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

## (1) A New Minimum and Kelvin Equation.

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## Abstract:

The main concern of classical homogeneous nucleation theory has been a thermodynamic description of initial stage of nucleation from embryo to nucleus with a little larger size over the critical one, thus, the change of parent phase in the system has been assumed to be negligible because of the largeness in volume and mass comparing that of nuclei. As a result, the nucleation curve (free energy change versus nucleus size) passes through well-known single maximum point corresponding to the critical size of the nucleus. In the present study, thermodynamics of the classical homogeneous nucleation was re-visited and developed a modified equation for multi-component solution and gas system with multi-component nuclei by taking into account the change of the free energy of parent phase. Using this equation, the calculation of nucleation curve beyond the size of critical nucleus became possible. A calculation of A-B binary solution system revealed a new minimum point in the nucleation curve, in addition to the maximum point. This minimum point indicates the theoretical possibility to stabilize a large amount of nano-nuclei in equilibrium with the supersaturated parent phase. In addition, Kelvin equation was proved at the extremum on the nucleation curve. Many scientists have misunderstood that Kelvin equation corresponds to the maximum state because they have unnoticed the presence of the minimum and its stability. At the minimum state, the nuclei should be more stable than those at the maximum state. Thus, Kelvin equation should correspond to the minimum state rather than the maximum state.

*Keywords*: classical homogeneous nucleation theory, supersaturation, nucleation, critical nucleus, free energy, Kelvin equation, equilibrium

## 1. Introduction.

Although a real nucleation phenomenon includes many processes and complicated factors, numerous studies concerning the phenomena have been reported in various fields [1-9]. Even though classical homogeneous nucleation theory [1-9] describes the microscopic nucleation phenomenon through a macroscopic thermodynamic approach and there is argument [6,10-11] against the theory on the standpoint of molecular dynamics, it contains essence of nucleation phenomena in simple and clear manner with deep insight in it, thus, it has been used widely for analyzing the real nucleation phenomenon and fulfilled a big role for understanding it.

The generally-used classical homogeneous nucleation theory describes the Gibbs free energy change during nucleation of a spherical nucleus made of pure liquid phase $A$ with radius $r$ under a constant temperature and a pressure condition as [1-4]:

$$\Delta_{nucl}G = 4 \cdot \pi \cdot r^2 \cdot \sigma - \frac{4 \cdot \pi \cdot r^3}{3 \cdot v_A} \cdot R \cdot T \cdot \ln \boldsymbol{S}_{\boldsymbol{ini.}} \quad , \tag{1.1}$$

where $v_A$ is the molar volume of pure component $A$ in the liquid state, $R$ the gas constant, $T$ the absolute temperature, $\sigma$ the interfacial tension between the drop and the parent phase, and $\boldsymbol{S}_{\boldsymbol{ini.}}$ is the initial supersaturation degree of component $A$ in parent phase over the spherical drop of radius r, compared to the saturation limit for the flat surface, i.e. when $r \rightarrow \infty$. This equation is derived on an assumption of unchanged free energy in parent phase. The $\Delta_{nucl}G$ plotted as a function of $r$ show a curve with a maximum as shown in Fig.1. The maximum point corresponds to the socalled critical radius ($r_{cr}$) of the nucleus. However, nuclei with an over-critical size will grow without stabilization of their size in a nanometer scale.

In the previous report [12], the nucleation curve of Fe-Al-O liquid alloy system, in which alumina nuclei are formed, calculated by taking into account the free energy change of parent phase, revealed the presence of a minimum in the curve. The minimum did not appear if the free energy change of parent phase was disregarded. Consequently, the long-pending question for this system, namely, the reason of persistence of supersaturated oxygen state, was clearly settled by the minimum. There is a few report concerning the minimum except that of Fe-Al-O liquid alloy, that is, the minimum in free-energy change for metal-hydrogen system calculated by P.S.Popel et al. [13], that for closed one-component vapor system under isochoric-isothermal conditions reported by J. Schmeltzer et al. [14]. The result suggests the possibility of the presence of minimum in nucleation curves for various other systems.

During the last decades nano-science and nano-technology (i.e. the science and technology of nanometer sized phases) has been playing an increasing role in different branches of materials science and technology. One of the most straightforward ways to produce nano-phases is to grow them from an oversaturated parent phase. Thus, the minimum in nucleation processes from an oversaturated parent phase would provide a theoretical possibility to stabilize nano phases.

In the present study, a modified classical homogeneous nucleation theory was developed for multi-component solution and gas systems forming multi-component nuclei by taking into account the change of the free energy of parent phase and it proved a new minimum in the nucleation curve through numerical calculation for A-B binary dilute solution.

On the other hand, many textbooks [2,7-9] wrote that Kelvin equation holds at a maximum in nucleation curve expressed as Fig. 1. Then, how does it at a minimum? Since the nucleus should be in equilibrium with the parent phase at both of the maximum and minimum states, both states should be described by Kelvin equation. Further, the minimum state should be more stable than the maximum state. Thus, Kelvin equation could be realized rather in the minimum state. However, there is limited information [14] on the relation between the minimum and Kelvin equation. Therefore, the present study attempted to derive Kelvin equation through the modified classical homogeneous nucleation theory without approximation at both of the extremum. This procedure is necessary for a proof of the modified theory and also for an appeal that the minimum state could often be come across in natural phenomena even though it passes unnoticed, because the state described by Kelvin equation frequently occurres in nature.

## 2. A Minimum in Nucleation Curve

### 2.1 Helmholz Free Energy and Gibbs Free Energy in Nucleation Process for Multi-Component System.

Let us consider a nucleation of liquid or solid spherical nuclei with radius $r$ under a constant temperature ($T$) in a closed multi-component system: the system includes $m$ components and is composed of spherical nuclei, parent phase and interface; nucleus is assumed to be entirely homogeneous from the center to the interface; nucleus includes $c$ components; the $m$ and $c$ are integers and $m \geq c$.

Helmholtz free energy before nucleation (the initial state of nucleation) is expressed as:

$$F_{ini.} = \sum_i n_i \mu_i - PV , \qquad (2.1)$$

where $P$, $V$ represent the pressure, and volume of the system respectively, $\mu_i, n_i$ are the chemical potential and mole number of component $i$. Helmholtz free energy during and after nucleation is expressed as:

$$F = \sum_{i=1}^{c} n_i^n \mu_i^n(P^n) + \sum_i n_i^* \mu_i^* + \sum_i n_i^I \mu_i^I + \sigma A - (P^n V^n + P^* V^*) . \qquad (2.2)$$

The superscripts $*$, $^n$ and $^I$ attached in the parameters ($P$, $V$ $\mu_i, n_i$) indicate the parent, nucleus and interfacial phases. The $\sigma$ and $A$ are the interfacial tension and total area of interface between nuclei and parent phase, respectively. Since $P^n$ is higher than $P^*$, which is predicted by Laplace equation, the chemical potential of component $i$ in nucleus phase is expressed as $\mu_i^n(P^n)$. The thickness of the interface is taken as zero and the interface corresponds to the surface of tension in a model by Gibbs which is described by Defay and Prigogine [9], and Abraham [7], in which the interface satisfies Laplace equation. The volume difference before and after nucleation can be written as:

$$\Delta V = V^n + V^* - V . \qquad (2.3)$$

The total mole number of each component in the system remains constant, thus:

$$n_i = n_i^n + n_i^* + n_i^I , \qquad \sum_{i=1}^{c} n_i = \sum_{i=1}^{c} n_i^n + \sum_{i=1}^{c} n_i^* + \sum_{i=1}^{c} n_i^I ,$$

$$\sum_{i=c+1}^{m} n_i = \sum_{i=c+1}^{m} n_i^* + \sum_{i=c+1}^{m} n_i^I . \qquad (2.4)$$

Helmholtz free energy change which should be used as potential energy change under a constant temperature and volume condition ($\Delta V = 0$) is expressed as [9,15]:

$$\begin{aligned}\Delta F &= F - F_{ini.} \\ &= \sum_{i=1}^{c} n_i^n \mu_i^n(P^n) + \sum_i n_i^* \mu_i^* + \sum_i n_i^I \mu_i^I - \sum_i n_i \mu_i + \sigma A - (P^n V^n + P^* V^* - PV) . \qquad (2.5)\end{aligned}$$

For a system under a constant pressure ($P = P^*$), Gibbs free energy should be used as potential energy [9,15]:

$$\begin{aligned}\Delta G &= \Delta F + P\Delta V \\ &= \sum_{i=1}^{c} n_i^n \mu_i^n(P^n) + \sum_i n_i^* \mu_i^* + \sum_i n_i^I \mu_i^I - \sum_i n_i \mu_i + \sigma A - (P^n - P^*) V^n . \qquad (2.6)\end{aligned}$$

Here, the following equations are written:

$$\mu_i^n(P^n) = \mu_i^n + v_i^n (P^n - P_0) , \qquad (2.7)$$

$$\sum_{i=1}^{c} n_i^n \mu_i^n(P^n) = \sum_{i=1}^{c} n_i^n \mu_i^n + V^n (P^n - P_0) , \qquad (2.8)$$

$$V^n = \sum_{i=1}^{c} v_i^n n_i^n = v^n \sum_{i=1}^{c} n_i^n , \qquad (2.9)$$

where $v_i^n$ is the partial molar volume of component $i$ in nucleus and $v^n$ is the molar volume of nucleus. Since nucleus is in the solid or liquid state, the compressibility can be neglected [9,10], and the $v_i^n$ and $v^n$ are approximately constant for the change

of pressure. The $\mu_i^n$ in Eqs. (2.7) and (2.8) is the chemical potential of component $i$ in nucleus under pressure $P_0$. The $P_0$ value can be selected arbitrary but when considering Kelvin equation, it should be the final pressure over the flat nucleus ($1/r \approx 0$). Under a constant pressure condition, $P_0$ equals $P$.
Therefore, Eq. (2.5) can be rewritten:

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

$$= -(\sum_{i=1}^{c} n_i^n)RT\ln \boldsymbol{S}_{ini.} + \sum_i\{n_i^*(\mu_i^* - \mu_i)\} + \sum_i\{n_i^l(\mu_i^l - \mu_i)\} + \sigma A + K\,. \quad (2.5.a)$$

Further, $\Delta F$ can be also written as follows:

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

$$= -(\sum_{i=1}^{c} n_i^n)RT\ln \boldsymbol{S} + \sum_i\{n_i(\mu_i^* - \mu_i)\} + \sum_i\{n_i^l(\mu_i^l - \mu_i^*)\} + \sigma A + K\,. \quad (2.5.b)$$

Here:

$$K = -(P_0 - P)V^n - (P^* - P)V^*\,. \quad (2.10)$$

Therefore, similarly:

$$\Delta G = -(\sum_{i=1}^{c} n_i^n)RT\ln \boldsymbol{S}_{ini.} + \sum_i\{n_i^*(\mu_i^* - \mu_i)\} + \sum_i\{n_i^l(\mu_i^l - \mu_i)\} + \sigma A\,, \quad (2.6.a)$$

$$\Delta G = -(\sum_{i=1}^{c} n_i^n)RT\ln \boldsymbol{S} + \sum_i\{n_i(\mu_i^* - \mu_i)\} + \sum_i\{n_i^l(\mu_i^l - \mu_i^*)\} + \sigma A\,, \quad (2.6.b)$$

where $\boldsymbol{S}$ is the supersaturation degree and $\boldsymbol{S}_{ini.}$ is the initial supersaturation degree before nucleation. When the parent phase is the liquid and solid phase, $\mu_i^*$ and $\mu_i^n$ can be written as:

$$\mu_i = \mu_i^\circ + RT\ln a_i\,, \quad (2.11)$$

$$\mu_i^* = \mu_i^\circ + RT\ln a_i^*\,, \quad (2.12)$$

$$\mu_i^n = \mu_i^\circ + RT\ln a_i^{sat}\,. \quad (2.13)$$

When the parent phase is the gas phase:

$$\mu_i = \mu_i^+ + RT\ln P_i\,, \quad (2.14)$$

$$\mu_i^* = \mu_i^+ + RT\ln P_i^*\,, \quad (2.15)$$

$$\mu_i^n = \mu_i^+ + RT\ln P_i^{sat}\,, \quad (2.16)$$

where $\mu_i^\circ$ and $\mu_i^+$ are the standard chemical potentials, $a_i$ and $P_i$ are the activity and partial pressure of component $i$ in the supersaturated system before nucleation, $a_i^*$ and $P_i^*$ are the activity and partial pressure of component $i$ in the parent phase during nucleation and $a_i^{sat}$ and $P_i^{sat}$ are the saturated values being equilibrium with the flat nucleus under the pressure $P_0$. When the parent phase is the liquid and solid phase, $\boldsymbol{S}_{ini.}$ and $\boldsymbol{S}$ can be expressed as:

$$S_{ini.} = \prod_{i=1}^{c} (a_i)^{x_i^n} / \prod_{i=1}^{c} (a_i^{sat})^{x_i^n} , \qquad (2.17)$$

$$S = \prod_{i=1}^{c} (a_i^*)^{x_i^n} / \prod_{i=1}^{c} (a_i^{sat})^{x_i^n} . \qquad (2.17.a)$$

When the parent phase is the gas phase:

$$S_{ini.} = \prod_{i=1}^{c} (P_i)^{x_i^n} / \prod_{i=1}^{c} (P_i^{sat})^{x_i^n} , \qquad (2.18)$$

$$S = \prod_{i=1}^{c} (P_i^*)^{x_i^n} / \prod_{i=1}^{c} (P_i^{sat})^{x_i^n} . \qquad (2.18.a)$$

Here, $x_i^n$ is the molar fraction of component $i$ in nucleus and is constant because of the assumption of homogeneous nucleus phase.

For one-component nucleus system, the following equations can be written:

$$A = 4\pi r^2 N , \qquad (2.19)$$

$$n_1^n = 4\pi r^3 N/(3v_1) , \qquad (2.20)$$

where $N$ is the total number of nuclei in the system. Therefore, if ignoring the third and fourth terms ($\sum_i \{n_i^*(\mu_i^* - \mu_i)\} + \sum_i \{n_i^l(\mu_i^l - \mu_i)\}$), Eq. (2.6.a) agrees with Eq. (1.1). Thus, Eq. (1.1) can be obtained if the change of parent phase and interfacial term is ignored.

When nucleus is a kind of compound:

$$\Delta F = -n^n RT \ln S + \sum_i \{n_i(\mu_i^* - \mu_i)\} + \sum_i \{n_i^l(\mu_i^l - \mu_i^*)\} + \sigma A + K , \qquad (2.5.c)$$

$$\Delta G = -n^n RT \ln S + \sum_i \{n_i(\mu_i^* - \mu_i)\} + \sum_i \{n_i^l(\mu_i^l - \mu_i^*)\} + \sigma A , \qquad (2.6.c)$$

where $n^n$ is the mole number of the compound. The supersaturation degrees for the liquid and solid parent phase and for the gas parent phase can be written as the following equations, respectively:

$$S = \prod_{i=1}^{c} (a_i^*)^{q_i} / \prod_{i=1}^{c} (a_i^{sat})^{q_i} , \qquad (2.21)$$

$$S = \prod_{i=1}^{c} (P_i^*)^{q_i} / \prod_{i=1}^{c} (P_i^{sat})^{q_i} , \qquad (2.22)$$

where $q_1, q_2, q_3, \ldots q_c$ are integers and show the stoichiometric ratio of the compound. For instance, the compound is expressed as $A_{q1}B_{q2}$ when it is composed of A and B component.

By the way, Abraham pointed that disregarding the final term in Eq. (2.6) is in error [7]. Gibbs free energy before nucleation is expressed as:

$$G_{ini.} = \sum_{i=1}^{m} n_i \mu_i . \qquad (2.23)$$

Thus, Gibbs free energy during and after nucleation is described as:

$$G = \sum_{i=1}^{c} n_i^n \mu_i^n (P^n) + \sum_{i=1}^{m} n_i^* \mu_i^* + \sum_{i=1}^{m} n_i^l \mu_i^l + \sigma A - (P^n - P^*) V^n$$

$$= \sum_{i=1}^{c} n_i^n \mu_i^n + \sum_{i=1}^{m} n_i^* \mu_i^* + \sum_{i=1}^{m} n_i^l \mu_i^l + \sigma A. \qquad (2.24)$$

Equation (2.24) means that the last term $(P^n - P^*)V^n$ corresponds to the increase of Gibbs free energy of nuclei due to the increase of pressure which is disappeared by the transformation using Eq. (2.8).

## 2.2 Nucleation Curve for a Pure Solid Nucleus in Binary Liquid Solution.

In this section, let us calculate numerically the Gibbs free energy change during nucleation of solid nuclei composed of A from 1 mole of liquid binary A-B solution. However, an assumption of $\sum_i \{n_i^l(\mu_i^l - \mu_i^*)\} \approx 0$ for Eq. (2.6.b) was used. As for the Gibbs free energy change for one nucleus, the following equation is obtained:

$$\Delta G / N \equiv \Delta_{nucl} G = 4\pi r^2 \sigma - (n_A^n RT/N) \ln S$$
$$+ (n_A RT/N) \ln(a_A^*/a_A) + (1 - n_A)(RT/N) \ln(a_B^*/a_B)\ , \qquad (2.25)$$

where following equations are used:

$$S = a_A^* / a_A^{sat}, \qquad (2.26)$$
$$A = 4\pi r^2 N. \qquad (2.27)$$

In case of ideal solution, each activity equals to the mole fraction. Thus:

$$a_A = x_A = n_A, \qquad (2.28)$$
$$a_B = x_B = n_B = 1 - n_A, \qquad (2.39)$$
$$a_A^* = x_A^* = n_A^* / (1 - n_A^n) = (n_A - n_A^n)/(1 - n_A^n), \qquad (2.30)$$
$$a_B^* = x_B^* = n_B / (1 - n_A^n). \qquad (2.31)$$

Here, $x_A$ and $x_B$ are the initial mole fractions and $x_A^*$ and $x_B^*$ are the mole fractions in the parent phase, respectively, of A and B components. Therefore, Eq. (2.25) can be simplified to:

$$\Delta_{nucl} G = 4\pi r^2 \sigma - (n_A^n RT/N) \ln S_{ini.}$$
$$+ (n_A - n_A^n)(RT/N) \ln\{(1 - n_A^n/n_A)/(1 - n_A^n)\} + (1 - n_A)(RT/N) \ln\{1/(1 - n_A^n)\}. \qquad (2.25.a)$$

Since $a_A^{sat}$ equals the saturated mole fraction ($x_A^{sat}$), $S_{ini.}$ can be expressed as:

$$S_{ini.} = (n_A / x_A^{sat}). \qquad (2.32)$$

The total mole number of nuclei can be expressed with radius ($r$) and molar volume ($v_A$), as follows:

$$n_A^n = 4\pi r^3 N / (3 v_A). \qquad (2.33)$$

Therefore, Eq.(2.25.a) is a function of $r$, if the values of $v_A$, $n_A$, $n_B$, $a_A^{sat}$, $\sigma$, $T$ and $N$ are given, and $\Delta_{nucl} G$ can be calculated for A-B ideal solution.

In many cases nucleation is taking place in dilute solution. In this case, Henry's law is valid, and activity coefficient of A component ($r_A^\circ$) have a constant value and that of B component is nearly equal to 1. Then:

$$a_A \approx r_A^\circ x_A, \qquad (2.34)$$
$$a_A^* \approx r_A^\circ x_A^*, \qquad (2.35)$$

$$a_B \approx x_B, \qquad (2.36)$$

$$a_B^* \approx x_B^*. \qquad (2.37)$$

Equation (2.25.a) also satisfies this dilute condition.

The last two terms of Eqs. (2.25) and (2.25.a) come from the Gibbs free energy change of the parent phase during nucleation. The sum of the last two terms is positive, and becomes significant at relatively high values of $r$. Thus, these last two terms will lead to the appearance of a minimum point in the nucleation curve at relatively large values of $r$.

In Fig.2, a nucleation curve calculated by Eq. (2.25.a), by using the parameters of $n_A = x_A = 10^{-4}$, $x_A^{sat} = 10^{-5}$ and $N = 10^{14}$ in dilute A-B binary solution. The initial supersaturation degree ($S_{ini.}$) equals 10. A minimum is observed where $a_A^* (= x_A^*)$ does not reach the value of $a_A^{sat} (= x_A^{sat})$. The minimum state should be stable, thus, the system would stay at the minimum for a longer time.

In Fig.3 the evolution of the nucleation curve is shown with increasing amount of nuclei ($N$). It is clear that with decreasing $N$, the radius at the minimum point increases. Therefore, the stirring of the system will promote the collision and coalescence and subsequently causes the decrease of $N$, growing of nuclei, moving of the system to the more stable minimum position. For the limiting case with $N = 1$, the nucleus at the minimum shows the final state with $a_A^* = a_A^{sat}$. In contrast, when $N$ increases so much that the maximum and the minimum meet and nucleation curve extends to positive direction, once formed nuclei will be decomposed.

## 3. Mathematical Prove that the Kelvin Equation Corresponds to Extremum of the Nucleation Curve.

### 3.1 Derivative of Eqs. (2.5) and (2.6).

Here, in this section, we derive Kelvin equation through derivative of Eqs. (2.5) and (2.6).

The following equations can be written:

$$v_i^n = \left(\frac{\partial V^n}{\partial n_i^n}\right)_{P^n}, \quad v^n = \sum_{i=1}^{c} v_i^n x_i^n, \quad V^n = \sum_{i=1}^{c} v_i^n n_i^n = v^n \sum_{i=1}^{c} n_i^n = 4\pi r^3 N/3. \qquad (3.1)$$

From Eqs.(2.19) and (3.1):

$$\delta V^n = \sum_{i=1}^{c} v_i^n \delta n_i^n = v^n \sum_{i=1}^{c} \delta n_i^n, \quad \delta A = \frac{2}{r}\delta V^n = \frac{2}{r}\sum_{i=1}^{c} v_i^n \delta n_i^n. \qquad (3.2)$$

Therefore, at extremum, from Eq.(2.5), under the constant volume condition, the following equation can be obtained:

$$\delta(\Delta F) = \sum_{i=1}^{c}\left\{(\mu_i^n(P^n) - \mu_i^*) + (2\sigma/r - P^n + P^*)v_i^n\right\}\delta n_i^n + \sum_{i=1}^{m}(\mu_i^l - \mu_i^*)\delta n_i^l$$
$$- V^n \delta P^n + \sum_{i=1}^{c} n_i^n \delta\{\mu_i^n(P^n)\} - V^* \delta P^* + \sum_{i=1}^{m} n_i^* \delta\mu_i^* + \sum_{i=1}^{m} n_i^l \delta\mu_i^l + A\delta\sigma = 0.$$

(3.3)

This equation should be written for the extremum in any arbitrary stage in nucleation process, that is, for the extremum on every nucleation curves with different $N$ value, or any arbitrary system and, thus, for arbitrary value of $\delta n_i^n$ and $\delta n_i^l$. Therefore, the following equations are concluded:

$$(\mu_i^n(P^n) - \mu_i^*) + (2\sigma/r - P^n + P^*)v_i^n = 0\,, \tag{3.4}$$

$$\mu_i^I - \mu_i^* = 0\,, \tag{3.5}$$

$$-V^n\delta P^n + \sum_{i=1}^{c} n_i^n \delta\{\mu_i^n(P^n)\} - V^*\delta P^* + \sum_{i=1}^{m} n_i^*\delta\mu_i^* + \sum_{i=1}^{m} n_i^I\delta\mu_i^I + A\delta\sigma = 0\,. \tag{3.6}$$

From Eqs.(3.4), (3.5) and Laplace equation ( $2\sigma/r - P^n + P^*$ ):

$$\mu_i^n(P^n) = \mu_i^I = \mu_i^*\,. \tag{3.7}$$

Equation (3.7) shows the equilibrium condition. Consequently, the extremum in nucleation curve corresponds to the equilibrium state of the system. In addition, Eq. (3.6) corresponds to Gibbs-Duhem relation in the present total system. According to Defay and Prigogine [9], the equation can be seperated into three relations corresponding to nucleus, parent, and interfacial phases, respectively, under equilibrium condition:

$$-V^n\delta P^n + \sum_{i=1}^{c} n_i^n \delta\{\mu_i^n(P^n)\} = 0\,, \tag{3.8}$$

$$-V^*\delta P^* + \sum_{i=1}^{m} n_i^*\delta\mu_i^* = 0\,, \tag{3.9}$$

$$\sum_{i=1}^{m} n_i^I\delta\mu_i^I + A\delta\sigma = 0\,. \tag{3.10}$$

From Eqs. (2.7) and (3.4):

$$-(\mu_i^n - \mu_i^*) = \ln(P_i^*/P_i^{sat}) = RT\ln \boldsymbol{S_i} = v_i^n\{(2\sigma/r) - (P_0 - P^*)\}\,, \tag{3.11}$$

where $P_0$ is the final pressure over the flat nucleus and $\boldsymbol{S_i}$ is the supersaturation degree for *i* component. Equation (3.11) agrees with Kelvin equation for *i* component in multi-component system [9]. Multiplying it by $x_i^n$ and summation leads to:

$$RT\ln\{\prod_{i=1}^{c}(P_i^*)^{x_i^n} / \prod_{i=1}^{c}(P_i^{\;sat})^{x_i^n}\} = RT\ln \boldsymbol{S} = v^n\{(2\sigma/r) - (P_0 - P^*)\}\,. \tag{3.12}$$

Under a constant temperature and pressure condition, the $\delta(\Delta G)$ can be expressed by the same terms in Eq. (3.3). Thus, putting $P_0 = P^*$ in Eqs. (3.11), (3.12), the following is obtained.

$$\ln(P_i^*/P_i^{sat}) = RT\ln \boldsymbol{S_i} = v_i^n(2\sigma/r)\,, \tag{3.13}$$

$$RT\ln\{\prod_{i=1}^{c}(P_i^*)^{x_i^n} / \prod_{i=1}^{c}(P_i^{sat})^{x_i^n}\} = RT\ln \boldsymbol{S} = v^n(2\sigma/r)\,. \tag{3.14}$$

When the parent phase is the liquid and solid solution phase under constant temperature and pressure condition,

$$\ln(a_i^*/a_i^{\;sat}) = RT\ln \boldsymbol{S_i} = v_i^n\{2(\sigma/r)\,, \tag{3.15}$$

$$RT\ln\{\prod_{i=1}^{c}(a_i^*)^{x_i^n} / \prod_{i=1}^{c}(a_i^{sat})^{x_i^n}\} = RT\ln \boldsymbol{S} = v^n(\frac{2\sigma}{r})\,. \tag{3.16}$$

For compound-nucleus, $\{\prod_{i=1}^{c}(P_i^*)^{q_i} / \prod_{i=1}^{c}(P_i^{sat})^{q_i}\}$ and $\{\prod_{i=1}^{c}(a_i^*)^{q_i} / \prod_{i=1}^{c}(a_i^{sat})^{q_i}\}$ should be used as $S$. All the equations from (3.11) to (3.16) could be regarded as Kelvin equation (c.f. Appendix). Therefore, Kelvin equation could be derived correctly from the modified classical homogeneous nucleation theory.

### 3.2 Consideration on Eq. (1.1) and Kelvin equation.

The critical maximum state in nucleation curve is the equilibrium state and often described by the following equation involving the critical radius ($r_{cr}$)derived through taking the derivative of the $\Delta_{nucl}G$ in Eq.(1.1) with respect to $r$ as zero:

$$\frac{R \cdot T}{v_A} \cdot \ln \boldsymbol{S}_{ini.} = \frac{2 \cdot \sigma}{r_{cr}} \tag{3.17}$$

It seems that Eq. (3.17) corresponds to Kelvin equation. However, the derivation of Eq. (3.17) was performed based on an assumption of constant $\boldsymbol{S}_{ini.}$ coming from the assumption of unchanged parent phase. Thus, the $\boldsymbol{S}_{ini.}$ in Eq. (3.17) is taken to be $P_A / P_A^{sat}$, where $P_A$ is the supersaturated pressure of $A$ in parent phase before nucleation, which is entirely different from Kelvin equation. Thus, the confusion in Eq. (1.1) will occur. As Defay and Prigogine [9] expressed for the small nucleus, the assumption of unchanged parent phase might be reasonable. However, strictly speaking, the assumption is not adequate and, thus, Eq. (3.17) based on the assumption does not correspond to Kelvin equation.

On the contrary, Kelvin equation can be derived in fully correct manner from the present study and a minimum in nucleation curve was confirmed in A-B binary dilute solution system. A nucleus could stay at the minimum for a considerable time, which contrasts markedly with a nucleus at a maximum that should instantly decompose or grow. It indicates that Kelvin equation should correspond to the minimum state in nucleation curve rather than the maximum unstable state.

Recently there is argument against the classical homogeneous nucleation theory expressed by Eq. (1.1). The argument is for a nucleus with around a critical size and a smaller size than it, and includes the following points: the composition of a nucleus is not homogeneous, thus, the pressure of the nucleus is different from the value corresponding to the homogeneous bulk composition, and surface tension should change with radius. These points of argument would be reasonable and a main part of it would refer to the vagueness of difference between interfacial zone and inner part of a nucleus when the nucleus is small. In the present modified theory, the interfacial term is included in Eqs. (2.5) and (2.6), although it stands on the assumptions of entirely homogeneous nucleus and zero volume of the interface according to the Gibbs model. However, the interfacial term was ignored in Eq. (2.25) for a numerical calculation. In the present stage, numerical estimation of the interfacial term is difficult. We expect further progress of the procedure based on molecular dynamics for the correct estimation of interfacial influence. However, the main concern of our present study focuses on a minimum in nucleation curve where nucleus size is fairy large and, thus, it will be free from the points of the argument for a small nucleus. As for the influence of the change of surface tension with curvature, it would be discussed in the next report.

## 4. Conclusion.

The neglect of the free energy change in parent phase in classical homogeneous nucleation process has caused oversight of an important phenomenon, which is the presence of a minimum in nucleation curve. In the present study, the modified theory of classical homogeneous nucleation of multi-component nuclei or compound nuclei from the multi-component solution and gas phase was developed, taking the change of parent phase into consideration, and proved a minimum in the nucleation curve in A-B binary solution. In addition, the modified theory proved that Kelvin equation, which describes the state of oversaturated vapor pressure over small spherical droplet, could describe the states at both of the maximum and minimum points in nucleation curve.

The following conclusions are made:

(1) Helmholtz free energy change and Gibbs free energy change during classical homogeneous nucleation process for multi-component solution and gas systems with multi-component nuclei or compound nuclei were developed.

(2) The calculated nucleation curve from the modified theory for A-B dilute solution system has a minimum point, in addition to a maximum point. The minimum state should be in more stable condition compared to the unstable maximum state. The decrease of the number of nuclei, *N*, in the nucleation process through collision and coalescence causes transformation of the system into further stable minimum state. However, when the system reaches to the considerable dilute state in which the collision and coalescence would rarely happened, the system would stay at the minimum state for a long time.

(3) The derivative of the above free-energy changes at extremum with respect to nuclear radius proved the equilibrium state at the extremum and the relations corresponding to Kelvin equation.

(4) Kelvin equation corresponds to the minimum and maximum state, showing the importance of the minimum state because of the more stable condition of the minimum state.

(5) The Gibbs free energy change by classical homogeneous nucleation theory ignoring the change of parent phase essentially includes an assumption of constant supersaturation degree, thus, the use of the theory has been restricted only in the initial stages of nucleation. Therefore, the well known equation obtained at the maximum assuming the constant supersaturation degree does not correspond to Kelvin equation in theoretically strict manner and can not describe the minimum state.

## Appendix.

Defay et al. [9] explained generalized Kelvin equation from Laplace equation for the multi-component system on the assumptions that the liquid phase is incompressible and that the vapor phase behaves as an ideal gas.

Laplace equation expresses the relation between the pressure in spherical drop and its vapor pressure as follows:

$$P^n - P^* = 2\sigma / r . \qquad (A.1)$$

The superscript $^n$ and $^*$ express the values in the drop phase and the parent phase respectively. From equality of the chemical potentials in both phases in equilibrium:

$$\mu_i^n = \mu_i^* . \qquad (A.2)$$

From Eqs. (A.1) and (A.2), we obtain:

$$\delta P^n - \delta P^* = \delta(\frac{2\sigma}{r}) , \qquad (A.3)$$

$$\delta\mu_i^n = \delta\mu_i^* . \qquad (A.4)$$

Under a constant temperature and constant composition [9]:

$$(\partial\mu_i^n / \partial P^n)_{T, x_i^n} = v_i^n . \qquad (A.5)$$

Thus,

$$\delta\mu_i^n = v_i^n \delta P^n . \qquad (A.6)$$

Further,

$$\mu_i^n = \mu_i^+ + RT \ln P_i^* . \qquad (A.7)$$

From Eqs. (A.6), (A.7):

$$\delta P^n = \delta\mu_i^n / v_i^n = (RT / v_i^n) \delta \ln P_i^* . \qquad (A.8)$$

Using Eq. (A.3), we obtain:

$$\delta(\frac{2\sigma}{r}) = (RT / v_i^n) \delta \ln P_i^* - \delta P^* . \qquad (A.9)$$

The integration from zero curvature, which corresponds to flat surface of drop phase ($1/r$=0, $P_i^{sat}$, $P_0$ ), to the other state ($1/r$, $P_i^*$ , $P^*$ ), gives:

$$\frac{2\sigma}{r} = \frac{RT}{v_i^n} \ln \frac{P_i^*}{P_i^{sat}} - (P^* - P_0) . \qquad (A.10)$$

Therefore:

$$RT \ln \frac{P_i^*}{P_i^{sat}} = v_i^n \{ \frac{2\sigma}{r} - (P_0 - P^*) \} . \qquad (A.11)$$

Eqation (A.11) is regarded as the generalized Kelvin equation for multi-component system. The second term in the right hand side in Eq. (A.11) is negligible compared to the first term and, in the case under constant pressure condition, $P_0$ equals $P^*$ . Then, Eq. (A.11) can be transformed as:

$$RT \ln \frac{P_i^*}{P_i^{sat}} = v_i^n \frac{2\sigma}{r} . \qquad (A.12)$$

Equation (A.12) is also regarded as Kelvin equation.

## Reference.

[1] Huimin Liu and David S. Dandy, Diamond Chemical Vapor Deposition, Noyes Publications, U.S.A.,1995, pp.46-78.

[2] Nikola Kallay, Interfacial Dynamics, Marcel Dekker, Inc., New York ,1999, pp.435-474.

[3] Lawrence E. Murr, Interfacial Phenomena in Metals and Alloys, Addison-Wesley Publishing Company, 1975, pp.259-358.

[4] Robert D.vold and Marjorie J.Vold, Colloid and Interface Chemistry Addison-Wesley Publishing Company, 1983 pp.289-339.

[5] Michael C. Weinberg, Nucleation and Crystallization in Liquids and Glasses, The American Ceramic Society, Westerville,Ohio, 1993.

[6] A.C.Zettlemoyer, Nucleation Phenomena, Elsevier Scientific Publishing Company, Amsterdam, 1977, pp.205-222.

[7]F.F.Abraham, Homogeneous Nucleation Theory, Academic Press, New York and London, 1974, pp.9-30 and pp.225-237.
[8]Arthur W.Adamson and Alice P.Gast, Physical Chemistry of Surfaces, John Wiley & Sons, Inc., USA, 1997, pp.328-336.
[9] R.Defay, I.Prigogine and A.Bellemans, Surface Tension and Adsorption, Translated by D.H.Everett, Longman Green & Co Ltd., London, 1966, pp217-222, pp.256-258, pp.259-261 and pp.319-320.
[10] K.Nishioka and I.Kusaka, J. Chem. Phys. 96(1992), pp.5370-5376.
[11] Jin-Song Li, K.Nishioka and Eric R.C.Holocomb, J. Cryst. Growth, 171(1997) , pp.259-269.
[12] K. Wasai and K. Mukai, Metall. Mater. Trans.B, 30B(1999), pp.1065-1074.
[13] P.S.Popel and S.N.Kuzin, Proc.Int.Conf.High Temperature Capillarity, Edited by N.Eustathopoulos and N. Sobczak, 29 June-2 July ,1997, Cracow, Poland.
[14] J.Schmelzer and H.Ulbricht, J.Coll. Inter. Sci. 1987, vol.117, No.2, pp. 325-338.
[15] I.Prigogine and R.Defay, Thermodynamique Chimique, Translated into Japanese by M.Seo, Third Edition, Misuzu Shobo, Tokyo, 1970, P.70 (Eqs. (6.24),(6.25)).

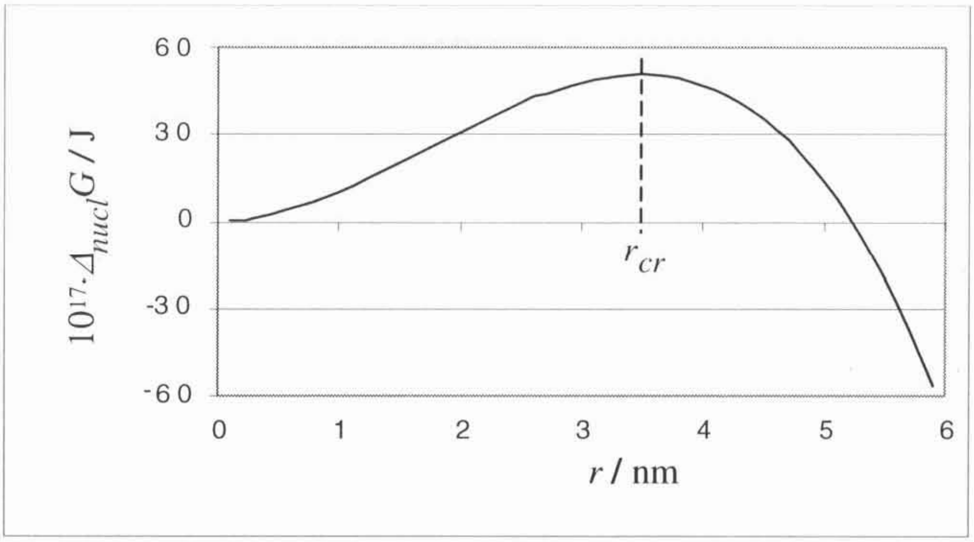

Fig.1. The nucleation curve, calculated from Eq. (1.1) and with the following parameters: $\sigma = 1$ J/m$^2$, $v_A = 10^{-5}$ m$^3$/mol, $T = 300$ K, $S_{ini.} = 10$.

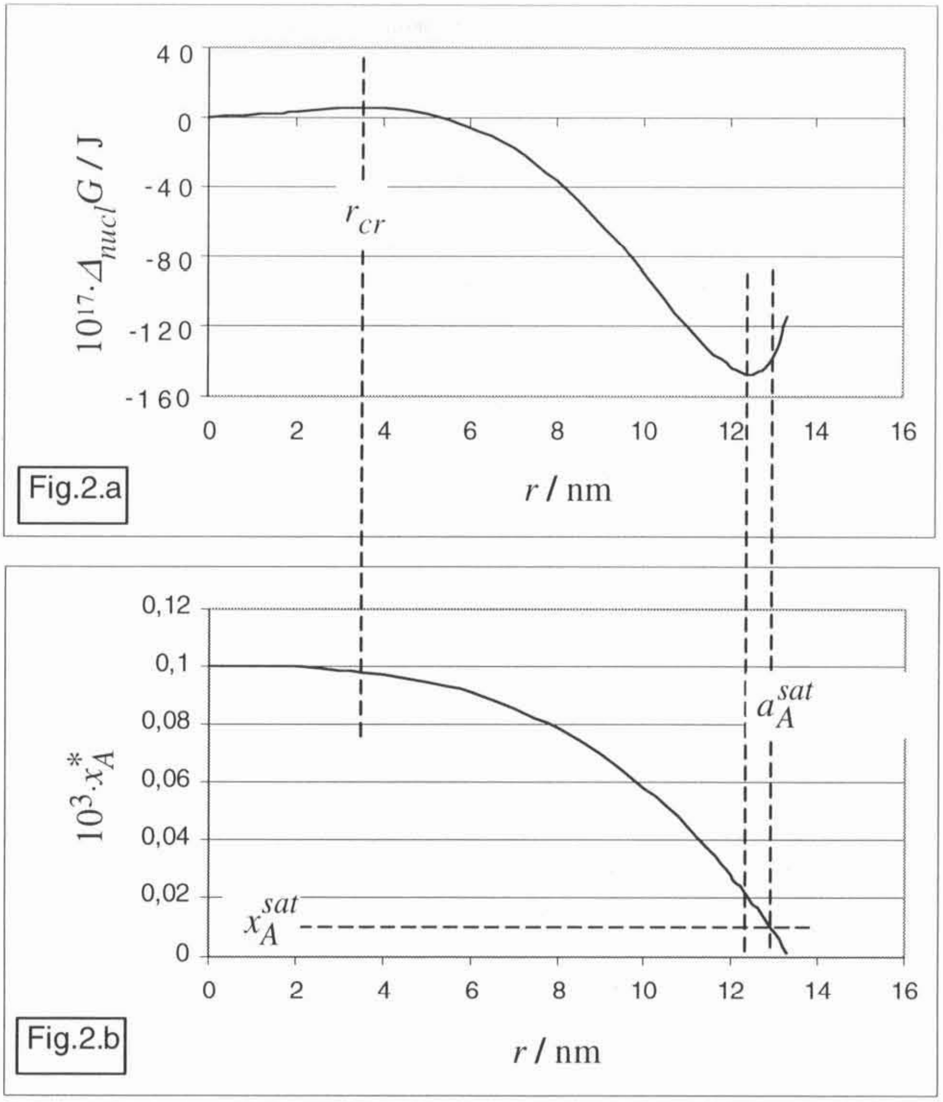

Fig.2. The nucleation curve, calculated by Eq. (2.25.a) and with the following parameters: $\sigma$ = 1 J/m$^2$, $v_A$ = $10^{-5}$ m$^3$/mol, $T$ = 300 K, $n_A = x_A = 10^{-4}$, $N$ = $10^{14}$, $x_A^{sat}$ = $10^{-5}$, $S_{ini.}$ = 10 ($r_{cr}$ = 3.48 nm ). Fig.2.a shows the nucleation curve, while Fig.2.b shows the mole fraction of component A in parent phase.

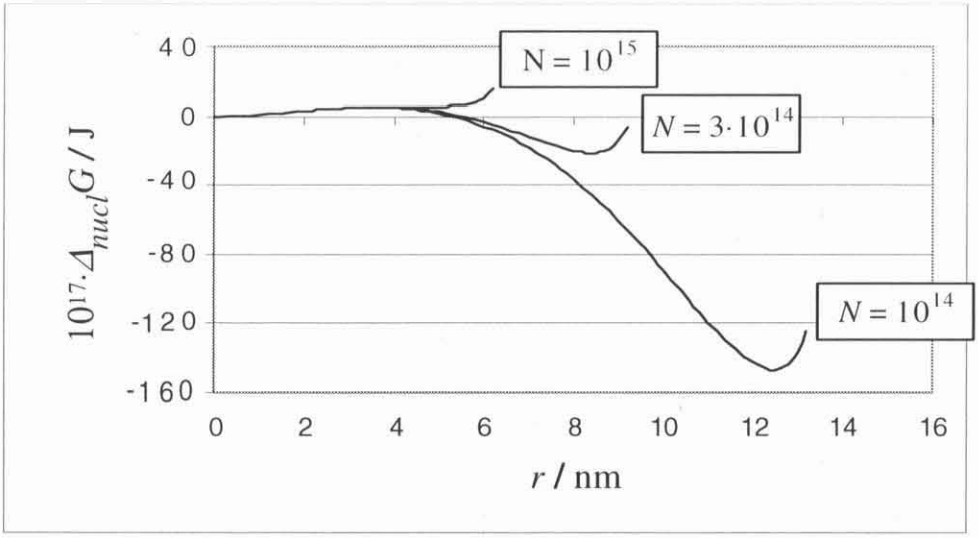

Fig.3. The nucleation curve, calculated by Eq. (2.25.a) and with the following parameters: $\sigma$ = 1 J/m$^2$, $v_A$ = $10^{-5}$ m$^3$/mol, $T$ = 300 K, $n_A = x_A = 10^{-4}$, $x_A^{sat}$ = $10^{-5}$, $S_{ini.}$ = 10 and different values of $N$, indicated on the curves