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Progress in Crystal Growth and Characterization of Materials 62 (2016) 43–57

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Review

Thermodynamics -for understanding crystal growth-

Tatau Nishinaga *

Department of Electronic Engineering, Graduate School of Engineering, The University of Tokyo, Bunkyo, Tokyo 113-8656, Japan

Available online 7 June 2016

Abstract

To understand what entropy is, thermodynamical entropy was derived from Boltzmann's entropy formula. After defining the Helmholtz and the Gibbs free energies, we calculated the formation Gibbs free energies of an equilibrium and a non-equilibrium nucleus following Toschev's approach taking a water droplet as an example. It is demonstrated that the Gibbs free energy for the formation of a cluster takes the maximum as the cluster radius is increased. The cluster at this maximum is called critical nucleus.

Thermodynamics is also a useful tool to obtain the rate of crystal growth in a vapor phase. The partial pressures of all gaseous species are calculated by solving equations given by the law of mass action and the initial conditions. The mathematical formulas to give the growth rates in a closed tube and in a gas flow system are derived.
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Keywords: thermodynamics; Boltzmann's entropy formula; free energy; chemical potential; nucleation; critical nuclei; law of mass action; vapor growth; chemical transport reaction

1. Introduction

Crystal growth has had a huge impact on the present society through the inventions and the developments of electronic and optical devices. For further advancement in the art and science of crystal growth, understanding of crystal growth is essential [1]. Thermodynamics is one of the most important tools to understand crystal growth. To understand the growth of snow crystals in the sky, we should understand what the water vapor is in the sky, how the nucleation of ice crystal occurs under a certain temperature and how the growth of snows proceeds from their nuclei. All these matters are understood by employing fully or partly the thermodynamics. In the melt and the vapor growths of semiconductors, the state of surface or interface affects strongly the growth. Depending on the temperature, the crystal surface changes from atomically smooth to completely atomically rough. Thermodynamics also can be applied to understand the state of the crystal surface. Including the above examples, thermodynamics is essentially important to solve the problems in crystal growth.

Thermodynamics and statistical physics treat common problems in the system of the many particles, where the former discusses from the macroscopic point of view while the latter does by starting from the microscopic view and ending at the macroscopic one. Therefore, many text books describe both thermodynamics and statistical mechanics in series in a single book. Traditionally, there are many good text books of thermodynamics and statistical mechanics. Among them, the book written by Sekerka [2] is one of the best books published recently.

The most important and sometimes the most difficult concept in thermodynamics is entropy. Hence, in this lecture, we start to explain entropy, which was defined by Boltzmann and then proceed to derive the thermodynamic entropy.

* Professor Emeritus, Department of Electronic Engineering, Graduate School of Engineering, The University of Tokyo, Bunkyo, Tokyo 113-8656, Japan. Tel.: +81 4 7176 1610; fax: +81 4 7176 1610.

E-mail address: tatau-n@td6.so-net.ne.jp.

http://dx.doi.org/10.1016/j.pcrysgrow.2016.04.001

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Although thermodynamics can be applied to understand almost all problems of crystal growth, in this lecture, due to the time constraint, we restrict our subjects only to the nucleation and the rate of the growth in vapor phase. In addition to these two examples, thermodynamics is also applied to obtain phase diagram, to understand stoichiometry of the compounds, defect concentration etc. Good examples for the application of thermodynamics to understand the crystal growth and related problems between growth are found in Reference [3].

2. Entropy and heat

Vapor phase is composed of gaseous atoms or molecules. If one can assume them as independent particles, namely, if these particles have no attractive or repulsive forces between them, we can express the gas as ideal. Such particles are called free particles. A free particle moves straight until it hits a wall or another particle. Even under the free particle approximation, chemical reaction takes place when the particles hit each other.

In ideal gas approximation, if each particle has the same mass of m and if the velocity of the i-th particle is denoted by v_i, the kinetic energy of the i-th particle is given as,

$$\varepsilon_i = mv_i^2 / 2. \tag{1}$$

When the number of the particles is expressed by N, the total kinetic energy of the ideal gas, U, is written as,

$$U = \sum_i^N \varepsilon_i. \tag{2}$$

U is called the internal energy and is a sum of the kinetic energy of the particles. When the particles are kept under the temperature of T, under the assumption that the particles obey Boltzmann statistics, the average kinetic energy of the particle is given by $(3/2)kT$, where k is the Boltzmann constant. The calculation is carried out in standard text books of thermodynamics or statistical mechanics. Then, one gets,

$$U = 3NkT / 2. \tag{3}$$

When the total number of the particles is 1 mol, N should be the Avogadro constant and Nk is equal to the gas constant, R.

Another important quantity to express the behavior of many particles is entropy. To understand entropy, let us see Fig. 1. In room 1, the particles of A are contained separately from the particles of B in room 2 as shown in the figure. The rooms are separated by a board a–b. Once the board a–b is removed, everyone knows that these two kinds of particles start to mix and finally they are mixed completely as shown in Fig. 2. If the particles are free, there is no change

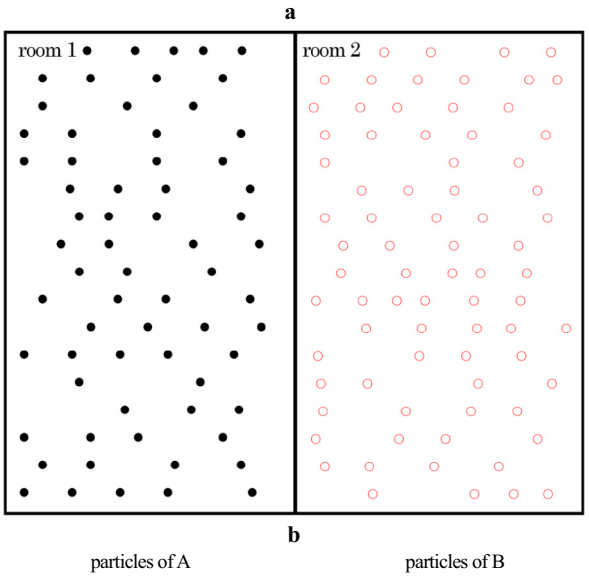


Fig. 1. Particles of A and B are separated by a board a–b and contained in different rooms.

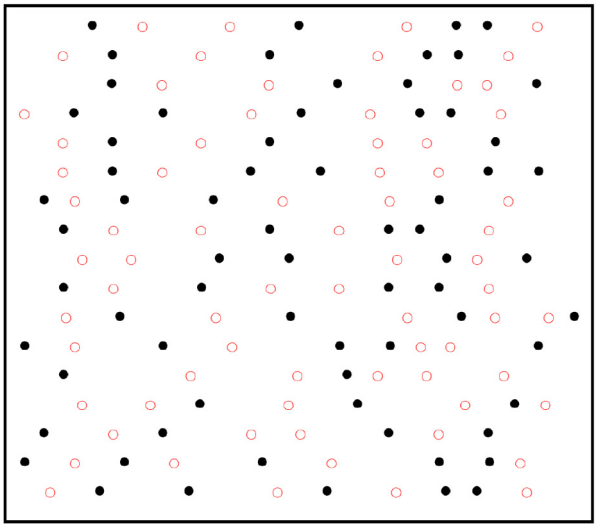


Fig. 2. After the removal of the board a–b, particles of A and B start to mix and finally they are mixed completely.

in internal energy, U, before and after the mixing. However, the state of the many particle system has changed very largely. The change is expressed by the increase of the entropy. The entropy, S, is defined by,

$$S = k \ln M, \tag{4}$$

where M is the number of the states. Equation (4) is known as Boltzmann's entropy formula.

For understanding the mixing phenomena, we take a simple example in which 2 particles each of A and B are

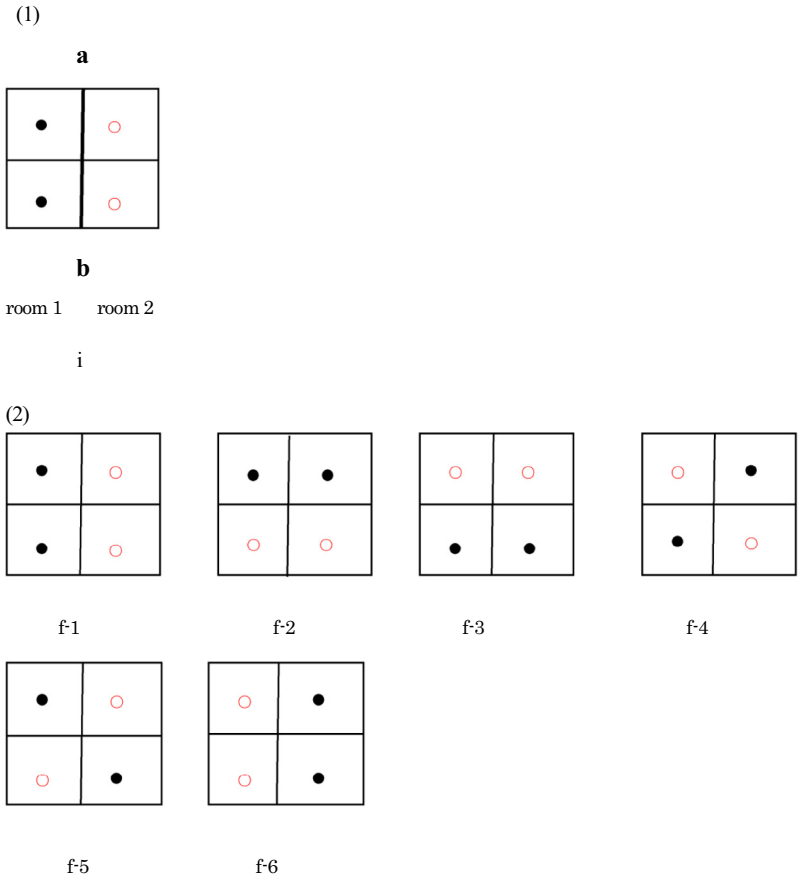


Fig. 3. As an initial state i, we consider 2 particles each of A and B are contained respectively in room 1 and room 2 (1). The room is separated by board a–b. At a certain time, the board a–b is removed (2). Then, the 6 states, from f-1 to f-6, appear with an equal probability.

contained respectively in room 1 and room 2. We divide each room into two small cells, the size of which is just to be able to contain one particle as shown in Fig. 3(1). We assume room 1 and room 2 are separated at first by the board a–b, the state of which is denoted as i. At a certain time, the board a–b is removed. Then, each particle starts to exchange positions by thermal vibration. Since each cell can contain only one particle, a total 6 states, f-1 to f-6, appear with an equal probability as shown in Fig. 3(2). If one observes the system for a certain period, for instance 60 seconds, one sees that each of f-1 to f-6 states appears equally in total for 10 seconds. Among them, the state of f-1, which is same as the initial state, appears for 10 seconds in total. However, the states of mixing, f-2 to f-5, appear in a total of 40 seconds. After the removal of the board, there is possibility that the particles are not mixed but for the most of the observation time, the particles are mixed, although in this simplified example, the period of mixing is only 4 times longer than the non-mixing period. When the number of particles is very large as the events in nature, the observation period of mixing like Fig. 2 is tremendously longer than the period of non-mixing state given in Fig. 1.

In Fig. 3, we define the entropy of the initial state as S_i. Then, by Eq. (4), one gets,

$$S_i = k \ln M_i. \tag{5}$$

The entropy of the mixing states is given by,

$$S_f = k \ln M_f. \tag{6}$$

Since M_i and M_f are respectively 1 and 4, one gets,

$$\Delta S = S_f - S_i = k \ln 4. \tag{7}$$

Hence, the entropy increases after the removal of the board a–b. The change from Fig. 1 to Fig. 2 is also expressed as the increase of the entropy.

Now, the expansion of gas is also expressed as the increase of the entropy. Fig. 4 shows a simple example of

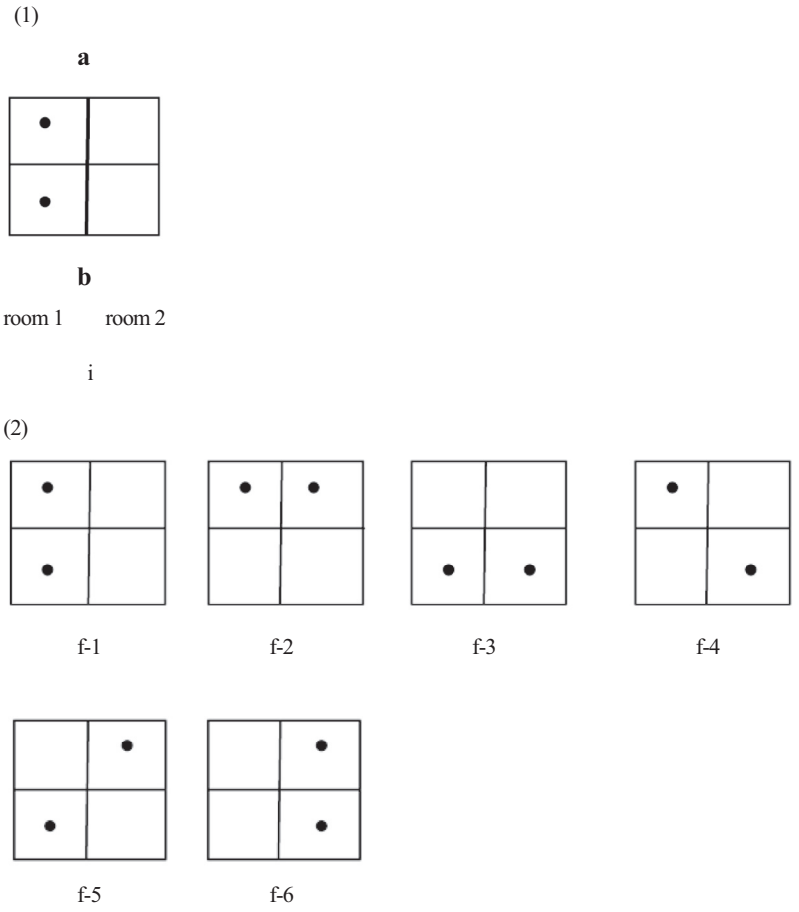


Fig. 4. In the initial state i, two particles are contained in room 1. After a certain time, the board a–b is removed. Then, the particles expand and 6 states, from f-1 to f-6, appear with an equal probability like the case of Fig. 3. The states of f-2 to f-5 can be taken as expanded with respect to the board a–b which has been removed.

the expansion. As an initial state i, 2 particles are contained in room 1 which is separated from room 2 by a board a–b as shown in Fig. 4(1). At a certain time, the board a–b is removed, then, 6 states, from f-1 to f-6, appear with an equal probability as shown in Fig. 4(2). Hence, if we observe the system for some period, each state appears for one sixth of the period. The state of expansion can be regarded as those from f-2 to f-5 with respect to the board a-b which has been removed and the state of non-expansion corresponds to f-1. Therefore, one observes mostly the states of expansion although in this simple system, the observing period of expansion is only 4 times longer than the observing period of non-expansion state. The entropy change after the removal of the board a–b is again $\Delta S = k$ ln 4 like the mixing problem explained by Fig. 3.

Let us scale up the models employed in Fig. 4. As shown in Fig. 5, we assume that there is a small room of volume V_1 which contains 4 particles. The small room

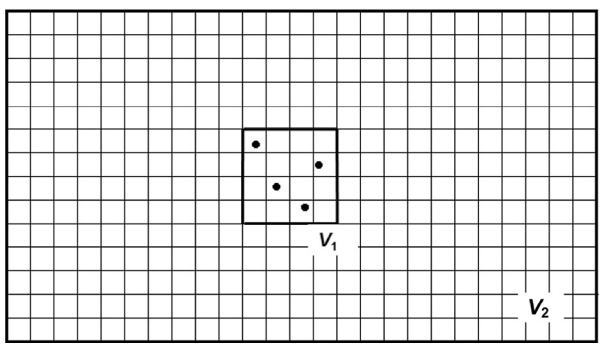


Fig. 5. In the initial state, 4 particles are contained in a small room inside a larger room. The volumes of the small and the larger rooms are given respectively as V_1 and V_2.

is located inside a larger room of volume V_2. After the removal of the boundary that surrounds the small room, 4 particles expand in the whole space of the larger room as shown in Fig. 6. To find the entropy change before and

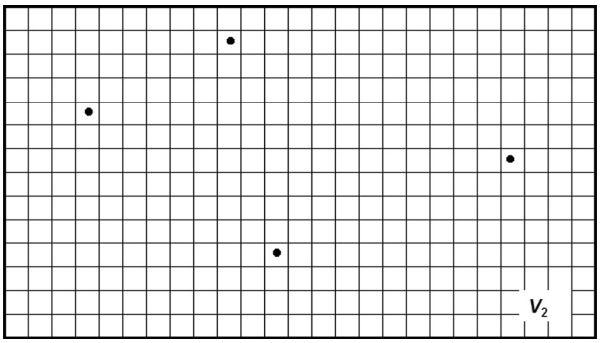


Fig. 6. After the removal of the boundary that surrounds the small room, 4 particles expand in the whole space of the larger room.

after the expansion, we divide both rooms into cells, the size of which is limited to contain only one particle. Now, we assume the size of each cell is v_0 and the number of cells in the small room is N_1. The number of ways to arrange 4 particles in the small room is given by,

$$M_i = {}_{N1}C_1 \cdot {}_{N1-1}C_1 \cdot {}_{N1-2}C_1 \cdot {}_{N1-3}C_1 = N_1 \cdot (N_1-1) \cdot (N_1-2) \cdot (N_1-3) \cong N_1^4 \quad (8)$$

where

$${}_nC_m = n!/(n-m)!\,m! \quad (9)$$

is the number of the combination and $N_1 \gg 1$ is assumed.

After the boundary of the small room is removed, the 4 particles expand to the whole space of the larger room as shown in Fig. 5. The number of ways to distribute 4 particles in the larger room, M_f, is given like Eq. (8) as,

$$M_f \cong N_2^4. \quad (10)$$

The change of the entropy in the expansion is given by,

$$\Delta S = S_f - S_i = k \ln M_f - k \ln M_i = k \ln (M_f / M_i) = 4k \ln (N_2 / N_1) = 4k \ln (V_2 / V_1). \quad (11)$$

where we have employed the relation of $V_1 = v_0 N_1$ and $V_2 = v_0 N_2$ with cell volume of v_0. If the number of the particles is N, Eq. (11) can be written as

$$\Delta S = Nk \ln (V_2 / V_1). \quad (12)$$

For the gas of one mol, N should be the Avogadro number and we have,

$$\Delta S = R \ln (V_2 / V_1). \quad (13)$$

where R is gas constant.

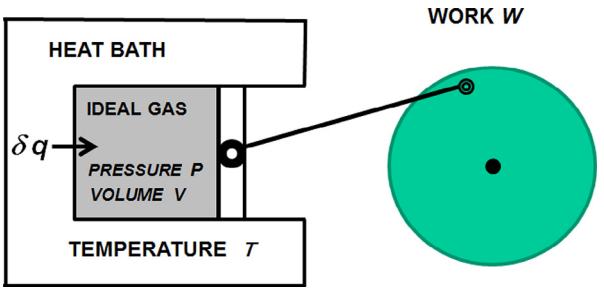


Fig. 7. Ideal heat engine in which there is no heat loss. The heat δq from the heat bath is converted completely to the work, W.

Now, to find the relation between the heat and the entropy, we use the ideal heat engine in which there is no heat loss. The engine is schematically given in Fig. 7. In the cylinder of the engine, we put the ideal gas of one mol. Then, we let the piston move to do the work, W. The gaseous particles hit the wall of the piston to let it move with the pressure P. If the gas pushes the piston, the particles lose the kinetic energy. This makes the temperature of the gas low. However, since the cylinder is in contact with the thermal bath of the temperature T, the gaseous particles in the cylinder receive the heat δq so that the temperature of the gaseous particle is kept constant. According to the law of Boyle–Charles,

$$PV = NRT, \quad (14)$$

the work, W, done by the expansion of the gaseous particles of one mol from V_1 to V_2 is given by,

$$W = \int_{V_1}^{V_2} P\,dV = RT \int_{V_1}^{V_2} (1/V)\,dV = RT \ln (V_2 / V_1). \quad (15)$$

From Eqs. (13) and (15), one gets,

$$W = T\Delta S. \quad (16)$$

As we saw, W is done by the heat from the heat bath and since there is no heat loss in this ideal heat engine, W should be equal to δq. Hence, we get from Eq. (16).

$$\delta q = T\Delta S. \quad (17)$$

Namely,

$$\Delta S = \delta q / T \quad (18)$$

is obtained. Eq. (18) is that given in usual text books of thermodynamics. When the heat engine is ideal we get Eq. (18), but if it is not ideal, the entropy change should be larger than the heat transfer so that one gets,

$$\Delta S \geqq \delta q / T. \tag{19}$$

In the extreme case, if the gas expands without work (free expansion), the entropy increases while there is no work done for the expansion and hence δq is zero. This is an extreme case of Eq. (19).

In the above discussion, the expansion took place under constant temperature and the entropy change occurs as the volume is changed. However, if the temperature is changed, the entropy may not be increased even if the volume is increased. So far we assumed the expansion occurs in a position space. However, the motion of a particle should be described in a position–momentum space, namely, a phase space of 6 dimensions. Hence, the expansion of particles should occur in the space of x, y, z, p_x, p_y, and p_z, where x, y and z denote the positions, and p_x, p_y and p_z denote respectively the momentums in x, y and z directions. Again we divide the phase space in small cells, the size of which is limited to contain one particle. According to the uncertainty principle, the cell size should be $\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z \cong h^3$, where h is the Planck constant. In phase space, the expansion of gas occurs in both the position and the momentum spaces. The expansion in position space means the increase of the volume, V, while the expansion in momentum space means the increase of internal energy, U. The expansion of gas in both spaces gives the increase of the entropy.

According to statistical mechanics, the entropy of ideal gas of 1 mol is given by,

$$S = R\{(3/2)\ln U + \ln V + (3/2)\ln(4\pi m / 3h^2) + 5/2\}. \tag{20}$$

We see in Eq. (20) that U and V take the equivalent position to the entropy. Hence, even if V increases, if U decreases by a corresponding amount, S will be not changed. This is the case of adiabatic expansion where no heat is supplied; hence, the temperature of the gas should be decreased in the expansion. In this case, $\delta q = 0$ and all the work should be done by consuming internal energy, namely,

$$P\mathrm{d}V = -\mathrm{d}U. \tag{21}$$

is derived. From Eq. (20), we get

$$\mathrm{d}S = R\{(3/2)\mathrm{d}U / U + \mathrm{d}V / V\} \tag{22}$$

in derivative form. One can show $\mathrm{d}S = 0$ by substituting Eqs. (3), (14) and (21) into Eq. (22).

3. Free energy

A single particle tends to decrease its energy to take the minimum, due to the loss of energies. As to the many-particle system, U is to decrease to take the minimum due to the loss of energies. On the other hand, as we have seen, the entropy should increase to reach equilibrium. Hence, we should take into account two thermodynamic quantities of U and S to express the behavior of the many-particle system. Now, we define the Helmholtz free energy by:

$$F = U - TS. \tag{23}$$

The minus sign before the entropy is due to the opposite tendency of S to go to an equilibrium. When many-particle system goes to an equilibrium under a constant temperature without changing the volume, F goes to the minimum. On the other hand, if the system changes with the change of the volume under a constant pressure, the system does the work and U should be changed. In this case,

$$G = U + PV - TS \tag{24}$$

goes to minimum at an equilibrium. G is called the Gibbs free energy. Here,

$$H = U + PV \tag{25}$$

is called the enthalpy. At an equilibrium, we obtain,

$$\mathrm{d}F = 0 \tag{26}$$

and

$$\mathrm{d}G = 0. \tag{27}$$

After the equilibrium is attained, if a virtual disturbance is given to the system, we see:

$$\mathrm{d}S < 0, \tag{28}$$

$$\mathrm{d}F > 0 \quad (T, V : \text{constant}) \tag{29}$$

and

$$\mathrm{d}G > 0. \quad (T, P : \text{constant}) \tag{30}$$

If the many-particle system is composed of one kind of particle, an increment of the Gibbs free energy by adding one mol of the particle is defined as the chemical potential.

$$\mu = G / N, \tag{31}$$

where N is the total mol of the particles in the system. If many species of the particles are contained in the system, the chemical potential of the i-th species is given by

$$\mu_i = (\partial G / \partial N_i)_{T,P,N_j(\neq N_i)}. \quad (32)$$

Under a constant temperature, we get:

$$V\mathrm{d}P + P\mathrm{d}V = 0 \quad (33)$$

from Eq. (14). Since $\mathrm{d}U = 0$ for the constant temperature, Eq. (24) gives

$$\mathrm{d}G = -T\mathrm{d}S. \quad (34)$$

Hence, under constant temperature the change of the Gibbs free energy is given by the change of the entropy only.

4. Nucleation

4.1. What is nucleation?

As an application of thermodynamics to understand crystal growth, we study the nucleation following the approach given by Toschev [4]. Now, we study the nucleation phenomenon taking a birth of a water droplet in the vapor phase as an example. One can imagine the generation of rain drops in the sky. Often they nucleate around small dusts or some foreign molecules. If nucleation occurs around such foreign particles or molecules, it is called heterogeneous nucleation, whereas if the nucleation happens without the foreign particles and molecules, it is called homogeneous nucleation. In the following, we limit our discussion to homogeneous nucleation.

Homogeneous nucleation of water droplet happens if the vapor pressure of water is higher than the equilibrium vapor pressure, p_{eq}, that is defined as the equilibrium vapor pressure to an infinitely large water plane. In Fig. 8, one sees the schematic relationship between the radius of water droplet and the ambient vapor pressure at an equilibrium. The mathematical expression for the curve will be given later by Eq. (66). The radius of droplet in equilibrium with the ambient pressure is called the radius of critical nucleus and is denoted by r^*. The droplets with the size smaller than r^* will disappear under the ambient pressure on the broken line in the figure because keeping them stable at a higher ambient pressure is required. On the other hand, the droplets with the size larger than r^* will grow alone in size because the ambient pressure is higher than the equilibrium pressure of the droplets. Hence, the curve in Fig. 8 gives an unstable equilibrium condition for the droplet. This is the reason why the droplet on the curve is called critical.

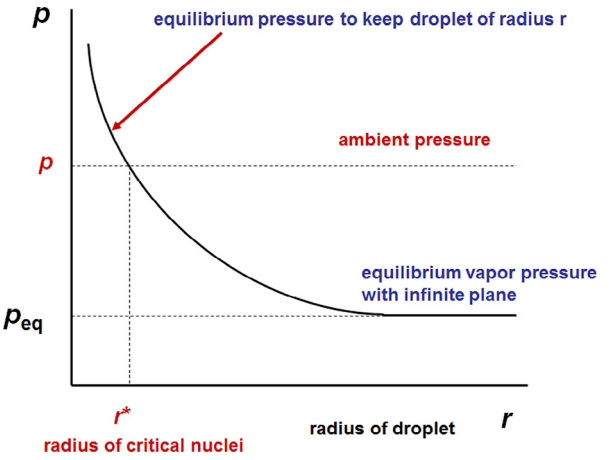


Fig. 8. Droplet radius r vs. equilibrium pressure p. p_{eq} is the equilibrium vapor pressure for infinitely large plane. The equilibrium droplet under a certain ambient pressure is called a critical nuclei and its radius is denoted by r^*.

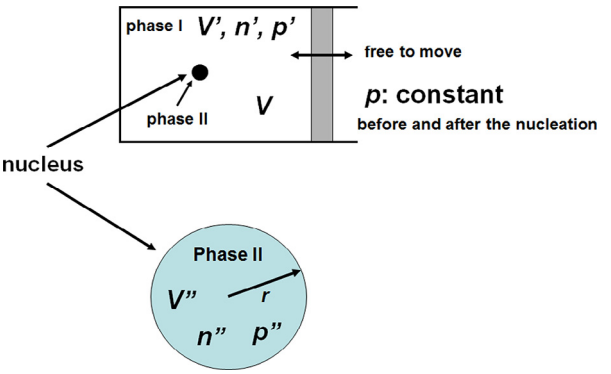


Fig. 9. Thermodynamic model of nucleation. A chamber of volume V is terminated by a freely movable piston at one end. In the chamber, water vapor of n' mol and of the pressure p' is contained (phase I, volume V') together with a water droplet of n'' mol and pressure p'' (phase II, volume V''). The outside of the chamber is surrounded by a very large volume of the pressure p.

4.2. Thermodynamics of nucleation

Now, let us consider a chamber ended by a freely movable piston as shown in Fig. 9. In the following, we will discuss the nucleation of water droplet from its vapor in mind to understand the nucleation phenomenon more easily. However, the understanding of the water nucleation can be applied for any other materials and phases.

As shown in Fig. 9, we consider a chamber of volume V in which water vapor (phase I, volume V') of n' mol and pressure p' and a nucleus (phase II, volume V'') of n'' mol and pressure p'' are contained. The Helmholtz free energy of the system, F, is given by:

$$\left.\begin{aligned} F &= F' + F'' + F_s \\ F_s &= \phi \end{aligned}\right\} \quad (35)$$

where F', F'' and F_s are respectively the Helmholtz free energy of phase I, that of phase II and the surface

free energy of the nucleus. When the system changes under a constant pressure, the Gibbs free energy takes the minimum. According to the definition of the Gibbs free energy, its change under constant pressure is given by

$$dG = dF + pdV, \tag{36}$$

where dF is given by

$$dF = dF' + dF'' + dF_s. \tag{37}$$

Here, dF', dF'', dF_s and dV are written down as:

$$\left.\begin{aligned} &dF' = \mu'(p')dn' - p'dV', \\ &dF'' = \mu''(p'')dn'' - p''dV'', \\ &dF_s = d\phi \\ &\text{and} \\ &dV = dV' + dV'' \end{aligned}\right\} \tag{38}$$

where $\mu'(p')$ and $\mu''(p'')$ denote respectively the chemical potentials of phase I and phase II. Hence, by substituting Eq. (38) into Eqs. (36) and (37), one gets

$$\begin{aligned} dG = {} & \mu'(p')dn' + \mu''(p'')dn'' + (p - p')dV' \\ & + (p - p'')dV'' + d\phi. \end{aligned} \tag{39}$$

Before and after the nucleation, the total number of water molecules is unchanged. Hence, the total mol of water molecules, n:

$$n = n' + n'' \tag{40}$$

should be constant. Now, we find

$$\left.\begin{aligned} &dn = dn' + dn'' = 0 \\ &dV' = n'dv' + v'dn' = n'dv' - v'dn'' \\ &\text{and} \\ &dV'' = n''dv'' + v''dn'' \end{aligned}\right\} \tag{41}$$

where v' and v'' are respectively molar volumes for phase I and phase II. Substituting Eq. (41) into Eq. (39) and using $dG = 0$ for an equilibrium, we get

$$\begin{aligned} & (p - p')n'dv' + \{[\mu''(p'') - \mu'(p')] + (p - p'')v'' \\ & \quad - (p - p')v' + (d\phi / dV'')v''\}dn'' \\ & \quad + [(p - p'') + d\phi / dV'']n''dv'' = 0. \end{aligned} \tag{42}$$

Eq. (42) should be true for any change of the system and this leads to:

$$\left.\begin{aligned} &p = p' \\ &\mu'(p') = \mu''(p'') \\ &\text{and} \\ &p'' - p' = d\phi / dV''. \end{aligned}\right\} \tag{43}$$

Eq. (43) indicates that (a) the pressure of phase I is equal to that of the outside, (b) the chemical potential of phase I is the same as that of phase II and (c) the outside and inside pressures of the liquid droplet are not the same but there is a difference which is given by the last equation of Eq. (43).

Assuming that the droplet is spherical (of diameter r) and that the surface free energy of the droplet is given by γ per unit area, we obtain:

$$\left.\begin{aligned} &\phi = 4\pi r^2\gamma \\ &\text{and} \\ &V'' = 4\pi r^3 / 3. \end{aligned}\right\} \tag{44}$$

Hence, we get:

$$d\phi / dV'' = 2\gamma / r = p'' - p'. \tag{45}$$

Here, we assume γ is constant and not the function of r. From Eq. (45), one sees the pressure difference between the inside and the outside of the droplet becomes small as r increases. In the extreme case where r goes to infinitely large, the pressure difference given by Eq. (45) vanishes namely at infinitely large water plane the outside and the inside pressure becomes equal and the outside vapor pressure is called as an equilibrium vapor pressure of the water.

4.3. Formation energy of critical nucleus

Again we consider a chamber which is ended by a movable piston like Fig. 9. We put n mol of water vapor in the chamber as shown in Fig. 10(a). Before nucleation, the system has the volume of V_1 and the pressure p which is the same as that of the outside as was shown in the previous section. At a certain time, a nucleus, which is a small water drop, is generated as shown in Fig. 10(b). All the variables before and after the nucleation are denoted respectively by suffixes of 1 and 2. Now, let us calculate the change of the Gibbs free energy, ΔG, before and after the nucleation, which will be given by:

$$\Delta G(n'') = G_2 - G_1 = F_2 - F_1 + p(V_2 - V_1) \tag{46}$$

where G_2, G_1, F_2 and F_1 are respectively the Gibbs free energies and the Helmholtz free energies after and before

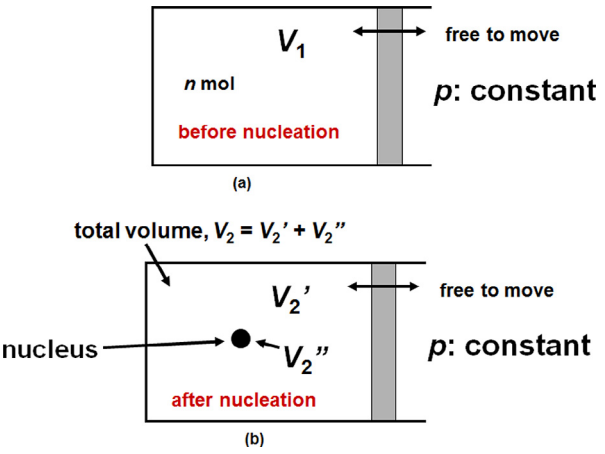


Fig. 10. Water vapor is contained in a chamber terminated by a freely movable piston. The upper (a) and the lower (b) figures denote the system respectively before and after the nucleation.

the nucleation. ΔG should be the function of the size of the nucleus and hence of n''. F_1 and F_2 are written as

$$\left.\begin{aligned} &F_1 = n\mu(p) - pV_1 \\ &\text{and} \\ &F_2 = n'\mu'(p) + n''\mu''(p'') - pV_2' - p''V_2'' + \phi, \end{aligned}\right\} \tag{47}$$

where μ denotes the chemical potential which is the Gibbs free energy of 1 mol and the marks ' and '' show the values respectively outside and inside of the nucleus. For simplicity, the subscripts for n and p are not used. We assume that the size of the nucleus is very small so that the vapor pressure before and after the nucleation is unchanged, namely it remains as p after the nucleation. Hence, we get

$$\left.\begin{aligned} &V_2 = V_2' + V_2'' \\ &n = n' + n'' \\ &V_2 \cong V_1 \\ &\text{and} \\ &\mu(p) \cong \mu'(p). \end{aligned}\right\} \tag{48}$$

By using Eqs. (47) and (48), one can rewrite Eq. (46) as:

$$\Delta G(n'') = [\mu''(p'') - \mu'(p)]n'' + (p - p'')V_2'' + \phi. \tag{49}$$

In Fig. 10(b), as previous calculation showed, if the nucleus is in equilibrium with the outside vapor phase, the chemical potential of the nucleus should be equal to that of the vapor phase, namely:

$$\mu''(p'') = \mu'(p). \tag{50}$$

Hence, the first term of the right hand side of Eq. (49) vanishes. Then, with Eqs. (44) and (45) we get the following equations for spherical nucleus,

$$\Delta G(n'') = \phi / 3 \tag{51}$$

and

$$\Delta G(r^*) = 4\pi r^{*2}\gamma / 3. \tag{52}$$

We have calculated the Gibbs free energy necessary to generate one nucleus which is in equilibrium to the ambient vapor phase. In other words, it is the Gibbs free energy required to generate a critical nucleus. To show this, we have used asterisk superscript in Eq. (52) as we saw in Fig. 8.

4.4. Free energy for creating non-equilibrium cluster

In the previous section, we obtained the Gibbs free energy for creating a nucleus which is in equilibrium with the ambient water vapor pressure. Hence, Eq. (52) is only valid on the curve in Fig. 8 which shows an equilibrium relationship between the water vapor pressure and the radius of the droplet. In this section, we calculate the Gibbs free energy for creating non-equilibrium cluster with radius smaller or larger than the critical radius. What is different from the discussion in section 4.3 is here we cannot use Eq. (50) to calculate Eq. (49). In other words, we are going to calculate the Gibbs free energy to generate a water cluster along the horizontal broken line in Fig. 8 which crosses the equilibrium curve at $r = r^*$.

For this calculation, we consider an infinitely large water plane with which water vapor is in equilibrium as shown in Fig. 11(a). We define the vapor pressure as p_{eq}. In the figure, Phase I and Phase II denote respectively vapor phase (mother phase) and liquid phase (growing phase). In (a), the vapor phase and the liquid phase are in equilibrium and hence, one gets:

$$\mu'(p') = \mu''(p''). \tag{53}$$

Furthermore, according to Eq. (45), we get:

$$\left.\begin{aligned} &p' = p'' = p_{eq} \\ &\text{and hence} \\ &\mu'(p_{eq}) = \mu''(p_{eq}). \end{aligned}\right\} \tag{54}$$

Therefore, for planer interface, at an equilibrium, both an inner pressure and an outer pressure take the same value which is the equilibrium pressure.

Now, let us consider the case where an ambient pressure, p, is higher than the equilibrium pressure, p_{eq}, and

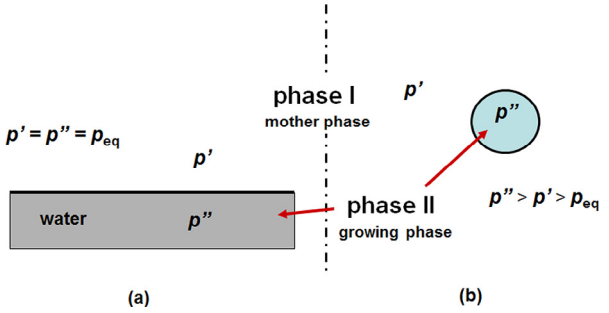


Fig. 11. Phase I is the mother phase, in this case water vapor, from which water droplet (phase II, growing phase) is generated. (a) When the pressure of the water vapor is in equilibrium with an infinitely large water plane, the pressure is called an equilibrium pressure and denoted by p_{eq} as we saw in Fig. 8. (b) When the vapor pressure is higher than p_{eq}, nucleation can happen. According to Eq. (45), inner pressure p'' is larger than the vapor pressure p'.

a cluster of radius r is generated as shown in Fig. 11(b). For such non-equilibrium cluster, one cannot assume that the first term in the right hand side of Eq. (49) is zero. Hence, the change of the Gibbs free energy before and after the generation of the cluster is given by:

$$\Delta G(n'') = [\mu''(p'') - \mu''(p_{eq})]n'' - [\mu'(p) - \mu'(p_{eq})]n'' + (p - p'')V'' + \phi \tag{55}$$

where we have used Eqs. (49), (54) and $p' = p$ and V'' instead of V_2'' which is the volume of the cluster. Assuming the liquid cluster is incompressible and the water vapor is ideal, we get, for the liquid cluster,

$$\mu''(p'') - \mu''(p_{eq}) = \int_{p_{eq}}^{p''} v''\mathrm{d}p = v''(p'' - p_{eq}) \tag{56}$$

and for the vapor phase,

$$\mu'(p) - \mu'(p_{eq}) = \int_{p_{eq}}^{p} v'dp = RT\ln(p / p_{eq}) \tag{57}$$

where v'' and v' are molar volumes respectively of the liquid cluster and the water vapor.

We define,

$$\Delta\mu = RT\ln(p / p_{eq}), \tag{58}$$

which is the difference in chemical potential of gases, the pressures of which are p and p_{eq}. Namely, $\Delta\mu$ is the chemical potential difference between the gas phases of (a) and (b) in Fig. 11. As is well known, $\alpha = p/p_{eq}$ and $\sigma = \alpha - 1$ are called respectively the supersaturation ratio and the supersaturation.

By substituting Eqs. (56) and (57) into Eq. (55) and with Eq. (58), one obtains:

$$\Delta G(n'') = [(p - p_{eq})v'' - \Delta\mu]n'' + \phi. \tag{59}$$

Since the molar volume of liquid is much smaller than that of the vapor, after some algebra one finds $(p - p_{eq})v'' \ll \Delta\mu$. This leads to:

$$\Delta G(n'') = \phi - \Delta\mu n''. \tag{60}$$

Hence, we get:

$$\Delta G(r) = 4\pi r^2\gamma - 4\pi r^3\Delta\mu / 3v''. \tag{61}$$

$\Delta G(r)$ is schematically drawn in Fig. 12. For $p > p_{eq}$, $\Delta\mu$ is positive and $\Delta G(r)$ takes maximum at $r = r^*$. At this radius,

$$d\Delta G(r) / dr|_{r=r^*} = 0 \tag{62}$$

should be held. Hence, we get

$$r^* = 2\gamma v'' / \Delta\mu \tag{63}$$

and

$$\Delta G^* = 16\pi v''^2\gamma^3 / 3\Delta\mu^2. \tag{64}$$

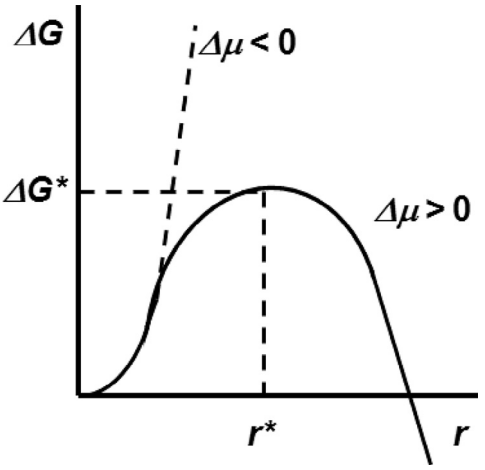


Fig. 12. The Gibbs free energy to generate a cluster of radius r under the vapor pressure of p. At an equilibrium, the Gibbs free energy takes an extremal value and its derivative becomes zero. This happens at $r = r^*$.

With Eqs. (63) and (64), one gets Eq. (52). Here, we have used ΔG^* for $\Delta G(r^*)$. This is the Gibbs free energy for generating a nucleus at an equilibrium with ambient vapor pressure, p. The cluster of $r < r^*$ once created by a local fluctuation of vapor pressure will disappear because the smaller cluster is more stable. In the same way, the cluster of $r > r^*$ will also disappear by increasing its size because the larger cluster is more stable. The cluster of $r = r^*$ is stable and is in equilibrium with the ambient vapor pressure. This cluster is called critical nucleus. For $\Delta\mu < 0$, as schematically shown by the broken curve in Fig. 12, there is no maximum and it means that no nucleus is generated.

With Eqs. (58) and (63), one gets:

$$RT\ln(p/p_{eq}) = 2\gamma v''/r, \tag{65}$$

and hence, p is given as a function of r as

$$p = p_{eq}\exp(2\gamma v''/RTr). \tag{66}$$

The curve which represents an equilibrium pressure in Fig. 8 is given by Eq. (66).

5. Thermodynamics for vapor growth

5.1. Law of mass action

Now, we consider one mol ideal gas. The volume, the temperature, the pressure, the internal energy and the entropy of the gas are denoted respectively by T, V, P, U and S. Then, we define the Gibbs free energy at a state 1 and 2 respectively by G_1 and G_2. The change of the Gibbs free energy between these two states under the same temperature is given by:

$$\begin{aligned} G_2 - G_1 &= U_2 - U_1 + P_2V_2 - P_1V_1 - TS_2 + TS_1 \\ &= -T(S_2 - S_1) \end{aligned} \tag{67}$$

where we have used the law of Boyle–Charles and the fact that U is constant under the constant temperature. By using Eq. (13) and the law of Boyle–Charles, we obtain

$$G_2 - G_1 = -RT(\ln P_1 - \ln P_2). \tag{68}$$

Taking the state 1 as a standard state, one gets the Gibbs free energy at an arbitrary state by:

$$G = (G_0 - RT\ln P_0) + RT\ln P \tag{69}$$

where G_0 and P_0 are respectively the Gibbs free energy and pressure at a standard state and G and P are those of the arbitrary state respectively.

Let us consider a chemical reaction of gases expressed for instance by:

$$aA(g) + bB(g) \Leftrightarrow cC(g) + dD(g) \tag{70}$$

where g denotes gas phase. Eq. (70) indicates that a mol of A and b mol of B react to give c mol of C and d mol of D. We denote the pressures of all gases at a standard state as $P_{0A} \sim P_{0D}$ and those at an arbitrary state as $P_{eA} \sim P_{eD}$. The Gibbs free energies of gases of A ~ D at an arbitrary state is given from Eq. (69) as

$$G_{ei} = (G_{0i} - RT\ln P_{0i}) + RT\ln P_{ei} \tag{71}$$

where the suffix i represents the gases of A ~ D.

If the reaction (70) proceeds toward the right hand side, the change of the Gibbs free energy of the whole system at an arbitrary state is given by:

$$\Delta G_e = -aG_{eA} - bG_{eB} + cG_{eC} + dG_{eD}. \tag{72}$$

At an equilibrium, ΔG_e should be zero. Hence, we get:

$$aG_{eA} + bG_{eB} = cG_{eC} + dG_{eD}. \tag{73}$$

By substituting Eq. (71) into Eq. (73), one gets:

$$\begin{aligned} &-aG_{0A} - bG_{0B} + cG_{0C} + dG_{0D} - RT\ln\left[(P_{0C})^c(P_{0D})^d / (P_{0A})^a(P_{0B})^b\right] \\ &= -RT\ln\left[(P_{eC})^c(P_{eD})^d / (P_{eA})^a(P_{eB})^b\right] = -RT\ln K. \end{aligned} \tag{74}$$

where K is an equilibrium constant. We choose all pressures at the standard state, P_{0i}, as 1 atm and by using

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 = -aG_{0A} - bG_{0B} + cG_{0C} + dG_{0D}, \tag{75}$$

we get

$$K = \exp(\Delta G_0/RT) = (P_{eC})^c(P_{eD})^d / (P_{eA})^a(P_{eB})^b, \tag{76}$$

which is well known as the law of mass action. Hence, if all G_{0i} at the temperature T and under 1 atm are given, one can calculate the equilibrium constant at the temperature T. One can find the table of equilibrium coefficients for almost all chemical reactions in data books or in journal papers.

5.2. Thermodynamic calculation of the vapor growth

5.2.1. Vapor growth in a closed tube

It is sometimes convenient to grow a crystal by a chemical reaction in an evacuated closed ampule because one

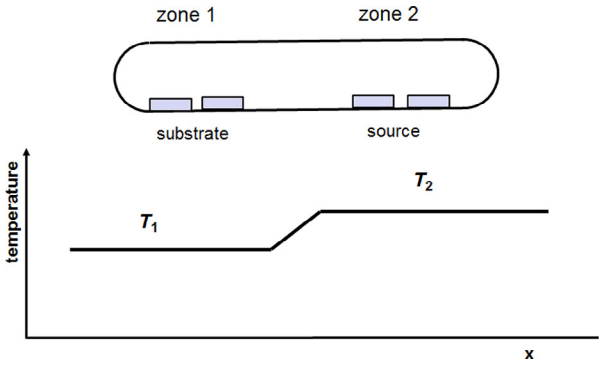


Fig. 13. Vapor growth in a closed tube. Typically source materials are put in a higher temperature zone kept at T_2 and substrate crystals are put in a lower temperature zone of T_1. In the tube some chemical such as halogen is put as a transport agent.

does not need to employ complicated gas flow system. Thermodynamic studies for obtaining the transport and the growth rates of materials have been conducted many years ago [5–8].

Let us consider the growth of GaAs by using iodine as a chemical transport agent [5]. Vapor growth in a closed tube is carried out in the temperature distribution as shown in Fig. 13. In this typical case, source materials are put in the higher temperature zone (zone 1) and the substrate crystals are put in the lower temperature zone (zone 1). According to the kind of reaction, the source materials are sometimes put in lower temperature zone. A chemical such as halogen is put in the tube to induce the material transport and the growth.

For the thermodynamic calculation, we assume,

(1) Chemical equilibrium is established in both zones,
(2) Gaseous molecules are transported by the concentration diffusion and the laminar flow which is caused by the volume change induced by the chemical reactions,
(3) The difference in T_1 and T_2 is not large, and
(4) Total pressure is constant in the whole tube.

Now, we consider the growth of a binary compound expressed as A_iB_h (s) by employing halogen. Then, we assume the chemical formula of the halide as $(A_i)_q X_{mi}$. In the usual case, often we see q = 1, so that we write the halide as $A_i X_{mi}$. For instance, when we use iodine for the growth of GaAs, the major gaseous halides are GaI and GaI_3. Therefore, if we denote them respectively as i = 1 and 2, $A_1 = A_2 = Ga$, X = iodine, $m_1 = 1$ and $m_2 = 3$. In the growth of compound semiconductors such as GaAs, the chemical reactions in the tube can be given by:

$$\left.\begin{aligned} &A_iB_h(s)+(1/2)m_iX_2(g)\Leftrightarrow A_iX_{mi}(g)+(1/k)B_{hk}(g)\\ &\text{and}\\ &B_h(s)\Leftrightarrow(1/k)B_{hk}(g)\Leftrightarrow(1/k')B_{hk'}. \end{aligned}\right\} \quad (77)$$

In the growth of GaAs, B_h is As and in typical case, k = 2 and k' = 4. In addition, a macroscopic stoichiometry of the compound requires:

$$\text{Total number of } A_i \text{ atoms} = \text{that of } B_h \text{ atoms in the whole tube,} \quad (78)$$

where we assumed source material is the same compound of the substrate crystal.

By giving an amount of halogen, one can calculate all partial pressures of gaseous species using Eqs. (77) and (78). In a practical calculation, one tentatively gives partial pressure of one species in one zone at first and calculates partial pressures of all other species in both zones then one calculates the amount of halogen in mol, M_X, to be put in the tube by:

$$M_X = \int (1/RT)\sum_i m_i p_i dv, \quad (79)$$

where the integral should be done in whole volume of the tube. Denoting $p_i^{(j)}$ as the partial pressure of the i-th species in j-th zone, we can approximate Eq. (79) by

$$M_X = \sum_{i,j} \left(V^{(j)}/RT^{(j)}\right) m_i p_i^{(j)}, \quad (80)$$

where $V^{(j)}$ and $T^{(j)}$ are respectively the volume and the temperature of the j-th zone.

The transport rate of the i-th gaseous species, J_i, is given by:

$$J_i = WC_i - D_i dC_i/dx, \quad (81)$$

where C_i, D_i and x are respectively the concentration and the diffusion coefficient of the i-th gaseous species and the position variable in the tube along the horizontal axis. C_i and its derivative by position are given as

$$\left.\begin{aligned} &C_i = p_i/RT\\ &\text{and}\\ &dC_i/dx = (1/RT)dp_i/dx. \end{aligned}\right\} \quad (82)$$

Then, we define T^{av} and p_i^{av} as the average values between two zones as:

$$T^{av} = \left(T^{(1)} + T^{(2)}\right)/2 \quad (83)$$

and

$$p_i^{av} = \left(p_i^{(1)} + p_i^{(2)}\right)/2. \tag{84}$$

The transport rate of halogen atoms included in the form of halides, in this case iodides, should be zero since iodine atoms are circulated in the closed tube and not deposited on the tube wall. Hence, we get:

$$\sum_i m_i J_i = 0. \tag{85}$$

Since the total pressure is constant everywhere, we get:

$$\sum_i dp_i / dx = 0. \tag{86}$$

By substituting Eq. (82) into Eq. (81) and using Eq. (85) we get W by:

$$W = \sum_i D_i m_i (dp_i / dx) \Big/ \sum_i m_i p_i. \tag{87}$$

If there are r species of halides (assume all gaseous species), in this case GaI and GaI_3, the transport rate of growth element in this case Ga, is expressed as:

$$J_{Ga} = \left(1/RT^{av}\right)\sum_i^r \left[-D_i (dp_i/dx) + p_i \sum_i D_i m_i (dp_i/dx) \Big/ \sum_i m_i p_i\right]. \left[\text{mol}/\text{cm}^2\text{s}\right] \tag{88}$$

We assume that all diffusion coefficients are equal and expressed by:

$$D = \left(T^{av}/T_0\right)^{1.5} D_0 \Big/ \sum_i p_i, \tag{89}$$

where D_0 is the diffusion coefficient at the temperature, T_0, and under the pressure of 1 atmosphere.

In Eq. (88), we employ the approximation,

$$dp_i / dx = \Delta p_i / L, \tag{90}$$

where L is the effective distance between two zones and Δp_i is given by

$$\Delta p_i = p_i^{(1)} - p_i^{(2)}. \tag{91}$$

Then, Eq. (88) is rewritten as:

$$J_{GaAs} = -\left(D_0 / LRT^{av}\right)\left(T^{av}/T_0\right)^{1.5} \sum_i^r \left[\left(\Delta p_i \sum_k m_k p_k^{av} - p_i^{av} \sum_j m_k \Delta p_k\right) / \sum_k p_k \sum_k m_k p_k^{av}\right]. \tag{92}$$

After the calculation of all $p_i^{(1)}$ and $p_i^{(2)}$, all values of Eq. (92) are known except D_0/L. Hence, by determining D_0/L by comparing the calculation with the experiment, one can obtain the transport rate, in this case, of GaAs which should be proportional to the growth rate.

5.2.2. *Vapor growth in a gas flow system*

When the vapor growth is carried out in an open tube as shown in Fig. 14, for the calculation of the growth rate, one assumes that a complete equilibrium is established in a central zone where substrates are located. We denote

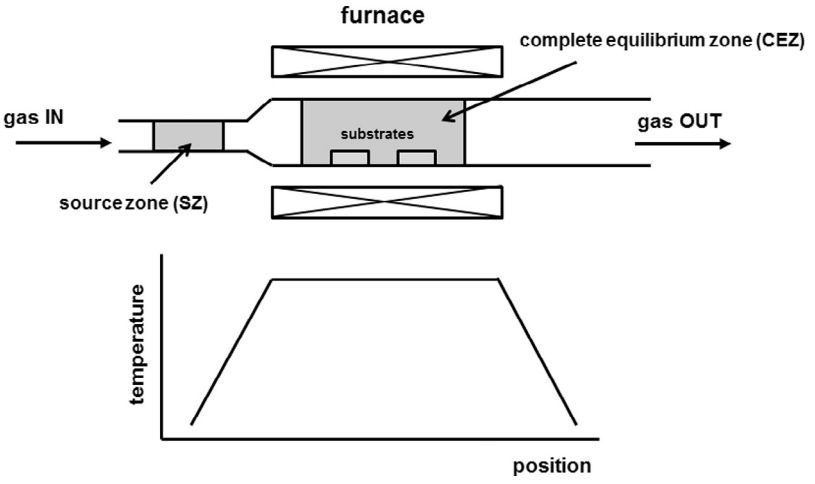


Fig. 14. Vapor growth in an open tube. For the analysis, we assume a central region in the tube is kept at an equilibrium.

the complete equilibrium zone as CEZ. In CEZ, the mass action law described by:

$$\ln K_i = \sum_j y_{ij} \ln p_j \tag{93}$$

is assumed to be established. Here, K_i, y_{ij} and p_j are respectively an equilibrium coefficient of the i-th chemical reaction, the numerical coefficient of each term (left-hand side negative and right-hand side positive) and pressure of the j-th gas species.

The total pressure,

$$P = \sum_j^n p_j \tag{94}$$

should be constant throughout the system and one atmosphere when the system is not evacuated nor pressurized.

Now, we take Si epitaxial vapor growth as an example and assume that $SiCl_4$ diluted in H_2 is introduced into the system. $J_{Si}{}^s$, the net flux of Si atoms in the source zone (SZ, see Fig. 14), which is involved in the form of $SiCl_4$ molecules, is given by:

$$J_{Si}^s = C_{Si}^s A^s v^s, \tag{95}$$

where $C_{Si}{}^s$, A^s, and v^s are respectively the concentration of Si atoms in the form of $SiCl_4$, a cross section of the tube and a flow velocity all in SZ.

In the same way, the net flux of Si at the exit of CEZ, $J_{Si}{}^g$, can be expressed by:

$$J_{Si}^g = C_{Si}^g A^g v^g, \tag{96}$$

where $C_{Si}{}^g$, A^g and v^g are respectively the concentration of Si atoms in the form of Si chlorides, the cross section of the tube and the flow velocity all at the exit of CEZ. The total amount of Si to be deposited in CEZ is given by $J_{Si}{}^s - J_{Si}{}^g$. One knows $C_{Si}{}^s$ and $C_{Si}{}^g$ by solving thermodynamic equations such as Eqs. (93) and (94) with initial conditions, but v^s and v^g are not easy to know because the chemical reactions will give volume changes. To avoid this difficulty, one can use the ratio of Si flux to the flux of an element which is not deposited in the CEZ. In this case, hydrogen and chlorine which do not deposit in the CEZ are such elements. We denote such an element by r. Then, the flux of r is given by

$$J_r^t = C_r^t A^t v^t, \tag{97}$$

where t denotes s or g.

Now, we take the ratio of $J_{si}{}^t$ to $J_r{}^t$, which is a normalized flux of Si, as:

$$q_{Si}^t = J_{Si}^t / J_r^t = C_{Si}^t / C_r^t = \sum_j^n \alpha_{jSi} p_j^t \Big/ \sum_j^n \alpha_{jr} p_j^t, \tag{98}$$

where α_{jk} shows the number of atom k contained in the j-th molecule and n is the total number of gaseous species involved in the calculation. For instance, for Si–HCl system, if k denotes Si and j does SiH_4, α_{jk} is 1, and if k denotes H, it is 4. By using the normalized flux, the condition for the growth to occur is given by

$$q_{Si}^s > q_{Si}^g. \tag{99}$$

For the atoms which are not deposited in CEZ, such as hydrogen and chlorine in this case, we have:

$$q_r^s = q_r^g, \tag{100}$$

for all r.

The growth rate of Si is given by:

$$G = J\alpha\beta, [\mathrm{g/min}] \tag{101}$$

where J, α and β are respectively, a flux of growth atoms in SZ, its fraction for the growth and a geometrical factor. J is given by

$$J = CMFX_{SiCl4} \tag{102}$$

where C, F and X_{SiCl4} are respectively, the concentration of total molecules in [mol/l], flow velocity [l/min] and mol fraction of $SiCl_4$ all in SZ and M is the atomic weight of Si. α is expressed as

$$\alpha = \left(q_{Si}^s - q_{Si}^g\right) / q_{Si}^s. \tag{103}$$

α is the factor calculated by the thermodynamics. The systematic calculation for the vapor growth of Si by using $SiCl_4$ source has been conducted by van der Putte et al. [9]. Hurle and Mullin carried out the thermodynamic calculation for the vapor growth of GaAs by GaAs–HCl system [10].

6. Summary

To understand the entropy, we have started from Boltzmann's entropy formula and showed that the entropy thus derived is identical with the entropy obtained thermodynamically. After defining the Helmholtz and the

Gibbs free energies, we calculated the Gibbs free energies for the formation of an equilibrium nucleus with ambient pressure following Toschev's approach taking a water droplet as an example. Then, the Gibbs free energy for the formation of a non-equilibrium cluster is calculated. It is demonstrated that the Gibbs free energy for the formation of the cluster takes the maximum as the radius is increased. The cluster at this maximum corresponds to a critical nucleus. The clusters smaller than the critical nucleus disappear while those larger grow continuously.

Thermodynamics is also a useful tool to obtain the rate of crystal growth in a vapor growth. The partial pressures of all gaseous species are calculated by solving equations given by the law of mass action and the initial conditions. The mathematical formulas for the growth rates in a closed ampoule and in an open tube are derived. In a closed ampoule, the materials are transported by the concentration diffusion and the laminar flow which is induced by the volume change of the reactions. The rate of the laminar flow is calculated by employing a conservation law of element which is not deposited in the system. The growth rate in gas flow system is also calculated by noting an element which is not deposited throughout the system. By calculating the ratio of the flux of growing element to that of non-depositing element, one can eliminate the effect of the geometrical change throughout the growth system.

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