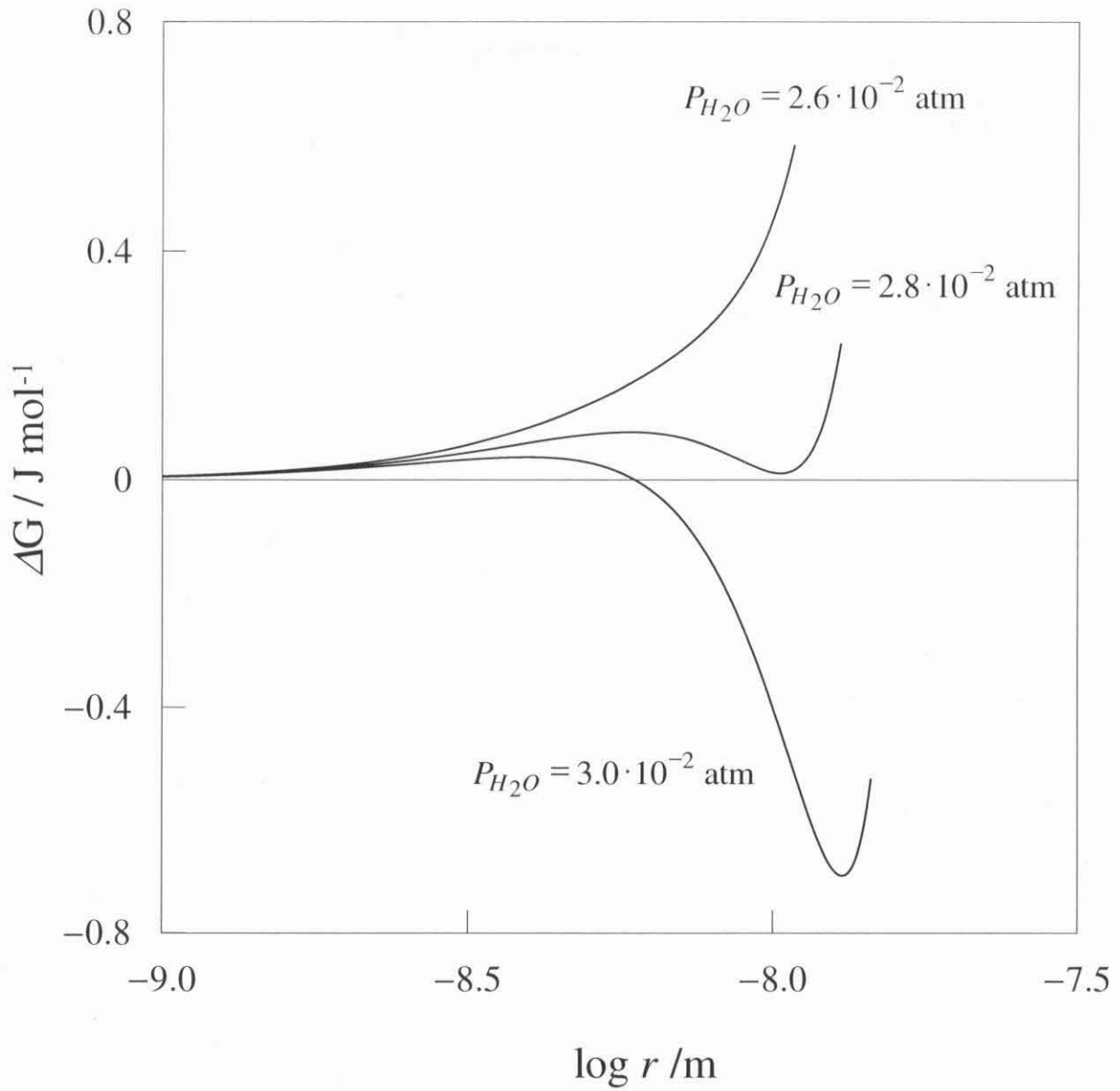


Fig.6 Gibbs free-energy change (ΔG) during nucleation of water from water-air pseudo-binary mixed gas system considering the dependence of interfacial tension on nuclear radius based on Eq. (3.3.1). Calculation was performed under the same condition as in Fig.4.