CHAPTER

# Introduction—An Overview of Microstructure in Materials

It is only with the heart that one can see rightly; what is essential is invisible to the eye. —Antoine de Saint-Exupéry, The Little Prince (Katherine Woods translation)

# 1.1 Matter and Materials

"What are materials?" To address this question, let us first consider the difference between *materials* and *matter*. These words and the distinction between them have been defined in various ways. This book distinguishes *materials* from *matter* through the concept of *microstructure*.

For example, when asked about carbon, the element with the atomic number 6, scientists who are interested in the essence of matter may describe it in terms of its crystal structure, the binding forces between the atoms, and so on, imagining a diamond or fullerene structure (Fig. 1.1a). Engineers or researchers who are more concerned with applications of carbon may discuss it in terms of the strength of its microstructure, imaging the array of approximately 1 nm thick graphite crystalline ribbons in the carbon fibers used for tennis rackets or golf club shafts (Fig. 1.1b).

In the latter case, carbon is recognized as a *material*, with attributes defined by its *microstructure*. In the former case, on the other hand, carbon is recognized as *matter*, and absolutely perfect single crystals are the ideal objects for study because the principal purpose of investigation is the fundamental essence of the substance.

Now, as another example, consider macromolecules (polymers). Macromolecules are *matter* with linearly or reticularly combined unit molecules (i.e., monomers) consisting of  $10^3$  atoms or more; homopolymers consist of a single type of monomer, and copolymers consist of two or more types of monomers (Fig. 1.2a). Because most macromolecules are



Fig. 1.1 The distinction between *matter* (characterized by structure) and *materials* (characterized by microstructure)





amorphous, it may be unreasonable to draw an analogy between them and metals or ceramics. However, if one thinks of a monomer as a unit of matter, one can regard a homopolymer as being roughly analogous to a pure metal and a copolymer to a solid solution. These polymer structures are called *primary structures* in polymer science. In the first generation of polymers, such as nylon, invented in 1939, the main problems were designing and controlling the primary structures. However, certain polymers developed after 1970, such as Kevlar and supertough nylon, have controlled higher-order structures. Many of these polymers have molecular orientations that align as shown in Fig. 1.2(b1); others are alloys—combinations of two or more types of polymers—as shown in Fig. 1.2(b3). These examples indicate that higher-order structures of polymers are analogous to microstructures of metals or ceramics. Therefore, recently developed advanced polymers can be regarded as new materials that have been developed by *microstructure control* as the key technology.

Based on the previous discussion, the discipline of *materials science* would not exist today if not for the concept of microstructure. Therefore, *materials science* is distinguished from *matter science* (the branches of physical science devoted to the fundamental nature of matter) in this book; materials science is defined by the keyword of *microstructure* and matter science is not.

# 1.2 Matter Science: Its Short History (Ref 1)

#### 1.2.1 Democritus's Atomic Theory

The starring actor in Act One of the history of matter science is the ancient Greek philosopher Democritus (Democritos), who studied and wrote on a wide range of disciplines, including physics, music, and ethics. Democritus is perhaps best known for his Theory of Atoms, which states that all matter is composed of *atoms*, which cannot be divided (a = not, tom = division).

His atomic theory was dismissed by Aristotle (Aristoteles) and his followers, who denied the concept of discontinuity. However, Democritus's theory later evolved to Sir Isaac Newton's corpuscular theory and A.L. Lavoisier's element theory. Some 2000 years after the Roman Era, with the intervening Middle Ages and Renaissance periods, these concepts have developed to the present theory of elementary particles, representing a splendid revival of Democritus's basic theory.

#### 1.2.2 The Birth of Modern Chemistry

Although matter science stagnated in the Middle Ages, it developed rapidly in the latter half of the 18th century. The turning point was the discovery of oxygen by K.W. Scheele and J. Priestley in 1772. This discovery clarified the true character of oxidation and greatly accelerated the pace of discovery of new elements (see Fig. 1.3). This period also was the active age for the two scientists who founded modern chemistry, A. Lavoisier and J. Dalton (sometimes spelled Doulton).



Fig. 1.3 The development of "matter science" (chemistry) versus that of physics

It is important to note that only 14 elements (the 11 in Fig. 1.3 plus As, Sb, and P) had been discovered by the time in the 17th century when Galileo (Galileo Galilei) and Newton founded physics. Matter science (chemistry), because of its complexity, was modernized at a pace far behind that of physics.

In 1789, the year of the French Revolution, Lavoisier, a hero of chemistry revolution, published his *Traité Élémentaire de Chimie (Elementary Treatise of Chemistry*) in which he presented the first table of the elements in history by grouping 33 elements (10 of which were not elements but compounds) into four groups. Dalton followed Lavoisier's unfinished work in his *New System of Chemical Philosophy* (1803), which presented atomic symbols and the atomic weights for 20 elements. D.I. Mendeleev, in 1869, completed the periodic law of the elements by consolidating the work of Lavoisier and Dalton.

After that, the existence of the electron and the atomic nucleus was confirmed by J.J. Thomson (1903) and E. Rutherford (1911). Act Two in the drama of matter science history reached its climax in 1913 when N.H.D. Bohr presented his Atom Model, which represents the atom as a small, positively charged nucleus orbited by electrons.

# 1.3 Establishment of Metallography

## 1.3.1 Discovery of Microstructure

A "microstructure world" exists between the "macroscopic world" of daily life and the "atomic and molecular world" of the fundamental elements of matter (Fig. 1.4). It was R. Hooke, famous for his law of elasticity, who first investigated this world of microstructure.

Hooke was an excellent experimental scientist of the same generation as Newton. He influenced scientists in many fields by publishing in



Fig. 1.4 The microstructure world. The words *micro* and *macro* come from the Greek words *mikros* and *makros*. Here, the boundary between both of them is set at the resolution of the naked eye (0.1 mm).



Fig. 1.5 Micrographia by R. Hooke. (a) Cover. (b) A sketch of cork cells by Hooke

1665 his spectacular book *Micrographia*, which was full of sketches of microscopic objects (Fig. 1.5). In particular, his sketches of living cells represented monumental discoveries that later became the foundation of histology and bacteriology (Ref 2).



**Fig. 1.6** Historically important microstructure and macrostructure. (a) The pearlite structure of carbon steel (microscope image of Sorby's sample owned by the University of Sheffield, 500×) (b) The Widmanstätten structure of iron-nickel meteoric iron (the section was polished and etched, and lithographically printed)

In 1863, 200 years after the publication of *Micrographia*, H.C. Sorby discovered that the microstructure world exists also in steel and that the strength of steel is remarkably affected by its microstructure (Fig. 1.6a). However, it was not easy for others to believe that a microstructure similar to that of living cells exists in a lump of iron appearing as flat and smooth as *Noppera-bo*, a Japanese mythological faceless creature. For this reason, it was not until 1885, 22 years after Sorby's discovery, that his micrographs were first printed in *Journal of the Iron and Steel Institute* (Ref 3–5).

As for the macroscopic structures of a metal, water patterns (ripple marks) in Japanese swords and Damascene swords had long been widely noted. Moreover, the macrostructure of the iron meteorite (Fig. 1.6b) that was presented in 1820 by A. von Widmanstätten, the superintendent at the Technical Museum, Vienna, is as beautiful as recent award-winning metallographic photographs. However, his contribution is just an episode in the history of understanding microstructure because it occurred before basic concepts of crystallography were established, such as Miller index (1839) and Bravais lattice (1848) (Ref 6).

On the other hand, Sorby, born and raised in the town of iron and steel, Sheffield, England, applied methods for observing the microstructure of a rock to steel. He succeeded in establishing the basic metallographic method that is used today, involving a series of operations: reveal microstructure by grinding and etching a sample cut on a plane and observe it using a reflecting microscope.

It is said, "Science begins by observation." Sorby followed this path and thus became the father of metallography.

#### 1.3.2 From Observation to Science

Hooke and Sorby opened the door to the "microstructure world." The resolving power of today's electron microscopes has brought observers to the threshold of the "atomic and molecular world," below the nanometer scale.

However, one cannot understand the essence of "things" only from accumulating the results of observation. A philosophy beyond observation, especially one based on thermodynamics, was needed so that metallography might be made a science instead of just a technique.

Thermodynamics, the branch of physics and of chemistry that studies the effects of changes in temperature, pressure, and volume on physical systems at the macroscopic scale, was developed during the Industrial Revolution, which started in the latter half of the 18th century. Its First Law, "the law of conservation of energy," states that the change in the internal energy of a closed system is equal to the sum of the amount of heat energy supplied to the system and the work done on the system. Next, the concept of *entropy* (a measure of the energy in a system or process that is unavailable to do work) was established through an effort to improve the efficiency of engines. The Second Law of Thermodynamics posits that the total entropy of any isolated thermodynamic system tends to increase over time, approaching a maximum value. Thermodynamics as a way of thinking based on these two laws spread to various fields of science from the latter half of the 19th century to the beginning of the 20th century. Since that time it has led to the development of concepts of chemical thermodynamics, where the primary object is analyzing chemical reactions, and statistical thermodynamics, in which thermodynamic principles are joined with statistical mechanics (Fig. 1.7).

The pioneer of *thermodynamics of microstructure* was J.W. Gibbs of Yale University in the United States. He published a series of papers from 1873 to 1879 collectively titled *On the Equilibrium of Heterogeneous Substances*. In these papers Gibbs established or clarified basic concepts such as *phase*, *phase equilibrium*, and *chemical potential*, which are necessary to grasp the essence of microstructure, and defined his Phase Rule. In addition, he paid special attention to the concept of *interfaces*, describing accurate examinations of adsorption at an interface and internal pressure by interface tension (Ref 7).

These papers by Gibbs were full of very important ideas, but they were too difficult for scientists at the time to understand. However, they were spread in Europe through a German version by F.W. Ostwald (1891), or other versions, and have since developed into a vast system of study as shown in Table 1.1.

Because the main topics in Table 1.1 are explained in detail in the following chapters, the historical overview is discussed a little more here.



Fig. 1.7 The genealogy of thermodynamics and its development into the thermodynamics of microstructures

Year (A.D.) 1800 1900	Researcher	Subject of study				
1800	Gibbs	Advocate of thermodynamics of microstructures				
	Austen	Phase diagram of Fe-C system				
1900	Tammann	Textbook on physical metallurgy				
1920	Volmer-Weber	Thermodynamics of nucleation				
	Bragg-Williams-Gorsky	Ordering in solid solutions				
	Johnson-Mehl-Avrami-Kolmogorov	Equation of transformation				
1940	Zener-Smith	Pinning of grain boundaries				
1940	Cottrell	Locking of dislocations				
	Jackson	Roughness of solid/liquid interface				
	Cahn-Hilliard-Hillert	Spinodal decomposition				
1960	Lifshitz-Wagner	Ostwald ripening				
	Kaufman-Hillert	Calculation of phase diagrams				

Table 1.1 Thermodynamics of microstructure chronology

# 1.4 Flowering of Materials Science

### 1.4.1 Progress of Steel Technology

The fundamentals of metallography and microstructure founded by Sorby and Gibbs brought a revolution to research and development of materials, and new materials were put to practical use one after another.

It was metals technology, especially that of steel, that reached maturity first. Various special steels, such as high-strength steels and stainless steels, were developed from the end of the 19th century to the beginning of the 20th century (Fig. 1.8). In Japan, Kotaro Honda and Hiroshi Takagi invented the Kichizaemon Sumitomo (KS) magnet steel in 1917 and thus left their immortal footprints on the history of magnetic materials.

Year (A.D).	Metals	Ceramics	Synthetic polymers		
1800	Lavoisier-Doulton: establis	hment of modern chemistry	Dumas: methyl group		
			ring structure		
1850	Sorby: Gibbs:		Establishment of organic chemistry		
	Establishment of metallography	Graham: advocate Sigmondy: ultram	 e of colloid icroscope		
1900 High-strength steel Duralmin 18-8 stainless steel KS magnetic steel	High-strength steels Duralmin 18-8 stainless steel KS magnetic steel	E: Zakariazen: glass structure	stablishment of colloid science		
1050	Grain-oriented electromagnetic steel	OP magnet	Nylon		
1950	Shape memory alloy	Transparent alumina Optical fiber	Glass fiber reinforced plastics Carbon fiber reinforced plastics		
	Microalloyed steel	High-strength zirconia Superconducting oxides	Multiphase polymers		

Fig. 1.8 History of development in new materials. OP, oxide powder

### 1.4.2 Progress in Synthetic Polymers and Ceramics

Steel is a foundation of contemporary civilization because it is the basis for much of its infrastructure, such as buildings, bridges, and vehicles. However, not all structural materials are steels. In particular, nylon, invented by W.H. Carothers in 1937, was the first synthetic polymer material in history; its development can be considered as the trumpet call signaling the dawn of a New Materials Age.

Polymer science is a rising field that was first advocated as a distinct discipline by H. Staudinger in Germany around 1920, but it did not really get established until after World War II, as indicated in the right side of Fig. 1.8. However, synthetic polymers quickly advanced to the status of being one three major industrial materials, along with metals and ceramics, within only a quarter of a century after the development of nylon.

Unlike synthetic polymers, ceramics have been used in conventional forms such as brick, cement, and pottery since ancient times. However, these materials also benefited from the establishment of microstructure science, and many fine ceramics with various advanced applications were developed starting in the 20th century. An early example is the oxide powder magnet announced by Yogoro Kato and Takeshi Takei in 1933, marking the beginning of ceramic magnet technology; ceramics are now the most widely used magnetic materials.

### 1.4.3 Establishment and Development of Materials Science

The rapid appearance of the aforementioned new materials challenged the scientific establishment to reconsider the way that materials were studied, and in response the discipline of Materials Science was born in the 1960s.

The most important aim of Materials Science is to formulate a unified system of science and technology by rearranging and combining, as it were, in a cross-disciplinary manner, the "vertically structured" knowledge and techniques that have been established separately for the study and development of metals, ceramics, and polymers.

In early Materials Science, the study of metals was relatively more advanced, but today both ceramic science and polymer science have caught up to metals science, and now all three major categories of materials contribute advances that enlighten the others. For example, "polymer alloy" is a new material that has been developed by applying traditional metallurgical alloying techniques to polymers. In another example, the exceptional strength of glass fiber reinforced plastics pointed out the importance of "structure designing," and these concepts became the foundation for the development of high-strength dual-phase steel, which has high strength as well as excellent ductility.

In future materials development, it is increasingly important that we pay attention to the influence of a material on the global environment at each step of manufacturing as well as its properties and characteristics for its intended application (Ref 8).

It thus will become more important from now on to learn and apply the universality and sense of balance peculiar to Materials Science covering a broad range of view, especially thermodynamics, the subject of this book.

# Appendix: The Glass Fiber Reinforced Plastic "Magic Wand"

New records in the pole vault were set one after another in the 1960s. The key factor was the appearance of a pole made of fiber reinforced plastics; at the time it was called a "magic wand" (Fig. 1.9a).

The mechanics of the pole vault are complicated, and assuming direct conversion from the kinetic energy  $(mV_0^2/2)$  to the potential energy (mgh), and a bar height (h) of 5.1 m at the highest point, one can go over



**Fig. 1.9** The impact of materials technology on the sport of pole vaulting. (a) Relation between pole vault record and pole materials. (b) Mechanics of pole vault. (c) Strength of glass fiber. (d) Strength of glass fiber/nylon composite

when one approaches at the speed of 10 m/s, but this does not explain the record height of S. Bubka (6.14 m). Perhaps, the conclusive factor may be the force supplied by the moderate "bendability" and "restoring force" of the pole (Fig. 1.9b).

Glass will become remarkably stronger when it is drawn at a temperature over the softening point (approximately 1100 K) (Fig. 1.9c). Glass fiber reinforced plastic (GFRP) is a composite materials in which this fiber is arranged into plastic on the basis of structure design (Fig. 1.9d).

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## EXERCISES FOR FURTHER STUDY

- **1.1** Investigate and describe the progress of microstructure observation from the magnifying glass to the electron microscope.
- **1.2** Various characteristics of a material are categorized roughly into ones that do not change so much, such as "specific gravity," and others that change remarkably according to its microstructure, such as hardness. The former are called "structure insensitive," and the latter "structure sensitive." Choose three kinds of each characteristic and explain their relation to microstructure.
- **1.3** Describe the following inventions and discoveries and their impact on Materials Science from the standpoint of metallography: (1) Duralumin (1906), (2) thoriated tungsten (1917), (3) glass fiber reinforced plastic (circa 1940), (4) spheroidal graphite cast iron (1948), and (5) high-strength zirconia (1975).

CHAPTER

# Free Energy of Pure Substances

Why does a ball tumble down a slope? This question can be answered easily using the idea of "energy" and conservation of energy. Why does water become steam when it is heated? The ability to answer this question requires knowledge of another basic thermodynamic concept "entropy," besides energy. For example, the stability of a water and steam system composed of an immense number of  $H_2O$  molecules depends on not only the energy level of each molecule, but also the stability of  $H_2O$  molecules as a group. This chapter describes the basics of energy and entropy, and "free energy" including both.

# 2.1 Energy Relating to Microstructure

# 2.1.1 Units of Energy

There are various kinds of energies such as thermal energy, chemical reaction energy, electric energy, nuclear energy, and action energy of a living cell. However, it was confirmed by the experiments of James Prescott Joule in 1843 that these different energies can be exchanged with each other, and the first law of thermodynamics, which is the energy-conservation law, was founded.

In the modern metric system, the SI unit of energy is appropriately the joule (J), and it has the following relation to other SI units:

$$\begin{array}{l} \overset{energy}{J} = \overset{power}{\underset{newton}{N}} \times \overset{distance}{\underset{meter}{m}} = \overset{mass}{Kg} \times \overset{acceleration}{m/s^2} \times \overset{distance}{m} = \overset{pressure}{\underset{pascal}{Paa}} \times \overset{volume}{m^3} \\ = \overset{magnetic}{\underset{weber}{Wb}} \times \overset{current}{A} = \overset{electric potential}{\underset{volt}{V}} \times \overset{current}{\underset{ampere}{A}} \times \overset{time}{\underset{second}{S}} = \overset{charge}{\underset{coulomb}{C}} \times \overset{potential}{\underset{volt}{V}} \\ \end{array}$$

$$\begin{array}{l} (Eq \ 2.1) \end{array}$$

Heat energy is expressed as the thermochemical calorie, which by definition is exactly 4.184 J. The calorie used is the field of nutrition (Calorie) is, in fact, a kilocalorie. A nutritional Calorie is 4184 J (Ref 1).

The concept of an energy field is useful to describe how the position of an object dictates the energy ascribed to that object. In a gravitational field, the kilogram force (kgf) is the force applied over one meter to move the kilogram object that meter. That energy 1 kgf  $\cdot$  m equals 9.80665 J. By definition, the Newton (N) equals 0.101972 kgf  $\cdot$  and 1 N  $\cdot$  m is 1 J.

Likewise in an electric field, a charge moving across a voltage requires energy. A Coulomb (C) of charge moved one volt is a Joule. At the atomic level, the electron volt is the amount of energy needed to move one electron through one volt, that is, increase its potential one volt. The charge on the electron is  $1.602 \times 10^{-19}$  C, so 1 eV equals  $1.602 \times 10^{-19}$  J.

The energy per electron can be converted to the energy per quantity of matter with the concept of the mole. A mole is the mass (in grams) numerically equal to the molecular mass (weight) of a substance. It is the amount of atoms in a system that contains as many elementary units (Avogadro's number,  $6.02 \times 10^{23}$ ) as there are atoms of carbon in 0.012 kg of the pure nuclide <sup>12</sup>C. The elementary unit may be an atom, molecule, ion, electron, photon, or specified group of such units (Ref 2).

In Fig. 2.1 the energy content of matter is expressed both as eV per atom and kJ per mole. The conversion factor is

$$1 \text{ eV/atom} = (1.602 \times 10^{-19} \text{ C}) \cdot \text{V} \cdot 6.02 \times 10^{23}/\text{mol} = 96.48 \text{ kJ/mol}$$
(Eq 2.2)





Fig. 2.1 Comparison of energies concerning microstructures of a material (converted into values per atom for energies of dislocation and grain boundary) with chemical energies

**[Exercise 2.1]** The energy required for severe plastic deformation of pure iron pieces (about 8 kJ/mol) is mostly consumed as thermal energy (about 95%), and only about 5% of the energy (about 400 J/mol) is stored in the pieces as lattice defects. The breakdown is presumed to be (i) about 75% to multiplied dislocation ( $\Delta E_d$ ,), (ii) about 10% to excess vacancy ( $\Delta E_v$ ,), and (iii) the remainder of about 15% to strain energy. Solve for the density of dislocation ( $\rho_d$ ), and density of vacancy ( $\rho_v$ ), formed by severe plastic deformation, assuming the energy of dislocation per line of unit length\* to be  $\Delta e_d = 5 \times 10^{-9}$  J/m, and the energy of vacancy formation to be  $\Delta e_v = 1.5$  eV. (See Exercise 2.9 for the formation energy and the equilibrium concentration of vacancies.)

**[Answer]** The total energy of multiplied dislocation is  $\Delta E_{\rm d} = 400 \times 0.75 \text{ J/mol} = 300 \text{ J/mol}.$ 

The density  $\rho_d$  can be obtained by dividing this energy by the molar volume of pure iron  $V (7 \times 10^{-6} \text{ m}^3/\text{mol})$  to convert it into the energy per unit volume, and dividing it again by the energy of dislocation line per unit length  $\Delta e_d (5 \times 10^{-9} \text{ J/m})$ .

$$\rho_{\rm d} = \frac{\Delta E_{\rm d}}{V \cdot \Delta e_{\rm d}} = \frac{300 \text{ J/mol}}{7 \times 10^{-6} \text{ m}^3/\text{mol} \cdot 5 \times 10^{-9} \text{ J/m}} = 9 \times 10^{15}/\text{m}^2$$

This value is close to the limiting value of the dislocation density in a metal  $(10^{16}/m^2)$ .

Next, the total energy of vacancy is  $\Delta E_v = 40$  J/mol. Because the energy per vacancy is  $\Delta e_v = 1.5$  eV  $\times 9.648 \times 10^4$  J  $\cdot$  atom/mol according to Eq 2.2, the density is

$$\rho_{\nu} = \frac{\Delta E_{\nu}}{\Delta e_{\nu}} = \frac{40 \text{ J/mol}}{1.5 \times 9.648 \times 10^4 \text{ J} \cdot \text{atom/mol}} = 3 \times 10^{-4}/\text{atom}$$

This value is about three times as much as the equilibrium density  $(\sim 10^{-4})$  at the temperature just below the melting point.

<sup>\*</sup>The elastic strain energy of a dislocation per unit length can be approximated by  $E\mathbf{b}^2/2(1 + v)$ , where *E* denotes Young's modulus, v denotes Poisson ratio, and **b** is Burgers vector. It can be estimated that  $\Delta e_d \approx 5 \times 10^{-9}$  J/m because  $E = 200 \times 10^9$  Pa,  $v \approx 0.28$ ,  $\mathbf{b} = 2.5 \times 10^{-10}$  m for body-centered cubic (bcc) Fe. The value can be converted into the dislocation energy per atom length (7.7 eV) if it is multiplied by one interatomic distance  $2.5 \times 10^{-10}$  m. The dislocation energy shown in Fig. 2.1 is the converted value.

# 2.1.2 Energy of Atoms and Molecules and Macroscopic Energy (Ref 3,4)

**Internal Energy of Gas Molecules.** The total of kinetic energy of atoms or molecules that compose a material and potential energy such as the binding energy between atoms is called internal energy (U). A physicist, D. Bernoulli, in 1738 in Switzerland related pressure of the gas and internal energy of the gas molecule and opened the way to "the kinetic theory of gases" by James Clark Maxwell after about 100 years.

**[Exercise 2.2]** Show that the internal energy of monatomic ideal gas can be expressed as Bernoulli's equation:\*

$$U$$
gas =  $(3/2)PV = (3/2)RT$  (Eq 2.3)

where P, V, and T are the system parameters (pressure, volume, and temperature) and R is the universal gas constant.

**[Answer]** If a monatomic gas is considered a group of point particles, each with mass (*m*) flying about in a disorderly manner, the internal energy per mole is the total kinetic energy of these particles, and it can be approximated by

$$U$$
gas =  $(1/2) m(\bar{v})^2 \cdot N_0$  (Eq 2.4)

Here,  $(\bar{v})^2$  is the mean (average) velocity of particles squared.  $N_0$  is Avogadro's constant.

As shown in Fig. 2.2(a), notice one of  $N_0$  particles (the black point) enclosed in a piston of height *h*, cross section *A*, and volume, V = Ah. Let the velocity components in the directions X-Y-Z be  $v_X v_Y v_Z$  (m/s). The frequency at which particles collide with the ceiling side of the piston at the unit time is  $v_Z/2h$ . The change in the momentum per collision is  $2mv_z$ . Therefore, the change of the momentum per unit time is  $2mv_z \cdot v_z/2h = mv_z^2/h$  (kg  $\cdot$  m/s<sup>2</sup>).

\*Equation 2.3 is applicable to the case of monatomic molecules (inert gases such as He, Ar, or metallic gases of Fe, Cu, and so on), and its general formula can be expressed as follows because energies of atomic vibration and rotation in molecules are to be added in cases of gases of polyatomic molecules (H<sub>2</sub>, H<sub>2</sub>O, and so on) that have more than two atoms bound together.

$$U^{\text{gas}} = (f/2)PV = (f/2)RT$$
 (Eq 2.3a)

Here, f is the degrees of freedom of motion in a molecule,  $f \approx 5$  in case of diatomic molecules such as H<sub>2</sub>, and f = 6 to 13 in cases of triatomic molecules such as H<sub>2</sub>O.



**Fig. 2.2** The internal energy  $(\Delta U)$  of monatomic ideal gases. (a) Gas at constant temperature (*T*) and pressure (*P*). The change in energy (*Q*) and temperature according to heating at (b) constant pressure and (c) constant volume.



Fig. 2.3 Enthalpy according to grain-boundary or interface tension, peculiar to microstructures.

Because the force (N) = the momentum change per unit time (kg  $\cdot$  m/s<sup>2</sup>) according to particle dynamics, the pressure (*P*) by collision of N<sub>0</sub> molecules (the force per unit area) can be expressed by

$$P = m \sum_{1}^{N_0} v_z^2 / Ah$$
$$P = \frac{m \cdot N_0 \bar{v}^2}{3V} \left( N/m^2 = Pa \right)$$
(Eq 2.5)

Here, it is assumed that

$$\sum_{1}^{N_0} v_z^2 = \sum_{1}^{N_0} v_x^2 = \sum_{1}^{N_0} v_y^2 = \frac{N_0}{3} \bar{v}^2$$

by isotropy at the speed.

From Eq 2.4 and 2.5, the relation of  $P = \frac{2}{3} Ugas/V$  can be obtained, and if the ideal gas equation PV = RT is used, Bernoulli's equation in question can be obtained.

Because  $m \cdot N_0 = M$  corresponds to molecular weight, the following relation is obtained by Eq 2.3 and 2.4:

$$\bar{v}^2 = 2U \text{gas}/M = 3RT/M \tag{Eq 2.6}$$

The mean square velocity of ideal gas molecules is understood to be proportional to the absolute temperature T.

**Enthalpy of Gas Molecules.** The energy H that is the combination of PV and internal energy U is called an enthalpy.\*

$$H = U + PV \tag{Eq 2.7}$$

The following exercise using the ideal gas helps explain the meaning of this energy.

**[Exercise 2.3]** Investigate the energy balance when the ideal gas is heated on the condition of (i) constant pressure ( $\Delta P = 0$ ) and (ii) constant volume ( $\Delta V = 0$ ), and compare the increases in temperature.

**[Answer]** (i) Because not only the internal energy of gas molecules increases from U to  $U + \Delta U$  but also the volume expands from V to  $V + \Delta V$ , the energy balance can be expressed at constant pressure:

Heat		Change		Work		Change	
quantity		of		to		of	
from		internal		outside		enthalpy	
outside		energy					
$\Delta Q$	=	$\Delta U$	+	$P \cdot \Delta V$	=	$\Delta H$	(Eq 2.8)

Therefore, the energy-conservation law at constant pressure holds with regard to H (Fig. 2.2b).

(ii) On the other hand, because the work to outside is  $P \cdot \Delta V = 0$  when it is heated without changing the volume, all of the energy by heating is converted into internal energy as in the following equation at constant volume:

<sup>\*</sup>The term *PV* in Eq (2.7) often plays the leading part in thermodynamics of microstructures. For example, a polycrystalline material of mean grain radius  $\bar{R}$  has an excessive enthalpy  $\Delta H = 2\sigma V/\bar{R}$  by internal pressure  $\Delta P = 2\sigma/\bar{R}$  according to grain-boundary tension  $\sigma$  to a single crystal (Fig. 2.3a). Crystal nuclei formed in a liquid phase (radius  $\bar{r}$ ) and apexes of crystals (radius of curvature  $\bar{r}$ ) also have an excessive enthalpy  $\Delta H =$  $2\sigma V/\bar{r}$  according to interface tension  $\sigma$  (Fig. 2.3 b). As a result, grain growth occurs in (a), and supercooling can be observed in (b). See Sections 5.2 "Gibbs-Thomson Effect" and 8.1 "Basic Subjects of Nucleation" for details.

Heat	Change of	
quantity	internal	
from	energy	
outside		
$\Delta Q$	$= \Delta U$	(Eq 2.9)

Therefore, the energy-conservation law at constant volume holds with regard to U (Fig. 2.2c).

When Eq 2.8 and 2.9 are applied to Bernoulli's equation (Eq 2.3) of monatomic ideal gas, the rise in temperature  $\Delta T$  by heating can be obtained:

(i) at constant pressure: 
$$\Delta Q = \Delta H = (5/2)R \cdot \Delta T$$
 (Eq 2.8a)

(ii) at constant volume: 
$$\Delta Q = \Delta U = (3/2)R \cdot \Delta T'$$
 (Eq 2.9a)

Therefore,  $\Delta T' = (5/3)\Delta T$  and the rise in temperature at constant volume is larger.

#### 2.1.3 Heat Capacity and Enthalpy of Transformation (Ref 5)

Heat Capacity at Constant Volume and Constant Pressure. The heat quantity (per mole) that is required to raise the temperature of a substance by 1 K is called the heat capacity. However, it is also called specific heat (per unit mass) or molar heat in physics.

There are two kinds of heat capacity:

Heat capacity at constant volume: 
$$C_V = \left(\frac{\Delta Q}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$
 (Eq 2.10)

Heat capacity at constant pressure: 
$$C_P = \left(\frac{\Delta Q}{\Delta T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$
 (Eq 2.11)

When these equations are integrated, one can obtain the equations to calculate U and H from the values of  $C_V$  and  $C_P$  respectively:

Internal energy: 
$$U = U_0 + \int_0^T C_V dT$$
 (Eq 2.12)

Enthalpy: 
$$H = H_0 + \int_0^T C_P dT$$
 (Eq 2.13)

Here  $U_0$  and  $H_0$  are values at T = 0 K.

Because the value of  $C_P$  under ordinary pressure has been measured precisely for years and an enormous store of data has accumulated, the value of *H* at each temperature can be obtained by Eq 2.13. On the other hand, because the analysis on the thermal vibration energy of a crystal is carried out on condition that interatomic distance is constant as described in Section 2.3, the obtained theoretical value is  $C_V$ .  $C_P$  and  $C_V$  are converted mutually by\*

$$C_P - C_V = \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \cdot \left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\alpha^2 V}{\beta} \right) T \qquad (\text{Eq 2.14})$$

Here,  $\alpha = (\partial V / \partial T)_P / V$  is the volumetric thermal expansion coefficient and  $\beta = -(\partial V / \partial T)_T / V$  is the isothermal compressibility.

**[Exercise 2.4]** Show that the following relation of J.R. Mayer (1842) is valid between  $C_P$  and  $C_V$  for the ideal gas.

$$C_P = C_V + R \tag{Eq 2.19}$$

**[Answer]** From the ideal gas equation PV = RT, the volumetric thermal expansion coefficient  $\alpha$  and the isotropic compressibility  $\beta$  of the ideal gas are

\*Equation 2.14 can be derived; at first, from Eq 2.11:

$$C_{\rm P} = (\partial H/\partial T)_P = (\partial U/\partial T)_P + P(\partial V/\partial T)_P$$
 (Eq 2.15)

If U is regarded as a function of V and T,

$$(\partial U/\partial T)_P = (\partial U/\partial V)_T \cdot (\partial V/\partial T)_P + (\partial U/\partial T)_V = (\partial U/\partial V)_T \cdot (\partial V/\partial T)_P + C_V$$
(Eq 2.16)

The first part of Eq 2.14 can be obtained by rearranging Eq 2.15 and 2.16.

Next, if the relation between entropy *S* and internal energy *U* (to be described later)  $\Delta U = T \cdot \Delta S - P \cdot \Delta V$  and one of Maxwell relations  $(\partial S/\partial V)_T = (\partial P/\partial T)_V$  are used:

$$(\partial U/\partial V)_T + P = T(\partial S/\partial V)_T = T(\partial P/\partial T)_V$$
 (Eq 2.17)

Because  $(\partial V/\partial T)_P dT + (\partial V/\partial P)_T dP = 0$  at constant volume ( $\Delta V = 0$ ),

$$(\partial P/\partial T)_V = -(\partial V/\partial T)_P/(\partial V/\partial P)_T = \alpha/\beta$$
 (Eq 2.18)

Rearranging Eq 2.17 and 2.18, the second part of Eq 2.14 can be obtained.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{T}$$
$$\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{P}$$

When these are substituted into Eq 2.14, Mayer's equation can be obtained:

$$C_P - C_V = \left(\frac{\alpha^2 V}{\beta}\right) \cdot T = \frac{PV}{T} = R$$

Because the heat capacity at constant volume of the ideal gas is  $C_V = (f/2) R$  according to Eq 2.3a, the difference (*R*) between  $C_P$  and  $C_V$  is quite large. However, in case of a solid, because  $C_V \approx 3R$  as mentioned in Section 2.3 but  $\alpha^2 V/\beta \approx 10^{-3} \text{ J/K}^{-2} \cdot \text{mol}$  in Eq 2.14, the difference between  $C_P$  and  $C_V$  is only about 10% even at temperatures near the melting point.

**Enthalpy of Transformation.** When a substance is heated or cooled, transformations such as fusion, solidification, evaporation, or condensation will occur, and absorption or emission of a specific heat quantity can be observed. This heat quantity was called "latent heat" in the past. However, because latent heat is the change of enthalpy in accordance with phase transformation as described, it has recently been called the enthalpy of melting, the enthalpy of evaporation, or the enthalpy of transformation as a generic name.

**[Exercise 2.5]** The enthalpy of boiling for H<sub>2</sub>O is  $\Delta H_b = 40.7$  kJ/mol, and the enthalpy of melting is  $\Delta H_m = 6.0$  kJ/mol. Investigate the components of these heat quantities.

**[Answer]** First, the enthalpy change in accordance with the phase transformation from water to water vapor can be classified as (i) the energy required to cut the mutual bindings of H<sub>2</sub>O molecules and to change them into vapor molecules  $\Delta U_{\rm b}$  and (ii) the energy required for the expansion of volume  $P \cdot \Delta V$ . Because  $\Delta V$ (water  $\rightarrow$  vapor)  $\approx V_{\rm vapor}$ , the value for (ii) can be estimated:

$$P \cdot \Delta V \approx P \cdot V_{\text{vapor}} \approx R \cdot T_{\text{b}} \approx 3.1 \text{ kJ/mol}$$

Therefore, most (about 90%) of  $\Delta H_b$  of boiling enthalpy is consumed by the internal energy change  $\Delta U_b$  to cut the intermolecular bindings of H<sub>2</sub>O.

$$\Delta H_{\rm b}(\text{water} \rightarrow \text{vapor}, 40.7 \text{ kJ/mol}) = \Delta U_{\rm b}(37.6 \text{ kJ/mol}) + P \cdot \Delta V(3.1 \text{ kJ/mol})$$



**Fig. 2.4** (a) Enthalpy ( $\Delta H$ ) at ordinary pressure and (b) heat capacity at constant pressure of H<sub>2</sub>O. The heat capacity of water is abnormally large. In case of mercury, for instance,  $C_P$  is 27.7 J/K mol.

Next, the volume change is  $\Delta V$  (ice  $\rightarrow$  water) < 0 in the case of phase transformation from ice to water. However, because  $P \cdot \Delta V = -0.17$  J/mol and it is very small, the enthalpy of melting  $\Delta H_{\rm m}$  is approximately equal to the change of internal energy  $\Delta U_{\rm m}$ .

$$\Delta H_{\rm m}({\rm ice} \rightarrow {\rm water}, 6.0 {\rm kJ/mol}) \approx \Delta U_{\rm m}$$

As is generally known, the heat capacity of water is  $C_P$  (water) =1 cal/g • K = 75.3 J/K mol. This value is about twice as large as the heat capacity of ice as shown in Fig. 2.4(b), and it is remarkably large compared to the values of heat capacity for ordinary liquids (0.9 to 1.2 times that of solids). The cause of this anomaly is thought to be the hydrogen bonds between H<sub>2</sub>O molecules.

The enthalpy of melting and the enthalpy of evaporation of a metal is in general approximately proportional to the melting point  $T_{\rm m}$  and the boiling point  $T_{\rm b}$  and the following general rules for them are: R.E. Richards' rule (1897) for enthalpy of melting:

$$\Delta H_{\rm m} \approx RT_{\rm m} \tag{Eq 2.20}$$

F.T. Trouton's rule (1884) for enthalpy of boiling:

$$\Delta H_{\rm b} \approx 92T_{\rm b} \tag{Eq 2.21}$$

Here, the coefficient R in the Richards rule is the gas constant (8.314 J/K  $\cdot$  mol).

According to Eq 2.22 in the next section, the ratio of the enthalpy change  $\Delta H$  and the temperature *T* corresponds to the change of "entropy"  $\Delta S$ . Therefore, Eq 2.20 and Eq 2.21 can be expressed as



Fig. 2.5 Richards' rule and Trouton's rule.

Entropy of melting:  $\Delta S_{\rm m} = \Delta H_{\rm m}/T_{\rm m} \approx R$ Entropy of boiling:  $\Delta S_{\rm b} = \Delta H_{\rm b}/T_{\rm b} \approx 92$ 

Metals fit well the Richards rule, as shown in Fig. 2.5(a). However, the value of  $\Delta S_{\rm m}$  of a semiconductor or a semimetal (Si or Bi) or a compound (NaCl, etc.) is considerably larger than *R*. Because "entropy" is the parameter of order, the entropy change of melting in the case of NaCl crystal of *B*1 structure or Si crystal of the diamond type is larger than that in the case of a metallic crystal of a simple structure.

On the other hand, the Trouton entropy rule can be applied to not only metals but also  $H_2O$  and NaCl as shown in Fig. 2.5(b). Perhaps it is supposed that the change of order is almost equal when a liquid is transformed into a gas because a liquid itself has no structure.

# 2.2 Entropy and Free Energy (Ref 3, 4)

The phenomenon of a ball rolling down a slope can be explained by the concept of "energy" as described in the opening of this chapter. However, why does the phase transformation happen? It is necessary to understand "entropy" in order to answer that question.

This "entropy S" was a name derived from a Greek word "trope" that means "change," and it was defined by R.J.E. Clausius in 1865 as

$$\Delta S = \Delta Q/T \tag{Eq 2.22}$$

Here,  $\Delta Q$  is the heat quantity that is absorbed quasi-statically by the system of interest.



Fig. 2.6 Stability condition of a substance at constant temperature and constant pressure

#### 2.2.1 Stability Condition in Thermal Equilibrium

In general, the second law of thermodynamics is called "law of increase of entropy" or "maximum entropy principle." However, because this law is the principle of an isolated system insulated from heat, one should consider "the total entropy increases" of both the sample and the heat bath in the case of a sample in a heat bath (Fig. 2.6). Therefore, a basic inequality is

$$\Delta S_{\text{total}} = \Delta S_{\text{sample}} + \Delta S_{\text{heat bath}} \ge 0 \tag{Eq 2.23}$$

Temperature *T* and pressure *P* do not change if the heat bath absorbs a very small amount of heat quantity  $\Delta Q$  from the sample because the heat capacity of the heat bath is usually very large compared to that of the sample. Therefore, by the definition of Eq 2.22,

$$\Delta S_{\text{heat bath}} = \frac{\Delta Q_{\text{(sample} \to \text{heat bath)}}}{T}$$
(Eq 2.24)

On the other hand, because the sample loses not only the heat quantity  $\Delta Q$  but also the energy of work  $P \cdot \Delta V_{\text{sample}}$ ,

$$\Delta U_{\text{sample}} = -\Delta Q_{\text{(sample} \rightarrow \text{heat bath)}} - P \cdot \Delta V_{\text{sample}}$$
(Eq 2.25)

When the enthalpy H = U + PV is used, Eq 2.25 can be rewritten as

$$\Delta Q_{\text{(sample} \rightarrow \text{heat bath)}} = -\Delta H_{\text{sample}}(\text{constant temperature and constant pressure})$$
(Eq 2.26)

When Eqs 2.23, 2.24, and 2.26 are rearranged, the following equation can be obtained:

$$\Delta S_{\text{total}} = \Delta S_{\text{sample}} - \frac{\Delta H_{\text{sample}}}{T} = -\frac{\Delta H_{\text{sample}} - T \cdot \Delta S_{\text{sample}}}{T}$$
(Eq 2.27)

 $\geq$  0(constant temperature and constant pressure)

Here, the Gibbs free energy G is defined:

$$G = H - TS \tag{Eq 2.28}$$

Because  $\Delta G = \Delta H - T \cdot \Delta S$  at a constant temperature and constant pressure, Eq 2.27 will become

$$\Delta G_{\text{sample}} \leq 0$$
 (constant temperature and constant pressure) (Eq 2.29)

Therefore, the only change that will occur is when Gibbs free energy G of the material decreases at a constant temperature and constant pressure. In other words, the following equation is the condition of stability in the state of the heat equilibrium.\*

 $G_{\text{sample}} = \text{minimum}$  at constant temperature and constant pressure (Eq 2.30)

**[Exercise 2.6]** Find out the relational equation between the Gibbs free energy G and the heat capacity at constant pressure  $C_P$ . Moreover, show that the relational curve between G (ordinate) and T (abscissa) is downward sloping and concave.

**[Answer]** The relational equation of the enthalpy at constant pressure H and the heat capacity  $C_P$  is according to Eq 2.13,

$$H = H_0 + \int_0^T C_P dT$$

Here,  $H_0$  is the value of H at T = 0 K. On the other hand, because the entropy change by heating is

$$\Delta S_{\text{sample}} = \Delta Q(\text{heat bath} \rightarrow \text{sample})/T = C_P \cdot \Delta T/T$$

the following equation can be obtained:

$$S = S_0 + \int_0^T (C_P/T) dT$$
 (Eq 2.31)

Here, the entropy  $S_0$  at T = 0 K is  $S_0 = 0$  according to the third law in the case of a pure substance.

\*The stability condition at constant temperature and constant volume is that Helmholtz free energy  $F = U - TS = \min$ .



**Fig. 2.7** Diagrams of (a) enthalpy, (b) entropy, and (c) free energy of a pure substance. Thick lines indicate the stable phase and the thin lines the metastable phase.

Therefore, the relational equation of G and  $C_P$  can be expressed as

$$G = H - TS = H_0 + \int_0^T C_P dT - T \int_0^T C_P / T dT$$
 (Eq 2.32)

When Eq 2.32 is differentiated with respect to T, the following two equations can be obtained:

$$\left(\frac{\partial G}{\partial T}\right)_{P} = -\int_{0}^{T} (C_{P}/T)dT = -S$$

$$\left(\frac{\partial^{2}G}{\partial T^{2}}\right)_{P} = -C_{P}T$$
(Eq 2.33)

Because both S and  $C_p$  always have positive values,  $(\partial G/\partial T)_P < 0$  and  $(\partial^2 G/\partial T^2)_P < 0$ . Therefore, the relation curve of G and T is downward sloping and concave as shown in Fig. 2.7(c).

Because the thermodynamic functions that indicate the stability of the substance were all present, consider why the phase transformation occurs. Since the stronger the binding between atoms in a phase becomes and the "denser" the phase becomes, the lower the enthalpy is, then  $H_{\text{solid}} < H_{\text{liquid}} < H_{\text{gas}}$  when the solid, the liquid, and the gas are compared. On the other hand, since the "coarser" the phase becomes the larger the entropy is, then  $S_{\text{solid}} < S_{\text{gas}}$ .

In the Gibbs free energy G = H - TS, the H term is a leading part in the low-temperature region where T is small. Because the term TS

becomes a leading part in the high-temperature region where T is large, the order of the G value is reversed.

```
Low temperature: G_{\text{solid}} < G_{\text{liquid}} < G_{\text{gas}}
High temperature: G_{\text{solid}} > G_{\text{liquid}} > G_{\text{gas}}
```

As a result, the phase will be transformed from the "dense" solid to the "coarse" liquid and farther to gas in accordance with the rise in temperature (Fig. 2.7).

#### 2.2.2 Boltzmann Entropy Relation

What is entropy? In 1877 Boltzmann presented a concise equation to quantify this difficult question:

$$S = k_{\rm B} \ln W \tag{Eq 2.34}$$

Here,  $k_{\rm B}$  is the Boltzmann constant and W is the total microscopic states of an atomic group forming a system. To understand the meaning of Eq 2.34, one should consider the following exercise.

**[Exercise 2.7]** Obtain the difference of entropies between the case I where a container of volume V is separated into two parts by a partition and  $N_0$  gas molecules occupy only one of the parts (A), and case II where the partition is removed and the gas molecules are equal in both parts A and B. Consider the Boltzmann relation (Eq 2.34). Moreover, obtain the entropy change by the Clausius equation (Eq 2.22) considering that the change of state I  $\rightarrow$  state II is an expansion of 1 mole of the ideal gas and compare it with the result above (Fig. 2.8).



Fig. 2.8 Comparison of entropies obtained from the Boltzmann relation and from classical thermodynamics.

**[Answer]** In case II where the partition is removed, there are two possibilities. The molecules exist in either A or B. If the total of microscopic states of I is  $W_{I}$ , the total of II is

$$W_{\mathrm{II}} = W_{\mathrm{I}} \times 2^{N_0}$$

Then the entropy in state II by Eq 2.34 is

$$S_{\mathrm{II}} = k_{\mathrm{B}} \ln W_{\mathrm{II}} = k_{\mathrm{B}} \ln W_{\mathrm{I}} + k_{\mathrm{B}} \ln 2^{N_0} = S_{\mathrm{I}} + k_{\mathrm{B}} \ln 2^{N_0}$$

Therefore, the difference of the entropy between I and II is

$$\Delta S(I \to II) = k_{\rm B} \ln 2^{N_0} = N_0 k_{\rm B} \ln 2$$
 (Eq 2.35)

On the other hand, the change of entropy according to the expansion of the ideal gas is, according to Eq 2.22:

$$\Delta S(\mathbf{I} \to \mathbf{II}) = \frac{\Delta Q(\mathbf{I} \to \mathbf{II})}{T} = \frac{\int_{\mathbf{I}}^{\mathbf{II}} P dV}{T} = \int_{\mathbf{I}}^{\mathbf{II}} \frac{R}{V} dV$$

$$= R \ln\left(\frac{V}{V/2}\right) = R \ln 2$$
(Eq 2.36)

Because  $N_0$  (Avogadro's constant)  $\times k_B$  (Boltzmann constant) = R (the gas constant), the entropy change obtained by the Boltzmann relation completely corresponds to the value by the Clausius equation.



Fig. 2.9 Various factors to increase entropy

As shown in Fig. 2.9, there are various phenomena that increase the entropy, and all of them are changes of states from dense to coarse or from order to disorder. Entropy is called "parameter of disorder" in this sense.

#### 2.2.3 Maxwell-Boltzmann Distribution Law (M-B Statistics)

The number of methods (W) of distributing  $N_0$  balls to two boxes by  $N_1$  and  $N_2 = N_0 - N_1$  is expressed by

$$W(N_1, N_2) = \frac{N_0!}{N_1! - (N_0 - N_1)!}$$
(Eq 2.37)

Figure 2.10(a) is a number of distribution methods for  $N_0 = 10$ , and the method of the distribution of 7 balls and 3 balls, for instance, is  $W(7, 3) = 10!/7! \cdot 3! = 120$ . The maximum is, of course, given by the case of uniform distribution of 5 balls to each,  $W(5, 5) = 10!/5! \cdot 5! = 252$ . Therefore, if 10 balls are distributed at random, the case of (5, 5) occurs at about twice the probability as the case of (7, 3).

Because the probability of uniform distribution grows rapidly as the number of balls increases, only uniform distribution can occur in the case of a huge group of atoms or molecules such as  $(N_0 \approx 10^{24})$  as a rule.

However, the situation changes completely when different states with different energy levels can coexist.

**[Exercise 2.8]** Find out the most stable method of distribution when  $N_0$  atoms are distributed to the two energy levels of  $\varepsilon_1$  and  $\varepsilon_2$ .



Fig. 2.10 Distribution to two energy levels. (a) Uniform distribution in cases where both of energy levels are equal. (b) Uneven distribution to the lower energy level at a low temperature in cases of unequal energy levels. Almost uniform distribution to both levels at a high temperature.

**[Answer]** The stable state of an atomic group is the state where the Gibbs free energy, including the energy (or enthalpy) and the number of distribution methods (or entropy), is the lowest.

First, the enthalpy is

$$H = \varepsilon_1 N_1 + \varepsilon_2 (N_0 - N_1) \tag{Eq 2.38}$$

On the other hand, according to Eq 2.34 and 2.37 the entropy is

$$S = k_{\rm B} \ln \frac{N_0!}{N_1! \cdot (N_0 - N_1)!} \approx k_{\rm B} [N_0 \ln N_0 - N_1 \ln N_1 - (N_0 - N_1) \ln (N_0 - N_1)]$$
(Eq 2.39)

Here, Stirling's approximation  $\ln N! \approx N \ln N - N$  is used.

The condition that the free energy G = H - TS becomes the lowest is

$$0 = \partial G / \partial N_1 = [\varepsilon_1 + k_B T \ln N_1] - [\varepsilon_2 + k_B T \ln (N_0 - N_1)]$$

By rearranging the above equation, a stable distribution rate to the energy levels of  $\varepsilon_1$  and  $\varepsilon_2$  can be obtained:

$$N_{1}/N_{0} = \exp\left(-\frac{\varepsilon_{1}}{k_{B}T}\right) / \left[\exp\left(-\frac{\varepsilon_{1}}{k_{B}T}\right) + \exp\left(-\frac{\varepsilon_{2}}{k_{B}T}\right)\right]$$

$$N_{2}/N_{0} = \exp\left(-\frac{\varepsilon_{2}}{k_{B}T}\right) / \left[\exp\left(-\frac{\varepsilon_{1}}{k_{B}T}\right) + \exp\left(-\frac{\varepsilon_{2}}{k_{B}T}\right)\right]$$
(Eq 2.40)

Figure 2.10(b) is a distribution rate on the assumption that  $\varepsilon_1 = 1000$   $k_{\rm B}$  and  $\varepsilon_2 = 1500$   $k_{\rm B}$ , and all atoms are unevenly distributed to the level of  $\varepsilon_1$  at T = 0 K. However, because the entropy increases and the free energy becomes lower if they are distributed to both the energy levels, the distribution will come close to uniform distribution at the high temperature.

It is assumed that there are two energy levels in this exercise; the case of more energy levels is basically same, and the distribution rate to the energy level of  $\varepsilon$  is proportional to exp ( $-\varepsilon/k_{\rm B}T$ ). This is called Maxwell-Boltzmann distribution law.\*

\*Elementary particles and atoms in the nature ought to obey either (i) Fermi-Dirac statistics (1926) or (ii) Bose-Einstein statistics (1924) and M-B statistics is, precisely speaking, an approximation. The former is indispensable for analyzing the behavior of electrons in a metal or a semiconductor, and the latter is for the behavior of photons or liquid helium, but almost all of the events dealt with in metallography can be analyzed enough by M-B statistics (for example, see Sections 2.3 "Statistical Thermodynamics of Thermal Vibration of Crystal" and 5.3 "Thermodynamics of Grain-Boundary Segregation").

**[Exercise 2.9]** Derive the equation that expresses the equilibrium concentration of vacancies (vacant lattice points) that exist in a crystal.

**[Answer]** When a vacancy is created in a crystal, the enthalpy increases. Since the probability that vacancies are in the neighborhood is very small, the increase of the enthalpy  $\Delta H$  is proportional to the number of vacancies *n*:

$$\Delta H = n \cdot \Delta e_{\rm v} \tag{Eq 2.41}$$

Here  $\Delta e_v$  is the energy of vacancy formation (per vacancy).

On the other hand, the entropy should increase only by the amount corresponding to W(N, n), the number of configuration of N atoms and n vacancies at N + n lattice points, and it can be approximated by

$$\Delta S_{\text{config}} = k_{\text{B}} \ln \left[ \frac{(N+n)!}{N! \cdot n!} \right]$$
  

$$\approx k_{B} [(N+n) \ln (N+n) - N \ln N - n \ln n] \qquad (\text{Eq 2.42})$$

Therefore, the change of free energy  $\Delta G = \Delta H - T \Delta S$  is

$$\Delta G = n \cdot \Delta e_{v} - k_{\mathrm{B}}T[(N+n) \ln (N+n) - N \ln N - n \ln n] \quad (\mathrm{Eq} \ 2.43)$$

and there is an equilibrium concentration of vacancies at which  $\Delta G$  = minimum as shown in Fig. 2.11(b). This equilibrium concentration can be obtained:

$$\frac{\partial \Delta G}{\partial n} = 0 \longrightarrow \frac{n}{N+n} \approx \frac{n}{N} = \exp\left(-\frac{\Delta e_v}{k_B T}\right)$$
(Eq 2.44)

If a vacancy is created in a crystal, the vibration frequency of the crystal around it changes and the entropy increases. When this influence is considered, Eq 2.43 that shows the change of free energy is modified:

$$\Delta G = n(\Delta e_{v} - T\Delta S_{vib}) - k_{B} \lfloor (N+n) \ln (N+n) - N \ln N - n \ln n \rfloor$$
(Eq 2.43a)

Here  $\Delta S_{\text{vib}}$  is the change of entropy of the vibration per vacancy (refer to Section 2.3.2).

According to Eq 2.43a, the equilibrium concentration of vacancies can be expressed as:

$$\frac{\partial \Delta G}{\partial n} = 0 \longrightarrow \frac{n}{N} \approx \exp\left(-\frac{\Delta S_{\text{vib}}}{k_{\text{B}}T}\right) \cdot \exp\left(-\frac{\Delta e_{\nu}}{k_{\text{B}}T}\right)$$
(Eq 2.44a)



Fig. 2.11 The equilibrium concentration of vacancies. (a) The increase in microscopic states by formation of vacancies. (b) The change in free energy according to vacancy formation. (c) The measured result of equilibrium concentration of vacancies

If the thermal expansion rate of the lattice constant by heating  $(\Delta a/a)$  and the thermal expansion coefficient of the sample  $(\Delta L/L)$  are measured, because the former is by the change of only the interatomic distance and the latter is by the change of both the interatomic distance and the concentration of vacancies, then the value of equilibrium concentration of vacancies can be obtained by:

$$\frac{n}{N} = \left(1 + \frac{\Delta L}{L}\right)^3 - \left(1 + \frac{\Delta a}{a}\right)^3 \approx 3\left(\frac{\Delta L}{L} - \frac{\Delta a}{a}\right)$$

As shown in Fig. 2.11(c),  $n/N \approx 1.7 \times 10^{-4}$  at the melting point (1234 K) in the case of pure silver, and it is estimated that  $\Delta e_{\rm v} \approx 1.09 \text{ eV} (= 97 \text{ kJ/mol}), \Delta S_{\rm vib}/k_{\rm B} \approx 1.5$ .

# 2.3 Statistical Thermodynamics of Thermal Vibration of Crystal (Ref 4,6)

Fundamental subjects of the internal energy U, the enthalpy H, the entropy S, the free energies G and F of a substance were presented in the previous section. In this section, the thermal vibration model

presented by Einstein in 1906 is the theme used to promote a better understanding of U, S, and F of the crystal.\*

#### 2.3.1 Energy of Thermal Vibration

Atoms comprising a crystal vibrate thermally around the lattice points. Think about the analysis of this thermal vibration in terms of classical mechanics in the following exercise.

**[Exercise 2.10]** Show that the vibration energy  $(U_{vib})$  and the heat capacity at constant volume  $(C_V)$  of a crystal (per mole) can be approximated if quantization of energy is not taken into consideration:

$$\begin{bmatrix} U_{\text{vib}} = 3RT \\ [C_{\text{vib}}]_{\nu} = 3R \end{bmatrix} \text{Dulong - Petit law(1819)}$$
(Eq 2.45)

**[Answer]** Consider a group of 3N one-dimensional oscillators instead of a three-dimensional crystal composed of N atoms. The energy of each oscillator is the sum of the kinetic energy and the potential energy, and it can be expressed by

$$\varepsilon = (1/2)mv^2 + (1/2)m\omega_0^2 x^2$$

Here *m* is the mass of an atom, *v* is the velocity, and  $\omega_0 = 2\pi v$  is the angular frequency.

If the distribution of the kinetic energy obeys the Maxwell-Boltzmann law, the mean value is

$$\frac{1}{2}m\bar{v}^2 = \int_{-\infty}^{\infty} \frac{m}{2}v^2 \cdot \exp\left(-\frac{mv^2/2}{k_{\rm B}T}\right)dv \Big/ \int_{-\infty}^{\infty} \exp\left(-\frac{mv^2/2}{k_{\rm B}T}\right)dv$$
$$= \frac{m}{2}\sqrt{\pi}\left(-\frac{2k_{\rm B}T}{m}\right)^{3/2} \Big/ \sqrt{\pi}\left(-\frac{2k_{\rm B}T}{m}\right)^{1/2} = \frac{k_{\rm B}T}{2}$$
(Eq 2.46)

Here integration formulas

$$\int_{-\infty}^{\infty} \exp(-\lambda y^2) dy = (\pi/\lambda)^{1/2}$$

<sup>\*</sup>A constant interatomic distance or a constant volume is assumed in the theory of vibration in crystals in order for the eigen frequency to be unchanged. As a result, the obtained energy is not H but U, and the obtained free energy is not G but Helmholtz free energy F.

 $\int_{-\infty}^{\infty} \exp(-\lambda y^2) dy = (1/2)(\pi/\lambda^3)^{1/2}$ 

are used and  $\bar{v}$  is the mean velocity.

The mean value of the potential energy by M-B statistics is  $k_{\rm B}T/2$  according to a similar calculation. Therefore, the average energy of each oscillator is  $\bar{\epsilon} = k_{\rm B}T$ , and internal energy and the heat capacity at constant volume of the total 3N one-dimensional oscillators are approximated by Eq 2.45.

The measured values of  $C_v$  at the temperature more than the ordinary temperature of various crystals are almost 3R, and Dulong-Petit law is approved. However, it was clarified that  $C_v < 3R$  at a temperature below the ordinary temperature by the progress of the low-temperature science. Einstein solved this contradiction by the quantization model.

Assumption (i): The energy of the oscillator is quantized, and it has discrete energies  $\varepsilon_n$ :

$$\varepsilon_n = \left(\frac{1}{2} + n\right) h v \ (n = 0, \ 1, \ 2, \ \dots)$$
 (Eq 2.47)

Here  $h \approx 6.626 \times 10^{-34}$  J · s is the Planck constant, v is an eigenfrequency, *n* is a quantum number, and  $\varepsilon_0 = hv/2$  is called the zero-point vibration energy.

Assumption (ii): An eigenfrequency v is a constant independent of temperature.

Assumption (iii): The energy distribution of the oscillators obeys the Maxwell-Boltzmann law.

Total energy of the 3N oscillators can be approximated (iii) according to assumption as

$$U_{\rm vib} = 3N \cdot \left(\sum_{n=0}^{\infty} \varepsilon_n \cdot f_n\right)$$
 (Eq 2.48)

Here,  $f_n$  is the fraction of oscillators that exist in the *n*th energy level, and it can be expressed by

$$f_n = \frac{\exp(-\varepsilon_n/k_{\rm B}T)}{\sum\limits_{m=0}^{\infty} \exp(-\varepsilon_m/k_{\rm B}T)} = \frac{\left[\exp(-h\nu/k_{\rm B}T)\right]^n}{\sum\limits_{m=0}^{\infty} \left[\exp(-h\nu/k_{\rm B}T)\right]^m}$$
(Eq 2.49)

Equation 2.49 looks very complex, but if two formulas about infinite series

and

$$\sum_{n=0}^{\infty} y^m = \frac{1}{(1-y)}$$

and

 $\sum_{n=0}^{\infty} ny^n = \frac{y}{\left(1-y\right)^2}$ 

are used, it will become a simple equation:

$$U_{\rm vib} = 3R\Theta_{\rm E} \left[ \frac{1}{2} + \frac{1}{\exp(\Theta_{\rm E}/T) - 1} \right]$$
 (Eq 2.50)

Here  $\Theta_{\rm E} = hv/k_{\rm B}$  is a parameter called the Einstein's characteristic temperature.

The heat capacity at constant volume can be obtained from Eq 2.50:

$$[C_{\rm vib}]_V = \frac{dU_{\rm vib}}{dT} = 3R \left(\frac{\Theta_{\rm E}}{T}\right)^2 \frac{\exp(\Theta_{\rm E}/T)}{\left[\exp(\Theta_{\rm E}/T) - 1\right]^2}$$
(Eq 2.51)

If the temperature *T* rises, then exp  $(\Theta_{\rm E}/T) \rightarrow 1 + \Theta_{\rm E}/T$ ; therefore,  $U_{\rm vib} \rightarrow 3RT$ ,  $[C_{\rm vib}]_V \rightarrow 3R$  and Eq 2.51 will approach the value by Dulong-Petit law (Fig. 2.12). On the other hand, when  $U_{\rm vib} \rightarrow 3R\Theta/2$ ,  $[C_{\rm vib}]_V \rightarrow 0$  for  $T \rightarrow 0$  K, and the value agrees well with the result of measurement. This was a remarkable result of the Einstein model in which the quantization of vibration energy was assumed.

It was assumed in the above model that the frequency v is constant, but Debye (1912) obtained the precise solution in consideration of a distribution function for v and found:

$$[C_{\rm vib}]_V^{\rm D} = 9R \left(\frac{T}{\Theta_{\rm D}}\right)^3 \int_0^{\Theta_{\rm D}/T} \frac{x^4 \exp(x)}{\left[\exp(x) - 1\right]^2} dx$$
 (Eq 2.52)

Here  $\Theta_D = h\nu/k_B$  is a Debye characteristic temperature (in short, Debye temperature).

Because the characteristic temperature of most crystals is several hundred K as shown in Table 2.1, the characteristic frequency is estimated as below.

$$v = \Theta \frac{k_{\rm B}}{h} = \Theta \frac{1.4 \times 10^{-23} \text{ J/K}}{6.6 \times 10^{-34} \text{ J} \cdot \text{s}} \approx 10^{13} \text{s}^{-1}$$

This frequency is a fundamental parameter that is often used when the mechanism of atomic diffusion or phase transformation in a crystal is considered.



Fig. 2.12 The energy and the heat capacity of the thermal vibration of a crystal. (a) The thermal vibration energy of a crystal. (b) The heat capacity of thermal vibration

Table 2.1 The typical Debye temperatures  $(\Theta_D)$  and melting points of crystals

	Pb	Al	Fe	Ti	W	NaCl	Diamond	Al <sub>2</sub> O <sub>3</sub>
$\Theta_{\rm D}$ , K	110	428	470	420	400	280	$\begin{array}{c} 2230 \\ {\sim}4000 \end{array}$	~1200
Melting point, K	600	933	1809	1953	3653	1074		2300

**[Exercise 2.11]** Investigate the distributions of thermal vibration energy at low temperature ( $T = \Theta_{\rm E}/2$ ) and high temperature ( $T = 2\Theta_{\rm E}$ ) according to the Einstein model.

[Answer] The fraction of the oscillators in the *n*th energy level can be obtained as follows if Eq 2.49 is rearranged by the formula on infinite series:

$$\sum_{m=0}^{\infty} y^m = 1/(1-y)$$

$$T = \frac{\Theta_E}{2}; f_n = \frac{[\exp(-2)]^n}{\sum_{m=0}^{\infty} [\exp(-2)]^m} = [1 - \exp(-2)][\exp(-2)]^n$$
$$= 0.865(0.135)^n$$

$$T = 2\Theta_E; f_n = \frac{[\exp(-0.5)]^n}{\sum_{m=0}^{\infty} [\exp(-0.5)]^m} = [1 - \exp(-0.5)][\exp(-0.5)]^n$$
$$= 0.393(0.607)^n$$

As shown in Fig. 2.13, most of the oscillators show n = 0 or zero-point vibration at low temperature  $(T = \Theta_E/2)$ , and there is no oscillator in the energy level of n > 3. However at high temperature  $(T = 2\Theta_E)$ , the distribution extends even to a higher energy level of around n = 8.


**Fig. 2.13** Distribution of vibration energy. Most of oscillators are on the level of n = 0 or 1 at a low temperature, but the distribution will extend to higher energy levels of around n = 8 at a high temperature.

# 2.3.2 Entropy and Free Energy of Thermal Vibration

The "total of microscopic states" of 3*N* oscillators can be expressed by the combination equation of arranging them to each energy level:

$$W_{\rm vib} = \frac{(3N)!}{N_1! \cdot N_2! \cdots N_\infty!}$$
(Eq 2.53)

The entropy of the group of oscillators can be obtained by Eq 2.53 and the Boltzmann relation (Eq 2.34).

$$S_{\text{vib}} = k_{\text{B}} \ln W_{\text{vib}} = k_{\text{B}} \left[ \ln (3N)! - \sum_{m=0}^{\infty} \ln N_m! \right] \approx -3Nk_{\text{B}} \left( \sum_{m=0}^{\infty} \frac{N_m}{3N} \ln \frac{N_m}{3N} \right)$$
$$= -3Nk_{\text{B}} \left( \sum_{m=0}^{\infty} f_m \ln f_m \right) = 3R \left\{ \frac{\Theta_{\text{E}}/T}{\exp(\Theta_{\text{E}}/T) - 1} - \ln \left[ 1 - \exp\left(-\frac{\Theta_{\text{E}}}{T}\right) \right] \right\}$$
(Eq 2.54)

Here,  $f_m$  is the fraction of oscillators in the *m*th level (Eq 2.49).  $\Theta_E = hv /k_B$  is an Einstein's characteristic temperature.

As shown in Fig. 2.14(a),  $S_{vib} = 0$  at T = 0 K. Because the energy of oscillators extends to a higher level when the temperature T rises, the entropy gradually increases.



Fig. 2.14 The entropy and the free energy of thermal vibration of a crystal (a) The entropy of thermal vibration. (b) The free energy of thermal vibration

Now that the approximations of the internal energy U and the entropy S of thermal vibration (Eq 2.50 and 2.54) have been obtained, the approximation of Helmholtz free energy (F) can be obtained by summarizing them both.

$$F_{\text{vib}} = U_{\text{vib}} - TS_{\text{vib}}$$
$$= 3R\Theta_{\text{E}} \left\{ \frac{1}{2} + \left( \frac{T}{\Theta_{\text{E}}} \right) \ln \left[ 1 - \exp\left( -\frac{\Theta_{\text{E}}}{T} \right) \right] \right\}$$
(Eq 2.55)

When Eq 2.55 is plotted, it will become a downward sloping and concave curve as shown in Fig. 2.14(b). This is similar to the case of the G-T curve in Exercise 2.6].

At high temperature ( $T \gg \Theta_{\rm E}$ ), because exp ( $\Theta_{\rm E}/T$ )  $\approx 1 + \Theta_{\rm E}/T$ , Eq 2.50, 2.54, and 2.55 are approximated as follows, respectively:

$$U_{\rm vib} \approx 3RT, \ S_{\rm vib} \approx 3R \left(1 + \ln \frac{T}{\Theta_{\rm E}}\right), \ F_{\rm vib} \approx -3RT \ \ln \frac{T}{\Theta_{\rm E}}$$
 (Eq 2.56)

# **2.4 Thermodynamics of Magnetic Transition** (Iron Hardens Twice!)

The magnetic transition is a unique transformation that can be observed only in magnetic materials. For this reason, there are many people who think it is a special subject that should be studied only by those involved in magnetic materials. However, one must not forget that magnetic transition plays an important role even in iron and steel for construction.

This section covers basic concepts of thermodynamics of magnetic transition and goes on to discuss the role and the meaning of magnetic transition in iron and steel.

# 2.4.1 Magnetic Domain Structure of Ferromagnetic Materials (Ref 7)

P. Weiss (1907) presented for the first time the concept that a ferromagnetic material (such as Fe, Co, Ni, and rare earths Gd, Dy) is an aggregate of "very small magnets" (magnetic domains). He solved the nature of the magnetic transition by thinking that this magnetic domain originates in spontaneous magnetization based on a magnetic moment of an atom comprising a ferromagnetic material. However, it was after 1950 that the substance of the magnetic domain was clearly observed with a microscope.

If a ferromagnetic material is not divided into magnetic domains, it has magnetostatic energy based on a magnetic pole NS as shown in Fig. 2.15(a). However, if a ferromagnetic material is divided into two domains with magnetization in the opposite directions on the right hand and left hand and the two domains of closure at the top and the bottom as shown in Fig. 2.15(b), it will stay in a stable state without any magnetostatic energy. This stabilization is the cause of magnetic domains and the boundaries of magnetic domains are called magnetic domain walls.

The magnetic domain walls have excessive energy as do the crystal surface and the crystal grain boundary. This is called the energy of magnetic domain wall, and the value is about  $10^{-3}$  to  $10^{-2}$  J/m<sup>2</sup>, far smaller than the grain-boundary energy (0.1 to 1 J/m<sup>2</sup>).

# 2.4.2 Magnetization and Magnetic Transition of Ferromagnetic Materials

Magnetization occurs when a ferromagnetic material is put in a magnetic field in "the state of demagnetization" such that the magnetic



**Fig. 2.15** The spontaneous magnetization (white arrows) and the domain structure of ferromagnetic materials. If a droplet of colloid liquid with magnetic particles is put on the surface of a sample whose strain layers have been removed by electrolytic polishing, etc., then the particles are attracted by domain walls, and the appearance of magnetic domains can be observed. (a) A single magnetic domain. (b) A single crystal with four domains. (c) The magnetic domain structure of a polycrystalline material

poles are eliminated by one another according to the formation of the magnetic domains. The mechanism is, the magnetic domains with spontaneous magnetization nearly in the direction of the magnetic field grow up as  $1 \rightarrow 2 \rightarrow 3$  in Fig. 2.16(a) absorbing the magnetic domains with the spontaneous magnetization of the opposite direction. This mechanism of magnetization is called the domain wall displacement.

When the magnetic field is strengthened further, the direction of the spontaneous magnetization rotates and it finally reaches saturation magnetization  $I_s$  (3  $\rightarrow$  4 in Fig. 2.16(a)) This mechanism is called the rotation magnetization. Materials that have domain walls that are easy to move (soft magnetic materials) are used for magnetic cores of transformers or telecommunications equipment because they are quickly induced by external magnetic field. On the other hand, materials that have domain walls that are difficult to move (hard magnetic materials) are used for recording elements or permanent magnets because they cannot be easily returned to a previous state of demagnetization once they are magnetized.

When a ferromagnetic material magnetized up to the saturation value  $I_s$  is heated in the magnetic field, the value  $I_s$  will decrease slowly in the range of low temperature; however, it will decrease rapidly and finally be annihilated approaching the Curie temperature  $T_c$ , and the material will become a paramagnetic substance. This change of ferromagnetism  $\Leftrightarrow$  paramagnetism is the "magnetic transition" (Fig. 2.16b). Here, the reason for describing "in the magnetic field" previously is to record the value  $I_s$  at which (the white arrows in the figure) is annihilated according to the temperature rise, and it should be noted that the magnetic field. The value of



Fig. 2.16 The mechanism of magnetization and the mechanism of magnetic transition White arrows indicate spontaneous magnetization. Black arrows indicate magnetic spins of atoms. (a) The magnetization curve. (b) The disordering of magnetic spins

the magnetic spin of each atom (black arrows in the figure) that bears the source of ferromagnetism is invariable even if it is inside or outside the magnetic field, and even if it is heated or cooled. What varies is the arrangement of magnetic spins, and all of the magnetic spins arrange parallel at low temperature. However, the arrangement falls into disorder gradually when the temperature rises, and it becomes completely disordered above  $T_{\rm C}$ . Therefore, the magnetic transition is a phenomenon of changing magnetic spins from an ordered arrangement into a disordered arrangement, and it is the same sort of "phase transition of second order" as "order  $\Leftrightarrow$  disorder transition" in Chapter 7.

# 2.4.3 Analysis of Magnetic Transition Using the Ising Model (Ref 4)

In order to understand the feature of the magnetic transition, think about an exercise of the concise spin model presented by E. Ising (1925).

**[Exercise 2.12]** Suppose N lattice points are occupied by magnetic spins  $(N_+ \text{ or } N_-)$ . The nearest spin pairs  $(\bigoplus \bigoplus \text{ or } \ominus \ominus)$  are granted an attractive energy  $(-\varepsilon)$ , whereas the spin pairs of different signs  $(\bigoplus \ominus)$  are burdened with a repulsive energy  $(+\varepsilon)$ . Derive the approximations of enthalpy H, entropy S, and free energy G of such a spin ensemble, and find out the numbers,  $N_+$  and  $N_-$ , in the state of G = minimum.

**[Answer]** The number of neighboring lattice points on each lattice point is assumed to be z(8 for body-centered cubic, bcc, 12 for face-centered cubic, fcc). Since the numbers of  $\oplus$  spins and  $\ominus$  spins among these z spins are  $z(N_+/N)$  and  $z(N_-/N)$  if the random distribution is assumed, the total of  $\oplus$   $\oplus$ ,  $\ominus \ominus$ ,  $\oplus$   $\ominus$  spin pairs can be approximated by\*

$$P_{+-} \approx N_{+} \cdot z(N_{+}/N)(\frac{1}{2}) \approx Nz \cdot (N_{+}/N)^{2}/2$$

$$P_{-} \approx N_{-} \cdot z(N_{-}/N)(\frac{1}{2}) \approx Nz \cdot (N_{-}/N)^{2}/2$$

$$P_{+-} \approx N_{+} \cdot z(N_{+}/N) \approx Nz \cdot (N_{+}/N)(N_{-}/N) \quad \text{(Eq 2.57)}$$

Here  $P_{++}$  and  $P_{--}$  are multiplied by  $\frac{1}{2}$  so as not to count the same spin in duplicate. Because the enthalpy  $H_{\text{mag}}$  is the total amount of the interaction energy between spins,

<sup>\*</sup>Because it is highly probable that  $\oplus$  exists next to  $\oplus$ , and  $\ominus$  exists next to  $\ominus$ , the random distribution assumption is not precisely valid. However, it is often adopted in statistical mechanics because of simplification. See Section 3.2.1 "Nearest–Neighbor Assumption and Random Distribution Assumption (Basic assumptions for B-W-G Model)."



Fig. 2.17 Analysis of magnetic transition according to the Ising model

$$H_{\text{mag}} = -\varepsilon (P_{++} + P_{--}) + \varepsilon P_{+-} \approx -\frac{Nz\varepsilon}{2} \left( \frac{N_{+}^2 + N_{-}^2 - 2N_{+}N_{-}}{N^2} \right)$$
$$= -\frac{Nz\varepsilon}{2} X^2$$
(Eq 2.58)

Here, because  $X = (N_+ - N_-)/N$  corresponds to the average magnetic spin (white arrows in Fig. 2.17(a, upper)) in the direction of  $\oplus$ , that is, spontaneous magnetization, it is called a ferromagnetic parameter.

Next, the entropy  $S_{\text{mag}}$  is given by the Boltzmann equation (Eq 2.34) as

$$S_{\text{mag}} = k_{\text{B}} \ln\left(\frac{N!}{N_{+}! \cdot N_{-}!}\right) \approx -N \ k_{\text{B}} \left(\frac{N_{+}}{N} \ln\frac{N_{+}}{N} + \frac{N_{-}}{N} \ln\frac{N_{-}}{N}\right)$$
$$\approx -Nk_{\text{B}} \left[\left(\frac{1+X}{2}\right) \ln\left(\frac{1+X}{2}\right) + \left(\frac{1-X}{2}\right) \ln\left(\frac{1-X}{2}\right)\right] \qquad (\text{Eq } 2.59)$$

The free energy  $G_{\text{mag}} = H_{\text{mag}} - TS_{\text{mag}}$  is approximated from Eq 2.59:

$$G_{\text{mag}} \approx -\frac{Nz\varepsilon}{2} X^2 + Nk_B T$$

$$\times \left[ \left(\frac{1+X}{2}\right) \ln\left(\frac{1+X}{2}\right) + \left(\frac{1-X}{2}\right) \ln\left(\frac{1-X}{2}\right) \right] \qquad \text{(Eq 2.60)}$$

The enthalpy H decreases when the ferromagnetic parameter X increases, as shown in Fig. 2.17(b). However, the entropy S becomes small, and the value of -TS rises because the disorder of the spin

arrangement decreases. A minimum point (data point  $\blacksquare$ ) exists in the free energy *G* that is the synthesis of these, and the next equation holds.

$$\left(\frac{\partial G_{\text{mag}}}{\partial X}\right)_{X_0} = 0 \quad \to \quad z\varepsilon \cdot X_0 = \frac{k_{\text{B}}T}{2} \left[\ln(1+X_0) - \ln(1-X_0)\right] \qquad (\text{Eq 2.61})$$

The relation between  $X_0$  obtained from Eq 2.61 and T (Fig. 2.17 a, lower) corresponds well to the relation curve between  $I_s$  and T in Fig. 2.16(b).

Since  $X_0 \ll 1$  in the neighborhood of the Curie point  $T_{\rm C}$ , the following relation can be obtained by approximating as  $\ln(1 + X_0) - \ln(1 - X_0) \approx 2X_0$  according to the Taylor expansion of the term ln in Eq 2.61.

$$z\varepsilon \cdot X_0 \approx k_{\rm B}T_{\rm C} \cdot X_0 \to T_{\rm C} \approx \frac{z\varepsilon}{k_B}$$
 (Eq 2.62)

If Eq 2.62 is applied to the case of bcc Fe, because  $T_{\rm C} = 1043$  K and z = 8, the interaction energy per spin pair can be estimated to be  $\varepsilon \approx 2 \times 10^{-21}$  J. When this value is multiplied by Nz/2 and converted into the ferromagnetic energy per mole of Fe, it becomes about 5 kJ/mol. The measured value is about 8 kJ/mol as shown in Fig. 2.19 described later, and it is 1.6 times as much as the estimation, but it can be said that it is a rather good estimation for such a simple model.

The magnetostatic energy that a ferromagnetic material exerts on its surroundings is no more than around 3 J/mol. On the other hand, the interaction energy of the source of spontaneous magnetization is about 8 kJ/mol as described previously, and it is about 2500 times greater. Why does so much energy act between spins? This difficult problem was solved by the idea of "exchange energy" based on the quantum theory that W. Heisenberg (1928) presented. Refer to Ref 7 for details.

#### 2.4.4 Thermodynamics of A<sub>3</sub> Transformation of Pure Iron

**Magnetic Transition and A<sub>3</sub> Transformation of Pure Iron.** Figure 2.18 illustrates the features of a phase transformation of the pure iron plainly, and it has been published in almost all the classic textbooks. First in Fig. 2.18(a), stagnation according to magnetic transformation appears rather clearly in the thermal analysis curve as shown by the hatching in the figure. It was misconceived in the pioneer days of metallurgy that Fe crystal had four phases,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ , and three kinds of allotropic transformations,  $A_2(\alpha \Leftrightarrow \beta)$ ,  $A_3(\beta \Leftrightarrow \gamma)$ , and  $A_4(\gamma \Leftrightarrow \delta)$  resulted. However, in Fig. 2.18(b) no change corresponding to  $A_2$  is observed in the thermal expansion curve. Thus, it was concluded that  $A_2$  is not an allotropic transformation but a magnetic transition.

Next, when the A<sub>3</sub> point is noted, the volume shrinks about 1% by  $\alpha \rightarrow \gamma$  transformation during the temperature rise. This shrinkage might be unexpected at first, but is a common sense metallurgical explanation. It has been



**Fig. 2.18** The thermal analysis curve (a) and the thermal expansion curve (b) for pure iron  $A_3$  transformation (circled) is an abnormal one progressing in the opposite direction (from "coarse" to "dense").

$\mathbf{fcc} \longrightarrow \mathbf{bcc}$	$hcp \longrightarrow bcc$
$\begin{array}{c} \alpha Ca & \overrightarrow{166} & \beta Ca \\ \gamma Fe & \overrightarrow{1667K} & \delta Fe \\ \gamma Mn & \overrightarrow{1416K} & \delta Mn \\ \alpha Sr & \overrightarrow{800K} & \beta Sr \\ \alpha Th & \overrightarrow{1335K} & \beta Th \end{array}$	$\begin{array}{c} \alpha Be  \overrightarrow{1543}\kappa  \beta Be \\ \alpha Hf  \overrightarrow{2028}\kappa  \beta Hf \\ \alpha Li  \overrightarrow{80\kappa}  \beta Li \\ \alpha Na  \overrightarrow{40\kappa}  \beta Na \\ \alpha Sc  \overrightarrow{160}\kappa  \beta Sc \\ \alpha Sc  (\beta Sc  \beta Sc  \beta Sc  \beta Sc \\ \alpha Sc  (\beta Sc  \beta S$
$ \begin{array}{c} \mathbf{bcc} \longrightarrow \mathbf{fcc} \\ \alpha \mathrm{Fe} \xrightarrow[1185]{}  \gamma \mathrm{Fe} \end{array} $	$\begin{array}{c} \alpha \Pi & 1155 & \beta \Pi \\ \alpha Y & 1751 K \\ \alpha Zr & 1136 K \end{array} \beta Y$

Table 2.2 The fcc  $\rightarrow$  bcc, hcp  $\rightarrow$  bcc, and bcc  $\rightarrow$  fcc transformations of pure metals

Rare earth metals (La, Ce, Sm, Gd, Tb, Dy) are omitted. fcc, face-centered cubic; bcc, body-centered cubic; hcp, hexagonal close-packed

explained that the shrinkage occurs because  $\gamma(\text{fcc})$  is "dense," while  $\alpha(\text{bcc})$  has a "coarse" or "open" structure. There are a lot of metals in which the transformation of "dense"  $\rightarrow$  "coarse" (fcc  $\rightarrow$  bcc or hcp  $\rightarrow$  bcc) occurs when temperature rises as shown in Table 2.2. However, Fe is the only metal in which the transformation of "coarse"  $\rightarrow$  "dense" occurs. These facts agree well with the general rule of phase transition considered in Section 2.2.1; a dense structure is stable at low temperature and a coarse structure is stable at high temperature. Therefore, the A<sub>3</sub> transformation of pure iron should be recognized as an abnormal transformation and a contradiction to the general rules of thermodynamics.

As is often said "there is no rule without exceptions"; of course, the  $A_3$  transformation of pure iron is not the only abnormal transformation. What is well known is the transformation of ice  $\rightarrow$  water, and the



**Fig. 2.19** Thermodynamic properties of magnetic materials. (a) The changes in the heat capacity (a1), the enthalpy (a2), and the free energy (a3) of bcc Fe according to magnetic transformation. (b) Unless magnetic transition occurs, A<sub>3</sub> transition will not occur. (c) Is hcp Fe nonmagnetic? See footnote on p. 47.

volume shrinks by as much as about 8%. Another exception is the fusion of silicon, and it shrinks by no less than 12%. There are clear reasons for these abnormal transformations; in the case of ice  $\rightarrow$  water, "hydrogen bonds" are the cause, and because ice has a "coarse" structure of a H<sub>2</sub>O molecule surrounded by only the four nearest-neighboring molecules with hydrogen bonds in the crystal, it becomes "dense" when it is transformed into water by fusion. In the case of silicon, because a diamond-type structure formed by "covalent bonds" is extremely "coarse" and the packing factor of atomic spheres is no more than 34%, the transformation of solid  $\rightarrow$  liquid will be abnormal ("coarse"  $\rightarrow$  "dense").

Then, what causes the  $A_3$  transformation of pure iron? The consideration is mentioned in the next section, but in conclusion the magnetic transition is the primary factor that causes "the abnormal  $A_3$  transformation."

**Change in Free Energy According to Magnetic Transition.** The measured values of the heat capacity change of pure iron during magnetic transition ( $\Delta C^{\alpha}_{mag}$ ) are described as the lambda-type curve shown in Fig. 2.19(a1). From the magnetic heat capacity, the changes of *H*, *S*, and *G* according to magnetic transition can be expressed numerically by Eq (2.13) and (2.31) as

$$\Delta H_{\rm mag}^{\alpha} = \int_{-\infty}^{T} \Delta C_{\rm mag}^{\alpha} dT$$
$$\Delta S_{\rm mag}^{\alpha} = \int_{-\infty}^{T} \left( \Delta C_{\rm mag}^{\alpha} / T \right) dT$$
$$\Delta G_{\rm mag}^{\alpha} = \Delta H_{\rm mag}^{\alpha} - T \cdot \Delta S_{\rm mag}^{\alpha}$$
(Eq 2.63)

Here, the reason they are integrated not from 0 to *T* but from  $\infty$  to *T* is because the paramagnetic state is taken as the standard. For example,  $\Delta G_{\text{mag}}^{\alpha}$  is -8.3 kJ/mol at 0 K means that the free energy will decrease by 8.3 kJ/mol when iron transits from a paramagnetic state (the arrangement of spins are at random) to a completely ferromagnetic state (the arrangement of spins is perfectly parallel).

**[Exercise 2.13]** Assume that the magnetic transition of the pure iron is the phase transition not of the second order but of the first order, and that the A<sub>2</sub> transformation ( $\alpha \Leftrightarrow \beta$ ) occurs at the temperature  $T_{\rm C}$ . Estimate the enthalpy change of this virtual transformation  $\Delta H^{\alpha \to \beta}$  according to the value of  $\Delta H^{\alpha}_{\rm mao}$ , that of the actual magnetic transition.

[Answer] Because it can be thought that the arrangement of spins will change from parallel to random all at once in this virtual transition of the first order, the changes of enthalpy and entropy are

$$\Delta H^{\alpha \to \beta} = -\left(\Delta H^{\alpha}_{\rm mag}\right)_{0\rm K} = 8.3 \, \rm kJ/mol$$

$$\Delta S^{\alpha \to \beta} = \frac{\Delta H^{\alpha \to \beta}}{T_{\rm C}} = 8.0 \,\mathrm{J/K} \cdot \mathrm{mol}$$

and the entropy change is almost equivalent to the melting entropy of metals;  $\Delta S_{\rm m} \approx R$  (Richards' rule, Eq 2.20).

The dotted lines of Fig. 2.19(a2) and (a3) are the changes of H and G if the magnetic transition is assumed to be the transition of the first order, and they indicate that the transition accompanies an energy change on a large scale comparable to melting. Therefore, it could be said "Fe coagulates at the melting point ( $T_{\rm m}$ ) and solidifies once again at the Curie point ( $T_{\rm c}$ )." This is, of course, just a figurative saying. Do not misunderstand it. In addition, assume that Fe is a nonmagnetic metal that does not undergo any magnetic transition.

Because the free energy of paramagnetic bcc Fe is, as shown by the dashed line in Fig. 2.19(b), higher than that of fcc Fe and metastable below the  $A_4$  point, the  $A_3$  transformation does not occur. To tell the truth, when this logic is promoted further, nonmagnetic fcc Fe is also



Fig. 2.20 States of matter. Amorphous is categorized into the solid region.

metastable, and one can come to the conclusion that  $\epsilon$ Fe of hcp is the most stable.\*

Therefore, if Fe were nonmagnetic, neither the  $A_3$  transformation, the  $A_4$  transformation, the pearlite transformation, nor the martensitic transformation would occur. It can be guessed that iron and steel might be dense materials that could not be compared with the actual ones.

# 2.5 Free Energy of Amorphous Phase

This section concludes the chapter with a general discussion of an amorphous phase from a thermodynamic viewpoint (Ref 10, 11).

### 2.5.1 Is the Amorphous a Solid Phase or a Liquid Phase?

Matter is classified into groups according to its features (Fig. 2.20). Because the amorphous order is not a fluid, it belongs to a solid, and it is called an amorphous solid or a glass phase. However, its microstructure is a random arrangement similar to a liquid phase, and it also has similar characteristics to a supercooled liquid phase.

<sup>\*</sup>Face-centered cubic Fe has magnetic spins of  $\Delta G_{\gamma mag} \approx 6$  kJ/mol, and it is thought to become antiferromagnetic below the Néel point ( $T_N \approx$ 80 K), so if such an amount of energy is added, hcp Fe becomes more stable than fcc Fe. Because Fe is surrounded by hcp metals in the periodic table as shown in Fig. 2.19(c), the hcp hypothesis of nonmagnetic Fe sounds true. See Ref 8 and 9 for details.

## 2.5.2 Is the Amorphous a Stable Phase or a Metastable Phase?

When the consideration in Section 2.2 is reviewed, crystals in which atoms are mutually bonded firmly have a "dense" structure, low enthalpy H, and small entropy S. On the other hand, liquids in which atoms are loosely bonded have a "coarse" structure, high H, and large S. Therefore, the free energy G = H - TS that is a standard of stability is lower in a crystal at low temperature, but it becomes lower in a liquid at the high temperature because -TS becomes a dominant term, and as a result, the change in state from crystal  $\rightarrow$  liquid takes place.

However, as for an amorphous phase, S is considerably near that of a crystal, while H is in the middle of a liquid and a crystal as shown in Fig. 2.21(a) and (b). Here, if  $(\partial G/\partial T) = -S$  (Eq 2.33) is recalled, G of the amorphous state and the crystal descends at a similar inclination by the temperature rise. As a result, as shown in Fig. 2.21(c), G of the crystal is lower than that of the amorphous state at the low temperature and G of the liquid phase is lower than that of the amorphous state at the high temperature. Thus, it can be concluded that the amorphous state is a metastable phase at any temperature.

The hatchings of Fig. 2.21 show the changes in H, S, and G according to the transformation of a liquid phase  $\rightarrow$  amorphous, and it is thought to be the same kind of "the phase transition of the second order" as the magnetic transition considered in the previous section.



**Fig. 2.21** The outlines of enthalpy, entropy, and free energy of amorphous phase and the measured samples of glass transition temperature. The nature of amorphous phase is not known well, and there are a lot of unknowns. (a) H-T. (b) S-T. (c) G-T. (d)  $T_g$ - $T_m$ 

Methods used to form an amorphous phase include (i) rapid cooling of a liquid phase, (ii) coagulation of a vapor phase, (iii) mechanical milling of a solid phase, and (iv) pyrolysis of a compound. Method (i) liquidphase rapid cooling is the most general. In this case, the temperature  $T_g$  at which the transformation of a liquid phase  $\rightarrow$  amorphous phase begins is called a glass-transition temperature; its ratio with the melting point  $T_m$  is  $T_g/T_m \approx 2/3$  (Fig. 2.21d).

Most chain macromolecules such as rubbers and polyethylene and silicates with a network structure based on  $SiO_2$  will form an amorphous phase. Sulfur, selenium, and carbon are, among the elements that become amorphous, and an amorphous phase is formed by random arrangement of chain molecules in the case of *S* and Se and of molecules with a network structure in the case of C (graphite). The amorphous phase of H<sub>2</sub>O is obtained by rapid cooling of steam down to about 110 K, but its characteristic still is not well known.

Finally, consider the following exercise quoted from Ref 4.

**[Exercise 2.14]** Let x be the distance between ends of a chain to which n segments (each length is a) are connected as shown in Fig. 2.22(a). Assume that the joints of the chain (data points  $\bigcirc$ ) can be bent freely, and obtain the tension to keep the chain length x.

**[Answer]** If the number of upward segments is named  $n_+$  and downward segments  $n_-$ , then the length of the chain is  $x = a(n_+ - n_-)$ . Since  $n = n_+ + n_-$ ,  $n_+$  and  $n_-$  can be expressed by

$$n_{+} = (na + x)/2a$$
  
 $n_{-} = (na - x)/2a$  (Eq 2.64)



**Fig. 2.22** The entropy elasticity of chain polymers. An spring is also an example of entropy elasticity. However, the entropy increases when air expands, contrary to the case of rubber. (a) The shorter *x* is, the larger entropy becomes. (b) The elastic coefficients of various matters

Because the number of microscopic states of the chain with the length of x, therefore with  $n_+$  and  $n_-$  segments is  $W = n! / [(n_+)! (n_-)!]$ , the entropy can be obtained by the Boltzmann relation (Eq 2.34):

$$S = k_{\rm B} \ln\left(\frac{n!}{n_+! \cdot n_-!}\right) = -k_{\rm B} \left[n + \ln\left(\frac{n_+}{n}\right) + n_- \ln\left(\frac{n_-}{n}\right)\right]$$
$$= -\frac{k_{\rm B}}{2a} \left[(na+x) \ln\left(\frac{na+x}{2na}\right) + (na-x)\ln\left(\frac{na+x}{2na}\right)\right]$$
(Eq 2.65)

Because the joint of the chain bends freely, the enthalpy H is irrelevant to X and the tension X depends only on an entropy term as given in

$$X = \left(\frac{\partial G}{\partial x}\right)_T = -T\left(\frac{\partial S}{\partial x}\right)_T = \frac{k_{\rm B}T}{2a} \ln\left(\frac{na+x}{na-x}\right) \approx \left(\frac{k_{\rm B}T}{na^2}\right) x \qquad ({\rm Eq} \ 2.66)$$

Here an approximation  $\ln[(1 + y)/(1 - y)] \approx 2y$  was used.

As shown in Fig. 2.10, the number of the ways of distributing balls into two boxes is the maximum in the case of uniform distribution. As for the chain, when the numbers of upward and downward segments  $n_+$  and  $n_-$  are equal, the value of W also becomes the maximum, and then the entropy S becomes the maximum. It can be seen that the length of the chain is x = 0 at this time, and the chain tends to be as short as possible. Thus, the elasticity caused by the tendency to increase entropy is called "the entropy elasticity" or "the rubber elasticity."

On the other hand, because the elasticity of the metal and ceramics is based on the binding energy between atoms, it is called "the energy elasticity." The differences between the elasticities are (i) the elastic coefficient of the energy elasticity is very large (Fig. 2.22b) and (ii) the higher the temperature, the smaller the coefficient of the energy elasticity becomes, but the larger that of the entropy elasticity becomes, which can be seen from Eq 2.66.

#### **EXERCISES**

**2.15** When fine particles with average radius  $\bar{r}$  are suspended in a liquid, show that the equilibrium distribution of the fine particles can be approximated, according to M-B statistics, as

$$\frac{n}{n_0} = \exp\left[-\frac{(4/3)\pi\bar{r}^3 (\rho - \rho_0) \cdot gh}{k_{\rm B}T}\right] \text{(equation of equilibrium suspension)}$$
(Eq 2.67)

Here,  $\rho$  and  $\rho_0$  are mass densities of the particles and the liquid, respectively. *h* is the height of position from the bottom of a container



**Fig. 2.23** A schematic of the distribution of fine particles. (a) The equilibrium suspension of fine particles showing particle density versus height. (b) Stokes floatation (the marks •) and Brownian motion (the marks ×) of Al<sub>2</sub>O<sub>3</sub> particles in molten iron.

(or from the liquid surface).  $n_0$  is the number of fine particles at H = 0.  $G = 9.80 \text{ m/s}^2$  is the acceleration of gravity (Fig. 2.23a).

Furthermore, from Eq 2.67, estimate the equilibrium distribution of such impure particles as those of  $Al_2O_3$  suspended in molten iron in the cases of  $\bar{r} = 1$ , 0.1, and 0.01 µm, respectively. The following values may be used in the calculation.

$$T = 1873 \text{ K}, \rho = 4000 \text{ kg/m}^3, \rho_0 = 7000 \text{ kg/m}^3$$

Note that the terminal speed of fine particles during floatation (or sedimentation) is approximated to

$$v \approx \frac{(4/3)\pi \bar{r}_3 \cdot (\rho - \rho_0) \cdot g}{6\pi \bar{r}\eta} = \frac{(2/9)(\rho - \rho_0) \cdot g}{\eta} \bar{r}^2 \text{ [Stokes' Law(1850)]}$$

Here  $\eta$  is the coefficient of viscosity for a liquid, and the value for molten iron is given as  $\eta = 5.5 \times 10^{-3} \text{ J} \cdot \text{s/m}^3$ .

In addition, fine particles may drift the following distance by Brownian motion.

$$\overline{X} \approx \left(\frac{k_{\rm B}T}{3\pi\bar{r}\eta}t\right)^{1/2}$$
 [Einstein's equation for Brownian motion(1905)]

In the case of  $\bar{r} < 1 \mu m$ , as shown in Fig. 2.23(b), the drift distance by both Stokes' floatation and Brownian motion is not more than a few mm per hour. Therefore, it takes a fairly long time to reach equilibrium suspension as shown in (Eq 2.67).

2.16 When pure iron is set in a magnetic field, A<sub>3</sub> transformation temperature will be (i) higher, (ii) lower, or (iii) unchanged. And why?2.17 Investigate the following matters about liquid crystal.

(i) Is the state of liquid crystal in a solid phase or a liquid phase? (ii) Is

the phase transformation, liquid crystal  $\rightarrow$  liquid first-order phase transition like ordinary melting, or second-order transition like magnetic transition? (iii) Is the state of liquid crystal in a stable phase or a metastable phase?

**2.18** When a substance in an amorphous phase is heated, it is "crystallized." Is the phase transformation first order or second order?

# Appendix: (Ref 9) Synthesis of Diamond by Very High Pressure

Development of very high pressure science and technology owes much to the efforts of P.W. Bridgman, (1881–1961). He discovered a new phase of ice (VI) different from ordinary ice (I), heavier than water and infusible at room temperature when water is pressurized at higher than  $10^9$  Pa (Fig. 2.24a). He also invented his unique anvil high-pressure apparatus aiming at conversion of graphite to diamond. Transformation of graphite by pressure needs very high pressure of more than  $10^{10}$  Pa. In addition, heating at higher than 3000 K is necessary for nucleation of diamond (Fig. 2.24b). For this, he had a hard time performing his



(c) The phase diagrams of solvent (M)-carbon system

**Fig. 2.24** High-pressure effects on water and carbon (a) and (b). Both H<sub>2</sub>O and carbon are transformed at very high pressure according to the *P*-*T* diagrams. However, it is difficult to convert graphite into diamond directly because the diffusion coefficient of C atoms in graphite is not more than 10<sup>-15</sup> m<sup>2</sup>/s even at 3000 K. (c) On the other hand, the diffusion coefficient in liquid metal is 10<sup>-8</sup> m<sup>2</sup>/s at 2000 K, and it is enough for synthesis and growth of diamond.

experiment, and diamond was finally synthesized in 1955 using a flux method developed by the General Electric Company in the United States.

In a flux method, diamond is crystallized by dissolving graphite into a metal M (Ni, Fe, etc.). The key to success was that a liquid phase was used as a reaction medium because atoms can move more rapidly there (Fig. 2.24c).

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CHAPTER 3

# Thermodynamics of Solutions

Combining a metal and an oxide, previously thought to be "unmixable," is now possible using new technologies of sputtering and mechanical alloying. New kinds of combined materials have been created one after another. The idea of "Solution Theory" in this chapter is important in order for one to understand the nature of these "mixed materials." It will keep playing an indispensible role in the materials science of the 21st century though it has classic roots.

# 3.1 Solutions, Mixtures, and Compounds

# 3.1.1 The Ways of Mixing of Atoms and Molecules

A lot of materials have been developed by melting and mixing different kinds of material. These materials made by "mixing" are divided roughly into three kinds: the solution, the mixture, and the compound (Fig. 3.1).

"Solution" is a matter in which the atoms or the molecules mix almost uniformly, and it is called a liquid solution for the liquid state and a solid solution in the case of a solid.

"Mixture" is a matter in which groups of the atoms or molecules (a phase) mix mechanically. An emulsion is a liquid/liquid mixture where one kind of liquid phase particle is dispersed in the other liquid phase. A colloid liquid is solid/liquid mixture where solid phase particles are dispersed and suspended in liquid phase. Precipitated alloy is a solid/ solid mixture where one kind of crystal particle is dispersed in the other crystal.

"Compound" is a matter in which two or more kinds of atoms or molecules are chemically bound in a specific integer ratio of their numbers, an ionic crystal such as NaCl and a covalent crystal such as SiC are



Fig. 3.1 Basic styles of "mixing" of different materials

examples. A compound, such as Al<sub>2</sub>Cu, in which metal elements are mutually bonded in an integer ratio of their numbers in a long-range-ordered crystal is called an intermetallic compound. Many intermetallic compounds with interesting attributes have been discovered in recent years. However, one is often formed without the integer ratio of the composition atoms. Ni<sub>1-x</sub> Al<sub>x</sub> (x = 0.3 to 0.6) of the CsCl-type structure is such an example, and it is called a nonstoichiometric compound. One can think of this compound as a kind of "solution" in terms of how it is mixed or as a compound from the style of bonding between atoms.

#### 3.1.2 Components, Systems, and Composition Axes

A constituent element of a mixed material is called a component. However, a component does not always mean an atomic element. For instance, the components of the solution of water and ethyl alcohol are  $H_2O$  and  $C_2H_5OH$ , but not H, O, or C. That is because neither the  $H_2O$ molecule nor the  $C_2H_5OH$  molecule is decomposed to their constituent elements, as long as one does not perform a special treatment such as electrolysis.

To show the composition of a two-element system (binary system) that consists of two components A and B in Fig. 3.2(a), one can plot the composition point (data point  $\odot$ ) dividing the composition axis with A and B components at the ends into two segments according to the fraction (or %) of A and B, by assuming the full length of the axis to be one (or 100%).

In the case of the A-B-C three-element system (ternary system), assuming each side length of the composition triangle to be as shown



Fig. 3.2 Diagram of the composition of (a) a binary system and (b) a ternary system. (A regular tetrahedron is used for a quaternary system.)

in Fig. 3.2(b) to be one (or 100%), the length of the line segment drawn from the composition point (data point  $\odot$ ) parallel to each side corresponds to the proportion of each element (or %).

#### 3.1.3 Entropy of Solutions and Mixtures

To understand the difference of how solutions and mixtures are mixed, think about entropy changes by "solid solution" and "dispersion" in the following two exercises.

**[Exercise 3.1]** Mix  $N_A$  A atoms and  $N_B$  B atoms, arrange them at  $N = N_A + N_B$  lattice points at random, and calculate the total number of microscopic states of the solid. Moreover, derive the change of entropy by "mixing" using the Boltzmann relation (Eq 2.34).

**[Answer]** The total number of configurations of B atoms numbered from 1 to  $N_{\rm B}$  at N lattice points at random is  $N \cdot (N - 1) \dots (N - N_{\rm B} + 1) = N!/(N - N_{\rm B})!$ . However, because B atoms cannot be distinguished from one another, the total of the arrangements should be divided by the total of permutations of B atoms,  $N_{\rm B}!$  It is expressed in the following equation and shown in Fig. 3.3:

$$W_{\rm config}^{\rm A-B} = \frac{N!}{(N - N_{\rm B})! \cdot N_{\rm B}!} = \frac{N!}{N_{\rm A}! \cdot N_{\rm B}!}$$
(Eq 3.1)

Here we do not have to consider the total of the configurations of A atoms, because A atoms can occupy only the lattice points where no B atoms are arranged.



Fig. 3.3 The number of arrangement configuration of two white balls and two black balls increases to six possibilities according to "mixing."

The total of microscopic states before mixing  $W_0$  is  $W_0 = 1$ , because there is only one configuration of identical atoms. Consequently, the entropy change by "mixing" according to Eq 2.34 is.

$$\Delta S_{\text{mix}}^{\text{A}-\text{B}} = k_{\text{B}} \ln W_{\text{arrange}}^{\text{A}-\text{B}} - k_{\text{B}} \ln W_{0}$$
  
=  $k_{\text{B}} \ln (N!/N_{\text{A}}! \cdot N_{\text{B}}!) = -k_{\text{B}}N\left[\left(\frac{N_{\text{A}}}{N}\right) \ln \left(\frac{N_{\text{A}}}{N}\right) + \left(\frac{N_{\text{B}}}{N}\right) \ln \left(\frac{N_{\text{B}}}{N}\right)\right]$   
(Eq 3.2)

Stirling's approximation,  $\ln N! \approx N \ln N - N$  was used in Eq 3.2.

Assuming the total amount of A and B atoms is 1 mole, because N equals Avogadro's constant and  $k_{\rm B} \cdot N = R$  (gas constant), the entropy change  $\Delta S_{\rm mix}^{\rm A-B}$  becomes

$$\Delta S_{\text{mix}}^{\text{A}-\text{B}} = -R(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}})$$
(Eq 3.3)

where  $x_A = N_A/N$  and  $x_B = N_B/N$  are the fractions of A and B atoms.

Generalizing Eq 3.3, the entropy of mixing for a random mixture of n kinds of atoms becomes

$$\Delta S_{\rm mix} = -R\left(\sum_{i=1}^n x_i \ln x_i\right) \tag{Eq 3.4}$$

Figure 3.4 shows entropies of mixing for A-B system and A-B-C system in an expression of composition as described in Chapter 2. Because the value of the equation in the parentheses in both Eq 3.3 and 3.4 is negative,  $\Delta S_{\text{mix}} \ge 0$ . It is as large as that of entropy of melting  $\Delta S_{\text{m}}$  (Eq 2.20). This indicates that "solution" and "melting" are state changes in almost the same scale.



Fig. 3.4 Entropy of mixing for a random solution of A-B system or A-B-C system

However, entropy change is very small for "mixing" groups of atoms (i.e., particles), rather than mixing on the atomic or molecular level as shown in the next exercise.

**[Exercise 3.2]** Calculate the total of microscopic states when granules Bn with n B atoms bound are dispersed in a crystal of A atoms and increase of entropy by dispersion (Fig. 3.5a).

**[Answer]** Because every *n* vacant lattice point will occupied when every particle is arranged, the total random configurations of  $N_{\rm B}$  particles of Bn at a total of  $N = N_{\rm A} + n N_{\rm B}$  lattice points is

$$W_{\rm config}^{\rm A-B} = \frac{n^{N_{\rm B}} \cdot (N/n)!}{[(N-nN_{\rm B})/n]! \cdot N_{\rm B}!}$$
(Eq 3.5)

Here the overlapping of particles was not checked in order to avoid complexity in calculation. Moreover, the number of configurations of A atoms was not considered because A atoms can only occupy vacant points without Bn particles, as described in Exercise 3.1.

When  $N_A \rightarrow 0$ , or  $N \rightarrow nN_B$  in Eq 3.5, the total configurations become  $\binom{W_{\text{config}}^{A-B_n}}{N_{A\rightarrow 0}} = n^{N_B}$ . Because it can be thought to correspond to the total configurations of Bn particles before mixing  $W_0$ , the entropy change for dispersing Bn particles in crystal A approximates to

$$\Delta S_{\text{disperse}}^{\text{A}-\text{B}_n} \approx k_{\text{B}} \ln W_{\text{config}}^{\text{A}-\text{B}_n} - k_{\text{B}} \ln W_0$$
  
=  $-k_{\text{B}} \left( \frac{N}{n} \right) \left[ \left( \frac{N_{\text{A}}}{N} \right) \ln \left( \frac{N_{\text{A}}}{N} \right) + \left( \frac{nN_{\text{B}}}{N} \right) \ln \left( \frac{nN_{\text{B}}}{N} \right) \right]$  (Eq 3.6)



**Fig. 3.5** Change in entropy of mixing B<sub>9</sub>, which is formed of nine B atoms bound together in crystal of A atoms (per one mole of total of both A and B atoms). (a) A-granular B<sub>9</sub> mixture. (b) A-chain B<sub>9</sub> solution. (c) Change in entropy of mixing chain B<sub>9</sub> can be expressed by Eq 3.67 in Exercise 3.13.

Assuming the total amount of A atoms and B atoms is 1 mole, because  $N = N_A + nN_B$  equals Avogadro's constant,  $k_B N = R$ , and  $N_A / N = x_A$  and  $nN_B / N = x_B$ , Eq 3.6 can be summarized:

$$\Delta S_{\text{disperse}}^{\text{A}-\text{B}_n} \approx -\frac{1}{n} R(x_{\text{A}}) \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}})$$
(Eq 3.7)

Since fine particles even 1 nm in diameter are composed of many of B atoms ( $n \approx 10^2$ ), the entropy change caused by the dispersion of particles is negligibly small compared to that of mutual mixing of atoms (Eq 3.3).

When Bn is a chain molecule as in Fig. 3.5(b), however, one should think of it as a solution because the entropy change by mixing is large. Polymer solutions are good examples, and they were analyzed thermodynamically by P.J. Flory et al. (see Eq 3.67 in Exercise 3.13).

# **3.2 Approximation of Free Energy by Regular Solution Model (Ref 1–5)**

As shown in Chapter 2, the Gibbs free energy G of a pure substance can be divided into an enthalpy term (H) and an entropy term (-TS). Similarly for a solution, it is easy to understand it if it is divided into an enthalpy term indicating the bond strength between atoms in a solution and an entropy term indicating disorder. In this section, consider the most basic approximation, the regular solution approximation.\*

# 3.2.1 Nearest-Neighbor Assumption and Random Distribution Assumption—Basic Assumptions for Bragg-Williams-Gorski (B-W-G) Model

It is difficult to solve enthalpy H and entropy S of solution precisely. However, on the two following assumptions, H and S can be easily derived.

- Nearest-Neighbor Assumption. Interactions with more distant atoms than the second-nearest neighbors are ignored, assuming that the bonding power between atoms acts only between the first-nearest neighbors in a crystal.
- Random Distribution Assumption. The existence probability of atom A or B at each lattice point is assumed to equal average density  $x_A$  or  $x_B$ , regardless of the kinds of nearest-neighbor atoms. Moreover, the energy distribution of thermal vibration of A and B atoms is assumed to be irrelevant to the existence of the other component atom.

This model was presented by Bragg, Williams, and Gorsky to analyze the ordering phenomena in solid solutions, and it is called the B-W-G model (see Chapter 7 "Thermodynamics of Ordering"). This model expresses the basic nature of actual solutions clearly, though there are many people who think little of it because it is too simplified a model. In addition, what one must remember is that this model is the starting point of the development of various kinds of exquisite theories.

## 3.2.2 B-W-G Approximation of Enthalpy in Solid Solution

There are only three kinds of nearest-neighbor pairs for substitutional solid solution ( $\alpha$  phase) of binary system A-B: A-A, B-B, and A-B. One assumes these binding energies per pair to be  $\varepsilon_{AA}$ ,  $\varepsilon_{BB}$ , and  $\varepsilon_{AB}$  (more negative energy means more intense binding), respectively. Assuming the totals of each pair to be  $P_{AA}$ ,  $P_{BB}$ , and  $P_{AB}$ , because the enthalpy is the summation of energy of atom pairs, it is expressed as

$$H^{\alpha} = \varepsilon_{AA} \cdot P_{AA} + \varepsilon_{BB} \cdot P_{BB} + \varepsilon_{AB} \cdot P_{AB} \qquad (Eq \ 3.8)$$

<sup>\*</sup>The name "regular solution" was advocated by J.H. Hildebrand (1929) from the viewpoint of experimental chemistry. See Section 3.2.4 for the definition, etc.



Fig. 3.6 The distances to and the number of the first-, second-, and third-nearest neighbor atoms in fcc, bcc, and hcp crystals. There are eight first-nearest neighbor atoms in bcc, but it is sometimes considered z = 14 including six second-nearest neighbor atoms very close to them.

Assuming z is the coordination number, that is, the number of nearest neighbors around an atom, z = 12 for fcc and hcp crystals, and z = 8 for bcc as shown in Fig. 3.6. On the random distribution assumption,  $zx_A$ of z positions are occupied by atoms A and  $zx_B$  by B, the totals of atom pairs are

$$\begin{array}{l}
P_{AA} = N_{A} \cdot zx_{A} \times (\frac{1}{2}) = (zN/2)x_{A}^{2} = (zN/2)(x_{A} - x_{A}x_{B}) \\
P_{BB} = N_{B} \cdot zx_{B} \times (\frac{1}{2}) = (zN/2)x_{B}^{2} = (zN/2)(x_{B} - x_{A}x_{B}) \\
P_{AB} = N_{A} \cdot zx_{B} = zNx_{A}x_{B}
\end{array} \right\}$$
(Eq 3.9)

Here the relation  $x^2 = x - x(1 - x)$  is used. In addition, the reason why  $P_{AA}$  and  $P_{BB}$  are multiplied by (1/2) is to avoid duplication of identical pairs A-A and B-B.

From Eq 3.8 and 3.9, one can obtain the approximation of the enthalpy of the  $\alpha$  phase:

$$H^{\alpha} = \frac{zN}{2} \varepsilon_{AA} \cdot x_{A} + \frac{zN}{2} \varepsilon_{BB} \cdot x_{B} + zN \left( \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) x_{A} x_{B}$$

$$= \underbrace{\underbrace{\overset{\circ}H^{\alpha}_{A} \cdot x_{A} + \overset{\circ}H^{\alpha}_{B} \cdot x_{B}}_{\text{Sum of enthalpy of component}} + \underbrace{\underbrace{\Omega^{\alpha}_{AB} \cdot x_{A} x_{B}}_{\text{Enthalpy of mixing}} \right\}$$
(Eq 3.10)



Fig. 3.7 Estimated values of Ω in liquid phases of Al-X system and Fe-X system. See periodic table in "Supplement" for periodic table group numbers. Source: Ref 6

where  ${}^{\circ}H_{\rm A}^{\alpha} = zN\varepsilon_{\rm AA}/2$  and  ${}^{\circ}H_{\rm B}^{\alpha} = zN\varepsilon_{\rm BB}/2$  are the enthalpies of crystals A and B, respectively. Moreover,

$$\Omega_{AB}^{\alpha} = zN \left( \epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right)$$
 (Eq 3.11)

is called interaction parameter, and  $\Omega_{AB}^{\alpha} < 0$  when atoms A and B are attractive because  $\varepsilon_{AB}$  is more negative than  $(\varepsilon_{AA} + \varepsilon_{BB})/2$ . On the contrary,  $\Omega_{AB}^{\alpha} > 0$  when they are repulsive.

In Eq 3.10, the third term,  $\Omega^{\alpha}_{AB} x_A x_B$  is called enthalpy of mixing.\*

Figure 3.7 shows the values of  $\Omega_{AB}^{L}$  in a liquid phase of Al-X and Fe-X systems estimated by A.R. Miedema and his group. In the case of transition metals in the center of the periodic table,  $\Omega^{L} < 0$  because they are easy to merge in both Fe and Al. However, in case of alkaline metals (Na, K, and so on) in the left end of the table and semimetals (Bi, Sb, and so on) in the right end,  $\Omega^{L} > 0$  and they are difficult to merge in them.

**[Exercise 3.3]** Show that the enthalpy of solid solution of a ternary system A-B-C can be approximated by the following equation according to the B-W-G model.

<sup>\*</sup>If water and alcohol are mixed, then "heat" is generated. Generation of "heat" means that the enthalpy of mixing is negative and water molecules and alcohol molecules will attract each other and they can be mixed well, because  $\Delta H_{\text{system}} < 0$  when  $\Delta Q_{(\text{system} \rightarrow \text{heat bath})} > 0$  according to Eq 2.26.

$$H^{\alpha} = {}^{\circ}H^{\alpha}_{A} \cdot x_{A} + {}^{\circ}H^{\alpha}_{B} \cdot x_{B} + {}^{\circ}H^{\alpha}_{C} \cdot x_{C} + \Omega^{\alpha}_{AB} \cdot x_{A}x_{B} + \Omega^{\alpha}_{BC} \cdot x_{B}x_{C} + \Omega^{\alpha}_{CA} \cdot x_{C}x_{A}$$
(Eq 3.12)

where  $\Omega^{\alpha}_{BC}$  and  $\Omega^{\alpha}_{CA}$  are the interaction parameters in B-C system and C-A system, respectively.

**[Answer]** The pairs of the nearest-neighbor atoms in a solid solution consisting of three components, A, B, and C are six kinds: A-A, B-B, C-C, A-B, B-C, and C-A. For example, the totals of the pair A-A and the pair B-C is described in the following equations according to the random distribution assumption.

$$P_{AA} = N_A \cdot zx_A \times (\frac{1}{2}) = (zN/2)x_A^2 = (zN/2)(x_A - x_A x_B - x_A x_C)$$
$$P_{BC} = N_B \cdot zx_C = zN \cdot x_B x_C$$

If we define the interaction parameters of the system B-C and C-A based on Eq 3.11 as:

$$\Omega_{\rm BC}^{\alpha} = zN[\varepsilon_{\rm BC} - (\varepsilon_{\rm BB} + \varepsilon_{\rm CC})/2], \quad \Omega_{\rm CA}^{\alpha} = zN[\varepsilon_{\rm CA} - (\varepsilon_{\rm CC} + \varepsilon_{\rm AA})/2]$$

we can obtain Eq 3.12 according to the same discussion as the derivation of Eq 3.10.

Figure 3.8 shows the enthalpies of substitutional solid solutions of a binary system A-B and a ternary system A-B-C calculated by Eq 3.10 and 3.12.



Fig. 3.8 Enthalpy of substitutional solid solution (at constant temperature and pressure). (a) A-B binary system. (b) A-B-C ternary system

## 3.2.3 B-W-G Approximation of Entropy in Solid Solution

We can obtain the entropy  $S^{\alpha}$  of substitutional solid solution of system A-B according to Exercise 3.1.

First,  $N_A$  atoms A and  $N_B$  atoms B distribute at random regardless of the existence of the other component atom. What is more, both atoms select their energy level of thermal vibration independently. The total of such microscopic states  $W^{\alpha}$  is expressed as the multiplication of three terms because the arrangement of atoms at lattice points and the selection of energy level of thermal vibration are independent events.

The total of microscopic states in solid solution  $\alpha$ ,  $W^{\alpha}$ 

- = [The total of microscopic states of thermal vibration of A atoms,  $W_A$ ]<sup>N<sup>A</sup></sup>
- $\times$  [The total of microscopic states of thermal vibration of B atoms,  $W_{\rm B}$ ]<sup>N<sup>B</sup></sup>
- $\times$  The total of mixing of A and B atoms,  $W_{\text{config}}^{\text{A-B}}$

(Eq 3.13)

Therefore, the entropy of solid solution  $\alpha$  is approximated as

$$S^{\alpha} = k_{B} \ln (W_{A})^{N_{A}} + k_{B} \ln (W_{B})^{N_{B}} + k_{B} \ln W_{\text{config}}^{A-B}$$
  
=  ${}^{\circ}S_{A}^{\alpha} \cdot x_{A} + {}^{\circ}S_{B}^{\alpha} \cdot x_{B} + \Delta S_{\text{mixing}}^{A-B}$   
=  ${}^{\circ}S_{A}^{\alpha} \cdot x_{A} + {}^{\circ}S_{B}^{\alpha} \cdot x_{B} - R(x_{A} \ln x_{A} + x_{B} \ln x_{B})$  (Eq 3.14)

Here  ${}^{\circ}S_{A}^{\alpha} = k_{B}N$  ln  $W_{A}$  and  ${}^{\circ}S_{B}^{\alpha} = k_{B}N$  ln  $W_{B}$  are the entropies of thermal vibration of 1 mole crystal A and crystal B (see section 2.3.2).

## 3.2.4 B-W-G Approximation of Free Energy in Solid Solution

From Eq 3.10 and 3.14, one can obtain the approximation of the free energy of the substitutional solid solution of a binary system A-B:

$$G^{\alpha} = H^{\alpha} - TS^{\alpha}$$

$$= \underbrace{\underbrace{G_{A}^{\alpha} \cdot x_{A} + G_{B}^{\alpha} \cdot x_{B}}_{\text{Sum of free energy of component atoms}}_{\text{Entropy of mixing}} + \underbrace{\underbrace{RT(x_{A} \ln x_{A} + x_{B} \ln x_{B})}_{\text{Entropy of mixing}}}_{\text{Entropy of mixing}} + \underbrace{\underbrace{RT(x_{A} \ln x_{A} + x_{B} \ln x_{B})}_{\text{Entropy of mixing}}}_{\text{(Eq 3.15)}}$$

where  ${}^{\circ}G_{A}^{\alpha} = {}^{\circ}H_{A}^{\alpha} - T^{\circ}S_{A}^{\alpha}$  and  ${}^{\circ}G_{B}^{\alpha} = {}^{\circ}H_{B}^{\alpha} - T^{\circ}S_{B}^{\alpha}$  are the free energies of 1 mole crystal A and crystal B.

Generalizing Eq 3.15 to n component system, the B-W-G approximation of the free energy of the substitutional solid solution can be described as

$$G^{\alpha} = \underbrace{\sum_{i=1}^{n} {}^{\circ}G_{i}^{\alpha} \cdot x_{i}}_{\text{Free energy of the components}} + \underbrace{\sum_{i,j} \Omega_{ij}^{\alpha} \cdot x_{i}x_{j}}_{\text{Enthalpy of mixing}} + \underbrace{RT\left(\sum_{i=1}^{n} x_{i} \ln x_{i}\right)}_{\text{Entropy of mixing}}$$
(Eq 3.16)

When there are no particular interactions between component elements, that is  $\Omega_{ij} = 0$ , a solution is generally called an ideal solution, and its free energy is expressed as

$$[G]^{\text{ideal}} = \sum_{i=1}^{n} {}^{\circ}G_i \cdot x_i + RT\left(\sum_{i=1}^{n} x_i \ln x_i\right)$$
 (Eq 3.17)

Based on this ideal solution, Eq 3.16 can also be expressed as

$$[G]^{\text{regular}} = [G]^{\text{ideal}} + \underbrace{\sum_{i,j} \Omega_{ij} \cdot x_i x_j}_{\text{Excess free energy term}}$$
(Eq 3.18)

A regular solution is the solution with a free energy that can be approximated by addition of the excess free energy term with the density product  $x_i x_j$  of each component to  $[G]^{ideal}$  as in Eq 3.18.\*

Figure 3.9 shows the values of free energy estimated by Eq 3.15 as a function of the temperature *T*: (a) an ideal solution ( $\Omega_{AB} = 0$ ), (b) a regular solution in which atoms A and atoms B are attractive ( $\Omega_{AB} < 0$ ), and (c) a regular solution in which atoms A and atoms B are repulsive ( $\Omega_{AB} > 0$ ).

<sup>\*</sup>It was a principle in the definition of regular solutions by Hildebrand that  $\Omega$  was a constant value independent of both temperature and concentration. However, the restrictions have been relaxed, and the regular solution approximation "in a broad sense" is generally adopted now in which  $\Omega$  is regarded as a function of *T* and  $x_i$ .



**Fig. 3.9** Free-energy curves for an ideal solution and a regular solution of A-B binary system. (a) Ideal solution,  $\Omega_{AB} = 0$ . (b) Solution with  $\Omega_{AB} < 0$  (c) Solution with  $\Omega_{AB} > 0$ . A concave region appears at the temperature below  $T_C = \Omega_{AB}/2R$  (see section 4.4).

It is often the case that a small amount of B and C are added to a principal component A in a practical material. In such a case, it is useful to describe the excess free energy as (see Exercise 3.9 in Section 3.4.2):

$$[G]^{\text{excess}} = \Omega_{\text{AB}} \cdot x_{\text{B}}(1 - x_{\text{B}}) + \Omega_{\text{AC}} \cdot x_{\text{C}} (1 - x_{\text{C}}) + W_{\text{BC}} \cdot x_{\text{B}}x_{\text{C}} \quad (\text{Eq 3.19})$$

where  $W_{BC} = \Omega_{BC} - \Omega_{AB} - \Omega_{AC}$  is the interaction parameter between component B and component C in a solution whose principal component is A.

# **3.3 Approximation of Free Energy by Sublattice Model**

The B-W-G approximation method is originally a model of the solid solution where atom A and atom B are equally substituted for each other. However, Hillert and Staffansson (Ref 7) showed that it is possible to apply the method even to solutions that have special restrictions in arrangement of composition atoms such as an interstitial solution and a compound solution by supplementary consideration of sublattice idea.

## 3.3.1 Free Energy of III-V Compound Solutions

As for III-V compounds (i.e., InAs, GaSb) in which atoms of 3B group in the periodic table (see "Supplement" at the back of the book), Al, In, and Ga, are bound with atoms of 5B group, P, As, and Sb, in the ratio 1:1, In and Ga, or As and Sb in a same group can substitute for each other, respectively, to form a complex compound (In, Ga)(As, Sb).

The crystal structure is the cubic ZnS, which is composed of two fcc sublattices (I and II) diagonally displaced by  $\frac{1}{4}$  unit from each other as shown in Fig. 3.10(a), and atoms of 3B group (data point  $\circ$ ) located only



Fig. 3.10 Crystal structure and composition square of III-V compound solution. (a) Crystal structure. (b) Composition square

on the lattice I and atoms of 5B (data point •) on II. Then, assuming the fractions and B(Ga) on the lattice I to be  $y_A = 1 - y_B$  and  $y_B$ , C(As) and D(Sb) on the lattice II to be  $y_C = 1 - y_D$  and  $y_D$ , the composition of a complex compound can be displayed by the data point  $\odot$  in a composition square whose axes are  $y_B$  and  $y_D$  (Fig. 3.10b).

**Approximation of Enthalpy.** The number of the near neighbors  $\circ$ - $\bullet$  is 4 (hereafter described as z') in a unit cell and the near neighbors  $\circ$ - $\circ$  and  $\bullet$ - $\bullet$  is 12 (hereafter described as z). Suppose that the lattice constant is a, then the interatomic distance of the pair  $\circ$ - $\bullet$  is  $(\sqrt{3}/4)a = 0.43a$  because it is the first-nearest neighbor. The distance of the second-nearest neighbors,  $\circ$ - $\circ$  and  $\bullet$ - $\bullet$ , is  $(1/\sqrt{2})a = 0.71a$ . The total binding energy is approximated up to the second-nearest neighbors below.

First, there are four kinds of first-nearest neighbors: A-C, B-C, A-D, and B-D, and the total of the pair A-C,  $P_{AC}$ , is  $P_{AC} = N_A z' y_C = z' N \cdot y_A y_C$ , for example, by the random distribution assumption. Here N is the total of the lattice on the sublattice I. We can have the number of other pairs similarly, and the total binding energy of the first-nearest neighbors  $H_1$  is approximated as

$$H_1 = z'N(\varepsilon_{AC}y_Ay_C + \varepsilon_{BC}y_By_C + \varepsilon_{AD}y_Ay_D + \varepsilon_{BD}y_By_D)$$
(Eq 3.20)

Next we will consider the second-nearest neighbors  $\circ \circ \circ$  (A-A, B-B, A-B) and  $\bullet \bullet \bullet$  (C-C, D-D, C-D). For example, because the energy of A-A pair depends on whether an atom 1' neighboring the pair A-A

(1)-3) of Fig. 3.10a) is C or D and is assumed to be  $\epsilon_{AA}^{C}$  or  $\epsilon_{AA}^{D}$ , the total energy of A-A pair can be approximated by the random distribution assumption:

$$H_2^{A-A} = \left( \varepsilon_{AA}^{C} \cdot N_A \cdot zy_A y_C + \varepsilon_{AA}^{D} \cdot N_A \cdot zy_A y_D \right) \times (1/2)$$
  
=  $(zN/2) \left[ \varepsilon_{AA}^{C} y_A (1-y_B) y_C + \varepsilon_{AA}^{D} y_A (1-y_B) y_D \right]$  (Eq 3.21)

Considering other pairs similarly, the total energy of the second-nearest neighbors is

$$H_{2} = (zN/2) \begin{cases} \left[ \varepsilon_{AA}^{C} y_{A} + \varepsilon_{BB}^{C} y_{B} + \left( 2\varepsilon_{AB}^{C} - \varepsilon_{AA}^{C} - \varepsilon_{BB}^{C} \right) y_{A} y_{B} \right] y_{C} \\ + \left[ \varepsilon_{AA}^{D} y_{A} + \varepsilon_{BB}^{D} y_{B} + \left( 2\varepsilon_{AB}^{D} - \varepsilon_{AA}^{D} - \varepsilon_{BB}^{D} \right) y_{A} y_{B} \right] y_{D} \\ + \left[ \varepsilon_{CC}^{A} y_{C} + \varepsilon_{DD}^{A} y_{D} + \left( 2\varepsilon_{CD}^{A} - \varepsilon_{CC}^{A} - \varepsilon_{DD}^{A} \right) y_{C} y_{D} \right] y_{A} \\ + \left[ \varepsilon_{CC}^{B} y_{C} + \varepsilon_{DD}^{B} y_{D} + \left( 2\varepsilon_{CD}^{B} - \varepsilon_{CC}^{B} - \varepsilon_{DD}^{B} \right) y_{C} y_{D} \right] y_{B} \end{cases}$$
(Eq 3.22)

Unifying and rearranging both Eq 3.20 and 3.22 allows one to obtain an approximation of the enthalpy *H*:

$$H = H_{1} + H_{2}$$

$$= \underbrace{\frac{H_{AC}y_{A}y_{C} + H_{BC}y_{B}y_{C} + H_{AD}y_{A}y_{D} + H_{BD}y_{B}y_{D}}{\text{Sum of each enthalpy of component compounds}} + \underbrace{\frac{(L_{AB}^{C}y_{C} + L_{AB}^{D}y_{D})y_{A}y_{B}}{\text{Enthalpy of mixing on the lattice I}} + \underbrace{\frac{(L_{CD}^{A}y_{A} + L_{CD}^{B}y_{B})y_{C}y_{D}}{(Eq 3.23)}}$$

Here, for example,  $H_{AC}$  and  $L_{AB}^{C}$  are

$$H_{AC} = z'N\varepsilon_{AC} + (zN/2)\varepsilon_{AA}^{C} + (zN/2)\varepsilon_{CC}^{A}$$

$$L_{AB}^{C} = zN[\varepsilon_{AB}^{C} - (\varepsilon_{AA}^{C} + \varepsilon_{BB}^{C})/2]$$
(Eq 3.24)

and  $H_{AC}$  means the enthalpy per 1 mole compound AC (= InAs).  $L_{AB}^{C}$  is the interaction parameter between A-B(In-Ga) on lattice I when all of lattice II is occupied by C atoms.

Approximation of Entropy. Because both the thermal vibrations of each component and the configuration of sublattices I and II are considered independent events in the B-W-G approximation, all of the microscopic states of a complex compound can be expressed by the product of three terms:

The total number of microscopic states of (A, B)(C, D); W

- = The total of microscopic states in thermal vibrations of AC, BC, AD and BD
- $\times$  The total of configuration of A, B on the lattice I
- $\times$  The total of configuration of C, D on the lattice II

(Eq 3.25)

Π

Therefore, the entropy  $S = k_{\rm B} \ln W$  can be approximated:

$$S = \frac{\sum_{AC} y_A y_C + S_{BC} y_B y_C + S_{AD} y_A y_D + S_{BD} y_B y_D}{\text{Total of entropy of each component compound}}$$
$$- \frac{R(y_A \ln y_A + y_B \ln y_B)}{\text{Entropy of mixing on the lattice I}}$$
$$- \frac{R(y_C \ln y_C + y_D \ln y_D)}{\text{Entropy of mixing on the lattice II}}$$
(Eq 3.26)

**Approximation of Free Energy.** Unifying Eq 3.23 and 3.26 allows one to obtain an approximation of the free energy G:

$$G = G_{AC}y_{A}y_{C} + G_{BC}y_{B}y_{C} + G_{AD}y_{A}y_{D} + G_{BD}y_{B}y_{D} + (L_{AB}^{C}y_{C} + L_{AB}^{D}y_{D})y_{A}y_{B}$$
$$+ (L_{CD}^{A}y_{A} + L_{CD}^{B}y_{B})y_{C}y_{D} + RT(y_{A} \ln y_{A} + y_{B} \ln y_{B} + y_{C} \ln y_{C} + y_{D} \ln y_{D})$$
$$(Eq 3.27)$$

where  $G_{AC} = H_{AC} - TS_{AC}$  is the free energy per 1 mole compound AC (per 2 mole component atoms), and so on.

Generalizing Eq 3.26, the free energy of the complex compound  $(A, B)_m (C, D)_n$  formed of  $A_m C_n$  and  $B_m D_n$  is approximated:

$$G = G_{A_m C_n} y_A y_C + G_{B_m C_n} y_B y_C + G_{A_m D_n} y_A y_D + G_{B_m D_n} y_B y_D + m (L^C_{AB} y_C + L^D_{AB} y_D) y_A y_B + n (L^A_{CD} y_A + L^B_{CD} y_B) y_C y_D + RT [m (y_A \ln y_A + y_B \ln y_B) + n (y_C \ln y_C + y_D \ln y_D)]$$
(Eq 3.28)

Equations 3.27 and 3.28 are also discussed in Section 4.4.2 in Chapter 4 "Thermodynamics of Phase Diagrams," a slightly more simplified exercise is considered here.

**[Exercise 3.4]**  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> are oxides having same crystal structure (corundum type) and can form a solid solution at any ratio. Obtain an approximation describing the free energy of this complex compound (Al,Cr)<sub>2</sub>O<sub>3</sub> (This complex oxide is used in ruby crystals for laser oscillators.)

**[Answer]** If one supposes that the crystal lattice of  $(Al,Cr)_2O_3$  consists of two sublattices, sublattice I with Al atoms and Cr atoms arranged on it and sublattice II with only O atoms arranged on it, one can obtain the answer by substituting the symbols in Eq 3.28 as follows: A = Al, B = Cr, C = O, m = 2, n = 3,  $y_C = 1$ , and  $y_D = 0$ .

$$G = G_{Al_2O_3} \cdot y_{Al} + G_{Cr_2O_3} \cdot y_{Cr} + 2L_{AlCr}^O \cdot y_{AI} y_{Cr} + 2RT(y_{Al} \ln y_{Al} + y_{Cr} \ln y_{Cr})$$
(Eq 3.29)



**Fig. 3.11** Composition and free-energy curve of a complex oxide (Al, Cr)<sub>2</sub>O<sub>3</sub>. (a) Composition of (Al, Cr)<sub>2</sub>O<sub>3</sub>. (b) Free-energy curve of Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> pseudobinary system (schematic illustration)

Equation 3.29 is of the same form as Eq 3.15 in the previous section and can be considered a binary solution composed of both  $Al_2O_3$  and  $Cr_2O_3$ . This kind of multicomponent solution that can be dealt with in exactly the same way as a binary solution is called a pseudobinary solution (Fig. 3.11).

 $G_{Al_2O3}$  and  $G_{Cr_2O3}$  in Eq 3.29 are the free energies per 1 mole Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>. Moreover, the factor 2 of the enthalpy term of mixing and the entropy term of mixing are derived from the fact that lattice I consists of 2 mole Al or Cr atoms.

# 3.3.2 Free Energy of Interstitial Solutions

Carbon atoms can dissolve interstitially into  $\gamma$ Fe crystal having fcc structure in a solid state at the maximum of 2 mass% (about 10 at. %). This interstitial solid solution was named austenite after its discoverer W. Roberts-Austen (1897). An interstitial solid solution can occur in a wide range of composition even in a binary system such as  $\gamma$ Fe-N, Ti-O, Ti-H, and so on.

In the solid solution of the  $\gamma$  Fe-C system, as shown in Fig. 3.12(a), carbon atoms intrude into the middle point of the edge (data point •) or the center of the body (data point  $\odot$ ) of the fcc lattice. These intrusion points form another fcc lattice (dotted line) that is a parallel displacement by a half unit along an edge from the unit cell of  $\gamma$ Fe crystal, and the total of such points is equal to the total number of Fe atoms  $N_{\text{Fe}}$ .

Then, as in the case of the afore-mentioned III-V compounds, assuming that the lattice comprises two fcc sublattices (I and II), and that Fe atoms are arranged on sublattice I, C atoms and the vacancies (v) on the sublattice II, one can obtain the free energy of the solution.

First, by replacing the symbols in Eq (3.27) as A = Fe,  $y_A = 1$ ,  $y_B = 0$ , C = C (carbon), D = v (vacancy), the following equation is obtained:



**Fig. 3.12** Crystal structure and free energy of the interstitial solid solution of γFe-C system (austenite). Because interstitial sites of C atom is in the center of the octahedron of Fe atoms, it is called an octahedral interstice. (a) Crystal structure of γFe-C. (b) Interstitial sites of C atom. (c) The free energy curve (1273 K)

$$[G^{\gamma}]_{\text{Fe}} = G^{\gamma}_{\text{FeC}} \cdot y_{\text{C}} + G^{\gamma}_{\text{Fe}_{\text{v}}} \cdot y_{\text{v}} + L^{\gamma\text{Fe}}_{\text{C}_{\text{v}}} \cdot y_{\text{C}}y_{\text{v}} + RT(y_{\text{C}} \ln y_{\text{C}} + y_{\text{v}} \ln y_{\text{v}})$$
(Eq 3.30)

Here  $[G^{\gamma}]_{\text{Fe}}$  is the free energy when the number of Fe atoms = N, the number of C atoms  $= N \cdot y_{\text{C}}$ , and the number of vacancies in the interstitial site  $= N \cdot y_{\text{v}}$ . However, because a free energy is ordinarily obtained as a value for

the number of 
$$\text{Fe} = N_{\text{Fe}} = N(1 - x_{\text{C}})$$
  
the number of  $\text{C} = N_{\text{C}} = N_{x_{\text{C}}}$  the total N,

 $[G^{\gamma}]_{\text{Fe}}$  should be multiplied by  $(1 - x_{\text{C}})$ . Moreover,  $y_{\text{C}}$  and  $y_{\text{v}}$  are in the following relation to the molar fraction of C atom  $x_{\text{C}}$ :

$$y_{\rm C} = x_{\rm C}/(1-x_{\rm C}), \quad y_{\rm v} = 1 - y_{\rm C} = (1-2x_{\rm C})/(1-x_{\rm C})$$
 (Eq 3.31)

In summary, the free energy per mole of  $\gamma$ Fe-C solid solution can be expressed by

$$G^{\gamma} = [G^{\gamma}]_{\text{Fe}} \cdot (1 - x_{\text{C}})$$

$$= \underbrace{\underbrace{\circ G_{\text{Fe}}^{\gamma}(1 - x_{\text{C}}) + \Delta G_{\text{C}}^{\gamma\text{Fe}}x_{\text{C}}}_{\text{Total of free energies for component atoms Interaction energy of C - C pair}_{+ \underbrace{RT[x_{\text{C}} \ln x_{\text{C}} + (1 - 2x_{\text{C}}) \ln (1 - 2x_{\text{C}}) - (1 - x_{\text{C}}) \ln (1 - x_{\text{C}})]}_{\text{Term of entropy of mixing}}$$

(Eq 3.32)

Here  ${}^{\circ}G_{\text{Fe}}^{\gamma} = G_{\text{Fev}}^{\gamma}$  is the free energy per mole of fcc Fe, and the superscript  ${}^{\circ}$  indicates "pure substance."  $\Delta G_{\text{C}}^{\gamma\text{Fe}} (= L_{\text{Cv}}^{\gamma\text{Fe}} + G_{\text{Fe}}^{\gamma} - G_{\text{Fev}}^{\gamma})$  is the free energy per mole of solute C atoms.  $L_{\text{Cv}}^{\gamma\text{Fe}}$  is the interaction parameter for a C atom and a vacancy, and  $L_{\text{Cv}}^{\gamma\text{Fe}} < 0$  means that the energy of a C atom and a vacancy is attractive, and that of C atoms is repulsive.

The lattice constant of  $\gamma$ Fe crystal is presumed to be a = 0.355 nm at room temperature. The diameter of Fe atom is d = 0.254 nm, and the size of interstitial site for C atom is a - d = 0.10 nm. On the other hand, the diameter of C atom is  $d_{\rm C} = 0.15$  nm. Then, interstitial solid solution of C atoms will cause compulsive expansion of  $\gamma$ Fe lattice. This energy is the aforementioned  $\Delta G_{\rm C}^{\gamma {\rm Fe}}$ , and it is calculated at + 22 kJ  $\cdot$  mol<sup>-1</sup>(0.2 eV per C atom) at 1273 K. Also, the repulsive energy of C-C pair is

$$-L_{Cv}^{\gamma \text{Fe}} = 36 \text{ kJ } \cdot \text{mol}^{-1}$$
$$-L_{Cv}^{\gamma \text{Fe}}/(z/2)N = 0.06 \text{ eV per pair (refer to Exercise 3.8).}$$

Figure 3.12(c) shows the free-energy curves for  $\gamma$ Fe-C austenite calculated by Eq 3.32, and one can see that the increasing energies by lattice strain and C-C pairs are offset by the decreasing energy by the contribution of entropy of mixing, and that, on the whole, the free energy decreases by the interstitial solid solution of C atoms (below 15 at. %).

# 3.4 Chemical Potential

### 3.4.1 Partial Molar Quantity

What is chemical potential? To answer this question, consider the molar volume of the solution of water (A) and alcohol (B). If this is an ideal solution, the molar volume (V) is linear as shown by the dot-dash line in Fig. 3.13(a). However, because a water molecule and an alcohol molecule attract each other and the intermolecular distance becomes shorter, the substantial volumes of each molecule become smaller than the molar volumes  ${}^{\circ}V_{A}$  of pure water and  ${}^{\circ}V_{B}$  of pure alcohol, respectively. Such substantial volumes of components A and B in a solution are called partial molar volumes and expressed by  $\bar{V}_{A}$  and  $\bar{V}_{B}$ .

**[Exercise 3.5]** Show the following relation between a molar volume V of A-B solution and partial molar volumes of both components  $\bar{V}_A$  and  $\bar{V}_B$ .

$$V(x_{\rm A}, x_{\rm B}) = \bar{V}_{\rm A} \cdot x_{\rm A} + \bar{V}_{\rm B} \cdot x_{\rm B}$$
 (Eq 3.33)

The left side of Eq 3.33 corresponds to the data point  $\odot$  in Fig. 3.13(a).  $\bar{V}_{A}$  and  $\bar{V}_{B}$  on the right side of Eq 3.33 correspond to the data points  $\triangle$  and  $\blacktriangle$  in the Figure. This is called Roozeboom's diagram (1904).


**Fig. 3.13** Relationship between the molar volume of A-B solution (*V*) and the partial molar volumes ( $\bar{V}_{A'}$ ,  $\bar{V}_{B}$ ). (a) Molar volume of a solution. (b) Partial molar volumes of components A and B

**[Answer]** Consider a solution of  $m_A$  moles of component A and  $m_B$  moles of component B. The volume V is an extensive quantity,\* and because when the moles of both components increase by a factor  $\varphi$ , then so does the value of V, the following equation can be obtained:

$$\varphi \cdot V(m_{\rm A}, m_{\rm B}) = V(\varphi m_{\rm A}, \varphi m_{\rm B})$$
 (Eq 3.34)

Differentiate both sides of Eq 3.34 by  $\phi$  and then replace  $\phi = 1$  to obtain

$$V(m_{\rm A}, m_{\rm B}) = \left(\frac{\partial V}{\partial m_{\rm A}}\right) \cdot m_{\rm A} + \left(\frac{\partial V}{\partial m_{\rm B}}\right) \cdot m_{\rm B}$$
(Eq 3.35)

Because  $V(m_A, m_B) = (m_A + m_B) \cdot V(x_A, x_B)$ ,  $(\partial V / \partial m_A)$  and  $(\partial V / \partial m_B)$  will become:

$$\left. \begin{array}{l} \left( \frac{\partial V}{\partial m_{\rm A}} \right) = V(x_{\rm A}, x_{\rm B}) + \left( m_{\rm A} + m_{\rm B} \right) \left( \frac{\partial V}{\partial x_{\rm B}} \right) \left( dx_{\rm B}/dm_{\rm A} \right) \\ = V(x_{\rm A}, x_{\rm B}) - \left( \frac{\partial V}{\partial x_{\rm B}} \right) \cdot x_{\rm B} = \bar{V}_{\rm A} \\ \left( \frac{\partial V}{\partial m_{\rm B}} \right) = V(x_{\rm A}, x_{\rm B}) + \left( m_{\rm A} + m_{\rm B} \right) \left( \frac{\partial V}{\partial x_{\rm B}} \right) \left( dx_{\rm B}/dm_{\rm B} \right) \\ = V(x_{\rm A}, x_{\rm B}) - \left( \frac{\partial V}{\partial x_{\rm B}} \right) \cdot \left( 1 - x_{\rm B} \right) = \bar{V}_{\rm B} \end{array} \right\}$$
(Eq 3.36)

Here we use the relations  $x_B = m_B/m_A + m_B$ ,  $dx_B/dm_A = -x_B/(m_A + m_B)$ , and  $dx_B/dm_B = (1 - x_B)/(m_A + m_B)$ .

\*Volume and free energy are in proportion to the amount of substance and called extensive quantities. Pressure and temperature are qualitative parameters of a substance, and they are classified as intensive quantities.



**Fig. 3.14** Relation between the free energy ( $G^{\alpha}$ ) and chemical potentials ( $\mu_A^{\alpha}$ ,  $\mu_B^{\alpha}$ ,  $\mu_C^{\alpha}$ ) of a solution of (a) A-B system and (b) A-B-C system

From Eq 3.35 and 3.36 we can obtain Eq 3.33; that is:

$$V(m_{\rm A}, m_{\rm B}) = \bar{V}_{\rm A} \cdot m_{\rm A} + \bar{V}_{\rm B} \cdot m_{\rm B}$$

Generalizing this, when an extensive quantity Q of *n*-component system is distributed to each component according to its molar fraction as in the following equation, the distributed value is called  $\bar{Q}_i$  a partial molar quantity of component *i*.

$$Q = \sum_{i=1}^{n} \bar{Q}_i \cdot x_i \tag{Eq 3.37}$$

Now back to the first question after a very long explanation, "chemical potential" is the partial molar quantity  $\bar{G}_i^{\alpha}$  of the free energy  $G^{\alpha}$  of  $\alpha$ solution, and it was advocated and expressed as  $\mu_i^{\alpha}$  by J.W. Gibbs (1876).

Figure 3.14(a) is the relation between the free energy of A-B solution and the chemical potentials of both components; it is clear from Eq. 3.33and 3.36 that the relation can be expressed by

$$G^{\alpha} = \mu_{\rm A}^{\alpha} \cdot x_{\rm A} + \mu_{\rm B}^{\alpha} \cdot x_{B} \qquad ({\rm Eq} \ 3.38)$$

$$\mu_{\rm A}^{\alpha} = G^{\alpha} - \left(\frac{\partial G^{\alpha}}{\partial x_{\rm B}}\right) \cdot x_{\rm B} \mu_{\rm B}^{\alpha} = G^{\alpha} - \left(\frac{\partial G^{\alpha}}{\partial x_{\rm B}}\right) \cdot x_{\rm B} + \left(\frac{\partial G^{\alpha}}{\partial x_{\rm B}}\right)$$
 (Eq 3.39)

**[Exercise 3.6]** Show that the chemical potential of  $\alpha$  solution of *n*-component system can be expressed by

$$\mu_{1}^{\alpha} = G^{\alpha} - \sum_{i=2}^{n} \left( \frac{\partial G^{\alpha}}{\partial x_{i}} \right) \cdot x_{i}$$

$$\mu_{j}^{\alpha} = \mu_{1}^{\alpha} + \left( \frac{\partial G^{\alpha}}{\partial x_{j}} \right)$$
(Eq 3.40)

[Answer] Generalizing Eq 3.38 to *n*-component system and the term of the fundamental component 1 separated,

$$G^{\alpha} = \sum_{i=1}^{n} \mu_{i}^{\alpha} \cdot x_{i} = \mu_{1}^{\alpha} + \sum_{i=2}^{n} \left( \mu_{i}^{\alpha} - \mu_{1}^{\alpha} \right) \cdot x_{i}$$
 (Eq 3.41)

For example, in the case of component B of A-B-C ternary system,  $\mu_i^{\alpha} - \mu_1^{\alpha}$  in Eq 3.41 is correspondent with 2-10 in Fig. 3.14(b) and is described by

$$\mu_i^{\alpha} - \mu_1^{\alpha} = \left(\frac{\partial G^{\alpha}}{\partial x_i}\right) \tag{Eq 3.42}$$

Equation 3.40 can be derived by arranging Eq. 3.41 and 3.42.

**[Exercise 3.7]** Approximate the chemical potentials of components A and B of A-B solution by the regular solution model.

**[Answer]** From Eq 3.15, the regular solution approximation of the free energy for  $\alpha$  solution of A-B system is

$$G^{\alpha} = {}^{\circ}G^{\alpha}_{A}(1-x_{B}) + {}^{\circ}G^{\alpha}_{B}x_{B} + \Omega^{\alpha}_{AB}x_{B} (1-x_{B})$$
$$+ RT[(1-x_{B}) \ln (1-x_{B}) + x_{B} \ln x_{B}]$$

Calculate  $(\partial G^{\alpha} / \partial x_{\rm B})$  from the above equation and substitute it into Eq (3.39), and one will obtain.

$$\mu_{\rm A}^{\alpha} = {}^{\circ}G_{\rm A}^{\alpha} + \Omega_{\rm AB}^{\alpha}x_{\rm B}^{2} + RT \ln(1 - x_{\rm B}) \mu_{\rm B}^{\alpha} = {}^{\circ}G_{\rm B}^{\alpha} + \Omega_{\rm AB}^{\alpha}(1 - x_{\rm B})^{2} + RT \ln x_{\rm B}$$
 (Eq 3.43)

Figure 3.15(a) illustrates the relation between  $\mu_{\rm B}^{\alpha}$  and  $x_{\rm B}$  on the assumption that  $\Omega_{\rm AB}^{\alpha} = +1.5RT$ , 0, or -2.5RT. Notice that  $\mu_{\rm B}^{\alpha} \to -\infty$  when  $x_{\rm B} \to 0$ , and  $\mu_{\rm B}^{\alpha} \to {}^{\circ}G_{\rm B}^{\alpha}$  when  $x_{\rm B} \to 1$ .



**Fig. 3.15** The chemical potential  $(\mu_{B}^{\alpha})$  and the activity  $(a_{B})$  of B component in a regular solution of A-B system.  $\mu_{B}^{\alpha}$  is shown as the value divided by *RT* assuming  $^{\circ}G_{B}^{\alpha} = 0$ . (a) Chemical potential. (b) Activity (Raoult's standard)

#### 3.4.2 Activity and Activity Coefficient of Solute Atoms

Activity is as important a concept for components in a solution as chemical potential, and a view point advocated by G.N. Lewis (1907) (Ref 1). As for A-B solution, the activities of A and B components  $a_A$  and  $a_B$  are defined by

$$\mu_{\rm A}^{\alpha} = {}^{\circ}G_{\rm A}^{\alpha} + RT \ln a_{\rm A}, \quad \mu_{\rm B}^{\alpha} = {}^{\circ}G_{\rm B}^{\alpha} + RT \ln a_{\rm B}$$
 (Eq 3.44)

Compared with Eq 3.43 when describing A-B system by the regular solution model, the following relation between the activity and the interaction parameter  $\Omega^{\alpha}_{AB}$  can be obtained:

$$a_{\rm A} = x_{\rm A} \cdot \exp\left[\frac{\Omega_{\rm AB}^{\alpha}}{RT}x_{\rm B}^2\right], \ a_{\rm B} = x_{\rm B} \cdot \exp\left[\frac{\Omega_{\rm AB}^{\alpha}}{RT}(1-x_{\rm B})^2\right]$$
 (Eq 3.45)

Figure 3.15(b) illustrates the relation between  $a_{\rm B}$  and  $x_{\rm B}$  when  $\Omega_{\rm AB}^{\alpha} = +1.5RT$ , 0, or -2.5RT. If  $\alpha$  phase is an ideal solution, then  $\Omega_{\rm AB}^{\alpha} = 0$  and the activity  $a_{\rm B}$  is equal to the molar fraction  $x_{\rm B}$ . However, when A and B atoms attract each other ( $\Omega_{\rm AB}^{\alpha} < 0$ ), the activity  $a_{\rm B}$  (the apparent concentration) is less than the concentration of its original meaning  $x_{\rm B}$ . When A and B atoms repulse each other ( $\Omega_{\rm AB}^{\alpha} > 0$ ), the activity  $a_{\rm B}$  is larger than the original concentration  $x_{\rm B}$  (data point  $\blacksquare$  in Fig. 3.15b).

Thus, an activity means "an apparent concentration converted on the basis of an ideal solution," and the conversion factor  $\gamma_i = a_i / x_i$  is called an activity coefficient.\*

**[Exercise 3.8]** Estimate the activity coefficient of C atom in  $\gamma$ Fe-C solution (an austenite) using the data at 1273 K shown in Section 3.3.2.

**[Answer]** From the approximation of the free energy of  $\gamma$ Fe-C solid solution (Eq 3.32), we can obtain the chemical potential of C atom:

$$\mu_{\rm C}^{\gamma} = G^{\gamma} - \left(\frac{\partial G^{\gamma}}{\partial x_{\rm C}}\right) x_{\rm C} + \left(\frac{\partial G^{\gamma}}{\partial x_{\rm C}}\right)$$
$$= \Delta G_{\rm C}^{\gamma} - 2L_{\rm C_v}^{\gamma \rm Fe} x_{\rm C} / (1 - x_{\rm C}) + RT [\ln x_{\rm C} - \ln (1 - 2x_{\rm C})]$$
$$\approx \Delta G_{\rm C}^{\gamma} - 2\left(L_{\rm C_v}^{\gamma \rm Fe} - RT\right) x_{\rm C} + RT \ln x_{\rm C} \qquad ({\rm Eq} \ 3.48)$$

Here, the terms including  $x_{\rm C}^2$  are omitted and  $\ln(1 - 2x_{\rm C}) = -2x_{\rm C}$ .

On the other hand, when the free energy of graphite is based, for example, on  ${}^{\circ}G_{C}^{gr} = 0$ , the activity of C atom  $a_{C}$  is defined by

$$\mu_{\rm C}^{\gamma} = RT \ln a_{\rm C} \tag{Eq 3.49}$$

From both sides of Eq 3.49 one can obtain the expression of the activity coefficient of C atom as

$$\gamma_{\rm C} = \frac{a_{\rm C}}{x_{\rm C}} \approx \exp\left(\frac{\Delta G_{\rm C}^{\gamma}}{RT}\right) \cdot \exp\left[-2\left(\frac{L_{\rm C_v}^{\gamma {\rm Fe}}}{RT} - 1\right) x_{\rm C}\right]$$
 (Eq 3.50)

\*Activity defined in Eq 3.44 is based on the experimental rule of F.M. Raoult (1887), and it is called "activity referred to Raoult's standard." Another useful activity is "activity referred to Henry's standard," which is based on the experimental rule of W. Henry (1805), and the activity coefficient  $f_{\rm B}$  is determined as  $a_{\rm B}^{\rm H}/x_{\rm B} \rightarrow 1$  for  $x_{\rm B} \rightarrow 0$  as shown in Fig. 3.16 (b). The relation between  $f_{\rm B}$  and  $\gamma_{\rm B}$  is:

$$f_{\rm B} = \gamma_{\rm B} \exp(-\Omega_{\rm AB}/RT) \tag{Eq 3.46}$$

"Activity referred to Henry's standard expressed in mass%" is used regularly in chemical engineering and extractive metallurgy. The coefficient of this activity  $f_B(\%)$  is determined as  $a_B^H(\%)/c_B \rightarrow 1$  when  $c_B \rightarrow 0$  as shown in Fig. 3.16(c). The relation of  $f_B(\%)$  and  $f_B$  is as follows if atomic weights of a solvent and a solution are presumed to be  $w_A$  and  $w_B$ :

$$f_{\rm B}(\%) = f_{\rm B} \cdot \left[ (100x_{\rm B}/c_{\rm B})(w_{\rm A}/w_{\rm B}) \right]$$
 (Eq 3.47)



Fig. 3.16 The definition of the activity of solute atoms (see Ref 8 for details). (a) Raoult's standard. (b) Henry's standard. (c) Henry's standard (mass%)



**Fig. 3.17** The activity of C atoms in γFe-C austenite *a*<sub>C</sub> (graphite standard). The data can be obtained by measured values of partial pressure of CO and CO<sub>2</sub> in CO-CO<sub>2</sub> atmosphere. (The marks • are the data from Ref 9.)

The first term on the right side is the activity coefficient for a dilute solution ( $x_{\rm C} \rightarrow 0$ ), and because  $\Delta G_{\rm C}^{\gamma} \approx 22 \,\text{kJ/mol}$  is estimated, the value of the first term is 8.0 (at 1273 K). The second term expresses the repulsive interaction between C atoms, and because  $L_{C_v}^{\gamma \text{Fe}} = -36 \,\text{kJ/mol}$  is measured, the value is 1.55 (at 1273 K) in the case of  $x_{\rm C} = 0.05$  (about 1 mass%). Therefore, the activity coefficient is 8.0 × 1.55 ≈ 12.

Putting the above more simply, C atoms confined in  $\gamma$ Fe crystal have a very high activity because it is narrower than in the state of graphite. As a result, it is observed to include apparently 12 times as many C atoms (Fig. 3.17). **[Exercise 3.9]** When the third element M is added to Fe-C system, investigate the influence of M on the chemical potential and the activity coefficient of C atoms in  $\gamma$ Fe-C-M austenite.

**[Answer]** Replace the symbols in Eq 3.27 by the sublattice model as follows: A = Fe, B = M, C = C (carbon), D = v (vacancy). Also, convert the fraction  $y_i$  in a sublattice into the molar fraction  $x_i$  in an austenite.

$$y_{\rm C} = x_{\rm C}/(1-x_{\rm C}), \quad y_{\rm v} = 1 - y_{\rm C} = (1-2x_{\rm C})/(1-x_{\rm C})$$
  
 $y_{\rm M} = x_{\rm M}/(1-x_{\rm C}), \quad y_{\rm Fe} = x_{\rm Fe}/(1-x_{\rm C})$ 

Moreover, multiply G in Eq 3.27 by  $(1 - x_c)$  to obtain each free energy per mole of Fe, C, and M atoms, omit the terms including higher than third order of the concentrations, and obtain

$$G^{\gamma} \approx {}^{\circ}G^{\gamma}_{\text{Fe}} \cdot x_{\text{Fe}} + {}^{\circ}G^{\gamma}_{\text{M}} \cdot x_{\text{M}} + \Delta G^{\gamma\text{Fe}}_{\text{C}} \cdot x_{\text{C}} - L^{\gamma\text{Fe}}_{\text{Cv}} \cdot x^{2}_{\text{C}}/(1 - x_{\text{C}}) + \Omega^{\gamma}_{\text{FeM}} \cdot x_{\text{M}}(1 - x_{\text{M}}) + W^{\gamma}_{\text{MC}} \cdot x_{\text{M}}x_{\text{C}} + RT[x_{\text{Fe}} \ln x_{\text{Fe}} + x_{\text{M}} \ln x_{\text{M}} + x_{\text{C}} \ln x_{\text{C}} + (1 - 2x_{\text{C}}) \ln (1 - 2x_{\text{C}}) - 2(1 - x_{\text{C}}) \ln (1 - x_{\text{C}})]$$
(Eq 3.51)

Here  $W_{MC}^{\gamma} = \Delta G_C^{\gamma M} - G_C^{\gamma Fe} + L_{FeM}^{\gamma C} - \Omega_{FeM}^{\gamma}$  is a parameter that describes the interaction between C atoms and M atoms in the austenite (refer to Eq 3.19).

The chemical potential of C atoms is obtained by Eq 3.51 and Eq 3.40 as

$$\mu_{\rm C}^{\gamma} = G^{\gamma} - \left(\frac{\partial G^{\gamma}}{\partial x_{\rm M}}\right) x_{\rm M} - \left(\frac{\partial G^{\gamma}}{\partial x_{\rm C}}\right) x_{\rm C} + \left(\frac{\partial G^{\gamma}}{\partial x_{\rm C}}\right)$$

$$\approx \Delta G_{\rm C}^{\gamma {\rm Fe}} - 2 \left(L_{\rm Cv}^{\gamma {\rm Fe}} - RT\right) x_{\rm C} + RT \ln x_{\rm C} + W_{\rm MC}^{\gamma} \cdot x_{\rm M} (1 - x_{\rm C})$$
(Eq 3.52)

Compared with  $\mu_C^{\gamma}$  in Fe-C system (Eq 3.48), one can understand that the final term  $W_{MC}^{\gamma} x_M (1 - x_C)$  indicates the influence of M addition.

From the definition of Eq 3.50, the activity coefficient of C atoms (graphite standard) is expressed by\*

$$\underbrace{\gamma_{\rm C} = \frac{a_{\rm C}}{x_{\rm C}} \approx \exp\left(\frac{\Delta G_{\rm C}^{\gamma {\rm Fe}}}{RT}\right) \cdot \exp\left[-2\left(\frac{L_{\rm CV}^{\gamma {\rm Fe}}}{RT} - 1\right)x_{\rm C}\right]}_{\text{Activity coefficient of } \gamma {\rm Fe-C system}} \cdot \underbrace{\exp\left(\frac{W_{\rm MC}^{\gamma}}{RT} \cdot x_{\rm M}\right)}_{\text{(Eq 3.53)}}$$

\*The activity coefficient of C atom in a dilute solution of Fe-C- $M_1$ - $M_2$  system can be approximated by (Ref 8):

$$\gamma_{\rm C} \approx (\gamma_{\rm C})_0 \cdot \exp\left(\sum_{j=1}^n \varepsilon_{\rm C}^{{\rm M}_j} \cdot x_{{\rm M}_j}\right)$$
 (Eq 3.54)

	Elei	ments dec	reasing ac	ctivity of c	arbon ato	Elements increasing activity of carbon atoms				
	Ti	Nb	V	Cr	Mo	Mn	Со	Ni	Cu	Si
$W_{\rm MC}^{\gamma}$ , kJ/mol	-570	-610	-305	-110	-115	-42	+24	+46	+25	+112
Source: Ref 11										

Table 3.1 Carbon-metal interaction parameter,  $W_{MC}^{\gamma}$  in austenite (1273 K)

Table 3.1 shows the values of interaction parameter  $W_{MC}^{\gamma}$  in  $\gamma$ Fe - C - M system.

# 3.5 Nonrandom Distribution of Solute Atoms

In the previous sections, the B-W-G model was analyzed on the assumption that the component atoms may be randomly distributed in a solution. However, in the microstructure of the materials, a nonrandom distribution will occur such as (i) segregation of solute atoms in grain boundaries or dislocations or (ii) ordering of solid solution, and it may have a remarkable influence on various characteristics of the materials.

For example, in a semiconductor, a complex defect—a combination of a solute atom and a lattice defect—dominates its electronic characteris-

Here  $(\gamma_C)_0$  is the activity coefficient of Fe-C system.  $\epsilon_C^{M_j}$  is a parameter called the interaction coefficient, and it is defined by

$$\varepsilon_{\rm C}^{\rm M_j} = \left[\frac{\partial}{\partial x_{\rm M_j}} (\ln \gamma_{\rm C})\right]_{x_{\rm M_j} \to 0} = W_{\rm M_j \rm C}/RT \qquad ({\rm Eq} \ 3.55)$$

 $\epsilon_{C}^{M_{j}}$  is also available as it is in the case of "activity referred to Henry's standard," but the interaction coefficient for mass % defined by common logarithm is used for "activity referred to Henry's standard expressed in mass %" as

$$e_{\rm C}^{\rm M_j} = \left[\frac{\partial}{\partial x_{\rm M_j} \to {\rm C}_{\rm M_j}} \ (\log f_{\rm C})\right]_{{\rm C}_{\rm M_j} \to 0\%}$$
 (Eq 3.56)

In order to convert between  $\varepsilon_{\rm C}^{{\rm M}_j}$  and  $e_{\rm C}^{{\rm M}_j}$ , the following equation presented by Lupis-Elliott et al. (Ref 10) can be used.

$$\varepsilon_{\rm C}^{\rm M_j} = 230 \frac{w_j}{w_{Fe}} e_{\rm C}^{\rm M_j} + \frac{w_{\rm Fe} - w_j}{w_{Fe}}$$
 (Eq 3.57)

Here  $w_i$  and  $w_{\text{Fe}}$  are the atomic weights of  $M_i$  and Fe.

tics (Ref 3,4). Among them, (i) grain-boundary segregation and (ii) ordering are explained in Chapters 5 and 7, and (iii) nonrandom distribution based on the interactions between solute atoms is considered here.

# 3.5.1 I-S Bonding between Interstitial Atoms (I) and Substitutional Atoms (S)

For example, C atoms should occupy interstitial positions close to Cr atoms with high probability because Cr-C bonding is strong in a solution of  $\gamma$ Fe - Cr - C system. Hereafter, let S, denote substitutional solute atoms and I denote interstitial solute atoms, and let  $N_{\text{Fe}}$ ,  $N_{\text{S}}$ , n, and N denote the number of Fe, S, I, and the total atoms. The interstitial positions of I atoms compose a fcc lattice as shown in Fig. 3.12(a) and (b), the total of the interstitial positions N' is equal to the total of the main lattice points,  $N_{\text{Fe}} + N_{\text{S}} = \text{N} - \text{n}$ .

First, let N' interstitial positions be divided into the I sites under the influence of S atoms (the total is  $N'_{\rm S} = z'N_{\rm S}$ ) and the I<sub>Fe</sub> sites free from the influence of S atoms (the total is  $N'_{\rm Fe} = N' - z'N_{\rm S}$ ) as illustrated in Fig. 3.18(a), and let  $n_{\rm S}$ ,  $n_{\rm Fe} = n - n_{\rm S}$  be the numbers of I atoms arranged in each of the sites. Also, the question of which ratio of  $n_{\rm S}$  and  $n_{\rm Fe}$  makes a solution the stablest is analyzed according to the Maxwell-Boltzmann distribution law.

**Enthalpy of I-S Bonding.** Letting  $\varepsilon_{FeI}$  and  $\varepsilon_{SI}$  be the bonding energies per pair of Fe-I and S-I, the total bonding energy is approximated by

$$H_{\rm I-S} \approx \varepsilon_{\rm FeI} \cdot n_{\rm Fe} + \varepsilon_{\rm SI} \cdot n_{\rm S} = \varepsilon_{\rm FeI} \cdot n + \Delta \varepsilon_{\rm I-S} \cdot n_{\rm S}$$
(Eq 3.58)

Here  $\Delta \varepsilon_{I-S} = \Delta \varepsilon_{SI} - \varepsilon_{FeI}$  is a parameter that denotes the strength of I-S bonding, and its large negative value means strong bonding.



**Fig. 3.18** I-S bonding in a solid solution of  $\gamma$ Fe-interstitial (I)-substitutional (S). (a) Classification of interstitial sites. (b) Numerical distribution. (c) Trap ratio related to temperature.  $f_1^{\rm S} = n_{\rm S}/n$ .

**Entropy of I-S Bonding.** The total number of microscopic states of I atoms is approximated by the multiplication of two terms as

$$W_{\text{config}}^{\text{I-S}} = \frac{N_{\text{S}}'!}{n_{\text{S}}! \cdot (N_{\text{S}}' - n_{\text{S}})!} \cdot \frac{N_{\text{S}}'!}{(n - n_{\text{S}})! \cdot (N_{\text{Fe}}' - n + n_{\text{S}})!}$$
(Eq 3.59)

Where the first half is the configuration of  $n_{\rm S}$  atoms on I sites, and latter half is the configuration of  $N_{\rm Fe}$  atoms on I<sub>Fe</sub> sites. Therefore, the entropy of configuration of I atoms is approximated as

Equilibrium Distribution and Trap Ratio of I atoms. According to the condition,  $(\partial G_{I-S}/\partial n_S) = 0$ , where a free energy  $G_{I-S} = H_{I-S} - TS_{I-S}$  becomes minimum, the equilibrium distribution of I atoms is given as

$$\frac{n_{\rm S}}{n_{\rm Fe}} = \left(\frac{N'_{\rm S} - n_{\rm S}}{N_{\rm Fe} - n_{\rm Fe}}\right) \exp\left(-\frac{\Delta\varepsilon_{\rm I-S}}{k_{\rm B}T}\right) \\\approx \left(\frac{z'x_{\rm S}}{1 - z'x_{\rm S}}\right) \cdot \exp\left(-\frac{\Delta\varepsilon_{\rm I-S}}{k_{\rm B}T}\right)$$
(Eq 3.61)

Here  $x_{\rm S} = N_{\rm S}/N$  is the molar fraction of S atoms.

Also, the ratio of I atoms trapped by S atoms is expressed by

$$f_{\rm I}^{\rm S} = \frac{n_{\rm S}}{n} = \frac{n_{\rm S}}{n_{\rm Fe}} / \left( 1 + \frac{n_{\rm S}}{n_{\rm Fe}} \right) \approx \frac{z' x_{\rm S} \exp(-\Delta\varepsilon_{\rm I-S}/k_{\rm B}T)}{1 - z' x_{\rm S} [1 - \exp(-\Delta\varepsilon_{\rm I-S}/k_{\rm B}T)]}$$
(Eq 3.62)

Figure 3.18(c) shows the result of the trap ratios when z' = 6,  $x_S = 0.01$ ,  $\Delta \varepsilon_{I-S} = -0.2$  eV (or -0.4 eV) calculated according to Eq 3.62.

#### 3.5.2 Estimation of I-S Bonding Energy ( $\Delta \varepsilon_{I-S}$ )

How can one estimate the value of  $\Delta \varepsilon_{\text{I-S}}$ ? What first comes to mind may be the C-M interaction parameter  $W_{\text{MC}}^{\gamma}$ , shown in Table 3.1. However, for example, when  $W_{\text{CrC}}^{\gamma} = -110 \text{ kJ/mol}$  (1273 K) is directly divided by the number of bonds (z' = 6) and Avogadro's constant N to

obtain the bond energy of a Cr-C pair,  $\Delta \varepsilon_{C-Cr} \approx -1$  eV and the trap ratio (Eq 3.62) will become  $f_C^{Cr} \approx 1$  even at a melting point ( $T_m \approx 1800$  K)! To inquire into this error, think about the following exercise.

**[Exercise 3.10]** Show the following relation between the interaction parameter of C atoms and M atoms in  $\gamma$  Fe-C-M austenite according to B-W-G model,  $W_{MC}^{\gamma}$  (Eq 3.51) and the afore-mentioned I-S bond energy,  $\Delta \varepsilon_{C-M}$  (Ref 12).

$$W_{\rm MC}^{\gamma}/RT = z'[1 - \exp(-\Delta\varepsilon_{\rm C-M}/k_{\rm B}T)]$$
 (Eq 3.63)

**[Answer]** First, examine the measurement of  $W_{MC}^{\gamma}$  (the diffusion couple method). For example, to obtain  $W_{CrC}^{\gamma}$ , as shown in Fig. 3.19(a), a Fe-C sample ( $\Delta$  denotes carbon concentration) and a Fe-C-Cr sample ( $\Delta$ )(the thickness of each is about 2 mm) are joined, enclosed in a silica capsule, and quenched rapidly after heating for hours at a given temperature. When a sample is heated for 100 h at 1273 K, C atoms diffuse about 4 mm in an austenite, but Cr atoms diffuse no more than about 0.01 mm. From this result, C atoms in a Fe-C sample are absorbed by Cr atoms, and C concentration is decreased to  ${}^{\circ}x_{C}^{E}$  ( $\odot$  in Fig. 3.19a). However, C concentration in a Fe-C-Cr sample is increased to  ${}^{1}x_{C}^{E}$  ( $\bullet$  in Fig. 3.19a), and both chemical potentials reach  ${}^{\circ}\mu_{C}^{\gamma} = {}^{1}\mu_{C}^{\gamma}$  and they reach equilibrium.

In this case, the following relation is approved (refer to Eq 3.48 and 3.52).



**Fig. 3.19**  $W_{MC}^{\gamma}$  in the regular solution model and  $\Delta \varepsilon_{C-M}$  in the nonrandom distribution model. (a) Measurement of  $W_{MC}^{\gamma}$  (diffusion couple method). (b) The relation between  $W_{MC}^{\gamma}$  and  $\Delta \varepsilon_{C-M}$ 

	$\Delta \epsilon_{IM},  kJ/mol  (eV)$									
	Ti	Nb	V	Cr	Мо	Mn	Co	Ni	Cu	Si
С	-24	-25	-18	-11	-11	-6	+2	+4	+2	$+19^{?}$
	(-0.25)	(-0.26)	(-0.19)	(-0.11)	(-0.11)	(-0.06)	(+0.02)	(+0.04)	(+0.02)	(+0.20)
Ν	-45	-27	-24	-20	-18	-10	+4	+5	+2	$+10^{?}$
	(-0.47)	(-0.28)	(-0.25)	(-0.21)	(-0.19)	(-0.11)	(+0.04)	(+0.05)	(+0.02)	(+0.10)

Table 3.2 Estimated values of interstitial-substitution bonding energy,  $\Delta\epsilon_{IM}$ , for Fe-M-C and Fe-M-N systems

$${}^{\circ}\mu_{\mathrm{C}}^{\gamma} = \Delta G_{\mathrm{C}}^{\gamma} - 2\left(L_{\mathrm{Cv}}^{\gamma} - RT\right) \cdot {}^{\circ}x_{\mathrm{C}}^{\mathrm{E}} + RT \ln {}^{\circ}x_{\mathrm{C}}^{\mathrm{E}}$$
  
=  ${}^{1}\mu_{\mathrm{C}}^{\gamma} = \Delta G_{\mathrm{C}}^{\gamma} - 2\left(L_{\mathrm{Cv}}^{\gamma} - RT\right) \cdot {}^{1}x_{\mathrm{C}}^{\mathrm{E}} + W_{\mathrm{CrC}}^{\gamma} \cdot x_{\mathrm{Cr}}\left(1 - {}^{1}x_{\mathrm{C}}^{\mathrm{E}}\right) + RT \ln {}^{1}x_{\mathrm{C}}^{\mathrm{E}}$   
(Eq 3.64)

Rearranging Eq 3.64 by omitting the small terms allows one to obtain the following equation, and the value of  $W_{CrC}^{\gamma}$  (110 kJ/mol at 1273 K) can be calculated from the values of  ${}^{\circ}x_{C}^{E}$ ,  ${}^{1}x_{C}^{E}$ , and  $x_{Cr}$ .

$${}^{1}x_{\rm C}^{\rm E} = {}^{\circ}x_{\rm C}^{\rm E} \left[ 1 - \left(\frac{W_{\rm CrC}^{\gamma}}{RT}\right) x_{\rm Cr} \right]$$
(Eq 3.65)

Next, replace  ${}^{\circ}x_{C}^{E}$  and  ${}^{1}x_{C}^{E}$  with parameters of the nonrandom distribution model.  ${}^{\circ}x_{C}^{E}$  is equal to the fraction of I atoms at I<sub>Fe</sub> site free from the influence of Cr atoms,  $n_{Fe}/N'_{Fe} \cdot {}^{1}x_{C}^{E}$  is equal to the average fraction of I atoms ( $n_{Fe} + n_{Cr}$ ) / N), because it is the average C concentration in an Fe-C-Cr austenite. Then, the following relation can be obtained from Eq (3.61):

$$\frac{{}^{1}x_{\rm C}^{\rm E}}{{}^{\circ}x_{\rm C}^{\rm E}} = \frac{n_{\rm Fe} + n_{\rm Cr}}{n_{\rm Fe}} \cdot \frac{N_{\rm Fe}^{'}}{N} \approx 1 - z^{\prime} x_{\rm Cr} \left[1 - \exp\left(-\frac{\Delta\varepsilon_{\rm C-Cr}}{k_{\rm B}T}\right)\right]$$
(Eq 3.66)

By comparing Eq 3.65 and 3.66, Eq 3.63 can be derived.

Besides, as shown by the dotted line in Fig. 3.19(b), the proportional relation between  $\Delta \varepsilon_{C-M}$  and  $W_{MC}^{\gamma}$  can be held only when  $|\Delta \varepsilon_{C-M}| \ll k_B T$ . Therefore, in the case of steel containing atoms such as Mn, which has weak I-S bonding, the distribution of C atoms is nearly random and can be approximated by the ordinary B-W-G model. However, in the case of steel containing such atoms as Cr, Mo, V, which have strong I-S bonding, one should think that C atoms distribute nonrandomly.

Table 3.2 shows the estimation of I-S bond energies for Fe-M-C (or N) system using Eq 3.63.

### Appendix: Hume-Rothery's 15% Rule

In the 1920s, x-ray analysis on crystals made it clear that the microstructures of solid solutions and intermetallic compounds in alloy



Fig. 3.20 (a) The relation between mutual solid solubility and atomic radius difference in Fe-X system. (b) Microstructure of alloys produced by mechanical alloying. Source: Ref 15



Fig. 3.21 The paths (point 1 to 2) of "mixing" and "dehydration" on composition triangles

systems can be expressed by the sphere-packing model with atoms having intrinsic radius. Integrating these experimental results, W. Hume-Rothery (1934) advocated a concise rule of thumb, "For two metals to form a solid solution, their atomic radius difference must be within 15%" and brought a landmark development in metallography.

The importance of this 15% rule was recognized again through the studies of amorphous alloys after about a half century. Figure 3.20 is the relation between the atomic radius factor  $\Delta r/\bar{r}$  and the interaction parameter  $\Omega$  of microstructure when mechanically alloying various kinds of mixed powder plotted in x-y plane and shows that it forms a solid solution when  $\Delta r$  is within 15%. It also forms an amorphous phase when  $\Delta r$  is more than 15%. In case of  $\Omega_{AB}^L > 0$ , which means that atoms are

repulsive, fine dispersion structure can be obtained regardless of  $\Delta r$ . Here,  $\Omega_{AB}^{L}$  is the interaction parameter in a liquid phase and the values by Miedema and his group are adopted (Fig. 3.7).

For details concerning why the critical factor of atomic radius is 15%, see Ref 16.

#### EXERCISES

**3.11** (a) How many kinds of ternary systems are there when 50 kinds of elements are available for the components? [Very many.]

(b) How many kinds of systems from binary to decanary (10-component) are there when 10 kinds of elements are available? [Unexpectedly few.]

**3.12** Show that the composition of solution is on the line  $\mathbb{O} \rightarrow \mathbb{Q}$  intersecting the vertex C of a composition triangle as in Fig. 3.21(a) when the third component C(Cr) is added to an A(Fe) and B(Ni) solution letting their ratio  $(x_A / x_B)$  be unchanged. Also, show that the composition of the residual solution is on the line  $\mathbb{O} \rightarrow \mathbb{Q}$  in Fig. 3.20(b) when C(H<sub>2</sub>O) is evaporated by heating the aqueous solution of A(NaCl) and B(KCl).

**3.13** Show that the entropy change will be approximated in the following equation when  $N_A$  atoms A and  $N_B$  chain molecules Bn are randomly mixed (Fig. 3.5b).

$$\Delta S_{\text{mixture}}^{\text{A-chainBn}} = -k_{\text{B}} \left[ N_{\text{A}} \ln \left( \frac{N_{\text{A}}}{N_{\text{A}} + nN_{\text{B}}} \right) + N_{\text{B}} \ln \left( \frac{nN_{\text{B}}}{N_{\text{A}} + nN_{\text{B}}} \right) \right]$$
  
=  $-R \left( x'_{\text{A}} \ln x_{\text{A}} + x'_{\text{B}} \ln x_{\text{B}} \right)$  [Flory-Huggins (1942) equation]  
(Eq 3.67)

Here  $x'_{\rm A} = N_{\rm A}/(N_{\rm A} + N_{\rm B})$  and  $x'_{\rm B} = N_{\rm B}/(N_{\rm A} + N_{\rm B})$  are the molar fractions of A atoms and Bn molecules.  $x_{\rm A} = N_{\rm A}/(N_{\rm A} + nN_{\rm B})$  and  $x_{\rm B} = nN_{\rm B}/(N_{\rm A} + nN_{\rm B})$  are the molar fractions of A atoms and B atoms.

[This is a difficult problem. See Ref 2 and 13 for details.]

**3.14** Show that the free energy of an  $\alpha$ Fe-C bcc solution is approximated in the following equation by the sublattice model.

 $G^{\alpha} \approx {}^{\circ}G^{\alpha}_{\text{Fe}}(1-x_{\text{C}}) + \Delta G^{\alpha\text{Fe}}_{\text{C}}x_{\text{C}} + RT[x_{\text{C}} \ln x_{\text{C}} - x_{\text{C}}(1+\ln 3)] \quad \text{(Eq 3.68)}$ 

Here,  $\Delta G_{\rm C}^{\alpha {\rm Fe}} = (G_{{\rm FeC}_3} - {}^{\circ}G_{{\rm Fe}}^{\alpha})/3 + L_{\rm Cv}^{\alpha {\rm Fe}}$  is the free energy per 1 mole atoms C dissolved into  $\alpha {\rm Fe}$  crystal, and estimated at 69 kJ mol (1000 K).

*Hint:* The number of interstitial sites of C atoms is three times the number of Fe atoms in a bcc crystal. Therefore, replace the symbols in

Eq 3.28 with A = Fe,  $y_{\text{Fe}} = 1$ ,  $y_{\text{B}} = 0$ , C-C (carbon), D = v (vacancy), m = 1, and n = 3. Because  $x_{\text{C}} \ll 1$ , Eq 3.68 can be obtained by omitting the  $x_{\text{C}}^2$  term.

**3.15** Let  $x_v^A$  be the equilibrium vacancy concentration in a pure A crystal, and  $\Delta \varepsilon_v^B$  be the binding energy between the alloy element B and the vacancy v. Show that the equilibrium vacancy concentration in A-B system solid solution where the fraction of component B is  $x_B$  is approximated by

$$x_{\rm v}^{\rm A-B} = x_{\rm v}^{\rm A} \left[ 1 + z x_{\rm B} \exp\left(-\frac{\Delta \varepsilon_{\rm Bv}}{k_{\rm B}T}\right) \right]$$
(Eq 3.69)

Here, z is the coordination number in crystal A (in case of fcc, z = 12).

For example, when  $\Delta \varepsilon_{Bv} = -0.1$  e V, how much does the vacancy concentration change with the addition of B having  $x_{\rm B} = 0.01$ ? [Answer: 1.4 times at 1000 K, 2.2 times at 500 K.]

**3.16** I atoms that dissolve interstitially will be trapped along the edge of a half atomic plane of edge dislocation and form Cottrell atmosphere (A.H. Cottrell, 1949). Show that the relation between the number of I atoms trapped on the dislocation line,  $n_D$  and the number of I atoms dissolved in a crystal,  $n_{\alpha}$  is approximated by

$$\frac{n_{\rm D}}{N_{\rm D}} \approx \frac{n_{\alpha}}{N_{\alpha}} \exp\left(-\frac{\Delta\varepsilon_{\rm I-D}}{k_{\rm B}T}\right) \tag{Eq 3.70}$$

Here  $\Delta \varepsilon_{I-D}$  is the binding energy between I atoms and the dislocations, and it is presumed that  $\Delta \varepsilon_{I-D} \approx -0.5$  eV in case of  $\alpha$ Fe-C system. Also,  $N_D$  is the number of trap sites along the dislocation line.  $N_{\alpha}$  is the number of solid solution sites in the crystal. Therefore,  $n_D/N_D$  on the left side of Eq 3.70 is the adhesion ratio of I atoms.  $n_{\alpha}/N_{\alpha}$  on the right side is the atomic fraction of dissolved I atoms.

The adhesion ratio in  $\alpha$ Fe-C system is about 0.7 at 500 K. See Ref 14 for details.

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CHAPTER **Z** 

# Thermodynamics of Phase Diagrams

A phase diagram has been called "a map" for materials. This "map" consisted only of the experimental data in former days, but in recent years an estimation of complicated data for a multicomponent system can be obtained by mutual support of experiments, computer models, and thermodynamics. However, a correct "map" may be just an ornament if one does not know how to use it. In this chapter, the significance of the "map" and methods to make a use of it for studies and development of new materials are explained.

# 4.1 Basic Rules of Heterogeneous Equilibrium

## 4.1.1 Common Tangent Law

For phase I and II of a one-component system (pure substance A) to be in equilibrium, as in Fig. 4.1(a), free-energy curves of both phases,  $G_A^I$  and  $G_A^{II}$  must intersect each other and the following equation must hold (see Fig. 2.7c).

 $G_{\rm A}^{\rm I} = G_{\rm A}^{\rm II}$  (phase equilibrium condition for one-component system) (Eq 4.1)

Then, how should the equilibrium condition be expressed for  $\alpha$  phase and  $\beta$  phase of A-B system? Gibbs published his timeless papers "On the Equilibrium of Heterogeneous Substances" in 1873 to 1879 and expressed the equilibrium condition between  $\alpha$  phase and  $\beta$  phase as in the simultaneous equations (Ref 1):

$$\begin{array}{l} \mu_{A}^{\alpha} = \mu_{A}^{\beta} \\ \mu_{B}^{\alpha} = \mu_{B}^{\beta} \end{array} \right\} \quad (equilibrium \ condition \ for \ binary \ system) \qquad (Eq \ 4.2)$$



**Fig. 4.1** Conditional equations of heterogeneous equilibrium in a unitary (a) and a binary (b) system. (a) Intersection of free-energy curves is the equilibrium temperature in a unitary system. (b) Points of contact ① and ② on the common tangent indicate each of the equilibrium compositions in a binary system.

As shown in Fig. 4.1(b), let  $\alpha$  phase and  $\beta$  phase consist of  $m_A^{\alpha}$  and  $m_A^{\beta}$  moles of atoms A, and of  $m_B^{\alpha}$  and  $m_B^{\beta}$  moles of atoms B, and let the total amount of A and B  $\left(m_A^{\alpha} + m_B^{\alpha} + m_A^{\beta} + m_B^{\beta}\right)$  be 1 mole. Using the chemical potential as discussed in Section 3.4, because  $\mu_i^{\alpha}$  is the substantial free energy per 1 mole of *i*th component atoms in  $\alpha$  phase, the total free energy of both phases  $\alpha + \beta$  can be expressed by

$$G^{\alpha+\beta} = \mu_{\rm A}^{\alpha} \cdot m_{\rm A}^{\alpha} + \mu_{\rm B}^{\alpha} \cdot m_{\rm B}^{\alpha} + \mu_{\rm A}^{\beta} \cdot m_{\rm A}^{\beta} + \mu_{\rm B}^{\beta} \cdot m_{\rm B}^{\beta}$$
(Eq 4.3)

In the state of equilibrium, because  $G^{\alpha + \beta} = \text{minimum}$  and  $d G^{\alpha + \beta} = 0$  by extreme value condition if very small amounts,  $dm_A$  and  $dm_B$  of components A and B are transferred from  $\beta$  phase to  $\alpha$  phase, the next equation can be obtained.

$$dG^{\alpha+\beta} = \mu_{A}^{\alpha} \cdot dm_{A}^{\alpha} + \mu_{A}^{\beta} \cdot dm_{A}^{\beta} + \mu_{B}^{\alpha} \cdot dm_{B}^{\alpha} + \mu_{B}^{\beta} \cdot dm_{B}^{\beta}$$
$$= (\mu_{A}^{\alpha} - \mu_{A}^{\beta}) \cdot dm_{A} + (\mu_{B}^{\alpha} - \mu_{B}^{\beta}) \cdot dm_{B} = O$$
(Eq 4.4)

For Eq 4.4 to hold for any  $dm_A$  and  $dm_B$ , Eq 4.2 must be satisfied. Therefore, Eq 4.2 is the condition of two-phase equilibrium.

Chemical potentials  $\mu_A^{\alpha}$  and  $\mu_B^{\alpha}$  are shown as intersections of the tangent to the free-energy curve of  $\alpha$  phase and the A axis and the B axis. Therefore, the data points  $\blacksquare$  and  $\bullet$  in Fig. 4.1(b) correspond to  $\mu_A^{\alpha(\beta)}$ and  $\mu_B^{\alpha(\beta)}$  on the common tangent to  $G^{\alpha}$  and  $G^{\beta}$  curves, and the points of contact ① and @ are equilibrium compositions of  $\alpha$  phase and  $\beta$  phase. This is called "common tangent law." **[Exercise 4.1]** Calculate a phase diagram where the solution (L) and the solid solution ( $\alpha$ ) of A-B system are ideal solutions.

Assume that entropy of melting of A and B is equal to the gas constant R by Richards' rule, and the free-energy difference between solid and liquid of A and B is proportional to the temperature difference from each melting point.

**[Answer]** According to Eq 3.43, the chemical potentials of components A and B in both the phases are

$$\mu_{\mathbf{A}}^{\mathsf{L}} = {}^{\circ}G_{\mathbf{A}}^{\mathsf{L}} + RT \ln (1 - x_{\mathbf{B}}^{\mathsf{L}}), \ \mu_{\mathbf{B}}^{\mathsf{L}} = {}^{\circ}G_{\mathbf{B}}^{\mathsf{L}} + RT \ln x_{\mathbf{B}}^{\mathsf{L}}$$

$$\mu_{\mathbf{A}}^{\alpha} = {}^{\circ}G_{\mathbf{A}}^{\alpha} + RT \ln (1 - x_{\mathbf{B}}^{\alpha}), \ \mu_{\mathbf{B}}^{\alpha} = {}^{\circ}G_{\mathbf{B}}^{\alpha} + RT \ln x_{\mathbf{B}}^{\alpha}$$

$$(Eq 4.5)$$

Let  $T_A$  and  $T_B$  be the melting points, and the free-energy differences between solid and liquid of both the components will become, by the assumption,

$${}^{\circ}G_{\rm A}^{\alpha} - {}^{\circ}G_{\rm A}^{\rm L} = R(T - T_{\rm A}), \; {}^{\circ}G_{\rm B}^{\alpha} - {}^{\circ}G_{\rm B}^{\rm L} = R(T - T_{\rm B})$$
 (Eq 4.6)

Equilibrium condition of L phase and  $\alpha$  phase is

$$\mu_{\rm A}^{\rm L} = \mu_{\rm A}^{\alpha}; RT \ln \left(1 - x_{\rm B}^{\rm L}\right) = RT \ln \left(1 - x_{\rm B}^{\alpha}\right) + R(T - T_{\rm A})$$

$$\mu_{\rm B}^{\rm L} = \mu_{\rm A}^{\alpha}; RT \ln x_{\rm B}^{\rm L} = RT \ln x_{\rm B}^{\alpha} + R(T - T_{\rm B})$$

$$\left. \right\}$$

$$(Eq 4.7)$$

By rearranging Eq 4.7, one can obtain equations representing the liquidus line and the solidus line:

Liquidus line: 
$$x_{\rm B}^{\rm L} = \left[1 - \exp\left(\frac{T - T_{\rm A}}{T}\right)\right] / \left[1 - \exp\left(\frac{T_{\rm B} - T_{\rm A}}{T}\right)\right]$$
  
Solidus line:  $x_{\rm B}^{\alpha} = \left[1 - \exp\left(\frac{T_{\rm A} - T}{T}\right)\right] / \left[1 - \exp\left(\frac{T_{\rm A} - T_{\rm B}}{T}\right)\right]$   
(Eq 4.8)

Figure 4.2(a) shows the calculated phase diagram on the assumption that the melting points of both components are  $T_A = 1000$  K and  $T_B = 500$  K. Figure 4.2(b) shows the free-energy diagram at T = 800 K.

#### 4.1.2 Enhancement to Multicomponent Systems

The equilibrium condition equation for a binary system (Eq 4.2) can be immediately enhanced to a multicomponent system. For example, equilibrium conditions between two phases  $\alpha/\beta$  and among three phases  $\alpha/\beta/\gamma$  in A-B-C ternary system can be expressed as Eq 4.9 and Eq 4.10, respectively.



Fig. 4.2 Calculated example (Exercise 4.1) of phase diagram for completely miscible type

$$\begin{array}{c} \mu_{A}^{\alpha} = \mu_{A}^{\beta} \\ \mu_{B}^{\alpha} = \mu_{B}^{\beta} \\ \mu_{C}^{\alpha} = \mu_{C}^{\beta} \end{array} \right\}$$
 (equilibrium condition between  
two phases in A-B-C ternary system) (Eq 4.9)

$$\mu_{A}^{\alpha} = \mu_{A}^{\beta} = \mu_{A}^{\gamma}$$

$$\mu_{B}^{\alpha} = \mu_{B}^{\beta} = \mu_{B}^{\gamma}$$

$$\mu_{C}^{\alpha} = \mu_{C}^{\beta} = \mu_{C}^{\gamma}$$

$$(equilibrium condition among$$

$$three phases in A-B-C ternary system)$$

$$(Eq 4.10)$$

Because there are innumerable common tangential planes to two curved surfaces, equilibrium between two phases  $\alpha/\beta$  can be expressed by tie lines connecting the pairs of contact points such as (1-2) and (1'-2)', which indicate equilibrium compositions of both phases as shown in Fig. 4.3(a). On the other hand, in the case of three-phase equilibrium  $\alpha/\beta/\gamma$ , there is only one common tangential plane that contacts three curved surfaces of free energy. Contact points (1-2)-(3) in Fig. 4.3(b) indicate the compositions of phases  $\alpha,\beta$ , and  $\gamma$ , which are mutually in equilibrium, and is called three-phase triangle.

**[Exercise 4.2]** Suppose that three components A-B-C can be mixed well and form an ideal solution in the state of liquid phase. Calculate the phase diagram where A, B, and C, however, do not form a solid solution at all in the state of solid phase. Assume that melting entropy of A, B, and C is equal to the gas constant R, and that free-energy difference between solid and liquid of each component is proportional to the temperature difference from each melting point.



**Fig. 4.3** Heterogeneous equilibrium in A-B-C ternary system (the common tangent law). The upper diagrams show free energy. The lower diagrams give a view of isothermal sections. (a) Two-phase equilibrium of  $\alpha/\beta$ . (b) Three-phase equilibrium of  $\alpha/\beta/\gamma$ 

[Answer] Chemical potential of each component in a liquid phase is

$$\mu_{\mathbf{A}}^{\mathbf{L}} = {}^{\circ}G_{\mathbf{A}}^{\mathbf{L}} + RT \quad \ln x_{\mathbf{A}}^{\mathbf{L}}, \quad \mu_{\mathbf{B}}^{\mathbf{L}} = {}^{\circ}G_{\mathbf{B}}^{\mathbf{L}} + RT \quad \ln x_{\mathbf{B}}^{\mathbf{L}},$$

$$\mu_{\mathbf{C}}^{\mathbf{L}} = {}^{\circ}G_{\mathbf{C}}^{\mathbf{L}} + RT \quad \ln x_{\mathbf{C}}^{\mathbf{L}}$$

$$(Eq 4.11)$$

And, according to the assumption in this exercise, there is the relation between the free energy of each component in a crystal and that in a liquid phase:

$$^{\circ}G_{A}^{S} = ^{\circ}G_{A}^{L} + R(T - T_{A})$$

$$^{\circ}G_{B}^{S} = ^{\circ}G_{B}^{L} + R(T - T_{B})$$

$$^{\circ}G_{C}^{S} = ^{\circ}G_{C}^{L} + R(T - T_{C})$$
(Eq 4.12)

From Eq 4.11 and 4.12, equilibrium equations of two phases between the crystal and the liquid phase of A, B, and C can be obtained:\*

<sup>\*</sup>Because the crystals have no solid solubility, for example, the chemical potential of B component in A crystal  $\mu_B^A$  has no meaning. Therefore, the equilibrium of A crystal with the liquid phase can be expressed not by such simultaneous equations as Eq 4.9, but only by Eq 4.13A.



**Fig. 4.4** Free-energy diagram for a eutectic ternary system. (a) Composition of a liquid phase (a liquidus surface or a primary crystallization surface of A) in equilibrium with A crystal. (b) Three-phase equilibrium of a liquid phase with A crystal and B crystal (a monovariant eutectic)

A/L equilibrium 
$$(\mu_A^L = {}^{\circ}G_A^S); x_A^L = \exp\left(\frac{T - T_A}{T}\right)$$
 (Eq 4.13A)

B/L equilibrium 
$$\left(\mu_{\rm B}^{\rm L} = {}^{\circ}G_{\rm B}^{\rm S}\right); x_{\rm B}^{\rm L} = \exp\left(\frac{T - T_{\rm B}}{T}\right)$$
 (Eq 4.13B)

C/L equilibrium 
$$\left(\mu_{\rm C}^{\rm L} = {}^{\circ}G_{\rm C}^{\rm S}\right); x_{\rm C}^{\rm L} = \exp\left(\frac{T - T_{\rm C}}{T}\right)$$
 (Eq 4.13C)

Figure 4.4(a) is the free-energy diagram indicating the equilibrium between the liquid phase and the crystal of A (Eq 4.13A) and 1-2-3-4-5 is the equilibrium compositions of the liquidus surface (or the primary crystallization surface) of crystal A.

Figure 4.4(b) is the free-energy diagram showing the equilibrium between liquid phase and crystals of A and B, and because it does not form a solid solution, Eq 4.10 expressing three-phase equilibrium can be simplified, and the equilibrium composition (6) can be obtained by solving the simultaneous equation:

A/B/L three-phase equilibrium 
$$\begin{pmatrix} \mu_{A}^{L} = {}^{\circ}G_{A}^{S} \\ \mu_{B}^{L} = {}^{\circ}G_{B}^{S} \end{pmatrix}$$
;  $\begin{cases} x_{A}^{L} = \exp(\frac{T-T_{A}}{T}) \\ x_{B}^{L} = \exp(\frac{T-T_{A}}{T}) \end{cases}$ 



**Fig. 4.5** Calculated examples of phase diagrams for a eutectic ternary system. (a) Projection of a primary crystallization surface. (b) View of isothermal section. (c) View of vertical section (30% C)

Because this equilibrium composition of liquidus line expresses the relation between the temperature and the composition produced by an eutectic reaction  $(L \rightarrow A + B)$  at solidification, it is called a monovariant eutectic line (see Section 4.1.3 Phase Rule "Gibbs" a monovariant system).

Figure 4.5 shows the calculated phase diagrams when the melting points of A, B, and C are  $T_A = 1000$  K,  $T_B = 800$  K, and  $T_C = 600$  K. As illustrated in Fig. 4.5(b) when one calculates and summarizes the composition in a liquid phase in equilibrium with a solid phase, one can obtain a liquidus surface as shown in Fig. 4.5(a) (also called a primary crystallization surface) and a eutectic point. The bottom of the ravine, E, where the primary crystallization surfaces of crystals A, B, and C intersect, shows the composition where the ternary eutectic reaction occurs (L  $\rightarrow$  A + B + C). The curved line,  $E_{AB}$ -E, where the primary crystallization surfaces of A and B intersect, shows the composition where the aforementioned monovariant eutectic reaction (L  $\rightarrow$  A + B) will occur. Moreover, Fig. 4.5(c) is the vertical section diagram along the proper compositions  $\mathbb{I}$ - $\mathbb{Q}$  and is often used to clearly explain three-dimensional phase diagrams of ternary systems.

#### 4.1.3 Gibbs Phase Rule

Consider conditions of multiphase equilibrium in *n*-component systems by extrapolating the phase equilibrium equation of A-B-C ternary system in Section 4.1.2.

The chemical potential of each component must be equivalent in order for heterogeneous equilibrium to be formed, and the total of conditions is the number of equal signs in the following simultaneous equations, n(q - 1). Here, q is the number of phases. Equilibrium equations:

Number of components 
$$n \underbrace{\begin{cases} \left(\mu_{A}^{1} = \mu_{A}^{2} = \cdot \cdot \cdot \cdot = \mu_{A}^{q}\right) \\ \left(\mu_{B}^{1} = \mu_{B}^{2} = \cdot \cdot \cdot = \mu_{B}^{q}\right) \\ \left(\mu_{n}^{1} = \mu_{n}^{2} = \cdot \cdot \cdot = \mu_{A}^{q}\right) \\ \hline \text{Number of equal signs; } n(q-1) \end{cases}$$

Composition variables:

Number of phases 
$$q \begin{cases} 1; x_{A}^{1}, x_{B}^{1}, \cdots, \cdots, x_{n}^{1} = 1 - \sum x_{i}^{1} \\ 2; x_{A}^{2}, x_{B}^{2}, \cdots, \cdots, x_{n}^{2} = 1 - \sum x_{i}^{2} \\ q; x_{A}^{q}, x_{B}^{q}, \cdots, x_{n}^{q} = 1 - \sum x_{i}^{q} \end{cases}$$

Total of composition variables; q(n-1)

Because the total of composition variables is q(n - 1) as mentioned previously, the number of independent composition variables is

$$f_{\rm C} = q(n-1) - n(q-1) = n - q$$
 (Eq 4.14)

Since phase equilibrium depends on not only composition but also temperature T and pressure P, the total of independent variables is

$$f = f_{\rm C} + 2 = n - q + 2$$
 [general phase equilibrium] (Eq 4.15)

However, because pressure P has nothing to do with the equilibrium between liquid phase and solid phase as long as P is not very high, the following equation fits in better with the reality.

f' = n - q + 1 [phase equilibrium when pressure is not thought to be a variable] (Eq 4.16)

Equations 4.15 and 4.16 are Gibbs phase rule; f (or f') is called the degree of freedom; a system is called a nonvariant system if the degree of freedom = 0 and a monovariant system if the degree of freedom = 1. For example:

- Nonvariant system: Figure 4.5(a) ternary eutectic point *E* (L, A, B, C, four-phase equilibrium) f' = 3 4 + 1 = 0
- Monovariant system: Figure 4.4(b) monovariant eutectic 1 (L, A, B, three-phase equilibrium) f' = 3 3 + 1 = 1

**[Exercise 4.3]** Correct errors in the binary phase diagram shown in Fig. 4.6(a).



**Fig. 4.6** An example of modifying an erroneous phase diagram (Exercise 4.3). Point 5 ( $\blacksquare$ ) indicates a peritectic reaction ( $\gamma + L \rightarrow \alpha$ ), and large supercooling can be caused easily. On the other hand, point 3 ( $\odot$ ) indicates a eutectic reaction ( $L \rightarrow \alpha + \beta$ ); it can make progress with small supercooling. (a) An erroneous phase diagram. (b) A modified phase diagram. (a') The free-energy diagram ( $T = T_1$ ). (b') The modified free-energy diagram

**[Answer]** The degree of freedom for a binary system is f' = 3 - q, and the number of phases in equilibrium with each other is  $q \leq 3$ .

If Fig. 4.6(a) is correct, the number of equilibrated phases exceeds the regulation by the phase rule because four phases, L,  $\alpha$ ,  $\beta$ , and  $\gamma$  have a common tangent as shown in the free-energy diagram Fig. 4.6(a') at  $T = T_1$ . Figures 4.6(b) and (b') are examples of corrected phase diagrams.

These kinds of errors are often seen in phase diagrams where experimental results are uncritically adopted.

#### 4.2 Liquidus Line and Solidus Line

#### 4.2.1 Phase Diagram of Completely Miscible Type

Understanding equilibrium between liquid phase and solid phase in a multicomponent system is indispensable to consideration and control of solidification and synthesis of compound from liquid phase. First, think about the following exercise concerning a phase diagram of a completely miscible type.

**[Exercise 4.4]** The width between liquidus line and solidus line is remarkably broad in a phase diagram of a semiconductor as shown in Fig. 4.7(a). Consider the cause of this breadth.

**[Answer]** When chemical potentials of both the components in a liquid phase L and a solid solution  $\alpha$  of A-B system are described by



**Fig. 4.7** Fundamental factors determining the shape of liquidus-solidus line. (a) Typical example of phase diagram for semiconductors. (b) Influence by entropy of melting. (c) Influence by interaction parameter

the regular solution approximation (Eq 3.43), the equilibrium conditions of both phases are expressed by

$$\mu_{\rm A}^{\rm L} = \mu_{\rm A}^{\alpha}; \ \ln \frac{1 - x_{\rm B}^{\alpha}}{1 - x_{\rm B}^{\rm L}} = \frac{\Delta S_{\rm A}^{\rm m}}{R} \left(\frac{T_{\rm A} - T}{T}\right) + \frac{\Omega_{\rm AB}^{\rm L}}{RT} \left(x_{\rm B}^{\rm L}\right)^2 - \frac{\Omega_{\rm AB}^{\alpha}}{RT} \left(x_{\rm B}^{\alpha}\right)^2 \quad (\text{Eq 4.17})$$

$$\mu_{\rm B}^{\rm L} = \mu_{\rm B}^{\alpha}; \ln \frac{1 - x_{\rm B}^{\alpha}}{1 - x_{\rm B}^{\rm L}} = \frac{\Delta S_{\rm B}^{\rm m}}{R} \left(\frac{T_{\rm B} - T}{T}\right) + \frac{\Omega_{\rm AB}^{\rm L}}{RT} \left(1 - x_{\rm B}^{\rm L}\right)^2 - \frac{\Omega_{\rm AB}^{\alpha}}{RT} \left(1 - x_{\rm B}^{\alpha}\right)^2 \quad ({\rm Eq} \, 4.18)$$

Here the melting entropies of A and B are written as  $\Delta S_A^m$  and  $\Delta S_B^m$ , and the free-energy difference between solid phase and liquid phase is approximated by

$$G_{\rm A}^{\alpha} - {}^{\circ}G_{\rm A}^{\rm L} = \Delta S_{\rm A}^{\rm m}(T - T_{\rm A}), \ {}^{\circ}G_{\rm B}^{\alpha} - {}^{\circ}G_{\rm B}^{\rm L} = \Delta S_{\rm B}^{\rm m}(T - T_{\rm B})$$
(Eq 4.19)

The width of liquidus-solidus is determined by (i) the entropies of melting of both components and (ii) the values of interaction parameters in both phases. First, when one assumes that  $\Omega^{L} = \Omega^{\alpha} = 0$  and  $\Delta S_{A}^{m} = \Delta S_{B}^{m} = 3R$  in order to examine the influence of melting entropy, as shown in Fig. 4.7(b), the width of liquidus-solidus (•-•) is about 3 times as much as the width when  $\Delta S_{A}^{m} = \Delta S_{B}^{m} = R$  (o-o).

Because Si, Ge, and InSb are covalent crystals and their entropies of melting are  $\Delta S_{\text{Si}}^{\text{m}} \approx 30$ ,  $\Delta S_{\text{Ge}}^{\text{m}} \approx 30$ , and  $\Delta S_{\text{InSb}}^{\text{m}} \approx 60 \text{ J/mol} \cdot \text{K}$  the

solutions containing them as components generally have rather broad width between the liquidus line and the solidus line.

Next, when one assumes that  $\Delta S_m = R$  and  $\Omega^L = \Omega^{\alpha} = 1000R$  in order to examine the influence of interaction between A and B atoms, as shown in Fig. 4.7(c), the free-energy curve forms a shallow round bottom and the common tangent ( $\blacktriangle$ - $\bigstar$ ) spreads to both sides.

In actual Ge-Si system,  $\Omega_{GeSi}^{L} \approx 9 \text{ kJ/mol}$  In the AlSb-InSb system,  $L_{AlIn}^{Sb} \approx 3 \text{ kJ/mol}$  ( $L_{AB}^{C}$  is the interaction parameter of the sublattice model. See Eq 3.24), and because Ge and Si and Al and In are repulsive to each other it is clear that the width between the liquidus line and the solidus line tends to be broader.

When the values of  $\Omega^{L}$  and  $\Omega^{\alpha}$  are remarkably different, the liquidussolidus line is likely to have the highest point or the lowest point. The conditions are discussed in Exercise 4.2.

# 4.2.2 Liquidus Line and Solidus Line at Low Concentration Region

What is important for usual alloys is the liquid-solid phase equilibrium in the region of low concentration of added elements. Therefore, Eq 4.17 and 4.18 are investigated in detail by rearranging them on the condition of  $x_{\rm B} \ll 1$ .

First, omit small terms including  $x_{\rm B}$  from Eq 4.17 and 4.18 and let ln  $(1 - x_{\rm B}) \approx -x_{\rm B}$ , then each of them can be simplified as

Composition width: 
$$\Delta x_{\rm B}^{\alpha/{\rm L}} = x_{\rm B}^{\rm L} - x_{\rm B}^{\alpha} = \frac{\Delta S_{\rm A}^{\rm m}}{RT_{\rm A}}(T_{\rm A} - T)$$
 (Eq 4.20)

Composition ratio:

$$k_{A-B}^{\alpha/L} = \frac{x_B^{\alpha}}{x_B^L} = \exp\left[-\frac{\Delta S_B^m}{R} \left(\frac{T_A - T_B}{T_A}\right) + \frac{\Omega_{AB}^L - \Omega_{AB}^{\alpha}}{RT_A}\right]$$
(Eq 4.21)

Equation 4.20 indicates that the composition width in the region of  $x_{\rm B} \ll 1$  is the proper value of component A, and it is independent of that of added element B. Next,  $k_{\rm A-B}^{\alpha/L}$  in Eq 4.21 is expressed as  $k_0$  and called the equilibrium partition ratio in solidification processing, and if this coefficient is smaller then solidification segregation occurs more remarkably.

In order to analyze solidification segregation, the gradient of liquidus line and the temperature gap (also called solidification interval) are important parameters as well as  $k_{A-B}^{\alpha/L}$ , and they can be obtained from Eq 4.20 and 4.21:

Liquidus line gradient: 
$$m_{A-B}^{L} = \frac{T_A - T^{\alpha}}{x_B^{L}} = \frac{RT_A}{\Delta S_A^{m}} \cdot \left(1 - k_{A-B}^{\alpha/L}\right)$$
 (Eq 4.22)

Temperature gap (solidification interval):

$$\Delta T_{A-B}^{\alpha/L} = T^{L} - T^{\alpha} = \frac{RT_{A}}{\Delta S_{A}^{m}} \cdot \frac{\left(1 - k_{A-B}^{\alpha/L}\right)^{2}}{k_{A-B}^{\alpha/L}} x_{B}^{\alpha}$$
(Eq 4.23)

As shown in Fig. 4.8(a1) and (a2), when the value of  $k_{A-B}^{\alpha/L}$  becomes smaller, the gradient (slope) of liquidus line will become larger. Particularly, when  $k_{A-B}^{\alpha/L} \rightarrow 0$  (therefore,  $x_B^{\alpha} \rightarrow 0$ ), one can obtain  $m_{A-B}^{\alpha/L} \rightarrow RT_A/\Delta S_A^m$ , and the liquidus line gradient cannot exceed this limit value.

Figure 4.8(b) is a summarization of liquidus lines of Fe-X systems; the equilibrium partition ratios are  $k_{\text{Fe}-X}^{\alpha/L} > 0.5$  for about 20 kinds of elements such as Cr and Ni, which locate near Fe in the center of the periodic table and their gradients of liquidus lines are small. On the other hand,  $k_{\text{Fe}-X}^{\alpha/L} < 0.5$  for nonmetals such as C, B, P, and S and 3A to 5A metals such as Zr, Ti, and Y; their gradients of liquidus lines are large; and they are used for producing Fe amorphous alloys. If an added element X has a low melting point, however, its gradient of liquidus line is not always large (for example, Fe-Al and Fe-Zn systems). The reason is apparently, from Eq 4.21, because the value of  $k_{A-B}^{\alpha/L}$  depends on not only  $(T_A - T_B)$  but also on the value of  $(\Omega_{AB}^L - \Omega_{AB}^{\alpha})$ .



Fig. 4.8 Relations between the gradient of liquidus line and the composition width, the temperature width

# 4.2.3 Primary Crystallization Line (Liquidus Line) of Compounds

The liquidus line is also called the primary crystallization line because it is the temperature at which a crystal begins forming when a liquid phase is cooled. Here, consider two exercises concerning the primary crystallization line of a compound AB.

**[Exercise 4.5]** Crystal A and crystal B do not form solid solution at all. However, if they form a compound with a concentration ratio of 1:1, AB( $\theta$  phase), calculate the primary crystallization line. Assume that the A-B liquid system is an ideal solution and let the energy of formation of the compound  $\Delta G_{AB}^{f} = G_{AB}^{\theta} - {}^{\circ}G_{A}^{S} - {}^{\circ}G_{B}^{S} = -25 \text{ kJ/mol}$ . The melting points of A and B are  $T_{A} = 1000 \text{ K}$  and  $T_{B} = 500 \text{ K}$ , respectively. Let the entropies of melting for A and B be  $\Delta S_{A}^{m} = \Delta S_{B}^{m} = R$  (the gas constant).

**[Answer]** The free energies of the liquid phase, the crystals A and B, and the compound AB can be approximated as

$$G^{L} = {}^{\circ}G^{L}_{A}(1 - x^{L}_{B}) + {}^{\circ}G^{L}_{B}x^{L}_{B} + RT\left[\left(1 - x^{L}_{B}\right) \ln\left(1 - x^{L}_{B}\right) + x^{L}_{B} \ln x^{L}_{B}\right]$$
  
$${}^{\circ}G^{S}_{A} = {}^{\circ}G^{L}_{A} + R(T - T_{A}), \ {}^{\circ}G^{S}_{B} = {}^{\circ}G^{L}_{B} + R(T - T_{B})$$
  
(Eq 4.24)

$$G_{AB}^{\theta} = {}^{\circ}G_{A}^{L} + {}^{\circ}G_{B}^{L} + R(T - T_{A}) + R(T - T_{B}) + \Delta G_{AB}^{f}$$
(Eq 4.25)

The equilibrium relation between the AB phase and the liquid phase can be expressed by the common tangents (1-2) and (2-3) in Fig. 4.9(a) and calculated by\*

$$G_{AB}^{\theta} = \mu_A^L + \mu_B^L = {}^{\circ}G_A^L + RT \ln \left(1 - x_B^L\right) + {}^{\circ}G_B^L + RT \ln x_B^L \qquad (\text{Eq 4.26})$$

By rearranging Eq 4.25 and 4.26, an equation expressing the primary crystallization line of the AB phase can be obtained:

$$\ln \left[ x_{\rm B}^{\rm L} \left( 1 - x_{\rm B}^{\rm L} \right) \right] = 2 - \frac{T_{\rm A} + T_{\rm B}}{T} + \frac{\Delta G_{\rm AB}^{\rm t}}{RT}$$
(Eq 4.27)

The calculated result is shown in Fig. 4.9(b).

**[Exercise 4.6]** Calculate a phase diagram in which the values in the former exercise are changed as follows.

<sup>\*</sup>The diagram for free energy shows the free energy of each phase for 1 mole of atoms. Therefore, the value of  $G_{AB}^{\theta}/2$  should be shown in the case of compound AB.



**Fig. 4.9** Calculation of primary crystallization line of a compound phase(I) eutectic type. This type of diagram can be often seen among those of III-V compounds (such as GaAs) and II-VI compounds (such as CdS). The free energy is shown as a value divided by the gas constant *R*.

The energy of formation of the compound :  $\Delta G_{AB}^{f} = G_{AB}^{\theta} - {}^{\circ}G_{A}^{S} - {}^{\circ}G_{B}^{S} = -5 \text{ kJ/mol}$ 

The melting points of A and B:  $T_A = 1500$ K,  $T_B = 600$ K

**[Answer]** The equation of the primary crystallization line of the compound AB (Eq 4.27) can hold as it is. However, because the melting point of A is high and the energy of formation of AB is small, the range will be extended where A begins crystallization and the range where a primary crystal of AB is formed is limited to the narrow one between  $T_{\rm P}$  (peritectic temperature) and  $T_{\rm E}$  (eutectic temperature) where the equilibrium relation holds as expressed by the common tangent @-\$ in Fig. 4.10(a).

In order to synthesize this kind of compound, such a means should be necessary as (i) mixing and pressing the powders of A and B at a ratio of 1:1, heating them under the eutectic temperature for hours, and developing the crystal AB, or (ii) rapidly cooling the liquid phase at a ratio of 1:1 down to lower than  $T_{\rm P}$ , preventing the creation of the crystal A, and crystallizing only the crystal AB.

# 4.3 Solubility Curve (Solid Solubility Curve)

Solubility curves or solid solubility curves are fundamental factors for designing microstructures of materials and showing the maximum of concentration of a component B that will dissolve into a component A. These solubility curves, in quite the same way as the case of solidus lines



**Fig. 4.10** Calculation of primary crystallization line of a compound phase (II) (peritectic + eutectic) type. This type of diagram can be often seen among those of compounds of rare earth-cobalt system (such as Sm-Co). The free energy is shown as a value divided by the gas constant *R*.

and liquidus lines described previously, can be expressed by contact points of common tangents to free-energy curves of both phases. Two typical examples are shown.

#### 4.3.1 Mutual Solubility Curve

**[Exercise 4.7]** Obtain an approximation that expresses a mutual solubility when A and B have different crystal structures.

**[Answer]** When free energy of  $\alpha$  phase and  $\beta$  phase are approximated by the regular solution model, the equilibrium equations of both phases are expressed as (see Eq 3.43):

$$\mu_{A}^{\alpha} = \mu_{A}^{\beta}; \ \mathcal{G}_{A}^{\alpha} + \Omega_{AB}^{\alpha} \left(x_{B}^{\alpha}\right)^{2} + RT \ln \left(1 - x_{B}^{\alpha}\right)$$

$$= \ \mathcal{G}_{A}^{\beta} + \Omega_{AB}^{\beta} \left(x_{B}^{\beta}\right)^{2} + RT \ln \left(1 - x_{B}^{\beta}\right)$$

$$\mu_{B}^{\alpha} = \mu_{B}^{\beta}; \ \mathcal{G}_{B}^{\alpha} + \Omega_{AB}^{\alpha} \left(1 - x_{B}^{\alpha}\right)^{2} + RT \ln x_{B}^{\alpha}$$

$$= \ \mathcal{G}_{B}^{\beta} + \Omega_{AB} \left(1 - x_{B}^{\beta}\right)^{2} + RT \ln x_{B}^{\beta}$$

$$\left. \right\}$$

$$(Eq 4.28)$$

If the interaction parameters of both phases  $\alpha$  and  $\beta$  are small, and  $\Omega_{AB}^{\alpha}$  and  $\Omega_{AB}^{\beta} \ll RT$ , and the free energies of the solid and the liquid have the same relations as in Eq 4.12,

$${}^{\circ}G_{\mathbf{A}}^{\alpha(\beta)} = {}^{\circ}G_{\mathbf{A}}^{\mathbf{L}} + R\left(T - T_{\mathbf{A}}^{\alpha(\beta)}\right), \ {}^{\circ}G_{\mathbf{B}}^{\alpha(\beta)} = {}^{\circ}G_{\mathbf{B}}^{\mathbf{L}} + R\left(T - T_{\mathbf{B}}^{\alpha(\beta)}\right)$$
(Eq 4.29)

then the following equations can be obtained from Eq 4.28 and 4.29:

$$\frac{1 - x_{\rm B}^{\alpha}}{1 - x_{\rm B}^{\beta}} \approx \exp\left(\frac{T_{\rm A}^{\alpha} - T_{\rm A}^{\beta}}{T}\right), \ \frac{x_{\rm B}^{\alpha}}{x_{\rm B}^{\beta}} \approx \exp\left(\frac{T_{\rm B}^{\alpha} - T_{\rm B}^{\beta}}{T}\right) \tag{Eq 4.30}$$

Figure 4.11(a) shows the calculated results when  $T_A^{\alpha} = 1000 \text{ K}$ ,  $T_A^{\beta} = 300 \text{ K}$ ,  $T_B^{\alpha} = 500 \text{ K}$ , and  $T_B^{\beta} = 800 \text{ K}$ . Lines 3–4 and 5–6 in Fig. 4.11(a) are the common tangents to the solid-phase/liquid-phase curves in a metastable region under the eutectic point (E = 690 K). This metastable equilibrium has an important meaning in a thermodynamic analysis. In 1970, Kaufman analyzed many metastable equilibria of binary component phase diagrams, estimated the melting points of naturally metastable crystals ( $T_A^{\beta}$  and  $T_B^{\alpha}$  in Fig. 4.11), and made a new departure in a calculation of phase diagram (Ref 2). Table 4.1 shows the estimated melting points of the typical metals in the states of bcc, fcc and hcp.

### 4.3.2 Solubility Curve of Compound

**[Exercise 4.8]** Obtain an approximation that expresses a solubility of a compound AmBn ( $\theta$  phase) to  $\alpha$  phase and  $\beta$  phase in A-B system.



**Fig. 4.11** Solubility curve in A-B system. (a) Mutual solubility curve where A and B have different crystal structures. (b) Solubility curve for a compound. The dotted lines in the phase diagrams indicate the equilibrium lines for metastable systems.

Element	bcc	fcc	hcp	Element	bcc	fcc	hcp	Diamond
Al	94	934	541	Nb	2750	919	1339	
Bc	1560	992	1545	Ni	1321	1728	1549	
Co	1435	1768	1701	Pb	347	601	500	
Cr	2180	1351	1379	Ru	1405	2104	2607	
Cu	1086	1358	1270	Si	442	-99	112	1687
Fe	1811	1801	1337	Sn(a)	332	330	329	505
Li	454	392	366	Ti	1943	1421	1693	
Mg	759	709	923	W	3695	1940	2249	

Table 4.1 The melting points of pure metals in the states of bcc, fcc, and hcp. Boldface type indicates the melting point of stable system.

bcc, body-centered cubic; fcc, face-centered cubic; hcp, hexagonal close-packed. (a) Si and Sn are semimetals; therefore the melting points of fcc Si and fcc Sn are estimated to be extraordinarily low. Source: Ref 3

**[Answer]** Because the chemical potentials of the components A and B in the  $\alpha$  (or  $\beta$ ) phase,  $\mu_A^{\alpha(\beta)}$  and  $\mu_B^{\alpha(\beta)}$ , can be approximated by Eq 3.43 according to the regular solution model, the equilibrium between  $\theta$  phase and  $\alpha$  (or  $\beta$ ) phase can be expressed by

$$G_{AmBn}^{\theta} = m\mu_{A}^{\alpha(\beta)} + n\mu_{B}^{\alpha(\beta)} = m^{\circ}G_{A}^{\alpha(\beta)} + n^{\circ}G_{B}^{\alpha(\beta)} + \Omega_{AB}^{\alpha(\beta)} \left[ m\left(x_{B}^{\alpha(\beta)}\right)^{2} + n\left(1 - x_{B}^{\alpha(\beta)}\right)^{2} \right] + RT \ln \left[ \left(1 - x_{B}^{\alpha(\beta)}\right)^{m} \left(x_{B}^{\alpha(\beta)}\right)^{n} \right]$$
(Eq 4.31)

The energy of formation of the compound AmBn is generally expressed by

$$\Delta G_{AmBn}^{f} = G_{AmBn}^{\theta} - m^{\circ} G_{A}^{\alpha} - n^{\circ} G_{B}^{\beta}$$
 (Eq 4.32)

According to Eq 4.31 and 4.32, the solubility of  $\theta$  phase to  $\alpha$  and  $\beta$  phases can be approximated:

$$\alpha/\theta$$
 equilibrium:  $x_{\rm B}^{\alpha} \approx \exp\left[\frac{\left(\Delta G_{\rm AmBn}^{\rm f}/n\right) + \left({}^{\circ}G_{\rm B}^{\beta} - {}^{\circ}G_{\rm A}^{\alpha}\right) - \Omega_{\rm AB}^{\alpha}}{RT}\right]$  (Eq 4.33)

$$\beta/\theta$$
 equilibrium:  $1 - x_{\rm B}^{\beta} \approx \exp\left[\frac{\left(\Delta G_{\rm AmBn}^{\rm f}/m\right) + \left({}^{\circ}G_{\rm A}^{\alpha} - {}^{\circ}G_{\rm A}^{\beta}\right) - \Omega_{\rm AB}^{\beta}}{RT}\right]$  (Eq 4.34)

When Eq 4.33 and 4.34 are obtained, they are rearranged by omitting the small terms including  $x_{\rm B}^{\alpha}$  or  $1 - x_{\rm B}^{\beta}$ .

Figure 4.11(b) shows the calculated results on AB compound, where m = n= 1, assuming that the energy of formation is  $\Delta G_{AB}^{f} = -12 \text{kJ/mol}$ ,  $T_{A}^{\alpha} = 1000 \text{K}$ ,  $T_{A}^{\beta} = 300 \text{K}$ ,  $T_{B}^{\alpha} = 500 \text{K}$ ,  $T_{B}^{\beta} = 800 \text{K}$ , and  $\Omega_{AB}^{\alpha(\beta)} = 0$ .

#### 4.3.3 Solubility Product of Compound

The solubility of a compound BC to an A-B-C ternary solution, for example Fe-TiC system or Fe-MnS system, is of practical importance. The gist of this kind of phase equilibrium is considered in the following exercise.

**[Exercise 4.9]** Let an A-B-C system solution ( $\alpha$  phase) be a regular solution. Obtain an equation expressing the solution of a compound BC ( $\theta$  phase) to  $\alpha$  phase, assuming that a component A never forms any solid solution into  $\theta$  phase.

**[Answer]** The regular solution approximation of the free energy of  $\alpha$  phase is expressed by (see Eq 3.16):

$$G^{\alpha} = {}^{\circ}G^{\alpha}_{A} \cdot x^{\alpha}_{A} + {}^{\circ}G^{\alpha}_{B} \cdot x^{\alpha}_{B} + {}^{\circ}G^{\alpha}_{C} \cdot x^{\alpha}_{C} + \Omega^{\alpha}_{AB}x^{\alpha}_{A}x^{\alpha}_{B} + \Omega^{\alpha}_{BC}x^{\alpha}_{B}x^{\alpha}_{C} + \Omega^{\alpha}_{CA}x^{\alpha}_{C}x^{\alpha}_{A} + RT(x^{\alpha}_{A} \ln x^{\alpha}_{A} + x^{\alpha}_{B} \ln x^{\alpha}_{B} + x^{\alpha}_{C} \ln x^{\alpha}_{C})$$
(Eq 4.35)

The chemical potentials of the components B and C in this  $\alpha$  phase are approximated by Eq 3.40:

$$\mu_{\rm B}^{\alpha} = G^{\alpha} + \frac{\partial G^{\alpha}}{\partial x_{\rm B}^{\alpha}} (1 - x_{\rm B}^{\alpha}) - \frac{\partial G^{\alpha}}{\partial x_{\rm C}^{\alpha}} x_{\rm C}^{\alpha}$$

$$= {}^{\circ}G_{\rm B}^{\alpha} + \Omega_{\rm AB}^{\alpha} x_{\rm A}^{\alpha} (1 - x_{\rm B}^{\alpha}) + \Omega_{\rm BC}^{\alpha} (1 - x_{\rm B}^{\alpha}) x_{\rm C}^{\alpha} - \Omega_{\rm CA}^{\alpha} x_{\rm C}^{\alpha} x_{\rm A}^{\alpha} + RT \ln x_{\rm B}^{\alpha}$$

$$\mu_{\rm C}^{\alpha} = G^{\alpha} - \frac{\partial G^{\alpha}}{\partial x_{\rm B}^{\alpha}} x_{\rm B}^{\alpha} + \frac{\partial G^{\alpha}}{\partial x_{\rm C}^{\alpha}} (1 - x_{\rm C}^{\alpha})$$

$$= {}^{\circ}G_{\rm C}^{\alpha} - \Omega_{\rm AB}^{\alpha} x_{\rm A}^{\alpha} x_{\rm B}^{\alpha} + \Omega_{\rm BC}^{\alpha} x_{\rm B}^{\alpha} (1 - x_{\rm C}^{\alpha}) + \Omega_{\rm CA}^{\alpha} (1 - x_{\rm C}^{\alpha}) x_{\rm A}^{\alpha} + RT \ln x_{\rm C}^{\alpha}$$

$$(Eq 4.36)$$

Therefore, the equilibrium equation between  $\alpha$  phase and  $\theta$  phase can be obtained by

$$\begin{aligned} G_{BC}^{\theta} &= \mu_{B}^{\alpha} + \mu_{C}^{\alpha} \\ &= {}^{\circ}G_{B}^{\alpha} + {}^{\circ}G_{C}^{\alpha} + \Omega_{AB}^{\alpha}x_{A}^{\alpha} \left(1 - 2x_{B}^{\alpha}\right) + \Omega_{BC}^{\alpha} \left(x_{B}^{\alpha} + x_{C}^{\alpha} - 2x_{B}^{\alpha}x_{C}^{\alpha}\right) \\ &+ \Omega_{CA}^{\alpha}x_{A}^{\alpha} \left(1 - 2x_{C}^{\alpha}\right) + RT \ln \left(x_{B}^{\alpha}x_{C}^{\alpha}\right) \end{aligned}$$
(Eq 4.37)

When the formation energy of the compound BC is expressed as  $\Delta G_{BC}^{f} = G_{BC}^{\theta} - {}^{\circ}G_{B}^{\alpha} - {}^{\circ}G_{C}^{\alpha}$ , Eq 4.37 can be rearranged as

$$x_{\rm B}^{\alpha} \cdot x_{\rm C}^{\alpha} = \exp\left[\frac{\Delta G_{\rm BC}^{\rm f} - \Omega_{\rm AB}^{\alpha} x_{\rm A}^{\alpha} \left(1 - 2x_{\rm B}^{\alpha}\right) - \Omega_{\rm BC}^{\alpha} \left(x_{\rm B}^{\alpha} + x_{\rm C}^{\alpha} - 2x_{\rm B}^{\alpha} x_{\rm C}^{\alpha}\right) - \Omega_{\rm CA}^{\alpha} x_{\rm A}^{\alpha} \left(1 - 2x_{\rm C}^{\alpha}\right)}{RT}\right]$$
(Eq 4.38)

Figure 4.12 shows the calculated results when  $\Delta G_{BC}^{f} = -20 \text{ kJ/mol}$ and  $\Omega_{AB}^{\alpha} = \Omega_{BC}^{\alpha} = \Omega_{CA}^{\alpha} = 0$ . If the solubility is small, Eq 4.38 can be simplified:

$$x_{\rm B}^{\alpha} \cdot x_{\rm C}^{\alpha} \approx \exp\left[\frac{\Delta G_{\rm BC}^{\rm f} - \Omega_{\rm AB}^{\alpha} - \Omega_{\rm CA}^{\alpha}}{RT}\right]$$
 (Eq 4.39)

In general, the solubility of a compound BmCn into a solution of A-B-C system can be approximated in an area of low concentration as



**Fig. 4.12** Solubility of a compound (BC) to α phase of A-B-C system. (a) Free energy diagram. (b) Isothermal section of solubility surface. (c) Vertical section of solubility surface. The shaded triangle in the diagram for free energy (a) is the common tangent plane of α phase ④ and BC phase. (b) shows the equilibrium of α phase and BC phase at 600 and 1000 K, and (c) is the vertical section diagram along A-BC line

Chemical engineers and extractive metallurgical engineers use the following solubility product in terms of common logarithms.

log 
$$[B\%]^m [C\%]^n = -\frac{\alpha_1}{T} + \alpha_2$$
 [equation of solubility product] (Eq 4.41)

Here,

$$\alpha_{1} = -\left[\left(\Delta G_{\rm BmCn}^{\rm f} - m\Omega_{\rm AB}^{\alpha} - n\Omega_{\rm CA}^{\alpha}\right)/R \ln 10\right]$$
  
$$\alpha_{2} = \log\left(\omega_{\rm B}^{\rm m} \cdot \omega_{\rm C}^{n}/\omega_{\rm A}^{m+n}\right) + 2(m+n)$$

where  $\omega_A, \omega_B, \omega_C$  are the atomic weights of each component.

### 4.4 Binodal Curve

#### 4.4.1 Miscibility Gap and Spinodal Curve

Mixing a liquid A and a liquid B sometimes results in a two-phase state where a solution  $L_1$  (the principal component of which is A) and a solution  $L_2$  (the principal component of which is B) can coexist under the critical temperature  $T_C$  (Fig. 4.13a). The area of this two-phase coexistence is called the miscibility gap, and the boundary curve is named the binodal curve. A binodal curve can be often seen in a solid solution as well as in a liquid solution, and a peculiar microstructure can be formed (it is called the spinodal decomposition).

An inverted image of a binodal curve can also be seen as shown in Fig. 4.13(b) for polymer composites and solutions of water and organic matters. These two types are discriminated from each other by calling the latter lower critical solution temperature (LCST) and the former upper critical solution temperature (UCST).



Fig. 4.13 Binodal curve of liquids (the hatched area indicates the miscibility gap). (a) Normal type of binodal curve of water and phenol. (b) Inverted type of binodal curve of polyvinyl methyl ether (PVME) (molecular weight 51,500) and polystyrene (PS) (molecular weight 20,400)
**[Exercise 4.10]** Analyze the binodal curve by the regular solution model.

**[Answer]** The free energy of A-B binary solution can be approximated by the regular solution approximation (Eq 3.16):

$$G^{\alpha} = {}^{\circ}G^{\alpha}_{A}(1-x_{B}) + {}^{\circ}G^{\alpha}_{B}x_{B} + \Omega^{\alpha}_{AB}x_{B}(1-x_{B}) + RT[(1-x_{B}) \ln (1-x_{B}) + x_{B} \ln x_{B}]$$
(Eq 4.42)

In this analysis, just the  $\alpha$  phase can be considered and it is not necessary to regard the differences of free energy from other phases. Therefore, it is enough to investigate the free energy when both  $\alpha$  phases of the components are determined as the standard states or  $G_A^{\alpha} = G_B^{\alpha} = 0$  (hereafter, it is described as  $\Delta G^{\alpha}$ ).

As shown in Fig. 4.14(b), because  $\Delta G^{\alpha}$  is symmetrical, the composition of the binodal curve (data point  $\Box$ ) is at the minimum point and it can be calculated by

$$0 = \frac{\partial \Delta G^{\alpha}}{\partial x_{\rm B}} = \Omega^{\alpha}_{\rm AB}(1 - 2x_{\rm B}) + RT \ln\left(\frac{x_{\rm B}}{1 - x_{\rm B}}\right) \text{[equation of binodal curve]}$$
(Eq 4.43)

The point of inflection (data point  $\times$ ) where the curve of  $\Delta G^{\alpha}$  changes from convex to concave downward can be obtained by

$$0 = \frac{\partial^2 \Delta G^{\alpha}}{\partial x_{\rm B}^2} = 2\Omega_{\rm AB}^{\alpha} + RT \left(\frac{1}{x_{\rm B}} + \frac{1}{1 - x_{\rm B}}\right)$$

or

 $2\Omega_{AB}^{\alpha} x_{B}(1 - x_{B}) = RT \text{ [equation of spinodal curve]}$  (Eq 4.44)



Fig. 4.14 Analysis of binodal curve and spinodal curve ( $\Omega^{\alpha}_{AB} = 2000R$ ). Each of the ordinates are shifted by 0.1 kJ/mol in (b).

The curve of the relation between the composition and the temperature at this inflection point is called the spinodal curve.\* As shown with the dashed curve in Fig. 4.14(a), a spinodal curve is parabolic, and it is inscribed in the binodal curve at its vertex ( $x_{\rm B} = \frac{1}{2}$ ). Therefore, the temperature at the vertex of the binodal curve  $T_{\rm C}$  can be expressed by

$$T_{\rm C} = \Omega_{\rm AB}^{\alpha}/2R$$
 [critical temperature of two – phase separation] (Eq 4.45)

In the analysis described previously, the interaction parameter  $\Omega_{AB}^{\alpha}$  is considered to be constant. If this restriction is loosened, an irregular binodal curve can be induced as in the following exercise (see Exercise 4.16).

**[Exercise 4.11]** Assuming the interaction parameter of the regular solution model to be a linear function of temperature T, consider the condition when the inverted type of binodal curve can be seen as in Fig. 4.13(b).

**[Answer]** In order to confirm whether the type of a binodal curve is normal or inverted, it is enough to investigate whether the spinodal curve is concave or convex. Then, investigate the following equation obtained by setting  $\Omega_{AB}^{\alpha} = {}^{0}\Omega + {}^{1}\Omega T$  in Eq 4.44.

$$2({}^{0}\Omega + {}^{1}\Omega T)x_{\rm B}(1 - x_{\rm B}) = RT$$
 (Eq 4.46)

The second differential of Eq 4.46 with respect to  $x_{\rm B}$  is

$$2^{1}\Omega x_{\rm B}(1-x_{\rm B})\frac{d^{2}T}{dx_{\rm B}^{2}} + 4^{1}\Omega(1-2x_{\rm B})\frac{dT}{dx_{\rm B}} - 4(^{0}\Omega + {}^{1}\Omega T) = R\frac{d^{2}T}{dx_{\rm B}^{2}} \quad ({\rm Eq} \ 4.47)$$

Because the composition at the vertex of the spinodal curve is  $x_{\rm B} = \frac{1}{2}$ , two equations can be obtained from Eq 4.46 and 4.47.

$$T_{\rm C} = \frac{{}^{0}\Omega}{2R - {}^{1}\Omega}$$

$$\left(\frac{d^2T}{dx_{\rm B}^2}\right)_{T_{\rm c}} = \frac{16RT_{\rm C}}{{}^{1}\Omega - 2R}$$
(Eq 4.48)

From these equations, the following conclusion can be obtained.

<sup>\*</sup>If the value of interaction parameter  $\Omega$  is negative or very small positive, then  $\mu_B^{\alpha}$  rises monotonically according to the decrease of  $\mu_A^{\alpha}$  as  $1 \rightarrow 2 \rightarrow 3$  in Fig. 4.15. However,  $\mu_A^{\alpha}$  and  $\mu_B^{\alpha}$  change complicatedly up and down as  $4 \rightarrow 5$  $\rightarrow 6 \rightarrow 7 \rightarrow 5 \rightarrow 8$  when of  $\Omega > 2RT$ . Because the chemical potential curve has spines particularly at 6 and 7 corresponding to the inflection point in the free-energy curve, the inflection point is called "a spinodal point," and the relation curve of composition and temperature at the inflection point is called "a spinodal curve." Corresponding to this, the two-phase separation curve is also called "a binodal curve" (Ref 4).

When

$$^{0}\Omega > 0, \ ^{1}\Omega < 2R, \ {
m if} \ {d^{2}T\over dx_{
m B}^{2}} < 0$$

a normal type of binodal curve can be seen. When

$${}^{0}\Omega < 0, {}^{1}\Omega > 2R, \text{ if } \frac{d^{2}T}{dx_{\mathrm{B}}^{2}} > 0$$

an inverted type of binodal curve can be seen. The typical calculations are shown in Fig. 4.16.

If one expands consideration of the miscibility gap in the afore-mentioned A-B binary system, one can also easily analyze the miscibility gap in a multicomponent system. For example, if atoms B and C are repulsive, because the free-energy curve of B-C binary system has a concave segment, the free-energy curved surface of A-B-C ternary system will be also concave on the side of B-C. Therefore, a common tangent exists between the free-energy curves in a solution of primary compo-



**Fig. 4.15** Relationship between  $\mu_A^{\alpha}$  and  $\mu_B^{\alpha}$  along the Gibbs energy curves  $G^{\alpha}$ ; 1-2-3 ( $\Omega \leq 2RT$ ) and 4-5-6-7-8 ( $\Omega > 2RT$ ). The word "spinodal" derives from the word "spine," stiff sharp-pointed parts (6 and 7) in this diagram. Source: Ref 4



Fig. 4.16 Binodal curve (bold solid lines) and the spinodal curve (dashed lines) where the interaction parameter is a linear function of temperature

nent B and a solution of C, and an area of two-phase separation is formed. Figure 4.17(b) shows the two-phase separation where B-C and C-A are repulsive. Fig. 4.17(c) shows the free-energy diagram (the upper) and isothermal phase diagram (the lower) where A, B, and C are mutually repulsive, and three-phase separation can be seen.

#### 4.4.2 Miscibility Gap Island (MGI)

**Miscibility Gap Island in Ternary System.** A miscibility gap can be usually seen when component atoms are mutually repulsive. However, if B-C is excessively attractive, a miscibility gap island (MGI) can be seen even in an A-B-C solution in which components are mutually attractive because the free energy on the side of B-C suddenly decreases and the middle part of the free-energy curved surface becomes concave as shown in Fig. 4.18(a). Meijering (Ref 5) found out that the temperature at the vertex of the island  $T_S$  can be expressed by analyzing this kind of abnormal two-phase separation area:\*

$$T_{\rm S} = -\frac{\left(\Omega^{\alpha}_{\rm AB} + \Omega^{\alpha}_{\rm CA} - \Omega^{\alpha}_{\rm BC}\right)^2 - 4\Omega^{\alpha}_{\rm AB}\Omega^{\alpha}_{\rm CA}}{8R\Omega^{\alpha}_{\rm BC}} \tag{Eq 4.49}$$



Fig. 4.17 Miscibility gap of A-B-C ternary system (the dashed line shows the spinodal curve). The upper figure is the free-energy surface. The lower figure is the isothermal phase diagram.

\*When  $\Omega^{\alpha}_{AB} \ll 0$ , an ordered phase ought to be formed in B-C system. Hardy (Ref 6) modified the analysis by Meijering in consideration of ordering and showed that MGI extends more remarkably (see Section 7.4 "Phase Separation due to Ordering"). **[Exercise 4.12]** Analyze the miscibility gap of A-B-C system when the interaction parameters of A-B, A-C, and B-C systems are  $\Omega^{\alpha}_{AB} = \Omega^{\alpha}_{AC} = 0$ ,  $\Omega^{\alpha}_{BC} = -8000 R$ .

**[Answer]** The free energy of  $\alpha$  phase composed of A, B, and C is approximated as the following equation, taking the  $\alpha$  of the components as the standard states:

$$G^{\alpha} = \Omega_{\rm BC}^{\alpha} x_{\rm B} x_{\rm C} + RT[x_{\rm A} \ln x_{\rm A} + x_{\rm B} \ln x_{\rm B} + x_{\rm C} \ln x_{\rm C}] \qquad ({\rm Eq} \ 4.50)$$

For easy analysis, think of the free energy along the composition line of B:C = 1:1 (A-D in Fig. 4.18b). First, if the scale y on the segment of this line is defined as Eq 4.51, then Eq 4.50 can be converted into Eq 4.52.

$$y = 1 - x_{\rm A} = 2x_{\rm B} = 2x_{\rm C}$$
 (Eq 4.51)

$$G^{\alpha} = \frac{\Omega_{\rm BC}^{\alpha}}{4} y^2 + RT[(1-y) \ln (1-y) + y \ln y - y \ln 2] \qquad ({\rm Eq} \ 4.52)$$



Fig. 4.18 Analysis of miscibility gap island (MGI) (see Fig. 7.13). (a) Free-energy surface. (b) Isothermal diagram. (c) Section of free energy along A-D. (d) View of vertical section

Illustrating Eq 4.52 as it is, as shown with A-D in Fig. 4.18(c), result in indistinct irregularities. Then, modify the free-energy curve by sub-tracting a linear function of y in order for the free energy at the point D to be zero [note 4.6].\*

$$\Delta G^{\alpha} = G^{\alpha} - \left[ \left( \Omega_{BC}^{\alpha}/4 \right) - RT \ln 2 \right] y$$
  
=  $- \left( \Omega_{BC}^{\alpha}/4 \right) y (1-y) + RT \left[ (1-y) \ln (1-y) + y \ln y \right]$  (Eq 4.53)

A-D' in Fig. 4.18(c) is the calculated result of Eq 4.53 at T = 800 K, and one can see the miscibility gap is in the range from 1' to 2'. Moreover, the critical temperature  $T_s$  is 1000 K, and it coincides with the value according to Eq 4.49 presented by Meijering.

**Two-Phase Separation of Complex Compounds (Ref 7–9).** Most III-V compounds in a ternary system, for example Ga(P,As), and most carbides in a ternary system, for example (Ti,Nb)C, can form solid solutions at all ratios. However, for composite systems of two kinds of 3B-5B compounds such as (Ga,In)(P, As) and of a carbide and a nitride such as (Ti,Nb)(C,N), one can often see an MGI (Fig. 4.19).

**[Exercise 4.13]** Describe the free energy of a complex compound (A,B) (C,D) using the sublattice model, and consider the condition for MGI to be seen.

[Answer] A III-V compound is a crystal type of a cubic ZnS structure (similar to that shown in Fig. 3.10), a carbonitride is of a NaCl structure, and the base compound (GaP or NbC) consists of the first nearest neighbor



Fig. 4.19 Miscibility gap island (MGI) of (Ga,In)(P,As)

\*If the linear function of *y* is omitted from the equation, the concavity or convexity of the curve does not change.



Fig. 4.20 Analysis of miscibility gap island in a composite system of compounds

pairs of atoms. On the other hand, the second nearest neighbor pairs (P-As or C-N) are farther from each other compared to the first ones, and their interactions are generally small. Therefore, the interactions between the second nearest neighbors ( $L_{AB}^{C}$ , etc. in Eq 3.27) are omitted here and the following equation is considered.

$$G = G_{AC}(1 - y_B)(1 - y_D) + G_{BC}y_B(1 - y_D) + G_{AD}(1 - y_B)y_D + G_{BD}y_By_D + RT[(1 - y_B) \ln (1 - y_B) + y_B \ln y_B + (1 - y_D) \ln (1 - y_D) + y_D \ln y_D] (Eq 4.54)$$

In Eq 4.54, for example  $G_{AC}$  is the free energy of the compound AC with 1 mole of A and 1 mole of B combined.  $y_{B}$  and  $y_{D}$  are the atomic fractions of B and D on the sublattice I and sublattice II.

When analyzing the irregularities of the free-energy surface, the origins of free energies for three components can be selected suitably. Then, if the plane including  $G_{AC}$ ,  $G_{BC}$ , and  $G_{AD}$  (the shaded plane in Fig. 4.20a) is set as a standard, Eq 4.54 can be rewritten as

$$\Delta G = G - [G_{AC}(1 - y_B - y_D) + G_{BC}y_B + G_{AD}y_D]$$
  
=  $\Omega_{y_By_D} + RT[(1 - y_B) \ln (1 - y_B) + y_B \ln y_B + (1 - y_D) \ln (1 - y_D) + y_D \ln y_D]$   
(Eq 4.55)

Here,

$$\Omega = (G_{\rm AC} + G_{\rm BD}) - (G_{\rm BC} + G_{\rm AD}) \tag{Eq 4.56}$$

Figure 4.20(b) is the calculated value of the free energy along the line AC-BD when  $\Omega = -400 R$ , T = 750 K, and a miscibility gap appears between 1 and 2. The vertex of this miscibility gap  $T_s$  has the following relation with  $\Omega$ :

$$T_{\rm S} = -\Omega/4R = [(G_{\rm BC} + G_{\rm AD}) - (G_{\rm AC} + G_{\rm BD})]/4R$$
 (Eq 4.57)

The afore-mentioned analysis is for the case when the compound BD is extremely stable and  $(G_{BC} + G_{AD}) \gg (G_{AC} + G_{BD})$ , but if the compound BC is extremely stable and  $(G_{BC} + G_{AD}) \ll (G_{AC} + G_{BD})$ , the miscibility gap along the line BC-AD can be seen.

The cause of MGI formation as mentioned previously is that the free energy becomes lower when the phase with primary component of BD (or BC) is separated than when A-B-C-D form a uniform solid solution because the bonding pair of B-D (or B-C) is strong.

Figure 4.21 shows the comparison of the typical examples for a usual miscibility gap and MGI.

It was A. J. Bradley (1949) (Ref 10) who first proved experimentally the appearance of MGI, and he confirmed that bcc Fe-Ni-Al phase decomposes into the  $\alpha_1$  phase with a primary element of Fe and the  $\alpha_2$ phase with a primary component of NiAl. This two-phase separation was reinvestigated in detail by Hao et al. (Ref 11). Additionally, the mechanism of the two-phase separation in bcc Fe-Cr-Co phase is also very interesting. Refer to Ref 3, 12, and 13 for details.



**Fig. 4.21** Miscibility gap of a solid solution is caused by the repulsive reaction between atoms. However, the miscibility gap island is caused by the difference in interatomic binding forces.

#### EXERCISES

**4.14** The phase diagram for a binary system shown in Fig. 4.22 is incorrect. Describe the reason.

**4.15** Show that the liquidus line and the solidus line in the phase diagram for a completely miscible A-B system will become such curves as in Fig. 4.23 by their magnitude relation between the interaction parameters  $\Omega^{L}$  and  $\Omega^{\alpha}$  according to the regular solution model. Here, let the entropies of melting for A and B be equal to the gas constant *R* by Richards' rule.

*Hints:* Think of the condition that an extreme value exists at the temperature  $T_0$  (long dashed, short dashed line) where the free energies of the liquid phase and solid phase become equivalent.

**4.16** The melting points of A, B, and C are 1000, 750, and 500 K, respectively. Confirm that the isothermal phase diagram for A-B-C system at 700 K can be calculated as in Fig. 4.24(a) when the liquid solution L and the solid solution  $\alpha$  are ideal solutions. Here, let the entropy of melting to be equal to *R*.



Fig. 4.22 Typical examples of incorrect phase diagrams for a binary system



Fig. 4.23 Relation between the interaction parameter and the shape of liquidus, solidus lines

**4.17** Induce the equation expressing the solubility product of a compound ABC with A:B:C = 1:1:1. Here, let the solid solution  $\alpha$  of A-B-C system be an ideal solution. Fig. 4.24(b) is a calculated example of the isothermal phase diagram.

**4.18** When the interaction parameter of A-B system is  $\Omega_{BC}^{\alpha} < 0$ , no binodal curve can be seen in general. Confirm that when  $\Omega_{BC}^{\alpha} = -1000R \cdot x_{B}$  a two-phase separation occurs; however, if  $\Omega_{BC}^{\alpha} < 0$  then the value of  $\Omega_{BC}^{\alpha}$  changes remarkably by the concentration of a solute (the result is shown in Fig. 4.24c).



Fig. 4.24 Answers to Exercises 4.16, 4.17, and 4.18. (a) Liquidus line-solidus line. (b) Solubility curve. (c) Binodal curve



**Fig. 4.25** Phase diagrams of typical ceramics. Metal oxide types: (a) M-MO basic type, (b) M-MO solid-solution type. (c) Zr-ZrO<sub>2</sub> dissolution type. Composite systems of ceramics: (d) Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2'</sub> (e) Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3'</sub> (f) Al<sub>2</sub>O<sub>3</sub>-AlN

### Appendix: The Phase Diagram of Ceramics

Because  $Al_2O_3$  is an ionic compound, it cannot dissolve into Al. Similarly, most of the phase diagrams for M-MO system show that the mutual solubility of the solution is small both in a liquid phase and in a solid phase as shown in Fig. 4.25(a).

However, Mg-MgO system and Ca-CaO system are exceptions, and they can dissolve into each other at all compositions beyond the melting point as in Fig 4.25(b). The Zr-ZrO<sub>2</sub> system (Fig 4.25c) is also an exception, and they not only can dissolve into each other in a liquid phase but also O atoms can form an interstitial solution with a solid crystal of Zr at a rather high concentration. On the side of ZrO<sub>2</sub> it can form  $\gamma$ ZrO<sub>2 - x</sub> phase, which has a nonstoichiometric composition lacking in O<sub>2</sub> ions.

Most of the combination of two kinds of ceramics often form a complex oxide such as mullite:  $3Al_2O_3 \cdot 2SiO_2$  of  $Al_2O_3$ -SiO\_2 system (Fig. 4.25d). Moreover, there are various cases such as  $Al_2O_3$ -Cr<sub>2</sub>O<sub>3</sub> system (Fig. 4.25e), which forms a quasi-binary solid solution ( $Al_1Cr$ )<sub>2</sub>O<sub>3</sub>,  $Al_2O_3$ -AlN system (Fig. 4.25f), which forms the Alon phase, a mixed compound with a solid solution of an oxide and a nitride, and so on. As for ( $Al_1Cr$ )<sub>2</sub>O<sub>3</sub>, see Fig. 3.11.

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CHAPTER

# Thermodynamics of Interfaces

When a microstructure is compared to a mosaic pattern, the constituent phase of the microstructure can be compared to pieces of beautiful glass and jewels or ceramic tiles coloring the mosaic. The group joining them together is the interface in a microstructure, and the interfaces are only "the subordinates" when contemplating the beauty of the pattern. However, it is the interface of group that must provide mechanical support to the pattern. Degradation of this joint would limit the enjoyment of the mosaic. This chapter considers various behaviors of the interface from a thermodynamics viewpoint.

## 5.1 Energy of Surface and Interface

Surface tension acts on the surface of water, and it tries to reduce the gross surface area as much as possible. Similarly, tension also acts on the surface of the crystal and the interface of a microstructure. These tensions are considered the excessive energy that the surface or the interface keeps. This energy is called surface energy or interface energy in thermodynamics.

Tension and energy are different concepts, but the unit that shows strength of the interfacial tension and the unit of energy possessed by the interface are identical as in the following equation, and they are not very different numerically.

Unit system	Interfacial tension		Interfacial energy	
SI	N/m	=	$J/m^2$	(Eq 5.1)
cgs	dyne/cm	=	erg/cm <sup>2</sup>	

Figure 5.1 shows the representative examples of a surface and an interface energy (Ref 1–4). These values are determined by the zero





**Fig. 5.1** Surface energies of various materials. (a) The surface energy of solids and liquids. It is greater for metals, and less for plastics. (b) The energy of solid/liquid or liquid/ liquid interface and random grain boundary. It varies according to the combination of substances and varies with melting points.

creep method (see Exercise. 5.21) or by the measurement of the contact angles, and one can estimate the approximate values based on the thermodynamic data as in the Exercise 5.1.

**[Exercise 5.1]** Show that the surface energy of a crystal can be estimated roughly by

$$\sigma_{\rm surface}^{\rm S} \approx (z'N^*/zN_0)\Delta H_{\rm S}$$
 (Eq 5.2)

Here,  $\Delta H_{\rm S}$  is the latent heat (per 1 mole) of the crystal when it sublimes, z is the number of the nearest-neighbor atoms in the crystal, z' is the number of free bonds of atoms on the crystal surface,  $N_0$  is Avogadro's constant and  $N^*$  is the number of atoms on the crystal surface (per unit area).

**[Answer]** Because the total of the nearest-neighbor pairs of atoms in 1 mole of the crystal is  $zN_0/2$ , the bonding energy per pair can be approximated by

$$\varepsilon_{\rm SS} \approx \Delta H_{\rm S}/(zN_0/2)$$
 (Eq 5.3)

When a crystal is cleaved, for example the bonds of A-B and A-C will be cut off as in Fig. 5.2(a) and the number of free bonds will be doubled.



**Fig. 5.2** Surface energy and grain boundary energy. If they are regarded as "surface," the energy of "atom bonds" crossing the surface is calculated. If they are regarded as "thin films," the energy of film "phase" is calculated. (a) Free bonds formed by cleavage. (b) Three-atom layer model for random grain boundary

Therefore, because the energy of the free bond  $\Delta \epsilon^{S/V}$  can be considered equal to  $\frac{1}{2}$  of  $\epsilon_{SS}$  mentioned previously, the surface energy can be approximated by the following equation and Eq. (5.2) as wanted in Eq 5.1 can be obtained.

$$\sigma_{\text{surface}}^{\text{S}} \approx z' N^* \cdot \Delta \varepsilon^{\text{S/V}} = (z' N^* / z N_0) \Delta H_{\text{S}}$$
 (Eq 5.4)

For example, in the case of (111) surface of Cu (fcc the lattice constant a = 0.37 nm), z = 12, z' = 3,  $N^* = 4/\sqrt{3}a^2 \approx 1.7 \times 10^{19} \text{m}^{-2}$ , and  $\Delta H_S = 319$  kJ/mol. Then, it is presumed that  $\sigma_{\text{surface}}^{\text{S}} \approx 2.3$  J/m<sup>2</sup>. This value is considerably larger than the measured value (1.7 J/m<sup>2</sup>) shown in Fig. 5.1(a), but it can be said that it is an unexpectedly good estimation by a simple model calculation.

Next, obtain the energy of the random grain boundary.

In general, "surfaces" do not have thickness, but because the grain boundary locates at the middle region of the crystal on both sides, if "a thin film" of proper thickness is imagined, it becomes easy to understand the essence of the grain boundary.

**[Exercise 5.2]** Find out the approximation of the grain-boundary energy  $\sigma^{gb}$  by considering the random grain boundary to be an amorphous phase with the thickness of 3 atoms placed with the crystals I and II. Here, it is assumed that the latent heat of transformation from the crystal to the amorphous phase is  $\frac{1}{2}$  of the latent heat of melting  $\Delta H_{\rm m}$  (see Section 2.5 "Free Energy of Amorphous Phase").

**[Answer]** If the energies of the atom pairs in the crystal and the grain boundary are  $\varepsilon_{SS}$  and  $\varepsilon^{gb}$ , the difference between them is

$$\Delta \varepsilon^{\rm gb} = \varepsilon^{\rm gb} - \varepsilon_{\rm SS} \approx (\Delta H_{\rm m}/2)/(zN_0/2) \tag{Eq 5.5}$$

Because the total of atoms existing in a unit area of the thin film with the thickness of 3 atoms is  $3 \times (N_0 / V)^{2/3}$  where V is the molar volume and the number of the atom pairs per 1 atom is z/2, the grain-boundary energy is

$$\sigma^{\text{gb}} \approx 3 \times (N_0/V)^{2/3} \cdot z/2 \cdot \Delta \varepsilon^{\text{gb}} \approx 3/2(N_0/V)^{2/3} \cdot \Delta H_m/N_0 \quad \text{(Eq 5.6)}$$

For example, in the case of pure Cu,  $\Delta H_{\rm m} = 13.1$  kJ/mol,  $V = 7.1 \times 10^{-5} {\rm m}^3$ /mol, and one can calculate  $\sigma^{\rm gb} \approx 0.62$  J/m<sup>2</sup>. This value is almost equal to the measured value shown in Fig. 5.1(b).

As mentioned previously, the interface energy of a pure substance can be estimated roughly based on the latent energy at state change. However, the interface energy of solid solutions in an alloy or of a ceramic and a metal is difficult to estimate because it is necessary to consider the chemical interactions between the atoms. The next exercise is the simplest example of calculation.

**[Exercise 5.3]** Show the interface energy of  $L_I/L_{II}$  when a liquid phase of A-B system is separated into two liquid phases  $(L_I + L_{II})$  can be approximated according to the regular solution model by

$$\sigma^{\text{I/II}} \approx \frac{z'N^*}{zN_0} \Omega_{\text{AB}}^{\text{L}} \left( x_{\text{B}}^{\text{II}} - x_{\text{B}}^{\text{I}} \right)^2 \text{ [Becker's equation (Ref 5)]}$$
(Eq 5.7)

Here  $N^*$  is the number of atoms on a unit area of the interface, z' is the number of bonds passing through the interface (per 1 atom),  $\Omega_{AB}^{L}$  is the interaction parameter between A and B atoms in the liquid phase, and  $x_{B}^{I}$  and  $x_{B}^{II}$  are the concentrations of B in L<sub>I</sub> and L<sub>II</sub>, respectively.

**[Answer]** Because  $L_I/L_{II}$  interface is regarded as the interface that is formed by cutting-off/joining both phases of  $L_I$  and  $L_{II}$  as shown in Fig. 5.3(a), it can be approximated by

$$\sigma^{\mathrm{I/II}} \approx z' N^* \Big[ \varepsilon^{\mathrm{I/II}} - \left( \varepsilon^{\mathrm{I/I}} + \varepsilon^{\mathrm{II/II}} \right) / 2 \Big]$$
 (Eq 5.8)

Here  $\varepsilon^{I/I}$ ,  $\varepsilon^{II/II}$ , and  $\varepsilon^{I/II}$  are the averaged energies per pair of atoms whose bonds pass through the cutting or joining section of both phases.

When the energy of each atom pair is  $\varepsilon_{AA}$ ,  $\varepsilon_{BB}$ , and  $\varepsilon_{AB}$ , respectively, by the random distribution assumption, one can obtain the following series of equations.



Fig. 5.3 Approximated calculation of the interface energy of two liquid phases in a binary system

$$\epsilon^{I/I} \approx \epsilon_{AA} (1 - x_B^I)^2 + \epsilon_{BB} (x_B^I)^2 + \epsilon_{AB} \left[ (1 - x_B^I) x_B^I + x_B^I (1 - x_B^I) \right] \epsilon^{II/II} \approx \epsilon_{AA} (1 - x_B^{II})^2 + \epsilon_{BB} (x_B^{II})^2 + \epsilon_{AB} \left[ (1 - x_B^I) x_B^{II} + x_B^{II} (1 - x_B^{II}) \right] \epsilon^{I/II} \approx \epsilon_{AA} (1 - x_B^I) (1 - x_B^{II}) + \epsilon_{BB} x_B^I x_B^{II} + \epsilon_{AB} \left[ (1 - x_B^I) x_B^{II} + x_B^I (1 - x_B^{II}) \right]$$

$$(Eq 5.9)$$

Consequently, the value in the brackets in Eq 5.8 will become

$$\epsilon^{I/II} - (\epsilon^{I/I} + \epsilon^{II/II})/2 \approx [\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2](x_B^{II} - x_B^I)^2 \qquad (\text{Eq 5.10})$$

Therefore, by rearranging them using the definition of the interaction parameter  $\Omega_{AB}^{L} = zN_0 [\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2]$  (Eq 3.11), Eq 5.7 in the exercise can be obtained. Becker introduced this equation when he was analyzing a homogeneous nucleation in a solution (Ref 5).

As an example, obtain the energy of the interface between two liquid phases in the Cu-Pb system (Fig. 5.3b).

When the arrangement of atoms on the interface is approximated by the arrangement of fcc (111), z' = 3,  $N^* \approx 1.7 \times 10^{19} \text{ m}^{-2}$ . The compositions of the two phases are  $x_{Pb}^{I} = 0.16$  and  $x_{Pb}^{II} = 0.65$ . The interaction parameter is  $\Omega_{CuPb}^{L} \approx 2RT_{C} \approx 21 \text{ kJ/mol}$  from Eq 4.45 using the critical temperature of two-phase separation:  $T_{C} \approx 1280 \text{ K}$ . Therefore, one can estimate that  $\sigma^{LCu/Pb} \approx 0.04 \text{ J/m}^2$ . This value is close to the measured value (0.06 J/m<sup>2</sup>) (Ref 6).

## 5.2 Gibbs-Thomson Effect

#### 5.2.1 Experiment on Soap Bubbles

The pressure inside a balloon is higher than that outside. When it is swollen, because the tension of elasticity increases, the pressure rises higher and higher. In the case of a soap bubble, the internal pressure is also higher than the external pressure. However, because the surface tension differs from the tension of elasticity, surface tension does not vary if the area increases; on the contrary, the pressure becomes less during swelling as shown in Exercise 5.4.

**[Exercise 5.4]** Show that the pressure as described will be caused by a surface energy  $\sigma$  inside a sphere with radius *r*.

$$\Delta P = 2\sigma/r \text{ [Laplace equation (1806)]}^* \qquad (\text{Eq 5.11})$$

[Answer] As shown in Fig. 5.4(a), the energy consumption is

$$\sigma \cdot d(4\pi r^2) = \sigma \cdot 8\pi r dr$$

When the surface of the sphere increases with the radius increasing by dr. On the other hand, when the pressure difference  $\Delta P$  is considered, the energy consumption according to the increase of the volume is

$$\Delta P \cdot d(4\pi r^3/3) = \Delta P \cdot 4\pi r^2 dr$$



**Fig. 5.4** (a) Illustrative explanation of Laplace equation, showing internal pressure by surface tension bubbles. (b) The experiment on two soap bubbles. The smaller soap bubble becomes smaller, and the larger bubble expands. The smaller bubble will disappear.

\*Laplace derived Eq 5.11 by considering dynamics. However, W. Thomson (later Lord Kelvin) derived the same equation thermodynamically, and it is also called the Thomson equation. Because these are equivalent, the following equation is formed and Eq 5.11 can be obtained.

$$\sigma \cdot 8\pi r dr = \Delta P \cdot 4\pi r^2 dr$$

Additionally, in the case of a soap bubble, the right-hand side of Eq 5.11 should be  $4\sigma/r$  because the surface tension acts on both sides of the soap film.

Figure 5.4(b) is a well-known illustration of an experiment on soap bubbles; because the pressure is higher in the smaller bubble, when the stop cock ③ is opened, air begins to flow into the larger bubble, the smaller bubble shrinks in a moment, and it disappears.

#### 5.2.2 Transformation Temperature and Pressure of Fine Particles

The internal pressure  $\Delta P$  based on the surface (interface) tension gives the following change to the free energy (G = U + PV - TS).

$$\Delta G = \Delta P \cdot V = \frac{2\sigma V}{r} \tag{Eq 5.12}$$

As a result, in the case of fine particles with radius  $r = 0.1 \ \mu m$  or less, the boiling point, the vapor pressure, and the solubility become different values from the usual ones.

**[Exercise 5.5]** Estimate the boiling point and boiling pressure of pure Cu particles with radius of 0.01 µm. Here, the surface energy of liquid Cu is  $\sigma = 1.3 \text{ J/m}^2$ . The molar volume is  $V^{\text{L}} = 7.9 \times 10^{-6} \text{ m}^3/\text{mol}$ . The boiling point is  $T_{\text{b}} = 2855 \text{ K}$  without any atomization. The enthalpy of boiling is  $\Delta H_{\text{b}} = 306 \text{ kJ/mol}$ .

**[Answer]** First, considering the boiling point at P = normal pressure, the equilibrium condition of the liquid drops and the gas phase is

$$(G - G_{\rm L})_{\rm normal \ pressure} = \frac{2\sigma V^{\rm L}}{r}$$
 (Eq 5.13)

The left side in Eq 5.13 can be approximated by a Taylor expansion as

$$(G^{g} - G^{L})_{\text{normal pressure}} \approx \left[ \left( \partial G^{g} / \partial T \right) - \left( \partial G^{L} / \partial T \right) \right]_{\text{normal pressure}} \times \Delta T$$
  
=  $-(S^{g} - S^{L})_{\text{normal pressure}} \cdot \Delta T = -(\Delta H_{b} / T_{b}) \Delta T$  (Eq 5.14)

Here, Eq 2.33;  $(\partial G/\partial T)_p = -S$  is used.

From Eq 5.13 and 5.14 as mentioned previously, the change of boiling point by atomization can be obtained

$$\Delta T = -\left(\frac{2\sigma V^{\rm L}}{r}\right) \left(\frac{T_{\rm b}}{\Delta H_{\rm b}}\right) \tag{Eq 5.15}$$

Substituting the values given in the exercise into Eq 5.15, it is presumed that the boiling point of Cu liquid droplets with radius  $r = 0.01 \ \mu m$  is  $\Delta T = -18.7 \ K$  lower than the usual boiling point (Fig. 5.5a).

Next, the conditional equation to obtain the change of the boiling pressure by atomization is expressed as

$$(G^{\rm g} - G^{\rm L})_{\rm boiling \ point} = \frac{2\sigma V^{\rm L}}{r}$$
 (Eq 5.16)

The left side of Eq 5.16, unlike Eq 5.14, can be approximated as follows according to  $(\partial G/\partial P) = V, V^g \gg V^L$ , and the ideal gas equation  $PV^g \gg RT$ .

$$(G^{g} - G^{L})_{\text{boiling point}} = \int_{P_{\infty}}^{P_{r}} (V^{g} - V^{L}) dP \approx \int_{P_{\infty}}^{P_{r}} \frac{RT_{b}}{P} dP$$
$$= RT_{b} \ln \frac{P_{r}}{P_{\infty}}$$
(Eq 5.17)



Fig. 5.5 Boiling point depression and elevation of boiling pressure by atomization. (a) At constant pressure (P = ordinary pressure). (b) At constant temperature (T = boiling point)

From Eq 5.16 and 5.17, the following equation can be obtained.

$$P_{\rm r} \approx P_{\infty} (= \text{normal pressure}) \cdot \exp\left(\frac{2\sigma V^{\rm L}}{RT_{\rm b}r}\right)$$
 (Eq 5.18)

When substituting the values given in the exercise into Eq 5.18 it is presumed that the boiling pressure of Cu liquid droplets with  $r = 0.01 \text{ } \mu\text{m} \text{ is } P_{\text{r}} = 1.09 \times 10^5 \text{ Pa}$  (Fig. 5.5b).

In order to find out the vapor pressure at the temperature T' below the boiling point, it is sufficient to substitute T' into  $T_b$  and the normal equilibrium vapor pressure  $P_{\infty}$  into  $P'_{\infty}$  (= normal pressure) in Eq 5.18.

This change of phase equilibrium by surface (interface) tension is generally called the Gibbs-Thomson effect.

#### 5.2.3 Solubility of Fine Particles

The next exercise is a typical example of the Gibbs-Thomson effect.

**[Exercise 5.6]** Show the increase in the solubility of  $\theta$  phase (AmBn) dispersed in  $\alpha$  phase as in the following equation when the radius of  $\theta$  phase *r* decreases.

$$[x_{\rm B}^{\alpha}]_r \approx x_{\rm B}^{\alpha/\theta} \cdot \exp\left[\frac{1}{nRT}\left(\frac{2\sigma V}{r}\right)\right]$$
 (Eq 5.19)

Here  $\sigma$  is the energy of interface  $\alpha/\theta$ . *V* is the molar volume of  $\theta$  phase.  $x_{\rm B}^{\alpha/\theta}$  is the equilibrium solubility (molar fraction).

**[Answer]** The true equilibrium between  $\theta$  phase and  $\alpha$  phase is expressed by (Eq 4.31):

$$G^{\theta} = m\mu_{\rm A}^{\alpha/\theta} + n\mu_{\rm B}^{\alpha/\theta} \tag{Eq 5.20}$$

Here  $\mu_A^{\alpha/\theta}$  and  $\mu_B^{\alpha/\theta}$  are the chemical potentials of components A and B in  $\alpha$  phase in equilibrium with  $\theta$  phase, and, as shown in Fig. 5.6(a), they correspond to the intersections (data point  $\triangle$ ) of the common tangent to  $G^{\alpha}$  and  $G^{\theta}$  and the A and B axes.

When  $\theta$  phase is a fine particle, because the free energy rises by the Gibbs-Thomson effect, the equilibrium equation can be expressed as follows and the values of chemical potential will shift to the data point  $\Delta$ :

$$[G^{\theta}]_{r} = G^{\theta} + \frac{2\sigma V}{r} = m[\mu_{A}^{\alpha/\theta}]_{r} + n[\mu_{B}^{\alpha/\theta}]_{r}$$
(Eq 5.21)

From Eq 5.20 and 5.21, one can obtain

$$\frac{2\sigma V}{r} = m([\mu_{\rm A}^{\alpha/\theta}]_r - \mu_{\rm A}^{\alpha/\theta}) + n([\mu_{\rm B}^{\alpha/\theta}]_r - \mu_{\rm B}^{\alpha/\theta})$$
(Eq 5.22)



**Fig. 5.6** The increase of solubility by atomization. See the footnote for Fig 4.9, where the reason that  $G^9$  and V are divided by (m + n) in the free-energy diagram is explained. (a) The free-energy diagram and the phase diagram. (b) The solubility of Fe<sub>3</sub>C particles to austenite of Fe-C system

In order to realize Eq 5.22, it can be expressed as the following equation by approximating  $\mu_A^{\alpha}$  and  $\mu_B^{\alpha}$  according to the regular solution model (Eq 3.43) and omitting the small terms on the assumption that  $x_B^{\alpha/\theta} \ll 1$ .

$$\mu_{\rm A}^{\alpha} \approx^{\circ} G_{\rm A}^{\alpha} + \Omega_{\rm AB}^{\alpha} \left( x_{\rm B}^{\alpha} \right)^2 + RT \ln \left( 1 - x_{\rm B}^{\alpha} \right) \approx^{\circ} G_{\rm A}^{\alpha} - RT \cdot x_{\rm B}^{\alpha}$$

$$\mu_{\rm B}^{\alpha} \approx^{\circ} G_{\rm B}^{\alpha} + \Omega_{\rm AB}^{\alpha} \left( 1 - x_{\rm B}^{\alpha} \right)^2 + RT \ln x_{\rm B}^{\alpha} \approx^{\circ} G_{\rm B}^{\alpha} + \Omega_{\rm AB}^{\alpha} + RT \ln x_{\rm B}^{\alpha}$$

$$\left. \left( \text{Eq 5.23} \right) \right\}$$

$$\left. \left( \text{Eq 5.23} \right) \right\}$$

Using these approximations, the difference of the chemical potential at the true solubility  $x_{\rm B}^{\alpha/\theta}$  from the one at the solubility of fine particles  $[x_{\rm B}^{\alpha/\theta}]_r$  can be described as

$$\left[ \mu_{\rm A}^{\alpha/\theta} \right]_r - \mu_{\rm A}^{\alpha/\theta} \approx 0 \\ \left[ \mu_{\rm B}^{\alpha/\theta} \right]_r - \mu_{\rm B}^{\alpha/\theta} \approx RT \ln\left( [x_{\rm B}^{\alpha/\theta}]_r / x_{\rm B}^{\alpha/\theta} \right)$$
 (Eq 5.24)

By substituting Eq 5.24 into Eq 5.22 and rearranging it, Eq 5.19 can be obtained.

Figure 5.6(b) is the calculated result showing that the solubility of the cementite (Fe<sub>3</sub>C) to the austenite ( $\gamma$  phase) in Fe-C system increases remarkably according to atomization of Fe<sub>3</sub>C. Here, the interface energy of the cementite is  $\sigma = 0.8$  J/m<sup>2</sup>. The molar volume is  $V = 23 \times 10^{-6}$  m<sup>3</sup>/mol.

# 5.3 Thermodynamics of Grain-Boundary Segregation

Solute atoms in a material tend to gather on the surface or the grain boundary. This is generally called "interface segregation."\* In this section, after learning the adsorption of the gas molecules to the crystal surface that has been investigated best in interface segregations, think about the segregation of the solute atoms in the grain boundary.

### 5.3.1 Monolayer Adsorption and Multilayer Adsorption

**[Exercise 5.7]** Show that the surface coverage  $\theta$  has the following relation with the partial pressure of adsorbed molecules *P* when the monatomic molecules adsorb the crystal surface and they form monolayer adsorption film.

$$\theta \approx \frac{kP}{1+kP}$$
 [Langmuir equation (1918)] (Eq 5.25)

**[Answer]** The number of gas molecules that coagulate on the crystal surface from the side of the gas phase (per unit area and unit time) is proportional to the rate of area  $(1 - \theta)$  that is not covered with the film, and the partial pressure *P*. However, the number of molecules that vaporize from the side of adsorption film to the side of gas phase is proportional to the rate of area of the adsorption film  $\theta$ . Because both of them are equal in equilibrium,

$$a(1-\theta)P = b\theta \tag{Eq 5.26}$$

*a* is the condensation coefficient, and *b* is the evaporation coefficient in Eq 5.26, and Eq 5.25 in the exercise can be obtained by rearranging it using the ratio of them, the adsorption equilibrium coefficient k = a/b.

The aforementioned Langmuir equation can hold in the case of "chemical adsorption" where the bond of the substrate crystal and the adsorbed atom is strong; the relation between the partial pressure and the coverage of the gas becomes a saturation type as shown in Fig. 5.7(a). On the other hand, in the case of "physical adsorption" where the bond of the adsorbed

<sup>\*&</sup>quot;Solidification segregation" caused during solidification of a solution will disappear by annealing for a long time because it is formed by nonequilibrium solidification. However, "interface segregation" is an equilibrium phenomenon, and the segregation ratio will come nearer to a specific value as a solid is heated more. Therefore, it is precisely correct to call it "equilibrium interface segregation."



**Fig. 5.7** (a) Monolayer adsorption model (chemical adsorption). (b) Multilayer adsorption model (physical adsorption)

atom and the substrate crystal is weak, the adsorption film comes to form a multilayer structure, and the relation between the amount of adsorption and the pressure becomes a nonsaturation type as shown in Fig. 5.7(b). The following Brunauer-Emmett-Teller (B-E-T) equation is a representative equation to describe this kind of multilayer adsorption.

$$\theta = \frac{k_1 P}{(1 - kP)[1 + (k_1 - k)P]}$$
 [the B-E-T adsorption equation (1938)] (Eq 5.27)

Here  $k_1 = a_1/b_1$  is the equilibrium coefficient of adsorption to the first layer. *k* is the equilibrium coefficient of adsorption to the second or more layer. As for induction of Eq 5.27, refer to Ref 7.

#### 5.3.2 McLean's Grain-Boundary Segregation Equation (Ref 8)

The grain-boundary segregation is a "chemical adsorption" in general, and the relation between concentration  $X^{\text{gb}}$  in the grain boundary and concentration  $x^{\alpha}$  in the inside of grain is expressed in a saturated curve of the same type as the Langmuir equation (Eq 5.25).

**[Exercise 5.8]** Let the total of atoms consisting of the grain boundary be  $N^{\text{gb}}$ . Let  $n^{\text{gb}}$  of them be the number of solute atoms segregated in the grain boundary. On the other hand, let the total of the atoms in the grain to be  $N^{\alpha}$ . Also, let  $n^{\alpha}$  of them be the number of solute atoms. Moreover, letting the energy of segregation in the grain boundary per solute atom be  $\Delta \varepsilon_X^{\text{gb}}$ , show that the following approximation can be approved if the distribution of the solute (X) follows Maxwell-Boltzmann statistics.

$$X^{\text{gb}} \approx \frac{x^{\alpha} \cdot \exp\left(\Delta \varepsilon_X^{\text{gb}}/k_B T\right)}{1 + x^{\alpha} \cdot \exp\left(\Delta \varepsilon_X^{\text{gb}}/k_B T\right)} [\text{McLean's equation (1948)}] \quad (\text{Eq 5.28})$$

**[Answer]** The change of free energy due to the segregation of  $n^{\text{gb}}$  atoms of X in the grain boundary is

$$\Delta G \approx \underbrace{\overbrace{-\Delta \varepsilon_{X}^{\text{gb}} \cdot n^{\text{gb}}}^{\text{Enthalpy change}} - T \cdot \underbrace{k_{\text{B}} \cdot \ln \left[ \frac{N^{\text{gb}}!}{n^{\text{gb}}! \cdot (N^{\text{gb}} - n^{\text{gb}})!} \cdot \frac{N^{\alpha}!}{n^{\alpha}! \cdot (N^{\alpha} - n^{\alpha})!} \right]}_{(\text{Eq 5.29})}$$

The term ln [ ] of Eq 5.29 can be approximated by Stirling's approximation:  $\ln N! \approx N \ln N - N$  as

$$\ln[] \approx -\left[n^{gb}\ln\left(\frac{n^{gb}}{N^{gb}}\right) + (N^{gb} - n^{gb})\ln\left(\frac{N^{gb} - n^{gb}}{N^{gb}}\right) + n^{\alpha}\ln\left(\frac{n^{\alpha}}{N^{\alpha}}\right) + (N^{\alpha} - n^{\alpha})\ln\left(\frac{N^{\alpha} - n^{\alpha}}{N^{\alpha}}\right)\right]$$
(Eq 5.30)

The minimum condition of  $\Delta G$  when  $n^{\alpha} + n^{\text{gb}}$  is constant is

$$0 = \frac{\partial \Delta G}{\partial n^{\text{gb}}} - \left(\frac{\partial \Delta G}{\partial n^{\alpha}}\right) \approx -\Delta \varepsilon_{\text{X}}^{\text{gb}} + k_{\text{B}}T \left[\ln\left(\frac{n^{\text{gb}}}{N^{\text{gb}}}\right) - \ln\left(\frac{N^{\text{gb}} - n^{\text{gb}}}{N^{\text{gb}}}\right) - \ln\left(\frac{n^{\text{gb}}}{N^{\text{gb}}}\right) + \ln\left(\frac{N^{\alpha} - n^{\alpha}}{N^{\alpha}}\right)\right] = -\Delta \varepsilon_{\text{X}}^{\text{gb}}$$

$$+ k_{\text{B}}T \cdot \ln\left[\left(\frac{n^{\text{gb}}}{N^{\text{gb}} - n^{\text{gb}}}\right) / \left(\frac{n^{\alpha}}{N^{\alpha} - n^{\alpha}}\right)\right]$$
(Eq 5.31)

When the variables are converted into the concentrations  $X^{gb} = n^{gb}/N^{gb}$ and  $x^{\alpha} = n^{\alpha}/N^{\alpha}$ ,

$$\frac{X^{\text{gb}}}{1 - X^{\text{gb}}} \approx \frac{x^{\alpha}}{1 - x^{\alpha}} \cdot \exp\left(\frac{\Delta \varepsilon_{\text{X}}^{\text{gb}}}{k_{\text{B}}T}\right)$$
 (Eq 5.32)

Because it is for a very small amount of impurities that the grainboundary segregation becomes a problem, by approximating  $1 - x^{\alpha} \approx 1$ , adding 1 to both sides, and rearranging it, we can obtain McLean's equation in the exercise.

Here the term of exp( ) in Eq 5.32 is called the grain-boundary segregation coefficient, and the segregation energy is often described by the value per mole,  $\Delta E_X^{gb}$  (=  $\Delta \varepsilon_X^{gb} \cdot N_0$ ).

Grain-boundary segregation coefficient: (Eq 5.33)

$$k_{\rm X}^{\rm go} = \exp\left(\Delta \varepsilon_{\rm X}^{\rm go}/k_{\rm B}T\right) = \exp\left(\Delta E_{\rm X}^{\rm go}/RT\right)$$

Using this  $k_{x}^{gb}$ , the equation of segregation becomes quite the same as the Langmuir equation

$$X^{\rm gb} \approx \frac{k_{\rm X}^{\rm gb} \cdot x^{\alpha}}{1 + k_{\rm X}^{\rm gb} \cdot x^{\alpha}} \tag{Eq 5.34}$$

Figure 5.8(b) is the calculated values of grain-boundary segregation when  $\Delta E_X^{gb} = 20$ , 60, and 100 kJ/mol, and the lower the temperature becomes, the greater the segregation becomes. However, because the diffusion rate is slow at low temperature, for example, the substantial segregation of very small amounts of *P* in steel becomes the most remarkable at about 850 K.

## 5.3.3 Analysis of Grain-Boundary Segregation by "Boundary Phase Model"

As described in Section 5.1, the energy of grain boundary calculated by considering the random grain boundary as an amorphous "boundary phase" with the thickness of  $\delta(3 \text{ atom width})$  is considerably close to the measured value. Hillert showed that useful results can be achieved



Fig. 5.8 McLean's grain-boundary segregation equation. The dashed curves in the figure (b) indicate the substantial segregations in consideration of the diffusion rate.

as follows by applying this "boundary phase model" to analysis of grain-boundary segregation (Ref 9, 10).

First, thinking of the equilibrium equation of boundary phase (gb phase) and grain phase ( $\alpha$  phase), because the sum of free energies of both the phases  $G^{\alpha+gb}$  is minimum in the equilibrium state, the free-energy change by transferring  $dm_A$  and  $dm_X$  of solvent A and solute X from  $\alpha$  phase to gb phase will become

$$dG^{\alpha+gb} = (\mu_{\rm A}^{gb} - \mu_{\rm A}^{\alpha})dm_{\rm A} + (\mu_{\rm X}^{gb} - \mu_{\rm X}^{\alpha})dm_{\rm X} = 0$$
 (Eq 5.35)

Here  $\mu_A$  and  $\mu_X$  are the chemical potentials of A and X (see Section 4.1 "Basic Rules of Heterogeneous Equilibrium").

Because we can choose  $dm_A$  and  $dm_X$  arbitrarily in a usual two-phase equilibrium, the solutions of Eq 5.35 are  $\mu_A^{II} = \mu_A^{II}$  and  $\mu_X^{II} = \mu_X^{II}$ ; that is, the common tangent law is the equilibrium condition. However, since the boundary phase considered here has the constant thickness of  $\delta$ , it is necessary that  $m_A^{gb} + m_X^{gb}$  is constant and  $dm_A + dm_X = 0$ . Therefore, in order that Eq 5.35 is approved, the following relation must hold.

 $\mu_A^{gb} - \mu_A^\alpha = \mu_X^{gb} - \mu_X^\alpha \quad [\text{Hillert's parallel tangents law (1975)}] \quad (\text{Eq 5.36})$ 

As shown in Fig. 5.9(a), since the free energy of gb phase  $G^{gb}$  is higher than  $G^{\alpha}$  by the grain-boundary energy, there is no common tangent. However, there are parallel tangents and they are in equilibrium at each composition of the contact point ( $X^{gb}$  and  $x^{\alpha}$ ).



**Fig. 5.9** Free-energy and grain-boundary energy diagrams. (a) The parallel tangents law regarding grain-boundary segregation. (b) The relation of grain-boundary energy  $(\sigma_{A,x})$  and grain-boundary segregation energy  $(\Delta E_g^{gb})$ 

**[Exercise 5.9]** Induce the grain-boundary segregation equation by approximating the free energies of  $\alpha$  phase and gb phase according to the regular solution model.

**[Answer]** We can describe the chemical potentials of A and X in  $\alpha$  phase and gb phase as follows by the regular solution approximation (see Eq 3.43).

$$\mu_{A}^{\alpha} = {}^{\circ}G_{A}^{\alpha} + \Omega_{AX}^{\alpha}(x^{\alpha})^{2} + RT \ln (1 - x^{\alpha}) \mu_{X}^{\alpha} = {}^{\circ}G_{X}^{\alpha} + \Omega_{AX}^{\alpha}(1 - x^{\alpha})^{2} + RT \ln x^{\alpha} \mu_{A}^{gb} = {}^{\circ}G_{A}^{gb} + \Omega_{AX}^{gb}(X^{gb})^{2} + RT \ln (1 - X^{gb}) \mu_{X}^{gb} = {}^{\circ}G_{X}^{gb} + \Omega_{AX}^{gb}(1 - X^{gb})^{2} + RT \ln X^{gb}$$
 (Eq 5.37)

When these are substituted into Eq 5.36 and the very small terms are omitted, the grain-boundary segregation equation can be obtained as

$$\frac{X^{\text{gb}}}{1 - X^{\text{gb}}} \approx \frac{x^{\alpha}}{1 - x^{\alpha}} \exp\left[\frac{({}^{\circ}G^{\text{gb}}_{\text{A}} - {}^{\circ}G^{\alpha}_{\text{A}}) - ({}^{\circ}G^{\text{gb}}_{\text{X}} - {}^{\circ}G^{\alpha}_{\text{X}}) - (\Omega^{\text{gb}}_{\text{AX}} - \Omega^{\alpha}_{\text{AX}})}{RT}\right]$$
(Eq 5.38)

Equation 5.38 is certainly the same type as McLean's equation (Eq 5.28), and the segregation energy has the following relation to the parameters of the regular solution model.

$$\Delta E_{\rm X}^{\rm gb} = (^{\circ}G_{\rm A}^{\rm gb} - ^{\circ}G_{\rm A}^{\alpha}) - (^{\circ}G_{\rm X}^{\rm gb} - ^{\circ}G_{\rm X}^{\alpha}) - (\Omega_{\rm AX}^{\rm gb} - \Omega_{\rm AX}^{\alpha})$$
(Eq 5.39)

Next, investigate the energy drop of grain boundary according to grain-boundary segregation using this "boundary phase model."  $\Delta G_{A-X}^{gb}$  shown as an arrow in Fig. 5.9(a) is the free-energy difference between gb phase and  $\alpha$  phase, and it can be expressed as follows according to the regular solution approximation.

$$\Delta G_{A-X}^{gb} = \mu_A^{gb} - \mu_A^{\alpha} \approx (^{\circ}G_A^{gb} - ^{\circ}G_A^{\alpha}) + RT \ln\left(\frac{1 - X^{gb}}{1 - x^{\alpha}}\right)$$
$$= \Delta G_A^{gb} - RT \ln\left(1 + k_X^{gb} \cdot x^{\alpha}\right)$$
(Eq 5.40)

Here the terms including  $(X^{\text{gb}})^2$  and  $(x^{\alpha})^2$  were omitted, and the relationship given by the McLean's equation:  $1 - X^{\text{gb}} = 1/(1 + k_x^{\text{gb}} \cdot x^{\alpha})$  was used.

Because the area of 1 mole of gb phase ( $\delta$  thick) is  $A^{\text{gb}} = V^{\text{gb}}/\delta$ , the grain-boundary energy of A-X system (per unit area) can be obtained by Eq 5.40 as in:

$$\sigma_{A-X} = \frac{\Delta G_{A-X}^{gb}}{A^{gb}} \approx \sigma_A - \frac{\delta RT}{V^{gb}} \ln (1 + k_X^{gb} \cdot x^{\alpha})$$
 (Eq 5.41)

Figure 5.9(b) is the calculated result when the segregation energy  $\Delta E_x^{gb} = 40$ , 60, and 80 kJ/mol, the dashed line in the figure is the gradient at  $x^{\alpha} \rightarrow 0$ , and it can be expressed by\*

$$\frac{\partial \sigma_{A-X}}{\partial x^{\alpha}} = -\frac{\delta RT}{V^{gb}} \left( \frac{k_X^{gb}}{1 + k_X^{gb} \cdot x^{\alpha}} \right), \ \left( \frac{\partial \sigma_{A-X}}{\partial x^{\alpha}} \right)_{x^{\alpha} \to 0} = -\frac{\delta RT}{V^{gb}} k_X^{gb}$$
(Eq 5.42)

The value of the grain-boundary segregation coefficient  $k_X^{gb}$  has been obtained by analysis of the grain-boundary composition with the Auger electron spectroscopy (AES) or the composition dependency of the grain-boundary energy  $\sigma_{A-X}$  (Ref 11-13). Figure 5.10 shows the measured values of Fe-X systems, and the less the solid solution limit is the larger the grain-boundary segregation coefficient is.

**[Exercise 5.10]** Consider the grain-boundary segregation when two kinds of solutes X and Y coexist. Estimate the concentrations of X and Y in the grain boundary when the segregation energies are  $\Delta E_X^{gb} = 30$ ,  $\Delta E_Y^{gb} = 60$  kJ/mol, and the concentrations in the grain are  $x^{\alpha} = 10^{-2}$  and  $y^{\alpha} = 10^{-4}$ .

**[Answer]** One can obtain Eq 5.45 by approximating the chemical potentials of components A, X, and Y in  $\alpha$  phase and gb phase according to the regular solution model, substituting them into the equation of the parallel tangents law below, and omitting very small terms.

$$\mu_A^{gb} - \mu_A^{\alpha} = \mu_X^{gb} - \mu_X^{\alpha} = \mu_{\gamma}^{gb} - \mu_{\gamma}^{\alpha} \text{ [equation of parallel tangent plain]} \quad (Eq 5.44)$$

$$\frac{X^{gb}}{1-X^{gb}-Y^{gb}} \approx \frac{x^{\alpha}}{1-x^{\alpha}-y^{\alpha}} \exp\left[\frac{({}^{\circ}G_{A}^{gb}-{}^{\circ}G_{A}^{\alpha})-({}^{\circ}G_{X}^{gb}-{}^{\circ}G_{X}^{\alpha})-(\Omega_{AX}^{gb}-\Omega_{AX}^{\alpha})}{RT}\right]$$

$$\frac{Y^{gb}}{1-X^{gb}-Y^{gb}} \approx \frac{y^{\alpha}}{1-x^{\alpha}-y^{\alpha}} \exp\left[\frac{({}^{\circ}G_{A}^{gb}-{}^{\circ}G_{A}^{\alpha})-({}^{\circ}G_{Y}^{gb}-{}^{\circ}G_{Y}^{\alpha})-(\Omega_{AY}^{gb}-\Omega_{AY}^{\alpha})}{RT}\right]$$
(Eq 5.45)

\*The decrease of interface energy by segregation or adsorption can be, in general, expressed by

$$\Gamma_{\rm X} = -(\partial \sigma / \partial \ln x)/RT$$
 [Gibbs' adsorption equation] (Eq 5.43)

Here  $\Gamma_X$  is the mole of X atoms adsorbing on the unit area of interface, and  $\Gamma_X = X^{\text{gb}}/(V^{\text{gb}}/\delta)$  using notations here. However, the right-hand side of Eq 5.43 becomes  $(\partial \sigma/\partial \ln x)/RT = -X^{\text{gb}}/(V^{\text{gb}}/\delta)$  according to Eq 5.42. Therefore, Eq 5.41 and 5.42 are considered practical formulas of Gibbs' adsorption equation.



**Fig. 5.10** The grain-boundary segregation coefficients of Fe-X systems (11)-(13). The smaller solid solution limits an element has, the larger its grain-boundary segregation coefficient becomes.

By rearranging after substituting  $k_X^{gb}$  and  $k_Y^{gb}$  for exp [ ] on the right side and  $1 - x^{\alpha} - y^{\alpha} \approx 1$  for the denominator on the right side, one can obtain the segregation equation of the same type as Langmuir's adsorption equation:

$$X_X^{\text{gb}} \approx \frac{k_X^{\text{gb}} \cdot x^{\alpha}}{1 + k_X^{\text{gb}} \cdot x^{\alpha} + k_Y^{\text{gb}} \cdot y^{\alpha}}, \quad Y_X^{\text{gb}} \approx \frac{k_Y^{\text{gb}} \cdot y^{\alpha}}{1 + k_X^{\text{gb}} \cdot x^{\alpha} + k_Y^{\text{gb}} \cdot y^{\alpha}} \quad \text{(Eq 5.46)}$$

Figure 5.11 shows the calculated result when the segregation energy and the concentration in the grain are set as the values in the exercise, and at high temperature  $X^{gb} > Y^{gb}$  similar to the magnitude relation of the concentrations in the grain, but at low temperature Y drives out X and occupies the grain boundary. Such a scramble for a grain boundary is called a "competitive segregation."

## 5.3.4 Relationship between Ultrarefinement of Grains and Grain-Boundary Segregation

At the end of this section, the grain-boundary segregation in the case of ultrarefinement of the grain is examined. Various investigations of this situation are being made corresponding to recent developments in nanotechnology.



**Fig. 5.11** The competitive segregation of two kinds of coexistent elements (At a higher temperature, *X*, the content of which is larger, has a higher segregation concentration. At a lower temperature,  $\Delta E_{Y}^{gb}$  is larger, and *Y* occupies grain boundaries.)

**[Exercise 5.11]** Analyze the relationship between the average radius of the crystal grains  $\overline{R}$  and the grain-boundary segregation by the "boundary phase model."

**[Answer]** Atomizing the crystal grains, the volume fraction of "boundary phase"  $f^{gb}$  increases as

$$f^{\rm gb} = \frac{(1/2)4\pi\bar{R}^2\delta}{(4/3)\pi\bar{R}^3} = \frac{3\delta}{2\bar{R}} \approx \frac{1.12 \times 10^{-9}[\text{m}]}{\bar{R}[\text{m}]}$$
(Eq 5.47)

Here the thickness of the grain boundary was set as  $\delta = 3$  atom width = 0.75 nm.

If the specific volumes inside the grain and in the grain boundary are equivalent, the average composition of the whole material  $x_0$  is

$$x_{0} = x^{\alpha}(1 - f^{gb}) + X^{gb}f^{gb} \\ X^{gb} = k_{X}^{gb}x^{\alpha}/(1 + k_{X}^{gb}x^{\alpha})$$
 (Eq 5.48)

Figure 5.12(a) shows the calculated result when the segregation energy is  $\Delta E_X^{gb} = 60$  KJ/mol, the average composition of the material is  $x_0 = 10^{-4}$ , and when the grain is refined to the size of  $\bar{R} = 1 \mu m$ , the volume fraction of the "boundary phase" increases to  $f^{gb} = 1.12 \times 10^{-3}$  and the grain-boundary segregation decreases to  $X^{gb} < 0.1$ .



Fig. 5.12 Grain-boundary segregation and temperature. (a) Reduction of grain-boundary

Summarizing the case of more ultrarefinement to  $\overline{R} < 5$  nm, the volume fraction of a "boundary phase" increases to  $f^{\rm gb} \approx 0.2$  by Eq 5.47. Moreover, the free energy of a "grain phase" increases by  $\Delta G^{\alpha} \approx 2\sigma V/\overline{R}$  according to the Gibbs-Thomson effect, as shown in Fig. 5.12(b, upper), the parallel tangents of the free-energy curves become a common tangent, and a usual condition of heterogeneous equilibrium  $\mu_A^{\rm gb} = \mu_A^{\alpha}$ ,  $\mu_X^{\rm gb} = \mu_X^{\alpha}$  holds.

As a result, as shown in Fig. 5.12(b, lower) in the model, it is presumed that the thickness of a grain boundary increases and finally the entire microstructure will become an amorphous phase (Ref 14).

## 5.4 "Roughness" and Mobility of Interface

#### 5.4.1 Smooth Interface and Rough Interface

An interface usually tends to become flat by action of an interface tension. However, although it looks smooth under an optical microscope, an interface often has a roughness when it is magnified to the atomic level. It was made clear by KA. Jackson (1958) that the solidification interface of a metal crystal (that is, solid/liquid interface), in particular, is a rough interface (Fig. 5.13).

In this section, think about the solid/gas interface of a pure metal as a representative example of a smooth interface first.



(a) Smooth interface



Fe-W-C alloy; primary carbide + eutectic



(b) Rough interface

Cu-P alloy; primary Cu phase + eutectic

Fig. 5.13 Morphology of interface in a solidification structure. (a) Interface between covalent compound and liquid phase, magnification  $150 \times$ . (b) Interface between metal crystal and liquid phase, magnification  $800 \times$ .

**[Exercise 5.12]** Estimate the distribution densities of adsorbed atoms, steps, and kinks on the (111) surface of a pure Cu when it is heated at 1200 K below the melting point (1356 K) according to the idea of free bonds [Exercise 5.1].

**[Answer]** When a Cu atom adsorbs on the (111) surface, it will have six free bonds. Because the energy of this free bond can be estimated as  $\Delta \varepsilon^{S/V} = \Delta H_S/zN_0 = 0.44 \times 10^{-19}$  J by Eq 5.3, the increase of energy per adsorbed atom is  $\Delta e_{ad} = 6 \times \Delta \varepsilon^{S/V} = 2.6 \times 10^{-19}$  J, and the distribution density at T = 1200 K will become as follows by the Maxwell-Boltzmann distribution law:

$$x_{\rm ad} = \exp\left(-\frac{\Delta e_{\rm ad}}{k_{\rm B}T}\right) = \exp\left(-\frac{6\Delta\varepsilon^{\rm S/V}}{k_{\rm B}T}\right) \approx 10^{-7}$$
 (Eq 5.49)

Therefore, there are very few adsorbed atoms and the terrace surface of the crystal is almost completely smooth.

However, an atom at a step has two extra free bonds compared to an atom that constitutes a terrace surface. Consequently, the extra energy a step atom has compared to a terrace atom is  $\Delta e_{\text{step}} \approx 2 \times \Delta \epsilon^{\text{S/V}}$  and according to the M-B distribution law,

$$x_{\text{step}} = \exp\left(-\frac{\Delta e_{\text{step}}}{k_{\text{B}}T}\right) = \exp\left(-\frac{2\Delta\varepsilon^{\text{S/V}}}{k_{\text{B}}T}\right) \approx \frac{1}{200}$$
 (Eq 5.50)

That is, a step exists approximately every 200 atoms.

Since a kink atom has one more extra free bond than a step atom, the density of kinks along a step is presumed to be:

$$x_{\text{kink}} = \exp\left(-\frac{\Delta e_{\text{kink}}}{k_{\text{B}}T}\right) = \exp\left(-\frac{\Delta \varepsilon^{\text{S/V}}}{k_{\text{B}}T}\right) \approx \frac{1}{14}$$
 (Eq 5.51)

That is, a kink exists approximately every 14 atoms.

A crystal surface consisting of smooth terraces, steps, and kinks as described above is called the Kossel model (1927).

Next, investigate Jackson's model concerning a rough solid/liquid interface.

**[Exercise 5.13]** Find out the free energy ( $\Delta G_{\text{rough}}$ ) using the B-W-G approximation where solid atoms S and liquid atoms L are randomly arranged, considering a solid/liquid interface as a two-dimensional lattice of a monatomic layer (the total of lattice points  $N^*$ , the number of the nearest-neighboring lattice points  $z^*$ ). Also, investigate the microscopic morphology of the interface according to the condition of  $\Delta G_{\text{rough}} = \text{minimum}$ .

**[Answer]** If the fractions of S atoms and L atoms on the two-dimensional lattice are  $x_S$  and  $x_L = 1 - x_S$ , the total energy of the atomic pairs can be approximated in the following equation using the nearest-neighbor assumption and the random distribution assumption in the same way as when inducing the enthalpy of A-B solid solution (Eq 3.10).

$$H^{*} = (z^{*}N^{*}/2)\varepsilon_{SS} \cdot x_{S}^{2} + (z^{*}N^{*}/2)\varepsilon_{LL} \cdot x_{L}^{2} + z^{*}N^{*}\varepsilon_{SL} \cdot x_{S}x_{L}$$
  
=  $(z^{*}N^{*}/2)\varepsilon_{SS} \cdot x_{S} + (z^{*}N^{*}/2)\varepsilon_{LL} \cdot x_{L} + z^{*}N^{*}[\varepsilon_{SL} - (\varepsilon_{SS} + \varepsilon_{LL})/2]x_{S}x_{L}$   
(Eq 5.52)

Because it can be considered that the first and second terms in Eq 5.52 correspond to the enthalpies of a two-dimensional solid and liquid phase area, and the third term corresponds to the enthalpy because of neighboring of S atom and L atom, that is, the one according to the roughness, the following equation can be obtained.

$$\Delta H_{\text{rough}} \approx z^* N^* [\varepsilon_{\text{SL}} - (\varepsilon_{\text{SS}} + \varepsilon_{\text{LL}})/2] x_{\text{S}} x_{\text{L}} \qquad (\text{Eq 5.53})$$

Next, the entropy according to the roughness of a solid/liquid interface can be thought the entropy due to mixing of S atoms and L atoms, and it can be obtained in the same way by inducing the mixing entropy of A-B solid solution.

$$\Delta S_{\text{rough}} \approx -N^* k_{\text{B}} (x_{\text{S}} \ln x_{\text{S}} + x_{\text{L}} \ln x_{\text{L}})$$
 (Eq 5.54)

From Eq 5.53 and 5.54, the free energy due to roughness of a solid/liquid interface at the melting point  $T_{\rm m}$  can be approximated:

$$\Delta G_{\text{rough}} \approx \Delta H_{\text{rough}} - T_{\text{m}} \cdot \Delta S_{\text{rough}}$$
  
=  $N^* k_{\text{B}} T_{\text{m}} (\alpha x_{\text{S}} x_{\text{L}} + x_{\text{S}} \ln x_{\text{S}} + x_{\text{L}} \ln x_{\text{L}})$  (Eq 5.55)

Here

$$\alpha = (z^* k_{\rm B} T_{\rm m})[\varepsilon_{\rm SL} - (\varepsilon_{\rm SS} + \varepsilon_{\rm LL})/2]$$
 (Eq 5.56)

If Eq 5.55 is illustrated,  $\Delta G_{\text{rough}} = \text{minimum}$  at  $x_{\text{S}} = x_{\text{L}} = 1/2$  for  $\alpha \leq 2$  as shown in Fig. 5.14(b). This indicates that a rough interface where S atoms and L atoms mix in confusion at a ratio of  $\frac{1}{2}$  is stable. On the other hand, when  $\alpha > 2$ ,  $\Delta G_{\text{rough}} = \text{minimum}$  at  $x_{\text{S}} \approx 0$  and  $x_{\text{L}} \approx 1$  similarly to the two-phase separation of a solid solution. In this case there is no adsorbed atom or almost all the interface lattice points are occupied by S atoms, and this corresponds to the smooth interface that was considered by Kossel et al.

As mentioned previously, because whether a solid/liquid interface is smooth or rough is determined by the value of  $\alpha$ , Jackson named it a "roughness parameter" (Ref 15).



Fig. 5.14 (a) Kossel's smooth interface. (b) Jackson's rough interface. Data points • in (b) indicate the minimum points.

Compared with Eq 5.2 and 5.8, it can be seen that this value of  $\alpha$  has the following relation with the latent heat of melting ( $\Delta H_{\rm m}$ ) or the interface energy ( $\sigma^{\rm S/L}$ ).

$$\alpha \approx \left(\frac{z^*}{z}\right) \frac{\Delta H_{\rm m}}{RT_{\rm m}} \approx \left(\frac{z^*}{z'}\right) \frac{\sigma^{\rm S/L}}{N^* k_{\rm B} T_{\rm m}} \tag{Eq 5.57}$$

The latent heat of melting of a metal is  $\Delta H_m \approx RT_m$  by the Richards' rule. The number of the nearest-neighboring atoms in a fcc crystal is z = 12. The number of the neighboring atoms on the (111) surface is  $z^* = 6$ . Therefore,  $\alpha \approx 0.5$  and a rough interface is stable.

However, in the case of covalent crystals or semimetal crystals such as Si, Ge, and Bi, as shown in Fig. 2.5(a),  $\Delta H_{\rm m} \approx RT_{\rm m} \approx 2.5$  and z = 4, then a smooth interface is stable. Moreover, usually  $\alpha > 5$  also in case of organic crystals and polymers and their solid/liquid interfaces are covered with flat terraces.\*

One would assume an interface to be a two-dimensional lattice of monoatomic layer in the Kossel and Jackson models, but later D.E. Temkin (1966), H.J. Leamy (1975), and others carried out analysis by computer simulation considering an interface as a multiatomic layer (Ref 17).

#### 5.4.2 Adhesion Growth and Lateral Growth

If a crystal is covered with a violently rugged interface, all the atoms hitting the interface will be built in the crystal as shown in Fig. 5.15(a), and the crystal will grow rapidly even at a low degree of supercooling. This is called an adhesion growth.

On the other hand, if an interface is smooth, atoms hitting the terrace will be reflected without building the crystal, and only atoms hitting the neighborhood of a step or a kink will be built up. Therefore, the crystal will grow by horizontal deposition on a step along a crystal face. This is called a lateral growth, the probability that the impacting atoms are built up in the crystal is called an "accommodation coefficient," and it is usually expressed by  $\kappa$ .

As described previously, because a solid/liquid interface of a metal crystal is very rough, it grows rapidly by a mechanism of adhesion. However, because a solid/liquid interface of a semiconductor crystal, an ionic compound or an organic compound is generally flat, the value of  $\kappa$  is often less than  $10^{-4}$ , and it will laterally grow slowly.

<sup>\*</sup>S/L interfaces of hexane ( $C_6H_{14}$ ) or carbon tetrabromide (CBr<sub>4</sub>) and so on are exceptionally rough interfaces in spite of organic compounds. Because they have transparency and low melting points, they have been actively used to simulate solidification of metals (Ref 16).


Fig. 5.15 Adhesion growth and lateral growth of crystals. (Stable faces have small mobility, but unstable faces have large mobility). (a) Adhesion growth ( $\kappa \approx 1$ ). (b) Lateral growth ( $\kappa \ll 1$ ). (c) The growth of an anisotropic crystal

As shown in Fig. 5.15(c), if each crystal face has a different "roughness" in an identical crystal, it will grow anisotropically such as tabularly or rodlike according to the difference of the growth mechanism.

## 5.4.3 Kinetic Description of Mobility of Interface

In the reaction kinetics advocated by S. Arrhenius (1889), H. Eyring (1964), and others, the transfer rate of an atom passing across I/II interface is analyzed as below.

As shown in Fig. 5.16(a), the rate of an atom getting over the activation barrier ( $\Delta G^*$ ) from side I and flowing to side II,  $V (I \rightarrow II)$  can be approximated as the following equation by multiplying the product of the frequency of jump due to thermal vibration v (s<sup>-1</sup>) and the jump distance  $\lambda$  (m) by the Boltzmann factor.

$$V(I \rightarrow II) \approx \nu \lambda \exp(-\Delta G^*/RT)$$
 (Eq 5.58)

Similarly, the rate of an atom flowing inversely from II to I is

$$V(I \to II) \approx \nu \lambda \exp\left[-(\Delta G^* + \Delta G^{I/II})/RT\right]$$
 (Eq 5.59)

Here  $\Delta G^{I/II}$  is the free-energy difference between phase I and II or the driving force.



Fig. 5.16 Analysis of interfacial transfer rate by reaction kinetics. (a) Elementary processes of atom transfer. (b) Success rate of atom transfer

The difference between these rates is the net transfer rate across the I/II interface and can be expressed by

$$V^{I/II} = V(I \to II) - V(II \to I)$$
  
=  $v\lambda \exp\left(-\frac{\Delta G^*}{RT}\right) \cdot \left[1 - \exp\left(\frac{\Delta G^{I/II}}{RT}\right)\right]$   
 $\approx \left\{\underbrace{\frac{\text{the mobility of interface}}{\sqrt{\lambda}RT} \exp\left(-\frac{\Delta G^*}{RT}\right)}\right\}^{\text{the driving force}} \Delta G^{I/II}$  (Eq 5.60)

Here the approximation  $1 - \exp(\Delta G^{I/II} RT) \approx \Delta G^{I/II} RT$  is used.\*

The term of  $\{ \}$  in Eq 5.60 is the parameter indicating the easiness with which I/II interface moves, and it is called the mobility of the interface. This is expressed hereafter as  $M^{I/II}$ .

In reaction kinetics, the barrier of activation ( $\Delta G^*$ ) is usually analyzed by decomposing it into the enthalpy of activation ( $\Delta H^*$ ) and the entropy term of activation ( $-T\Delta S^*$ ). According to this decomposition, the mobility of interface is decomposed into the accommodation coefficient

<sup>\*</sup>In general, the driving force on phase transformation is by far smaller compared with the driving force on chemical reaction and so on. For example, the driving force on solidification  $\Delta G^{L/S}$  is around  $\Delta G^{L/S}/RT \approx 0.25$  even at the maximum degree of supercooling, and the approximation mentioned previously can be approved.

 $\kappa = \exp (\Delta S^* / R)$ , the term of energy barrier including  $\Delta H^*$ , and the frequency factor according to thermal vibration (see Fig. 5.16b):

The mobility of interface:

$$M^{\text{I/II}} = \frac{\nu\lambda}{RT} \exp\left(\frac{\Delta G^*}{RT}\right)$$
$$= \frac{\begin{pmatrix} \text{Accommodation} \\ \kappa \end{pmatrix}}{\kappa} \cdot \frac{\langle \text{Frequency factor} \rangle}{RT} \cdot \exp\left(-\frac{\Delta H^*}{RT}\right) \qquad (\text{Eq 5.61})$$

Moreover, the diffusion coefficient in the solid phase or the liquid phase can be approximated according to kinetics (refer to the section 6.4 "Mechanism of Diffusion and Diffusion Coefficient") by

$$D \approx v\lambda^2 \exp\left(-\Delta H^*/RT\right)$$
 (Eq 5.62)

From Eq 5.61 and 5.62, the mobility of interface can be also expressed by:

$$M^{\mathrm{I/II}} \approx \kappa \left(\frac{D}{RT}\right) \frac{1}{\lambda}$$
 (Eq 5.63)

Here (D/RT) is the parameter that Einstein called the mobility of atoms.

# 5.4.4 Analysis of Velocity of Solidification

According to the kinetics described previously, the mobility of solid/ liquid interface or the velocity of solidification can be expressed by

$$V^{S/L} \approx \left[\kappa \left(\frac{D}{RT}\right) \frac{1}{\lambda} \cdot \right] \Delta G^{S/L}$$
 (Eq 5.64)

Think about the two following exercises using this equation.

**[Exercise 5.14]** Estimate the velocity of solidification when a pure metal is solidified by "adhesion growth."

**[Answer]** The solid/liquid interface of a pure metal is a "rough interface," and the accommodation coefficient is  $\kappa \approx 1$ . The diffusion coefficient in the liquid phase is  $D^{L} \approx 10^{-8} \text{ m}^2/\text{s}$  at the temperature near the melting point. If the jump distance of an atom that transfers from the liquid phase side to the solid phase side at a solidification is 1 interatomic distance,  $\lambda \approx 2.5 \times 10^{-10}$ m. The driving force of solidification is, according to the Richards' rule,  $\Delta G^{S/L} = (\Delta H_m/T_m) \cdot \Delta T \approx R \cdot \Delta T$ . By substituting them into Eq 5.64,

$$V^{\rm S/L} \approx 40 (\Delta T/T_{\rm m}) [{\rm m/s}]$$

For example, the growth velocity of solidification is presumed to be  $v^{S/L} \approx 20$  mm/s when a pure Ni ( $T_{\rm m} = 1726$  K) is solidified at a degree of supercooling  $\Delta T = 1$  K, and  $V^{S/L} \approx 1$  m/s at  $\Delta T = 50$  K.

In the actual solidification, most crystals will grow preferentially in a specific direction of the crystal axis ( $\langle 100 \rangle$  in case of fcc and bcc metals) and become dendritic crystals. The growth rate of the primary dendrite arm in this case is faster than the aforementioned estimation, and it is reported that in case of a pure Ni dendrite  $V_{\text{dendrite}} \approx 4 \text{ m/s}$  $\Delta T = 50 \text{ K}$  (Ref 18).

**[Exercise 5.15]** Show that the velocity of solidification is proportional to  $(\Delta T)^2$  according to the spiral growth model advocated by F.C. Frank (1949).

**[Answer]** Before answering the question, if the growth of a perfect crystal is summarized, the movement of solid/liquid is rate limited by the production frequency of two-dimensional nuclei on the interface (Fig. 5.17a). The critical radius  $\rho_c$  and the energy barrier of nucleation  $\Delta g_c$  in this case can be approximated by the following equations (see Chapter 8 "Thermodynamics of Nucleation").

$$\rho_{\rm c} = \sigma V / \Delta G^{\rm S/L}, \ \Delta g_{\rm c} = \pi a \sigma^2 V / \Delta G^{\rm S/L}$$
 (Eq 5.65)

Here  $\sigma$  is the interface energy, V is the molar volume, and a is the height of a step, which is equal to the atomic diameter.

Since the probability that atoms injected from the liquid phase side will be built in, the crystal can be regarded as the product of the number of lattice points neighboring on the external wall of critical nuclei



**Fig. 5.17** The model for solidification interface and the velocity of solidification. (a) A two-dimensional nucleus on the surface of a perfect crystal. (b) Spiral model. (c) The velocity of solidification of silicon (calculation)

 $(2\pi\rho_c/a)$ , and the production rate of the critical nuclei, the accommodation coefficient is

$$\kappa_{\text{perfect}} \approx \frac{2\pi\rho_{\text{c}}}{a} \exp\left(-\frac{\Delta g_{\text{c}}}{k_{\text{B}}T}\right)$$
 (Eq 5.66)

For example, in the case of solidification of pure Si, each parameter is  $\sigma = 0.22 \text{ J/m}^2$ ,  $V = 1.2 \times 10^{-5} \text{ m}^3/\text{mol}$ ,  $a = 1.9 \times 10^{-10} \text{ m}$ ,  $\Delta G^{\text{S/L}} = 23 \Delta T$  J/mol, and the value of the accommodation coefficient is estimated as:

$$(\kappa_{\rm Si})_{\rm perfect} \approx (3.8 \times 10^3 / \Delta T) \exp(-620 / \Delta T)$$

and as shown by the long-dashed short-dashed line in Fig. 5.17(c), the crystal hardly grows at  $\Delta T < 40$  K.

On the contrary, when "spiral steps starting at screw dislocations" advocated by Frank are formed on the crystal surface, because new steps gush out from the spiral core one after another as each step walks horizontally, there are steady steps at intervals of 4  $\rho_c$  on the interface (Fig. 5.17b). Therefore, if it is considered that atoms injected at the lattice points within three atoms from a step are built in a crystal, the accommodation coefficient is proportional to  $\Delta T$ , and consequently the velocity of solidification is proportional to  $(\Delta T)^2$ .

$$\kappa_{\rm spiral} \approx \frac{3a}{4\pi\rho_{\rm c}} \approx \frac{3a(\Delta H_{\rm m}/T_{\rm m})}{4\pi\sigma V} \cdot \Delta T$$
 (Eq 5.67)

$$V_{\rm spiral} \approx \kappa_{\rm spiral} \left( \frac{D^{\rm L}}{\lambda R T_{\rm m}} \right) \Delta G^{\rm S/L} \approx \frac{3D^{\rm L} (\Delta H_{\rm m}/T_{\rm m})^2}{4\pi \sigma V R T_{\rm m}} (\Delta T)^2$$
 (Eq 5.68)

Substituting the aforementioned parameters of a pure Si into it, it is estimated that the accommodation coefficient is  $(\kappa_{\rm Si})_{\rm spiral} \approx 4 \times 10^{-4} \cdot \Delta T$  and the growth rate is  $(v_{\rm Si})_{\rm spiral} \approx 35(\Delta T)^2 \ \mu m/s$  (the solid line in Fig. 5.17c).

# 5.5 Thermodynamics of Grain Growth

# 5.5.1 Grain Growth of Pure Substances

It is easy to understand the phenomenon of grain growth if the group of soap bubbles is observed. Certainly from the Laplace equation Eq 5.11, because a small bubble has a higher internal pressure than a large one, the air inside the small bubble flows into the large bubble through a soap film. As a result, because the small bubble shrinks and disappears, and the large bubble expands more and more, the average radius of the bubbles  $\bar{R}$  will become larger and larger (Fig. 5.18).



Fig. 5.18 The mechanism of the grain growth. Large grains (A) absorb surrounding grains and expand. Small grains (B) shrink and disappear.

When the grain growth as described is expressed by the basic rule of chemical kinetics (Eq 5.60),

$$\frac{dR_{\rm i}}{dt} = M^{\rm gb} \times \left(\frac{2\sigma V}{R_{\rm c}} - \frac{2\sigma V}{R_{\rm i}}\right) \tag{Eq 5.69}$$

Here  $M^{\text{gb}}$  is the mobility of the grain boundary,  $\sigma$  is the energy of the grain boundary, V is the molar volume, and  $R_c$  is the critical radius of the crystal grain that neither expands nor shrinks, and it is almost equal to the average radius  $\bar{R}$  (Ref 19).

If the radius of the *i*th crystal noticed here  $R_i$  is  $R_i > R_c$ , then  $dR_i/dt > 0$  and this grain will grow. On the contrary, if  $R_i < R_c$ , then  $dR_i/dt < 0$  and this grain will shrink, and Eq 5.69 describes the grain growth faithfully. However, it is necessary to analyze the statistical distribution of the grain radii to solve Eq 5.69, and it becomes very complicated (Ref 19, 20). Therefore, consideration will be continued in accordance with the simple model by J.E. Burke and D. Turnbull (1952) (Ref 21).

Without consideration of the expansion or shrinkage of individual crystal grains, if the average radius  $\bar{R}$  is noticed, this polycrystal structure has higher free energy by  $2 \sigma V/\bar{R}$  than a single crystal due to the Gibbs-Thomson effect. If the grain growth is considered one of interfacial transport phenomena driven by this excessive free energy, it can be expressed by the following rate equation (Fig. 5.19a).

$$\frac{d\bar{R}}{dt} = M_{\text{poly}}^{\text{gb}} \times \frac{2\sigma V}{\bar{R}}$$
 (Eq 5.70)

Here  $M_{\text{polycrystal}}^{\text{gb}}$  is the apparent mobility of grain boundary in a polycrystal structure.



Fig. 5.19 The growth rate equation of grain and an example of calculation (pure iron)

Since there are some crystal grains that grow and others that shrink, and a boundary of one grain is connected with a boundary of another neighboring grain, a polycrystal structure is surely more difficult to move than a single grain boundary. Hillert presented the following equation by analyzing the steady growth of a polycrystal structure (Ref 19).

$$M_{\rm poly}^{\rm gb} \approx (1/4) M^{\rm gb}$$
 (Eq 5.71)

The value of  $M^{\text{gb}}$  can be approximated in the following equation using Eq 5.63.

$$M^{\rm gb} \approx D^{\rm gb} / \delta RT$$
 (Eq 5.72)

Here  $D^{gb}$  is the grain-boundary diffusion coefficient.  $\delta$  is the thickness of a grain boundary (three-atom width for a random grain boundary).\*

<sup>\*</sup>When three balls are arranged in the series and another ball is made to collide with the ball on the right side, one ball will leap out toward the left side by the principle of billiards (Fig. 5.20a). In this process, the ball traverses the distance of three atoms at a collision, and the jump distance  $\lambda$  in Eq 5.63 is  $\delta = 3$  atom width. It is considered that the diffusion across the grain boundary and the diffusion along the grain boundary can be equally treated at a random grain boundary. Moreover, the accommodation coefficient of atom transfer across the grain boundary is presumed as  $\kappa \approx 1$ .



Fig. 5.20 Motion of solvent atoms and solute atoms according to the grain-boundary movement. (a) Transfer of solvent atoms. (b) Drag of solute atoms

Rearranging Eq 5.70, 5.71, and 5.72, the relation between the average radius of crystal grains  $\overline{R}$  and heating time *t* can be obtained:

$$\bar{R}^2 - \bar{R}_0^2 = (M^{\rm gb} \sigma V) \ t = \left(\frac{D^{\rm gb} \sigma V}{\delta RT}\right) t \tag{Eq 5.73}$$

Here  $\overline{R}_0$  is the initial value of  $\overline{R}$  before heating.

**[Exercise 5.16]** Calculate the grain growth of a polycrystal structure of a pure iron heated at 900, 1000, and 1100 K. Here, the parameters are assumed to have the following values.

The diffusion coefficient in the grain boundary  $D_{\rm Fe}^{\rm gb} = 8.8 \times 10^{-4} \exp(-167,000/RT) \,({\rm m}^2/{\rm s})$  (Ref 22), the thickness of the grain boundary  $0.75 \times 10^{-9}$  m, the energy of the grain boundary  $\sigma = 0.8$  J/m<sup>2</sup>, the molar volume  $V = 7.4 \times 10^{-6} \,({\rm m}^3/{\rm mol})$ .

**[Answer]** The result of calculation by Eq 5.73 shows curves obeying the <sup>1</sup>/<sub>2</sub>th power law when the initial grain radius is  $\bar{R}_0 = 0$ , as shown in Fig. 5.19(b), but the curves apparently obey the nearly linear law when  $\bar{R}_0 = 50 \ \mu\text{m}$ .

As far as practical iron and steel are concerned, the grain growth is far slower than this calculated value. The reason is investigated in the next sections.

#### 5.5.2 Solute Drag Effect

The growth rate of the crystal grains becomes remarkably slow by solution of a trace element. The solute atoms consume excessive energy when they are segregated and dragged into the grain boundary, and so the phenomenon was named the solute drag effect. References 23 to 25 discuss the precise analysis of this effect, and this section considers the case when segregation always reaches an equilibrium value (Ref 26).

Residence Time and Drag Distance of Segregated Atoms. Think about the grain-boundary movement in  $\alpha$  phase where a very small

amount of X forms a solid solution in A. First, as the solvent atom A is observed, if an A atom jumps into a grain boundary from the side of II, an A' atom will jump off to the side of I. By repetition of similar transport of atoms, the grain boundary I/II moves in the direction opposite to the transport of atoms. The velocity is

$$V = v_{\rm A} \cdot \delta \tag{Eq 5.74}$$

Here  $v_A$  (S<sup>-1</sup>) is the transport frequency of A atoms.

On the other hand, as the solute atom X is observed, an X atom on the side of II will be built in a grain boundary and left on the side of I before long (Fig. 5.20b). If the atomic fraction of X atoms in  $\alpha$  phase is  $x^{\alpha}$ , and the molar volume of  $\alpha$  phase is  $V^{\alpha}$ , the mole number of X atoms per unit volume is  $x^{\alpha} / V^{\alpha}$ . The flux of X atoms that are built in a grain boundary at a unit time is  $x^{\alpha}V/V^{\alpha}$  (mol/m<sup>2</sup> • s<sup>1</sup>).

If the molar volume of the grain boundary is  $V^{\text{gb}}$ , the fraction of X atoms is  $X^{\text{gb}}$ , and the mean residence time of these X atoms in the grain boundary is  $\tau_{\text{X}}$ , then the flux of X atoms in the grain boundary is  $X^{\text{gb}} (\delta / \tau_{\text{X}}) / V^{\text{gb}}$ , and the following equation is approved in the stationary state. Here,  $V^{\text{gb}} = V^{\alpha}$ .

$$X^{\rm gb}(\delta/\tau_{\rm X}) = x^{\alpha}V \tag{Eq 5.75}$$

If the grain-boundary segregation energy of X atoms is  $\Delta E_X^{gb}$ , and the equilibrium segregation coefficient is  $k_X^{gb} = \exp(\Delta E_X^{gb}/RT)$ , then according to the McLean's grain-boundary segregation equation (Eq 5.34),

$$X^{\rm gb} \approx k_X^{\rm gb} x^{\alpha} / (1 + k_X^{\rm gb} x^{\alpha}) \tag{Eq 5.76}$$

When Eq 5.74 to 5.76 are rearranged, the following result can be obtained.

Residence time: 
$$\tau_X \approx k_X^{gb} \delta/V$$
  
Drag distance:  $\lambda_X \approx V \tau_X \approx k_X^{gb} \delta$   
Transport frequency:  $\nu_X \approx 1/\tau_X \approx \nu_A/k_X^{gb}$ 
(Eq 5.77)

For example, if  $\Delta E_X^{gb} = 40 \text{ kJ/mol}$ ,  $k_X^{gb} \approx 120 \text{ at } T = 1000 \text{ K}$ . The residence time of X atoms is  $\tau_X \approx 9 \text{s}$  when the grain-boundary transports at a velocity of  $V = 0.01 \text{ }\mu\text{m/s}$ . The drag distance is  $\lambda_X \approx 0.09 \text{ }\mu\text{m}$ . The transport frequency is  $v_A \approx V/\delta \approx 13 \text{s}^{-1}$  for A atoms while  $v_X \approx 0.1 \text{s}^{-1}$  for X atoms.

**Decrease of Grain-Boundary Mobility by Segregation.** It is easy to understand the phenomenon that when solute atoms are segregated in a grain boundary the mobility  $M^{gb}$  will decrease by referring to Ohm's



**Fig. 5.21** (a) The model for solute drag effect on the migration of grain boundary (the solute drag effect decreases the mobility of the grain boundary M). (b) An electric circuit analogy

law of the series circuit. As shown in Fig. 5.21(b), the relation between the current and the voltage of the circuit in the series connected with electric wires of specific resistance  $\rho_1$  and  $\rho_2$  at a ratio of  $l_1$  and  $l_2$  is

Current Conductivity Voltage  

$$i = \left(\frac{1}{l_1\rho_1 + l_2\rho_2}\right) \times \Delta V$$
(Eq 5.78)

Because the movement of the grain boundary is the same transport phenomenon as an electric current, using the analogies of  $i \leftrightarrow V$ ,  $\rho \leftrightarrow 1/M^{\text{gb}}$ , and  $\Delta V \leftrightarrow \Delta G$ , the equation of the grain-boundary transport rate can be expressed as

$$V = \left[\frac{1}{(1 - X^{\rm gb})/M_{\rm A}^{\rm gb} + X^{\rm gb}/M_{\rm X/A}^{\rm gb}}\right] \times \Delta G$$
 (Eq 5.79)

Here  $M_A^{gb}$  is the grain-boundary mobility of a pure A.  $M_{X/A}^{gb}$  is the grainboundary mobility when the grain boundary of A-X system is covered with X atoms, and both of them are considered to be proportional to the transport frequency of A and X of which the grain boundary is composed ( $v_A$  and  $v_X$ ); therefore by the final expression of Eq 5.77,

$$M_{\rm X/A}^{\rm gb} \approx M_{\rm A}^{\rm gb}/k_{\rm X}^{\rm gb}$$
 (Eq 5.80)

In summary, the grain-boundary mobility of  $\alpha$  phase in A-X system can be obtained:

$$M_{X-A}^{gb} = \frac{1}{(1 - X^{gb})/M_A^{gb} + X^{gb}/M_{X/A}^{gb}} = \left[\frac{1 + k_X^{gb} x^{\alpha}}{1 + (k_X^{gb})^2 x^{\alpha}}\right] M_A^{gb}$$
(Eq 5.81)

**[Exercise 5.17]** Estimate the influence of segregated atoms on the energy and the mobility of a grain boundary in pure iron and investigate the solute drag effect on the grain growth. In this exercise, the parameters concerning the grain boundary are identical to those in Exercise 5.16.

**[Answer]** The energy and the mobility of the grain boundary in Fe-X system and the equation of the crystal grain growth can be presumed by the following equations, which can be derived from Eqs 5.41, 5.72, 5.73, and 5.81.

Grain-boundary energy: 
$$\sigma_{\text{Fe-X}} \approx \sigma_{\text{Fe}} - (\delta/V)RT \ln(1 + k_X^{\text{gb}}x^{\alpha})$$
  
Mobility of grain boundary:  $M_{\text{Fe-X}}^{\text{gb}} \approx D_{\text{Fe}}^{\text{gb}} / \left\{ \delta RT \left[ 1 + (k_X^{\text{gb}})^2 x^{\alpha} \right] \right\}$  (Eq 5.82)  
Equation of grain growth:  $\bar{R}^2 - \bar{R}_0^2 \approx (M_{\text{Fe-X}}^{\text{gb}} \cdot \sigma_{\text{Fe-X}} \cdot V)t$ 

As shown in Fig. 5.22, if the segregation energy is  $\Delta E_X^{gb} = 40 \text{ kJ/mol}$ , though the grain-boundary energy  $\sigma_{\text{Fe-X}}$  hardly changes, the mobility  $M_{\text{Fe-X}}^{gb}$  decreases remarkably. As a result, the growth of grains is also remarkably suppressed.

# 5.5.3 Grain-Boundary Pinning by Dispersed Particles

The solute drag effect in Section 5.5.2 is a phenomenon based on the grain-boundary segregation of solute atoms. Compared to this, the



**Fig. 5.22** Calculated examples of the drag effect due to solute atoms on the grain growth. (a) Energy and the mobility of boundary. (b) Grain growth

pinning effect described in this section is the one by dispersed particles, and it has already been applied to improvement of the life of tungsten wire used for an electric bulb by dispersing ThO<sub>2</sub> particles (Ref 27) and refinement of grains of iron and steel by dispersing AlN particles (Ref 28) and so on since around 1920. However, the analysis of the function of dispersed particle was carried out after many years; it is said that C.S. Smith (1948) was one of "the pioneers" who explained the idea of Zener's in his report (Ref 29) (Fig. 5.23).

**Zener-Smith Pinning Model.** When a spherical particle with a radius of  $\bar{r}$  is attached to a grain boundary, a conical dent of vertical angle  $2\theta$  will be made and a pinning force  $(F_{pin})$  will be caused in the direction opposite to the movement of the grain boundary. If the grain-boundary energy is  $\sigma$ , the value is

$$F_{\rm pin} = 2\pi \bar{r}\sigma \sin\theta \cdot \cos\theta = \pi \bar{r}\sigma \sin 2\theta$$
 (Eq 5.83)

and it will have the following maximum value at  $\theta = 45^{\circ}$  (Fig. 5.24a).

$$[F_{\rm pin}]_{\rm max} = \pi \bar{r} \sigma \, (J/m) \tag{Eq 5.84}$$

Next, find out the number of particles that are pinning the grain boundary  $(n^{\text{gb}})$ . To do it this, one must find the number of particles in a unit volume  $(n_{\text{V}})$ , and if the volumetric fraction of particles is  $f_{\text{V}}$ , then

$$n_{\rm V} = f_{\rm V} / (4\pi \bar{r}^3/3)$$

The number of particles on a section of this structure cut by a randomly selected plane (the dashed line in Fig. 5.24b) is equal to the number of



**Fig. 5.23** The retardation of grain growth by dispersed particles (the pinning effect decreases the driving force of the growth  $\Delta G$ ). (a) Dispersion structure vs the single-phase structure. (b) Model for pinning effect



Fig. 5.24 Zener-Smith pinning force and the number of pinning particles

particles in a thin layer of thickness  $2\overline{r}$ . Therefore, the average number of particles pinning a grain boundary in a unit area can be approximated by

$$n^{\rm gb} \approx n_{\rm V} \cdot 2\bar{r} \approx \frac{3}{2} \frac{f_{\rm V}}{\pi \bar{r}^2} \ ({\rm m}^{-2})$$
 (Eq 5.85)

From Eq 5.85, the pinning energy per 1 mole  $\Delta G_{\text{pin}}$  can be expressed in the following equation by multiplying of the total of the pinning force by the molar volume V.

Pinning energy: 
$$\Delta G_{\text{pin}} \approx [F_{\text{pin}}]_{\text{max}} \cdot n^{\text{gb}} \cdot V = \frac{3}{2} \frac{\sigma V f_V}{\bar{r}} (J/\text{mol})$$
 (Eq 5.86)

Because the driving force of grain growth is  $\Delta G = 2\sigma V/\bar{R}$  according to the Gibbs-Thomson equation, the relation between the radius of grains  $\bar{R}_{\rm P}$  and the radius of particles  $\bar{r}$  can be obtained by the equilibrium condition between the pinning energy and the driving force of the growth  $\Delta G_{\rm pin} = \Delta G$ .

$$\bar{R}_{\rm P} \approx \frac{4}{3} \frac{\dot{r}}{f_{\rm V}}$$
 [Zener-Smith equation for the grain radius under pinning (1948)]

(Eq 5.87)

**Modification of Zener-Smith Model (Ref 30, 31).** The value of the grain radius under pinning  $\bar{R}_{\rm P}$  is too much larger than the radius of actual grains. For example, the radius of grains is  $\bar{R}_{\rm P} \approx 130 \ \mu m$  (data point • in Fig. 5.25a) according to Eq 5.87 if the volume fraction of dispersed par-



Fig. 5.25 Calculated examples of pinning effect by dispersed particles on the grain growth

ticles is  $f_V = 10^{-3}$  and the radius is  $\bar{r} = 0.1 \,\mu\text{m}$ , and it is considerably larger than the grain size of a high-strength material for practical use.

This disagreement comes from Eq 5.85 in which it is assumed that the number of particles that pin a grain boundary  $(n^{\rm gb})$  is equal to the number of particles on a randomly selected flat plane. A grain boundary that is pinned and moving has ups and downs as shown in Fig. 5.26(a), and the number of pinning particles can be estimated as follows because  $\bar{\rho} \approx \bar{r}/f_{\rm V}^{1/3}$  if the depth of the ups and downs is considered to be identical to the territory radius of a dispersed particle  $\bar{\rho}$ .

$$n'^{\rm gb} \approx n_{\rm V} \cdot \bar{\rho} \approx \frac{3}{4} \frac{f_{\rm V}^{2/3}}{\pi \bar{r}^2} \,({\rm m}^{-2})$$
 (Eq 5.88)

Therefore, unless the factors except for the number of particles are changed, Eq 5.86 and 5.87 can be modified:

Pinning energy: 
$$\Delta G'_{\text{pin}} \approx [F_{\text{pin}}]_{\text{max}} \cdot n'^{\text{gb}} \cdot V = \frac{3}{4} \frac{\sigma V f_V^{2/3}}{\bar{r}}$$
 (Eq 5.89)

Radius of pinning particles: 
$$\bar{R}'_{\rm P} \approx \frac{8}{3} \frac{\bar{r}}{f_{\rm V}^{2/3}}$$
 (Eq 5.90)

Figure 5.25(a) shows the comparison of calculated radii of pinning particles by Zener-Smith equation (Eq 5.87) and its modified equation (Eq 5.88).



**Fig. 5.26** The ups and downs of interface and the number of pinning particles. (a)  $\gamma/\alpha$  interface of Fe-Mo alloy after carburization (1123 K). (b) The dotted circles show the territories of each dispersed particle.

This section concludes with an exercise about grain growth, considering the pinning effect.

**[Exercise 5.18]** The grain growth of a polycrystal structure in which fine particles are dispersed can be approximated by

$$\frac{d\bar{R}}{dt} = M_{\text{poly}}^{\text{gb}} \times \left(\frac{2\sigma V}{\bar{R}} - \Delta G_{\text{pin}}\right)$$
(Eq 5.91)

Using to this equation, calculate the grain growth at T = 1000 K when the volume fraction of particles is  $f_V = 10^{-3}$ , the particle radius is  $\bar{r} = 0.03 \,\mu\text{m}$ , and the initial grain radius before heating is  $\bar{R}_0 = 3 \,\mu\text{m}$ . Here, the values of  $M_{\text{poly}}^{\text{gb}}$ ,  $\sigma$ , and V are assumed to be identical to the values of a pure iron in Exercise 5.16.

**[Answer]** Because the pinning energy can be expressed as  $\Delta G_{\text{pin}} = 2\sigma V/\bar{R}_{\text{P}}$ , Eq 5.91 can be rewritten as

$$\frac{d\bar{R}}{dt} = a \left(\frac{1}{\bar{R}} - \frac{1}{\bar{R}_{\rm P}}\right), \text{ where } a = 2\sigma V M_{\rm poly}^{\rm gb}$$
(Eq 5.92)

If Eq 5.92 is integrated and the integration constant are determined to satisfy  $\bar{R} = \bar{R}_0$  at t = 0,

$$\ln\left(\frac{\bar{R}_{\rm P} - \bar{R}}{\bar{R}_{\rm P} - \bar{R}_0}\right) + \frac{\bar{R} - \bar{R}_0}{\bar{R}_0} = -\frac{a}{(\bar{R}_{\rm P})^2}t$$
(Eq 5.93)

Here the equilibrium radius of grains  $\bar{R}_{\rm P}$  is substituted by  $\bar{R}_{\rm P} = (4/3)\bar{r}/f_{\rm V}$  for Zener-Smith model, or  $\bar{R}_{\rm P} = (8/3)\bar{r}/f_{\rm V}^{2/3}$  for the modified model. The coefficient of grain growth rate *a* is  $a = 2\sigma V M_{\rm poly}^{\rm gb}$  for both models, and it is determined as follows according to the values shown in Exercise 5.16:

Zener-Smith: 
$$\bar{R}_{\rm P} = 40 \,\mu\text{m}$$
,  $a = 0.79 \,\mu\text{m}^2/\text{s}^1$ ,  $a/(\text{R}_{\rm P})^2 = 4.9 \times 10^{-4} \,\text{s}^{-1}$   
Modified model:  $\bar{R}_{\rm P}' = 8 \,\mu\text{m}$ ,  $a = 0.79 \,\mu\text{m}^2/\text{s}^1$ ,  $a/(\text{R}_{\rm P}')^2 = 1.2 \times 10^{-2} \,\text{s}^{-1}$ 

The calculated results using the above values are shown in Fig. 5.26(b).

#### EXERCISES

- **5.19** Two kinds of liquids with different specific gravity were strongly stirred in microgravity equipment to make a fine mixture (emulsion). However, when stirring was stopped, the liquids separated like an "egg" floating in water as shown in Fig. 5.27(c). Explain the reason and describe countermeasures.
- **5.20** Find out the pressure caused inside the fine particles of such shapes as shown in Fig. 5.28. Here, the surface tension  $\sigma$  is assumed to be the same on all the faces.

Answer: (a)  $\Delta P = 4\sigma/a$ , (b) $\Delta P = 2\sigma/\delta$ , (c) $\Delta P = 2\sigma/\rho$ 

**5.21** When a weight was hung on a pure Cu wire of radius r = 0.1 mm and held at a high temperature, the balanced load of the weight was  $\omega_0 = 5.5 \times 10^{-5}$  kg, which caused neither expansion nor shrinkage of the wire. Estimate the surface energy of pure Cu from this experimental value. This is called the zero creep method.



Fig. 5.27 The experiment on emulsion under microgravity. (a) Under gravity. (b) Immediately after stirring. (c) Under microgravity.



Fig. 5.28 Pressure in a fine particle? (a) Cube. (b) Sheet. (c) Wire

Answer: Because the radius of a round bar decreases by  $\Delta r = -(r/2l)\Delta l$ when the length of it is increased by  $\Delta l$ , the change of the surface area is  $\Delta A = \pi r \Delta l$ . Therefore, the kinetic balance equation between the gravity and the surface tension is w<sub>o</sub> (kg) = w<sub>o</sub> × 9.807 (J/m) =  $\pi r \sigma$  (J/m), and the surface tension can be estimated as  $\sigma = 1.7$  J/m<sup>2</sup>.

**5.22** The pattern of microstructure is often determined by the principle of "least interface energy." Consider the stability conditions of the microstructures shown in Fig. 5.29.

(a) Show that the total lengths of boundaries have the following ratio when a plane is divided by cells of triangles, squares, and hexagons, all of which have an identical area.  $L_3:L_4:L_6 = 1.14:1:0.93$ .

(b) Which is more stable, the microstructure where a plane is divided equally by n cells with an identical area or the one where it is divided unequally by n cells with a different area?

(c) Show that an  $\alpha + \beta$  dual-phase structure will become the most stable when the volume fractions of both phases  $f_{\alpha}$  and  $f_{\beta}$  and the average radius of crystal grains  $\bar{R}_{\alpha}$  and  $\bar{R}_{\beta}$  have the following relation.

$$ar{R}_lpha/\sqrt{f_lpha}~=~ar{R}_eta/\sqrt{f_eta}$$

*Hint:* If (b) and (c) are considered conditional extreme value problems and Lagrange's method of undetermined multipliers is used, we can solve them as follows.



**Fig. 5.29** (a) What division of cell structures is most stable: triangular, quadrangular, or hexagonal? (b) Which is more stable, equal cell or unequal cell structure? (c) What is the stable size ratio  $(\bar{R}_{\alpha};\bar{R}_{\beta})$  in a dual-phase structure?

The additional condition of (b) is that the total area

$$A = \sum_{i=1}^n \pi R_i^2$$

is constant and the total boundary length

$$L = (1/2) \sum_{i=1}^{n} 2\pi R_i$$

is minimum.

Lagrange's equation is  $\partial L/\partial R_i = \lambda(\partial A/\partial R_i) \rightarrow R_i = 1/2\lambda$ . Therefore, the case of equal cells is more stable.

(c) The feature of dual-phase structure is that both phases are equal and one locates on the other's grain boundary. Therefore, the additional condition is that the distance between two phases  $1 = \bar{R}_{\alpha} + \bar{R}_{\beta}$  is constant and the total area of the  $\alpha/\beta$  interface and the grain boundary  $A = (1/2)(4\pi \bar{R}_{\alpha}^2 \cdot n_{\beta}) = (3V/2)[(f_{\alpha} / \bar{R}_{\alpha}) + (f_{\beta} / \bar{R}_{\beta})]$  is minimum.

Lagrange's equation: 
$$\frac{\partial A/\partial R_{\alpha} = \lambda(\partial L/\partial R_{\alpha})}{\partial A/\partial R_{\beta} = \lambda(\partial L/\partial R_{\beta})} \rightarrow \bar{R}_{\alpha} / \sqrt{f_{\alpha}} = \bar{R}_{\beta} / \sqrt{f_{\beta}}$$



Fig. 5.30 Production of bubble-free crystal by pinning the crystal grain boundary

# **Appendix: Transparent Sintered Alumina**

Water is transparent but why is a snowman opaque? The reason is, of course, because the incident light is reflected diffusely by innumerable bubbles of air confined in crystal spaces.

It is difficult to get rid of these bubbles, and one of the methods is to melt the crystal first, to drive gas elements out of it, and to solidify it slowly.

Sintered compacts of ceramics are usually opaque, too. However, R.L. Coble of GE (1962) developed an epoch-making technology: add about 0.5% of MgO fine powder to  $Al_2O_3$  powder, pin the crystal grain growth at a sintering process, and remove gas elements (O, N) by grain-boundary diffusion. This method was not only applied to  $Al_2O_3$ but also developed to manufacture translucent sintered compacts such as ZrO<sub>2</sub>, SIAION (Si<sub>3</sub>N<sub>4</sub>-Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>), and GaAs. (Fig. 5.30).

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CHAPTER 6

# Thermodynamics of Diffusion

If red ink (B) is dropped quietly onto the surface of water (A) and a specific B molecule is tracked, it will move around right and left, up and down, in a quite disorderedly way. However, the movement of the group of B molecules is not disorderly at all; the area occupied by B molecules expands in proportion to  $\sqrt{t}$ , and finally all the water will become a uniform pink. An individual movement of the former is called a Brownian motion, a group movement of the latter is called "diffusion," and the transfer rate is described by the diffusion coefficient *D* (Fig. 6.1).

Most of the microscopic structures of materials are formed by "diffusion." Therefore, it is no exaggeration to say that phase diagrams are equivalent to maps, and tables of diffusion coefficients are like train or bus timetables. Both are the indispensable manuals of people who participate in materials science.

# 6.1 Brownian Motion and Diffusion

# 6.1.1 Random Walk Model

The botanist R. Brown in Britain discovered that pollen floating in water moved about in a disorderly fashion in 1827 and opened the gate to the kinetic theory of molecules developed later by Maxwell and others. Review "the random walk model" to understand this Brownian motion.

**[Exercise 6.1]** Find out the probability that a drunken man who has lost the sense of direction moves to the distance of z by n steps. Here, it is assumed that a man walks only in + or - direction on a straight line and his pace is  $\lambda$ .



Fig. 6.1 Brownian motion and diffusion. Both are transport phenomena according to thermal vibration of atoms or molecules.

**[Answer]** Assuming that  $n_+$  is the number of steps in + direction and  $n_-$  is in - direction among *n* steps, walking of this combination will occur in the following probability.

$$P(n_+, n_-) = (n!/n_+! \cdot n_-!) \cdot (1/2)^n$$
 (Eq 6.1)

Because the transfer distance from the starting point is  $z = (n_+ - n_-) \cdot \lambda$ and  $n_+ + n_- = n$ , the relations between  $n_+$  and  $n_-$ , and between n and z are

$$n_{+} = \frac{1}{2} \left( n + \frac{z}{\lambda} \right), \ n_{-} = \frac{1}{2} \left( n - \frac{z}{\lambda} \right)$$
(Eq 6.2)

In addition, because z increases by  $2\lambda$  when  $n_+$  increases by one step, the unit length of z is  $2\lambda$ . Therefore, "the probability that he moves to the distance of z by n steps" in the question can be obtained:

$$P(n,z) = \frac{1}{2\lambda} \cdot P(n_{+}, n_{-})$$
  
=  $\frac{1}{2\lambda} \cdot \frac{n!}{[(n+z/\lambda)/2]! \cdot [n-z/\lambda)/2]!} \left(\frac{1}{2}\right)^{n}$  (Eq 6.3)

The calculated values by Eq 6.3 when n = 10 and n = 90 are shown in Fig. 6.2(a).

If Eq 6.3 is rewritten using Stirling's approximation,  $\ln n! \approx n \ln n - n + \ln (2\pi n)^{1/2}$  as the number of steps *n* is considered an extremely large number to translate the above "random walk" into Brownian



**Fig. 6.2** Brownian motion and diffusion length. The diffusion length *z* is proportional to the square root of steps *n*. (a) The distance to which a drunken man moves. (b) The diffusion length of vacancies in Cu

motion, one can obtain the following equation of the same type as the normal distribution function familiar in the theory of errors.\*

$$P(n, z) \approx \frac{1}{\sqrt{2\pi n\lambda^2}} \cdot \exp\left(-\frac{z^2}{2n\lambda^2}\right)$$
 (Eq 6.4)

Furthermore, from Eq 6.4, the average movements (diffusion length) by Brownian motion can be obtained:

$$\bar{z} = (\bar{z}^2)^{1/2} = \left[\int_{-\infty}^{\infty} z^2 \cdot P(n, z) dz\right]^{1/2} = \sqrt{n} \ \lambda$$
 (Eq 6.5)

The arrows  $(\leftrightarrow)$  in Fig. 6.2(a) indicate the diffusion lengths  $\overline{z}$  when n = 10 and n = 90.

<sup>\*</sup>It is sufficient to use  $\ln!n \approx n \ln n - n$  for Stirling's approximation in many cases. However, if this approximation is used, then Eq 6.4 becomes  $P(n, z) \approx \exp(-z^2/2n\lambda^2)$ , and the contradiction of P = 1 at z = 0 may be caused. It is necessary to raise the precision to avoid this error, and the correct Eq 6.4 can be obtained by addition of the third term,  $\ln (2\pi n)^{1/2}$ . Here, when the diffusion length is obtained from Eq 6.4, the definite integral,  $\int_{-\infty}^{\infty} y^2 \exp(-\beta^2 y^2) dy = \sqrt{\pi}/2\beta^3$  is used.

#### 6.1.2 Einstein's Equation for Brownian Motion

Einstein analyzed Brownian motion in terms of statistical mechanics and showed that the mean distance of diffusion can be approximated by

$$\bar{z} \approx \sqrt{2Dt}$$
 [Einstein's equation for Brownian motion (1905)] (Eq 6.6)

Here, D is the diffusion coefficient and t is the diffusion time.

If it is compared with the afore-mentioned average movements by the random walk model (Eq 6.5), it can be seen that there is the following relationship among each of the parameters.

$$2Dt = n\lambda^2 \tag{Eq 6.7}$$

Since the mean frequency of walking in + direction is  $v_+ = n/2t$ in the one-dimensional random walk model, Eq 6.7 can be also expressed as

$$D = \left(\frac{n}{2t}\right)\lambda^2 = v_+ \cdot \lambda^2 \tag{Eq 6.8}$$

These are important related equations for understanding the import of diffusion coefficient D.

**[Exercise 6.2]** Vacancies (vacant lattice points) in a crystal are moved by the thermal vibration of the surrounding atoms in a three-dimensional Brownian motion path. Estimate the distance moved by a vacancy in a pure copper crystal in a second (rate of diffusion).

Here, let the interatomic distance be  $\lambda = 0.256$  nm, the activation energy of transfer to a neighboring lattice point be 1.0 eV (= 96.5 kJ/mol), and the frequency of thermal vibration be  $v_0 = 10^{13}$  s<sup>-1</sup>.

**[Answer]** If it is considered that the transfer frequency in the threedimensional Brownian motion  $v_+$  can be approximated as multiplication of the thermal frequency of a crystal  $v_0$ , the fraction of the vibration in +z direction (<sup>1</sup>/<sub>6</sub>), and the probability to go over the mount of activation, the diffusion coefficient of vacancies  $D_v$  can be estimated by Eq 6.8 as below.

$$D_{\rm v} \approx (1/6) \times 10^{13} \cdot \exp(-96, 500/RT) \times (0.256 \times 10^{-9})^2 \,({\rm m^2/s})$$
  
 $\approx 4.3 \times 10^{-16} \text{ for } T = 600 \,\mathrm{K}$   
 $6.9 \times 10^{-12} \text{ for } T = 1200 \,\mathrm{K}$   
 $2.1 \times 10^{-11} \text{ for } T = T_{\rm m} = 1356 \,\mathrm{K}$ 

Therefore, the diffusion length in a second can be obtained by Einstein's Equation (Eq 6.6):

 $ar{z} = \sqrt{2D_v} pprox 0.03 \,\mu{
m m}$  for 600 K 3.7  $\mu{
m m}$  for 1200 K 6.5  $\mu{
m m}$  for 1356 K

As shown in Fig. 6.2(b), the Brownian motion of vacancies is very small at the temperature below  $\frac{1}{2}$  of the melting point  $T_{\rm m}$ , but they diffuse 6.5 mm (about 25,000 interatomic distance) in a second at the temperature in the neighborhood of  $T_{\rm m}$ .

The production rate of vacancies also increases rapidly as the temperature rises, and a vacancy is produced every 10,000 atoms in the neighborhood of  $T_{\rm m}$  (see Exercise 2.9). As a result, "diffusion by vacancy mechanism" as mentioned later will progress.

# 6.2 Fick's Diffusion Laws

#### 6.2.1 The First Law and the Second Law (Ref 1)

Quantitative analysis on diffusion phenomena was started by the medical scientist A. Fick in Germany. He measured that the diffusion flux (J) of NaCl in a solution of salt is proportional to the gradient of concentration in a stationary state using an apparatus of a large vessel with a capillary tube (as illustrated in Fig. 6.3a) and presented the following equation.

Flux Diffusion × Gradient of  

$$J = \begin{array}{c} \text{Diffusion} \times \text{Gradient of} \\ -D \cdot (dc/dz) \end{array}$$
[Fick's first law (1855)] (Eq 6.9)

Here the flux is the amount of a solute through a unit cross section in a unit time and is expressed by the unit of  $(mol/m^2 \cdot s)$ . On the other hand, the gradient of concentration is the change of a concentration  $(mol/m^3)$  per unit length, and it has the unit of  $(mol/m^4)$ . Therefore, the unit of a diffusion coefficient is  $(m^2/s)$ .

Moreover, Fick considered diffusion in an unsteady state and presented

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2}$$
 [Fick's second law] (Eq 6.10)

This second law can be derived from the first law as follows.

Let  $J_z$  be the flux of a solution flowing in the area of a round rod with a unit cross section and the thickness of  $\Delta z$  from the left side, and  $J_{z+\Delta z}$  to be the flux flowing out to the right side (Fig. 6.3b). The difference between



**Fig. 6.3** Fick's diffusion experiment and derivation of his second law. The large vessel and the capillary tube were means to keep the boundary condition as  $c \approx 0$  at the top and also to prevent convection. (a) Fick's experiment (1855). (b) One-dimensional diffusion. (c) Diffusion in spherical coordinates

 $J_z$  and  $J_{z+\Delta z}$  has the following relation to the time variation of solute concentration in the disc with the thickness of  $\Delta z \ (\partial c/\partial t) \ (\text{mol/m}^3 \cdot \text{s})$ .

$$\left(\frac{\partial c}{\partial t}\right) \cdot \Delta z = J_z - J_{z+\Delta z} \approx J_z - \left(J_z + \frac{\partial J_z}{\partial z} \cdot \Delta z\right) = -\left(\frac{\partial J}{\partial z}\right) \cdot \Delta z \quad (\text{Eq 6.11})$$

Since it is thought that the instantaneous flux at a given place can be expressed by Eq 6.9 even if the diffusion is unsteady, the second law can be obtained from Eq 6.11 as

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial z} = \frac{\partial}{\partial z} \left( D \frac{\partial c}{\partial z} \right) \approx \left[ = D \frac{\partial^2 c}{\partial z^2}, \text{ if } D \text{ is constant} \right]$$
(Eq 6.12)

**[Exercise 6.3]** For the case of growth or dissolution of spherical particles, the analysis of diffusion flux in the spherical coordinate system is necessary. Show that it can be expressed by the following diffusion equation.

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial c}{\rho \partial \rho}\right)$$
[Fick's second law in the spherical coordinate system]  
(Eq 6.13)

**[Answer]** Consider a spherical shell with a thickness of  $\Delta \rho$  at a distance of  $\rho$  from the center of a spherical coordinate system (Fig. 6.3c). If  $J_{\rho}$  is the flux flowing in from the inside of this spherical shell and  $J_{\rho+\Delta\rho}$  is the flux flowing out from the outside, the change in the amount of solute in the spherical shell can be expressed by

$$\begin{pmatrix} \frac{\partial c}{\partial t} \end{pmatrix} \cdot 4\pi\rho^2 \cdot \Delta\rho = J_{\rho} \cdot 4\pi\rho^2 - J_{\rho+\Delta\rho} \cdot 4\pi(\rho + \Delta\rho)^2 \approx -\left(\frac{\partial J}{\partial\rho} + 2\frac{J}{\rho}\right) \cdot 4\pi\rho^2 \cdot \Delta\rho$$
 (Eq 6.14)

By rearranging Eq 6.14, Eq 6.13 can be derived as

$$\frac{\partial c}{\partial t} = -\left(\frac{\partial J}{\partial \rho} + 2\frac{J}{\rho}\right) = \frac{\partial}{\partial \rho} \left(D\frac{\partial c}{\partial \rho}\right) + D\frac{2}{\rho} \left(\frac{\partial c}{\partial \rho}\right)$$

$$\left[ = D\left(\frac{\partial^2 c}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial c}{\partial \rho}\right), \quad \text{when } D \text{ is constant} \right]$$
(Eq 6.15)

Because  $\partial u/\partial t = \rho(\partial c/\partial t)$ ,  $\partial u/\partial \rho = c + \rho(\partial c/\partial \rho)$ , and  $\partial^2 u/\partial \rho^2 = 2(\partial c/\partial \rho) + \rho(\partial^2 c/\partial \rho^2)$  when the variable  $u = c\rho$  is used, Eq 6.13 is rewritten as

$$\partial u/\partial t = D(\partial^2 u/\partial \rho^2)$$
, when  $u = c\rho$  (Eq 6.16)

which is quite the same type of equation as the diffusion law for onedimensional systems.

# 6.2.2. Examples of Analysis of Diffusion Law

**[Exercise 6.4]** Show that the concentration distribution of A and B can be expressed by the following equation when they are interdiffused if they can form a completely miscible solid solution and the diffusion coefficient is independent of the composition.

$$x_{\rm B} = \frac{1}{2} \left[ 1 + \operatorname{erf}\left(\frac{z}{2\sqrt{Dt}}\right) \right]$$
 (Eq 6.17)

Here  $x_B$  is the fraction of B component. erf is an abbreviation of the error function and is defined by

$$\operatorname{erf}(\zeta) = \frac{2}{\sqrt{\pi}} \int_0^{\zeta} \exp\left(-\zeta^2\right) d\zeta \qquad (\text{Eq 6.18})$$

**[Answer]** Equation 6.17 can be obtained in various ways, and the conversion of Fick's second law into an ordinary differential equation using a non-dimensional variable:  $\zeta = z/2\sqrt{Dt}$  is explained here.

Because the partial differentials of  $\zeta = z/2\sqrt{Dt}$  with respect to t and z are  $\partial \zeta/\partial t = -\zeta/2t$ ,  $\partial \zeta/\partial z = \frac{1}{2}\sqrt{Dt}$ , the partial differentials of the concentration  $x_{\rm B}$  with respect to t and z are

$$\frac{\partial x_{\rm B}}{\partial t} = \left(\frac{dx_{\rm B}}{d\zeta}\right)\frac{\partial\zeta}{\partial t} = -\left(\frac{dx_{\rm B}}{d\zeta}\right)\frac{\zeta}{2t}$$
$$\frac{\partial x_{\rm B}}{\partial z} = \left(\frac{dx_{\rm B}}{d\zeta}\right)\frac{\partial\zeta}{\partial z} = \left(\frac{dx_{\rm B}}{d\zeta}\right)\frac{1}{2\sqrt{Dt}}, \quad \frac{\partial^2 x_{\rm B}}{\partial z^2} = \left(\frac{d^2 x_{\rm B}}{d\zeta^2}\right)\frac{1}{4Dt}\right\}$$
(Eq 6.19)

Therefore, Fick's second law can be rewritten into an ordinary differential equation:

$$\frac{\partial x_{\rm B}}{\partial t} = D \frac{\partial^2 x_{\rm B}}{\partial z^2} \to \frac{d^2 x_{\rm B}}{d\zeta^2} + 2\zeta \frac{dx_{\rm B}}{d\zeta} = 0$$
 (Eq 6.20)

If the above equation is integrated twice,

First integration: 
$$\frac{dx_{\rm B}}{d\zeta} = K_1 \exp(-\zeta^2),$$
 (Eq 6.21)  
Second integration:  $x_{\rm B} = K_1 \int_0^{\zeta} \exp(-\zeta^2) d\zeta + K_2$ 

Because the values of integration constants  $K_1$  and  $K_2$  can be determined as  $K_1 = 1/\sqrt{\pi}$ , and  $K_2 = \frac{1}{2}$  according to (i) a boundary condition,  $x_B = \frac{1}{2}$  at z = 0, that is  $\zeta = 0$ , (ii) an initial condition  $x_B = 1$  at t = 0, that is  $\zeta = \infty$ , and a definite integral  $\int_0^\infty \exp(-\zeta^2) d\zeta = \sqrt{\pi}/2$ , Eq 6.17 in question can be obtained.

Figure 6.4(a) shows the concentration-distance curves in case of  $\sqrt{t} = 1$ , 2. The arrows ( $\leftrightarrow$ ) in the figure are the mean distances of diffusion  $\overline{z} = \sqrt{2Dt}$  in + direction and - direction and indicate rough estimations of diffusion area width.

If A and B with finite solid solubility are joined and interdiffused, "a concentration gap" will be caused at the  $\alpha/\beta$  interface as in Fig. 6.4(b). However, the concentrations of B in both of  $\alpha$  and  $\beta$  phases can be expressed by the following equations, which are the same type as Eq 6.17.

$$\alpha \text{ phase: } x_{B}^{\alpha} = x_{B}^{\alpha/\beta} \left[ 1 + \operatorname{erf}\left(\frac{z}{2\sqrt{D^{\alpha}t}}\right) \right] \qquad z \leq 0$$
  
$$\beta \text{ phase: } x_{B}^{\beta} = 1 - (1 - x_{B}^{\beta/\alpha}) \left[ 1 - \operatorname{erf}\left(\frac{z}{2\sqrt{D^{\beta}t}}\right) \right] \qquad z \geq 0$$
  
(Eq 6.22)



**Fig. 6.4** Interdiffusion in A-B system. (a) The concentration-distance curve for a completely miscible solid-solution system. Arrows are the values of mean distance of diffusion ( $\bar{z}$ ) divided by  $\sqrt{D}$ . (b) The concentration-distance curve in case of  $\alpha/\beta$  two-phase diffusion

Here  $x_{\rm B}^{\alpha/\beta}$  and  $x_{\rm B}^{\beta/\alpha}$  are compositions at the interface between  $\alpha$  and  $\beta$  phases, and  $D^{\alpha}$  and  $D^{\beta}$  are diffusion coefficients in both phases.

As for this kind of two-phase diffusion,  $\alpha/\beta$  interface moves because there is a difference between the flow rates of A and B atoms diffusing from  $\alpha$  side to  $\beta$  side (or from  $\beta$  side to  $\alpha$  side).

Next, consider an exercise concerning Fick's diffusion law in spherical coordinates: Eq 6.13 or Eq 6.16.

**[Exercise 6.5]** If  $\alpha$  solid solution of A-B system in which the concentration of B is  ${}^{\circ}x_{\rm B}^{\alpha}$  is heat treated and aged at the temperature *T*, show that the growth of precipitated particles ( $\theta$  phase) can be expressed by a  $\sqrt{t}$  rule.

**[Answer]** When a spherical particle of radius *r* grows at a rate of dr/dt, the balance between the flux of B atoms absorbed in the particle and that of B atoms supplied by diffusion from the side of  $\alpha$  phase can be expressed by

Volume	Concentration	Surface	Diffusion	
change	difference	area	flux	(Eq 6.23)
$4\pi r^2 (dr/dt) \times$	$(x_{\rm B}^{\theta} - x_{\rm B}^{\alpha/\theta})$	$= 4\pi r^2$	$\times D^{\alpha}_{\rm B}(\partial x^{\alpha}_{\rm B}/\partial \rho)_{\rho=r}$	· · · ·

Here  $x_{\rm B}^{\alpha/\theta}$  is the concentration on the side of  $\alpha$  at  $\alpha/\theta$  interface, and it is assumed that molar volumes of both  $\alpha$  and  $\theta$  phases are equal.

The final term of Eq 6.23 can be obtained using Fick's diffusion law in spherical coordinates (Eq 6.16) discussed in Exercise 6.3.

Because the composition on the side of  $\alpha$  at  $\alpha/\theta$  interface is shown as the data point  $\cdot$  in the phase diagram of Fig. 6.5(b) and is constant according to the local equilibrium, the concentration distribution of  $\alpha$ phase in the neighborhood of  $\theta$  particles should satisfy

$$D_{\rm B}^{\alpha} \left( \frac{\partial^2 u_{\rm B}^{\alpha}}{\partial \rho^2} \right) = \frac{\partial u_{\rm B}^{\alpha}}{\partial t} = 0 \qquad \text{(here } u_{\rm B}^{\alpha} = x_{\rm B}^{\alpha} \cdot \rho \text{)} \qquad \text{(Eq 6.24)}$$

The general solution of this equation is  $u_B^{\alpha} = k_1 \rho + k_2$ , that is,  $x_B^{\alpha} = k_1 + k_2 / \rho$ ; and if  $k_1$  and  $k_2$  are determined by the boundary conditions  $x_B^{\alpha} = x_B^{\alpha/\theta}$  at  $\rho = r$  and  $x_B^{\alpha} = {}^{\circ}x_B^{\alpha}$  as  $\rho \to \infty$ , one can obtain

$$x_{\rm B}^{\alpha} = {}^{\circ}x_{\rm B}^{\alpha} - \frac{\left({}^{\circ}x_{\rm B}^{\alpha} - x_{\rm B}^{\alpha/\theta}\right)r}{\rho} \tag{Eq 6.25}$$

Therefore, the concentration gradient on the side of  $\alpha$  in the neighborhood of  $\alpha/\theta$  interface can be expressed by

$$\left(\partial x_{\rm B}^{\alpha}/\partial \rho\right)_{\rho=r} = \left({}^{\circ}x_{\rm B}^{\alpha} - x_{\rm B}^{\alpha/\theta}\right)/r$$
 (Eq 6.26)

Rearranging Eq 6.23 and 6.26, the  $\sqrt{t}$  rule equation of particle growth can be obtained\*



**Fig. 6.5** Derivation of the growth equation for globular precipitates. (a) The concentration curve of a solute around precipitates. (b) The phase diagram

\*Because territories of each particles impinge on each other at the latter stage of growth, the boundary condition;  $x_B^{\alpha} = x_B^{\alpha}(\rho \to \infty)$  does not hold. As a result, the growth of particles wanders from the  $\sqrt{t}$  rule. See Johnson-Mehl-Avrami-Kolmogorov equation in Chapter 9 for such a growth rule at the latter state.

$$r\frac{dr}{dt} = D_{\rm B}^{\alpha} \left( \frac{{}^{\alpha}x_{\rm B}^{\alpha} - x_{\rm B}^{\alpha/\theta}}{x_{\rm B}^{\theta} - x_{\rm B}^{\alpha/\theta}} \right); \text{ that is, } r = \sqrt{2D_{\rm B}^{\alpha} \left( \frac{{}^{\alpha}x_{\rm B}^{\alpha} - x_{\rm B}^{\alpha/\theta}}{x_{\rm B}^{\theta} - x_{\rm B}^{\alpha/\theta}} \right) \cdot t} \quad (\text{Eq 6.27})$$

# 6.3 Review of Solid Phase Diffusion

The study of diffusion in a solid phase was begun far later than diffusion in a liquid phase, at the end of the 19th century. In the beginning, the method of estimating diffusion area by etching was attempted, and in 1930s the measurement of lattice constant by x-ray was pervaded, the concentration-distance curves of diffusion atoms were obtained, and the facts of diffusion were gradually cleared. The most impactive studies among them were confirmation of diffusion by vacancy mechanism published by Kirkendall, et al. immediately after the World War II (Ref 2), and thermodynamic analysis by Darken et al. (Ref 3,4).

# 6.3.1 Kirkendall Effect

E.O. Kirkendall, et al. in the United States (1947) manipulated a Cu-Zn sample as shown in Fig. 6.6(a) by plating 70-30 brass that was wound molybdenum wires around with Cu about 2.5 mm thick. They diffused this by heating at 1058 K for 1 to 56 days and measured the concentration-distance curve by x-ray and the intervals between Mo wires ( $\xi$ ) with a microscope. Molybdenum wires were markers chosen because they do not form any solid solution with Cu or Zn.



**Fig. 6.6** Kirkendall effect. (a) Composition of diffusion couple. (b) Transfer of the markers according to diffusion. According to the concentration-distance curve obtained by x-ray diffraction method, the diffusion length for 56 days was  $\bar{z} \approx \sqrt{Dt} \approx 2$  mm. Because the difference of atom diameters between Zn and Cu is around 6%, it is estimated that the transfer distance of the markers by "direct exchange mechanism" is  $\bar{z} \times$  concentration difference  $\times$  atomic diameter difference  $\approx 0.02$  mm. However, the measured value was 0.12 mm, about six times the above as shown in (b).

Because both 70-30 brass and pure Cu form fcc crystals, the lattice constant of the former is 0.368 nm, and the latter is 0.361 nm, the intervals between Mo wires would have been hardly varied if Cu atoms and Zn atoms had diffused into each other by mutual exchange of the positions. However, as in Fig. 6.6(b), the Mo wires obviously moved to the side of the brass, and moreover it was confirmed that the motion followed the  $\sqrt{t}$  rule. Therefore, it is obliged to conclude that "Zn atoms diffuse more rapidly than Cu atoms" concerning the interdiffusion in Cu-Zn system.

This simple and obvious experiment by Kirkendall et al. brings one to conclude that the interdiffusion in a metal crystal is promoted not by a direct exchange mechanism of  $A \xrightarrow{\leftarrow} B$  but by diffusion in which vacancies mediate, or diffusion by vacancy mechanism, which was proposed by C. Wagner et al. (1938).

# 6.3.2 Dependency of Interdiffusion Coefficient on Concentration

In 1948, the year after the Kirkendall effect was discovered, L.S. Darken clarified the importance of interdiffusion coefficient  $\tilde{D}$  by the investigation as follows.

If A and B that can form a completely miscible solid solution are joined and interdiffused along the z axis, the fluxes of both components can be expressed by the following equations, respectively, according to Fick's first law.

$$\vec{J}_{A} = -D_{A}\left(\frac{dc_{A}}{dz}\right) = D_{A}\left(\frac{dc_{B}}{dz}\right), \ \vec{J}_{B} = -D_{B}\left(\frac{dc_{B}}{dz}\right)$$
 (Eq 6.28)

If B atoms are easier to move than A atoms, because the flux in + direction  $\vec{J}_A$  is less sufficient than the flux in - direction  $\vec{J}_B$ , the flux of vacancies is caused in + direction as in (see also Fig. 6.7 a1):

$$\vec{J}_{\rm v} = -(\vec{J}_{\rm B} + \vec{J}_{\rm A}) = (D_{\rm B} - D_{\rm A}) \left(\frac{dc_{\rm B}}{dz}\right)$$
 (Eq 6.29)

The value of this vacancy flux  $\vec{J}_v(\text{mol/m}^2 \cdot s)$  divided by the total concentration of both components  $c_A + c_B \pmod{m^3}$  has a unit of (m/s) and should be equal to the aforementioned transfer rate of the marker  $\vec{V}_M$  measured by Kirkendall et al., and then one can obtain.

$$\vec{V}_{\rm M} = \frac{\vec{J}_{\rm v}}{c_{\rm A} + c_{\rm B}} = \left(\frac{D_{\rm B} - D_{\rm A}}{c_{\rm A} + c_{\rm B}}\right) \left(\frac{dc_{\rm B}}{dz}\right) \tag{Eq 6.30}$$



**Fig. 6.7** Analysis on interdiffusion of A-B system (a) The diffusion flow rates in the external coordinates and the marker coordinates. (b) The relation between the interdiffusion coefficient  $\tilde{D}_{Ni-Cu}$  and the diffusion coefficients of component atoms  $D_{Ni}$  and  $D_{Cu}$ 

By the way, because interdiffusion is a position exchange phenomenon of component atoms, the flux of interdiffusion is the flux of both components observed in the coordinates where the fluxes in + direction and - direction are equal, or the marker is set as a standard (it is called the marker coordinates) (Fig. 6.7a2). Letting these be  $\vec{J}_{A}$  and  $\vec{J}_{B}$ , because the fluxes of A and B atoms spontaneously caused by transition of the marker coordinates are  $c_A \vec{V}_M$  and  $c_B \vec{V}_M$ , they can be expressed by Eq 6.28 and 6.30:

$$\vec{J}_{A}^{'} = \vec{J}_{A} + c_{A}\vec{V}_{M} = -D_{A}\left(\frac{dc_{A}}{dz}\right) - (D_{B} - D_{A})\frac{c_{A}}{c_{A} + c_{B}}\left(\frac{dc_{A}}{dz}\right) = -D_{B}x_{A} + D_{A}x_{B}\left(\frac{dc_{A}}{dz}\right)$$
$$\vec{J}_{B}^{'} = \vec{J}_{B} + c_{B}\vec{V}_{M} = -D_{B}\left(\frac{dc_{B}}{dz}\right) + (D_{B} - D_{A})\frac{c_{B}}{c_{A} + c_{B}}\left(\frac{dc_{B}}{dz}\right) = -D_{B}x_{A} + D_{A}x_{B}\left(\frac{dc_{B}}{dz}\right)$$
(Eq 6.31)

Here,  $x_A$  and  $x_B$  are the atomic fractions of both components.

From the above consideration, Darken expressed the relation between the interdiffusion coefficient  $\tilde{D}_{A-B}$  and the diffusion coefficients of both component atoms  $D_A$  and  $D_B$  by

$$\tilde{D}_{A-B} = D_B x_A + D_A x_B$$
 (Darken's equation of interdiffusion coefficient)  
(Eq 6.32)

Figure 6.7(b) is a qualitative illustration about the interdiffusion coefficient  $\tilde{D}_{\text{Ni-Cu}}$  of the completely miscible solid solution, Ni-Cu system.

Since the value of interdiffusion coefficient, in general, depends strongly on not only a solute but also a solvent, the interdiffusion coefficients of the component atoms  $D_{\text{Ni}}^{\text{Ni}}$  and  $D_{\text{Cu}}^{\text{Ni}}$  in a solid solution of Ni base, which has a higher melting point than Cu, are smaller than the diffusion coefficients  $D_{\text{Ni}}^{\text{Cu}}$  and  $D_{\text{Cu}}^{\text{Cu}}$  in a solid solution of Cu base. As a result, the value of the interdiffusion coefficient for Ni-Cu system  $\tilde{D}_{\text{Ni}-\text{Cu}}$  increases upward according to Eq 6.32.

**[Exercise 6.6]** Estimate the interdiffusion coefficient for a solid solution of 70Cu-30Zn system  $\tilde{D}_{Cu-Zn}$ , and the ratio of diffusion coefficients of both components  $D_{Zn}/D_{Cu}$ , according to the data obtained by the diffusion experiment of Kirkendall et al. (at 1058 K for 56 days =  $4.84 \times 10^6$  s). The experimental data available here are (i) mean distance of diffusion  $\bar{z} \approx 2 \times 10^{-3}$ m and (ii) transfer distance of the marker  $(\Delta \xi/2) \approx 1.25 \times 10^{-4}$ m.

**[Answer]** First, the interdiffusion coefficient can be estimated as  $\tilde{D}_{\text{Cu-Zn}} \approx \bar{z}^2/2t \approx (2 \times 10^{-3})^2/2 \cdot 4.84 \times 10^6 \approx 4.1 \times 10^{-13} \text{m}^2/\text{s}$ , according to  $\bar{z} \approx \sqrt{2\tilde{D}t}$ .

Next, because the transfer rate coefficient of the marker can be obtained as  $k_{\rm M} \approx (\Delta \xi/2)/\sqrt{t} \approx 1.25 \times 10^{-4}/\sqrt{4.84 \times 10^6} = 5.7 \times 10^{-8} {\rm m/s}^{1/2}$ , the transfer rate of the marker is presumed to be  $v_{\rm M} \approx k_{\rm M}/2\sqrt{t} \approx 5.7 \times 10^{-8}/2\sqrt{4.84 \times 10^6} \approx 1.3 \times 10^{-11} {\rm m/s}$ .

On the other hand, if the general solution for the concentrationdistance curve in interdiffusion of A-B system (Eq 6.17) is applied to the diffusion in Cu-30%Zn system,

$$x_{\rm Zn} = (0.3/2) \left[ 1 + \operatorname{erf} \left( z/2\sqrt{\tilde{D}_{\rm Cu-Zn}t} \right) \right]$$

Then the gradient of concentration in the neighborhood of the marker is

$$\left(\frac{\partial x_{\text{Zn}}}{\partial z}\right)_{z=0} = \frac{0.3}{\sqrt{\pi}} \cdot \frac{1}{2\sqrt{\tilde{D}_{\text{Cu-Zn}}t}} \approx \frac{0.3}{\sqrt{\pi} \cdot 2(4.1 \times 10^{-13} \cdot 4.84 \times 10^{6})^{1/2}} \approx 60 \text{ m}^{-1}$$

Substituting the above values into Eq 6.30 and Eq 6.32, the two equations below can be obtained.

$$\begin{cases} D_{\rm Zn} - D_{\rm Cu} = V_{\rm M}/(dx_{\rm Zn}/dz) \approx 1.3 \times 10^{-11}/60 = 2.2 \times 10^{-13} {\rm m}^2/{\rm s}^1 \\ D_{\rm Zn} \cdot 0.85 + D_{\rm Cu} \cdot 0.15 = \tilde{D}_{\rm Cu-Zn} \approx 4.1 \times 10^{-13} {\rm m}^2/{\rm s}^1 \end{cases}$$

The solutions for this simultaneous equations are  $D_{\text{Cu}} \approx 2.2 \times 10^{-13} \text{m}^2/\text{s}$ and  $D_{\text{Zn}} \approx 4.4 \times 10^{-13} \text{m}^2/\text{s}$ . Therefore, it is presumed that  $D_{\text{Zn}}/D_{\text{Cu}} \approx 2$ .

#### 6.3.3 Uphill Diffusion

Diffusion is essentially a phenomenon that solute atoms transfer from a higher concentration region to a lower concentration region, and the composition becomes uniform in all regions. However, diffusion sometimes occurs in the opposite direction such that atoms climb from a lower concentration region to a higher region, and it is called uphill diffusion.

The most typical instance is the experiment of diffusion couple by Darken as shown in Fig. 6.8 (Ref 4). The sample used for the experiment was a diffusion couple with a piece of Fe-3.8%Si-0.48%C steel (I), and a piece of Fe-0.44%C steel without Si (II) joined. He heated the sample at 1323 K for 13 days  $(1.1 \times 10^6 \text{ s})$ , then scraped it off every about 2 mm up to 50 mm and analyzed carbon concentration. He confirmed that C atoms diffused inversely from the side of Fe-Si-C to the side of Fe-C.

Another typical instance of uphill diffusion is diffusion in spinodal decomposition of such an alloy as Fe-Ni-Cu system, and if a two-phase separation type of A-B alloy as shown in Fig. 6.9(a) is rapidly cooled from a single-phase state 1 to a two-phase region 2 and held as is, then a uniform solid solution gradually becomes ununiform by uphill diffusion and at last decomposes into  $\alpha_1$  rich in A and  $\alpha_2$  rich in B. (See Sections 4.4 and 9.1 for metallographic consideration of spinodal decomposition.



**Fig. 6.8** The diffusion of C atoms in diffusion couple of Fe-Si-C system (the diffusion of Si atoms is very small). (a) The uphill diffusion can be observed in the concentration-distance curve of C atom. However, if (b) is converted into the activity-distance curve of C atoms, it is an ordinary diffusion.



**Fig. 6.9** The uphill diffusion in the spinodal decomposition. When A-B is strongly repulsive, the diffusion coefficient will take a negative value. (a) The phase diagram. (b) The change in structure and composition. (c) The free energy and the diffusion coefficient

These uphill diffusion phenomena urged an essential investigation of Fick's diffusion law "Diffusion is proportional to the gradient of concentration."

# 6.3.4 Thermodynamic Modification of Fick's Diffusion Laws

In order to solve the aforementioned contradiction, Darken (Ref 3) thought that diffusion phenomena were driven not by the gradient of concentration but by the gradient of chemical potential and analyzed them according to the rate equation:

Diffusion rate Mobility Gradient of of atoms chemical potential (Eq 6.33)  $V = -m \times (\partial \mu / \partial z)$ 

In an  $\alpha$  solid solution of A-B system, if the chemical potentials of component atoms are approximated by the regular solution model, then according to Eq 3.43,

$$\begin{array}{l} \mu_{\rm A}^{\alpha} \approx^{\circ} G_{\rm A}^{\alpha} + \Omega_{\rm AB}^{\alpha} (1 - x_{\rm A})^2 + RT \ln x_{\rm A} \\ \mu_{\rm B}^{\alpha} \approx^{\circ} G_{\rm B}^{\alpha} + \Omega_{\rm AB}^{\alpha} (1 - x_{\rm B})^2 + RT \ln x_{\rm B} \end{array} \right\}$$
 (Eq 6.34)
From Eq 6.34, the gradient of chemical potential of B component can be obtained:

$$\frac{\partial \mu_{\rm B}^{\alpha}}{\partial z} = \frac{\partial \mu_{\rm B}^{\alpha}}{\partial x_{\rm B}} \cdot \frac{dx_{\rm B}}{dz} \approx \frac{RT}{x_{\rm B}} \left[ 1 - \frac{2\Omega_{\rm AB}^{\alpha}}{RT} x_{\rm B} (1 - x_{\rm B}) \right] \cdot \frac{dx_{\rm B}}{dz}$$
(Eq 6.35)

Because the diffusion flux of B component is the product of the concentration  $c_{\rm B}({\rm mol/m}^3)$  and the rate  $v_{\rm B}$  (m/s), it can be expressed according to Eqs 6.33 and 6.35:

$$J_{\rm B} = c_{\rm B} v_{\rm B} = -m_{\rm B} RT \left[ 1 - \frac{2\Omega_{\rm AB}^{\alpha}}{RT} x_{\rm B} (1 - x_{\rm B}) \right] \cdot \frac{dc_{\rm B}}{dz}$$
(Eq 6.36)

Here the following relationship equation with regard to the gradients of the atomic fraction  $x_B$  and the concentration  $c_B$  was used.

$$\frac{1}{x_{\rm B}} \left( \frac{dx_{\rm B}}{dz} \right) = \frac{1}{c_{\rm B}} \left( \frac{dc_{\rm B}}{dz} \right) \tag{Eq 6.37}$$

The terms of [ ] in Eq 6.35 and 6.36 are [ ]=1 for  $x_B \ll 1$ , or a dilute solution on the side of A. Referring to the definition of mobility of atoms by Einstein, m = D/RT, it is thought  $m_BRT = D_B$ , and it is concluded that the coefficient of Fick's diffusion law, Eq 6.9 should be modified:

$$D_{\rm B}({\rm Fick's\ diffusion\ law}) \to D_{\rm B} \left[ 1 - \frac{2\Omega_{\rm AB}^{\alpha}}{RT} x_{\rm B}(1 - x_{\rm B}) \right]$$
 (Eq 6.38)

According to the same analysis, it is necessary to modify the coefficient of diffusion law for A component:

$$D_{\rm A}(\text{Fick's diffusion law}) \to D_{\rm A} \left[ 1 - \frac{2\Omega_{\rm AB}^{\alpha}}{RT} x_{\rm B}(1 - x_{\rm B}) \right]$$
 (Eq 6.39)

Summarizing the above consideration and Eq 6.32, Darken expressed the coefficient of interdiffusion:

$$\tilde{D}_{A-B} = (D_B \cdot x_A + D_A \cdot x_B) \left[ 1 - \frac{2\Omega_{AB}^{\alpha}}{RT} x_B (1 - x_B) \right]$$
(Eq 6.40)

The term of [ ] in Eq 6.40 is called the thermodynamic factor of diffusion coefficient.\*

\*The thermodynamic factor was considered using the regular solution model here. In a general explanation, [ ] is expressed using the activity coefficient  $\gamma_{\rm B} = a_{\rm B}/x_{\rm B}$ :

[Thermodynamic factor] = 
$$[1 + x_B(\partial \ln \gamma_B / \partial x_B)]$$
 (Eq 6.41)

**[Exercise 6.7]** Explain according to Eq 6.40 that uphill diffusion is caused if A and B atoms are strongly repulsive.

**[Answer]** When  $\Omega_{AB}^{\alpha} > 2RT$ , as shown in Fig. 6.9(c), a "concave" region of composition appears in the free-energy curve, the interdiffusion coefficient becomes  $\tilde{D}_{A-B} < 0$ , and uphill diffusion from the side of low concentration to the side of high concentration will be caused. The limits of this composition region (data points  $\cdot$ ) correspond to the spinodal points (see Eq 4.44).

**[Exercise 6.8]** The chemical potential of C atoms in  $\gamma$ Fe-Si-C austenitic system can be approximated according to the regular solution model (Eq 3.52) by:

$$\mu_{\rm C}^{\gamma} \approx \Delta G_{\rm C}^{\gamma \rm Fe} - 2(L_{\rm Cv}^{\gamma \rm Fe} - RT)x_{\rm C} + W_{\rm SiC}^{\gamma} \cdot x_{\rm Si}(1 - x_{\rm C}) + RT\ln x_{\rm C} \qquad ({\rm Eq}\ 6.42)$$

Here  $L_{Cv}^{\gamma Fe}(=-36 \text{ kJ/mol})$  is the interaction parameter between C atoms, and the negative sign means that they are repulsive. Also,  $W_{SiC}^{\gamma}(=+112 \text{ kJ/mol})$  is the repulsive energy between Si atoms and C atoms. Verify the uphill diffusion experiment by Darken according to Eq 6.42.

**[Answer]** First, comparing the diffusion coefficients and distances of C atoms and Si atoms by this experiment (at 1323 K for 13 days),

$$D_{\rm C}^{\gamma {\rm Fe}} \approx 5 \times 10^{-11} {
m m}^2/{
m s}, \ \bar{z}_{\rm C} = \sqrt{2 D_{\rm C}^{\gamma {\rm Fe}} t} \approx 11 {
m mm}$$
  
 $D_{{
m Si}}^{\gamma {\rm Fe}} \approx 10^{-15} {
m m}^2/{
m s}, \ \bar{z}_{{
m Si}} = \sqrt{2 D_{{
m Si}}^{\gamma {\rm Fe}} t} \approx 0.05 {
m mm}$ 

Therefore, it can be thought that Si hardly diffused and only C diffused.

Next, obtain the gradient of chemical potential that drives the diffusion of C atoms from Eq 6.42,

$$\frac{\partial \mu_{\rm C}^{\gamma}}{\partial z} = \left(\frac{\partial \mu_{\rm C}^{\gamma}}{\partial x_{\rm C}}\right) \frac{dx_{\rm C}}{dz} + \left(\frac{\partial \mu_{\rm C}^{\gamma}}{\partial x_{\rm Si}}\right) \frac{dx_{\rm Si}}{dz}$$

$$= \left[\frac{RT}{x_{\rm C}} - 2(L_{\rm Cv}^{\gamma \rm Fe} - RT)\right] \frac{dx_{\rm C}}{dz} + W_{\rm SiC}^{\gamma} \frac{dx_{\rm Si}}{dz}$$
(Eq 6.43)

The first term on the right-hand side is the driving force by C atoms themselves, and the second term is the driving force onto C atoms by the concentration gradient of Si.

The driving force by Si is extremely large in the neighborhood of the joint interface of the pieces (I) and (II) of the above two, and if it is estimated by the mean distance of diffusion  $\bar{z}_{Si} \approx 0.05$  mm, then

$$W_{\rm SiC}^{\gamma} \frac{dx_{\rm Si}}{dz} \approx 112 \times \left(-\frac{0.072}{0.05}\right) \approx -160 \,\mathrm{kJ/mol} \cdot \mathrm{mm}$$

is presumed. This value is far larger than the driving force of normal diffusion of C atoms in the piece (I) or (II) (about 0.3 kJ/mol  $\cdot$  mm).

Therefore, it is considered that C atoms can get over the steep slope of C concentration from I side to II side, and "uphill diffusion" may make progress.

When the activity-distance curve of carbon is obtained by the relationship equation between the activity of C atoms  $(a_C^{\gamma})$  and the chemical potential  $\Delta \mu_C^{\gamma} = RT \ln a_C^{\gamma}$ , it will become a normal diffusion curve as shown in Fig. 6.8(b), and no uphill diffusion occurs.

# 6.4 Mechanism of Diffusion and Diffusion Coefficient

As for the measurement of solid phase diffusion, the precision was markedly improved by propagation of the tracer technique using a radio isotope invented by Hevesy (Ref 1, 5), and mechanisms of every kind were made clear. Important ones include Ref 6 and 7. As far as diffusion of ions in oxides or sulfides is concerned, refer to Ref 6 to 8.

# 6.4.1 Frequency Factor of Diffusion Coefficient and Activation Energy

As mentioned previously, the diffusion coefficient *D* is equal to the product of the jumping frequency in + direction  $v_+$  and the square of the jumping distance  $\lambda$  (Eq 6.8). Therefore, let the eigenfrequency of the crystal be  $v_0$ , and it will generally be expressed by

$$D = v_+ \ \lambda^2 = \frac{1}{6} v_0 \lambda^2 \exp\left(-\frac{\Delta G_d^*}{RT}\right)$$
(Eq 6.44)

Here the coefficient (%) is the fraction in + direction of three-dimensional vibration and  $\Delta G_d^*$  is the activation energy for an atom to transfer to the neighboring lattice point. If this  $\Delta G_d^*$  is divided into an enthalpy term and an entropy term and expressed as  $\Delta G_d^* = \Delta H_d^* - T\Delta S_d^*$ , then Eq 6.44 can be rearranged:

$$D = \left[\frac{1}{6}v_0\lambda^2 \exp\left(-\frac{\Delta S_d^*}{R}\right)\right] \cdot \exp\left(-\frac{\Delta H_d^*}{RT}\right) = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (\text{Eq 6.45})$$

 $D_0$  in Eq 6.45 is called the frequency factor of diffusion coefficient, and  $Q(=\Delta H_d^*)$  is called the activation energy of diffusion.

**[Exercise 6.9]** The self-diffusion coefficient of Cu atoms in pure Cu was measured at 1173 and 973 K by the tracer technique, and the following result was obtained.

(i) 
$$D_{\text{Cu}}^{\text{Cu}} = 3.2 \times 10^{-14} \text{m}^2/\text{s}$$
 (1173 K), (ii)  $D_{\text{Cu}}^{\text{Cu}} = 3.8 \times 10^{-16} \text{m}^2/\text{s}$  (973 K)

Evaluate  $D_0$  of the diffusion coefficient and Q according to these measured values.

[Answer] Equation 6.45 can be rewritten:

$$\ln D = \ln D_0 - \frac{Q}{R} \left(\frac{1}{T}\right), \quad \log D = \log D_0 - \frac{Q}{2.3R} \left(\frac{1}{T}\right)$$
(Eq 6.46)

Here  $\ln x = (\ln 10) \log x = 2.3 \log x$  was used.

Substituting the values in the question into Eq 6.46, one obtains  $D_0 \approx 8 \times 10^{-5} \text{m}^2/\text{s}$  and  $Q \approx 211 \text{ kJ/mol}$ . As shown in Fig. 6.10(b), if an "Arrhenius plot" is drawn by plotting log D in ordinate and 1/T in abscissa, the ordinate intercept at 1/T = 0 corresponds to log  $D_0$ . The gradient of a line connecting the plots indicates the amount of activation energy Q.

# 6.4.2 Diffusion by Vacancy Mechanism and Interstitial Diffusion

Let us consider diffusion by vacancy mechanism first. As shown in Fig. 6.11(a), in order for a substitutional atom B to transfer from the lattice point 1 to the lattice point 2, at the opportunity that a vacancy arrives at the lattice point 2, it must pass through the gap between the neighboring atoms 3 and 4. Therefore, the diffusion coefficient can be approximated by:



Fig. 6.10 The frequency factor and the activation energy of self diffusion for pure Cu



**Fig. 6.11** The elementary processes of diffusion of substitutional atoms (B) and interstitial atoms (I). (a) The model for diffusion by vacancy mechanism. (b) The model for interstitial diffusion. The bold dotted line in (a) is the energy curve when no vacancy exists on the lattice point 2.

Probability of vacancy formation × Probability of transfer  

$$D = \frac{1}{6} v_0 \lambda^2 \exp\left(-\frac{\Delta G_v^*}{RT}\right) \cdot \exp\left(-\frac{\Delta G_m^*}{RT}\right)$$

$$= \frac{1}{6} v_0 \lambda^2 \exp\left(-\frac{\Delta G_v^* + \Delta G_m^*}{RT}\right) \quad (Eq \ 6.47)$$

Here  $\Delta G_v^*$  is the energy of vacancy formation and  $\Delta G_m^*$  is the activation energy for transfer of atoms. Rearranging Eq 6.47 in the same way as Eq 6.45, it can be seen that the frequency factor of diffusion by vacancy mechanism  $D_0$  and the activation energy Q have the meaning:

$$D_0 = (\frac{1}{6})v_0\lambda^2 \exp\left[\left(\Delta S_v^* + \Delta S_m^*\right)/R\right], \ Q = \Delta H_v^* + \Delta H_m^* \qquad (\text{Eq 6.48})$$

Here  $\Delta S_v^*$  is the change in entropy of vibration in accordance with the formation of vacancies,  $\Delta S_m^*$  is the change in entropy in accordance with the transfer of atoms, and  $\Delta H_V^*$  and  $\Delta H_m^*$  are the enthalpies necessary for the formation of vacancies and the transfer of atoms.

[Exercise 6.10] Compare the self-diffusion coefficients of the six kinds of pure metals shown in Table 6.1.

**[Answer]** The stronger the bond between atoms forming a crystal is, the higher the melting point  $T_m$  is and the larger the activation energy

Metal (crystal structure)	$D_0, m^2/s$	Q, kJ/mol	T <sub>m</sub> , K	$Q/T_{\rm m}$ , J/mol · K
Al (fcc)	$1.7  imes 10^{-4}$	142	934	152
Cu (fcc)	$7.8  imes 10^{-5}$	211	1358	155
γ (fcc)	$8.9  imes 10^{-5}$	291	(1801)	162
α Fe (bcc)				
Paramagnetic	$2.0  imes 10^{-4}$	241	1811	133
Ferromagnetic	$1.0  imes 10^{-4}$	294		
Ta (bcc)	$1.2  imes 10^{-5}$	413	3263	127
Ge (diamond)	$7.8  imes 10^{-4}$	286	1232	232

Table 6.1 Typical self-diffusion coefficients of pure metals

of diffusion Q is. Therefore, the values of  $Q/T_{\rm m}$ , as shown in Table 6.1, are about 150 for the fcc metals and about 130 for the bcc metals. Therefore, the scattered data in the ordinary Arrhenius plot with 1/T in abscissa (Fig. 6.12a) are collected according to crystal structures as in Fig. 6.12 (b) if plotted with  $T_{\rm m}/T$  in the abscissa, and the diffusion coefficients of the fcc metals are a little smaller than those of the bcc metals because the former have a denser crystal structure than the latter. Although Ge of the diamond type has a coarse structure, the value of diffusion coefficient is far smaller than that of a metal because it is a covalent crystal. Because aFe becomes ferromagnetic and the interatomic binding force becomes larger below 1043 K, the diffusion coefficient becomes remarkably small, as shown by the hatching.

Interstitial diffusion is considered next.

The elements below have a small atomic radius, and they can form an interstitial solution in a metal crystal.

H (0.037), C (0.071), N (0.053), O (0.061)



**Fig. 6.12** The self-diffusion coefficients of various kinds of metals. (a) Arrhenius plot. (b) Normalized diagram according to the melting points. The hatching means the decrease of diffusion coefficient according to the magnetic transformation of  $\alpha$ Fe( $T_c = 1043$  K)

Here the values in the parenthesis are the atomic radii (nm), and they are less than  $\frac{1}{2}$  of an atomic radius of a metal.

Because these atoms, as in Fig. 6.11(b), transfer through the crystal lattice by induction of thermal vibration, the diffusion coefficient can be expressed by

$$D_{\rm i} = \left[\frac{1}{n}\nu_0\lambda^2 \exp\frac{\Delta S_{\rm im}^*}{R}\right] \cdot \exp\left(\frac{\Delta H_{\rm im}^*}{RT}\right) = D_{\rm io} \cdot \exp\left(\frac{\Delta Q_{\rm im}^*}{RT}\right) \quad ({\rm Eq} \ 6.49)$$

Here,  $Q_{\rm im} = \Delta H_{\rm im}^*$  is the activation energy to transfer from 1 to 2 through the lattice,  $\Delta S_{\rm im}^*$  is the activation entropy, and 1/n is the fraction of vibration in + direction and has a value between  $\frac{1}{4}$  to  $\frac{1}{12}$  depending on crystal structure.

If the coefficients of interstitial diffusion shown in Table 6.2 are plotted in Arrhenius plots, then they are remarkably different according to the metal system as in Fig. 6.13(a). However, if they are normalized according to the melting point of a solvent metal in the same manner as in the case of diffusion by vacancy mechanism, then the values will

Solute/solvent (crystal structure)	$D_{\rm io}, {\rm m}^2/{\rm s}$	$Q_{ m im}$ , kJ/mol	T <sub>m</sub> , K	$Q_{\rm im}/T_{\rm m}$ , J/mol · K
H/Pt (fcc)	$6 \times 10^{-7}$	24.7	2042	12
$C/\gamma$ Fe (fcc)	$4.7  imes 10^{-5}$	155	(1801)	86
$C/\alpha$ Fe (bcc)	$1.24 \times 10^{-5}$	99.5	1811	55
C/Ni (fcc)	$1.2 \times 10^{-5}$	142	1726	82
C/NbC (NaCl) (Ref 9)	$2.3  imes 10^{-5}$	345	3896	89
Li <sup>+</sup> /Ge (diamond) (Ref 10)	$2.5  imes 10^{-7}$	49.3	1232	40



Fig. 6.13 The interstitial diffusion coefficients. (a) Arrhenius plots. (b) Normalized diagram according to the melting points of solvent metals

become approximately equivalent among crystals of same structure (Fig. 6.13b).

Though the coefficients of interstitial diffusion at  $T = T_m/2$  range From  $10^{-14}$  to  $10^{-11}$ m<sup>2</sup>/s, the aforementioned coefficients of diffusion by vacancy mechanism range From  $10^{-21}$  to  $10^{-18}$ m<sup>2</sup>/s and there is a difference of about 10<sup>7</sup>. In particular, the interstitial diffusion of hydrogen atoms is abnormally rapid, and they diffuse to a good distance even at the ordinary temperature. Therefore, hydrogen accumulates at internal defects of structural materials and forms voids there and sometimes cause hydrogen embrittlement and other hydogen-induced defects.

Because  $Li^+$  (the atomic radius is 0.15 nm, but the ionic radius is 0.078 nm) diffuses rapidly by interstitial mechanism in Si or Ge crystal of the diamond structure as shown by the long-dashed short-dashed line in Fig. 6.13, it is very important to control the impurity Li in semiconductor devices.

### 6.4.3 Surface Diffusion and Grain-Boundary Diffusion

Diffusion along the surface or the grain boundary of a crystal is called short-circuit diffusion because it is far faster than diffusion by passing through in crystal grains (lattice diffusion) (Fig. 6.14). Those diffusion coefficients vary in the direction of crystallographic planes or grains, but they can be approximated roughly if the data in a random direction are summarized. (Ref 11, 12):



Fig. 6.14 The comparison of the surface diffusion, the grain-boundary diffusion, and the lattice diffusion. (a) Short-circuit diffusion. (b) Mechanism of surface diffusion

Surface diffusion coefficient:

$$D^{\text{surf}} \approx 7 \times 10^{-6} \exp\left[-\frac{56}{R} \left(\frac{T_{\text{m}}}{T}\right)\right]$$
 (Eq 6.50)

Grain-boundary diffusion coefficient:

$$D^{\text{gb}} \approx 4 \times 10^{-5} \exp\left[-\frac{82}{R} \left(\frac{T_{\text{m}}}{T}\right)\right]$$
 (Eq 6.51)

The surface diffusion makes progress by transfer of vacancies showing their faces on the crystal surface (terrace vacancies) as in Fig. 6.14(b2). However, at the temperature right below the melting point, the value of diffusion coefficient deviates from Eq 6.50 and becomes abruptly large because of increase in adherent atoms on the crystal surface as shown in Fig. 6-14(b1).

On the other hand, the grain-boundary diffusion coefficient almost coincides with the coefficient of diffusion in a liquid phase at the melting point  $T_{\rm m}$ . Moreover, the grain-boundary diffusion coefficient is almost equivalent even if the crystal structure is bcc or fcc. This indicates that the structure of random grain boundary is in an amorphouslike state analogous to a liquid.

[Exercise 6.11] Consider the apparent coefficient of diffusion in the case of an experiment on self-diffusion with polycrystal samples with the mean radius of crystal grains of 100, 10, and 1  $\mu$ m. Here, the grain boundary is assumed to be a random grain boundary with three atom width ( $\delta = 7.5 \times 10^{-10}$ m).

[Answer] Because it is complicated to analyze this problem rigorously, a simple method (Ref 7) can be applied here.

Regard a polycrystal as a compound of the prismatic crystal grains of 2  $\bar{R}$  thick and the platelike grain boundaries of  $\delta$  thick, the stationary diffusion in the direction of the principal axis of the prism will be analyzed (Fig. 6.15). The area of a crystal grain in the cross section perpendicular to the direction of diffusion is  $(2\bar{R})^2 = 4\bar{R}^2$ . Because the cross-sectional area of a grain boundary in every crystal grain is  $4 \times 2\bar{R} \times (\delta/2) = 4\bar{R}\delta$ , the fractions of cross-sectional areas for the grains and the grain boundaries are

$$f_{\text{lat}} = \frac{4\bar{R}^2}{4\bar{R}^2 + 4\bar{R}\delta} = \frac{\bar{R}}{\bar{R} + \delta}, \ f_{\text{gb}} = \frac{4\bar{R}\delta}{4\bar{R}^2 + 4\bar{R}\delta} = \frac{\delta}{\bar{R} + \delta}$$
(Eq 6.52)

In general, the additive rule is approved for a stationary transport phenomenon in a parallel complex, and the relation between the apparent



Fig. 6.15 Relation between the grain size and the apparent diffusion coefficient

diffusion coefficient D and the diffusion coefficients in the grain and the grain boundary  $D^{\text{lat}}$  and  $D^{\text{gb}}$  is as

$$D \approx f_{\text{lat}} \cdot D^{\text{lat}} + f_{\text{gb}} \cdot D^{\text{gb}} = \left(\frac{\bar{R}}{\bar{R} + \delta}\right) D^{\text{lat}} + \left(\frac{\delta}{\bar{R} + \delta}\right) D^{\text{gb}}$$
 (Eq 6.53)

Figure 6.15(b) shows the calculated result when the diffusion coefficients in the grain and the grain boundary are approximated by the following equations, and the influence of grain boundaries becomes remarkable when the mean radius of crystal grains is less than 10  $\mu$ m.

$$D^{\text{lat}} = 10^{-4} \exp\left[-\frac{150}{R}\left(\frac{T_{\text{m}}}{T}\right)\right], \ D^{\text{gb}} = 4 \times 10^{-5} \exp\left[-\frac{82}{R}\left(\frac{T_{\text{m}}}{T}\right)\right]$$

In order to carry out this type of experiment, it is necessary to suppress the growth of crystal grains by pinning effect with fine particles dispersed in a sample.

#### **EXERCISES**

**6.12** Einstein derived the following equation by analyzing Brownian motion of fine particles.

Average movements: 
$$\bar{z} = \sqrt{2Dt}$$
  
Diffusion coefficient:  $D = \frac{RT}{N_0} \cdot \frac{1}{6\pi r\eta}$ 

Here  $N_0$  is Avogadro's number, r is the radius of a particle, and  $\eta$  is the coefficient of viscosity.

Estimate the distance to which the fine particle  $(r = 0.1 \,\mu\text{m})$  suspended in water at 293 K (or molten iron at 1823 K) can move in 100 s. Here, the coefficient of viscosities are  $\eta(\text{water}) = 10^{-3}\text{Pa} \cdot \text{s}$ ,  $\eta$  (molten *iron*) = 5 × 10^{-3}\text{Pa} \cdot \text{s}.

**Answer:**  $\bar{z} \approx 20 \,\mu\text{m}$  for both water and molten iron.

**6.13** Which type is the diffusion couple of A and B joined that has such a phase diagram as shown in Fig. 6.16(a) and is heated for hours at the temperature *T*, type (a) or type (b) in Fig. 6.16(b)?

*Hint:* The thickness of each phase in a multiphase diffusion couple is almost proportional to the square root of the diffusion coefficient.

**6.14** When an alloy is annealed or tempered, almost identical microstructures can be obtained even if the heating temperature T and the heating time t are changed to T' and t' according to the following relationship. Consider the reason for it. Here, C is a characteristic value of a material.

 $T(\log t + C) = T'(\log t' + C)$  [Hollomon-Jaffe's equation (1945)]

*Hint:* Because the fundamental parameter of microstructure change according to diffusion is the diffusion distance,  $\bar{z} = \sqrt{2Dt}$ , take the logarithm of the relation between *T* and *t* included in 2*Dt*,  $t \exp(-Q/RT) = t_0$  and let  $C = -\log t_0$ , and  $T(\log t + C) = Q/R \ln 10$  in question can be derived.



Fig. 6.16 Construction of multilayer diffusion couple of A-B system and the concentration-distance curve

**6.15** Estimate the change of diffusion coefficient of C atom when 3 at. % Cr is added to  $\gamma$ Fe-C system. Here, the bond energy of C atom and Cr atom is

$$\Delta \varepsilon_{\rm CrC} \approx -1$$
 J/mol.

*Hint:* The rate of C atoms trapped by Cr atoms is as below according to Eq 3.62.

$$f_{\rm CrC} = \frac{z' x_{\rm Cr} \exp\left(-\Delta \varepsilon_{\rm CrC}/RT\right)}{1 - z' x_{\rm Cr} \left[1 - \exp\left(-\Delta \varepsilon_{\rm CrC}/RT\right)\right]} \approx 0.45 \ (T = 1000 \, K)$$

Here z' is the number of the interstitial sites closest to Cr atom (=6).

Assuming that the trapped C atoms cannot diffuse, the diffusion coefficient becomes:.

$$D_{\mathrm{C}}^{\gamma} \approx \left( D_{\mathrm{C}}^{\gamma} \right)_{\mathrm{Fe-C}} \cdot \left( 1 - f_{\mathrm{C}}^{\mathrm{Cr}} \right) \approx \left( D_{\mathrm{C}}^{\gamma} \right)_{\mathrm{Fe-C}} \cdot 0.55$$

However, because the activation energy of C atom diffusion is  $Q_{\rm C} \approx 155 \, \rm kJ/mol$ , and it is far larger than  $\Delta \varepsilon_{\rm CrC}$ , the aforementioned assumption is wrong and the value of  $D_{\rm C}^{\gamma}$  hardly changes by addition of Cr. In the case of diffusion of hydrogen in  $\alpha$ Fe, because  $\Delta \varepsilon_{\rm CrH} \approx -7 \, \rm kJ/mol$  while the activation energy is  $Q_{\rm H} \approx 8 \, \rm kJ/mol$ , the effect of trapping is remarkable.

# **Appendix: Diffusion Path**

If the changes of each phase by diffusion are plotted on a composition triangle and the diffusion path is drawn there, the importance of the diffusion process will be easy to understand. The typical examples are shown below.

**Detour of Diffusion Path: Fig. 6.17(a).** When steel sheets are dipped in a hot dip galvanizing bath, diffusion layers are formed where  $\Gamma(Fe_5Zn_8)$ ,  $\delta(FeZn_{10})$ , and so forth are laminated. However, these compounds are brittle, and detachment or cracks are caused during stamping after galvanization. So, if about 0.2% of Al is added in Zn bath, then Al concentrates at the interface between Fe and Zn, the thin film of B2 (FeAl) or  $\eta(Fe_2Al_5)$  is formed, and a great detour is made in the diffusion path. As a result, the growth of Zn diffusion layer is suppressed, and deterioration of workability can be reduced.

**Double Tracking of Diffusion Path: Fig. 6.17(b).** If Cu-Al solid solution is heated in a weak oxidizing atmosphere, then O atoms diffuse interstitially and form Al<sub>2</sub>O<sub>3</sub>. In this case, the diffusion path is bifurcated to the double track lines of  $2 \rightarrow 3 \rightarrow 4$  on the side of Cu and  $2' \rightarrow 3' \rightarrow 4'$  on the side of Al<sub>2</sub>O<sub>3</sub>, and the microscopic structure will become a dispersion structure with Al<sub>2</sub>O<sub>3</sub> particles precipitated in Cu substrate.



Fig. 6.17 (a) Diffusion path in hot dip galvanizing (several kinds of compounds are omitted). (b) Diffusion path in the internal oxidation of Cu-Al solution

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CHAPTER

# Thermodynamics of Ordering

From the 1930s through the 1960s, "solid state physics" flourished and the true characteristics of matters were elucidated using statistical thermodynamics. "Thermodynamics of ordering" is one of the important items, the exquisite theories including the B-W-G model were published one after another, and they remarkably contribute to the progress of materials science.

This chapter covers the gist of analytical methods these predecessors of ours developed. Many expressions appear, but it is important to see through the essence without being puzzled by the operations.

# 7.1 Ordering Phenomena

# 7.1.1 Ordering in Microscopic Structure

A different ordering phenomenon from an ordinary phase transformation often occurs in a microscopic structure. Figure 7.1 shows typical examples: Fig. 7.1(a) shows that the transition of a liquid crystal (nematic  $\rightarrow$  smectic) is the ordering in arrangement of long and slender macromolecules, Fig. 7.1(b) shows that the magnetic transition is the ordering in orientation of magnetic spins, and Fig. 7.1(c) shows the ordering in configuration considered in this chapter.

Because a disordered state is chaotic, entropy S is large and enthalpy H is high. However, S is small and H is low in an ordered state. As a result, the value of free energy G = H - TS is lower in a disordered state at high temperature and in an ordered state at low temperature, so the change in state mentioned below occurs in accordance with heating or cooling. This is called an order-disorder transformation or an order-disorder transition.

(Low temperature) ordered state  $\stackrel{\rightarrow}{\leftarrow}$  Disordered state (high temperature)

This ordering phenomenon was confirmed by x-ray diffraction in 1923. The discoverer was E.C. Bain, who later became famous for the study on



Fig. 7.1 The typical examples of ordering phenomena

bainite structure in steel. He discovered diffraction lines that were not expected in solid solutions of fcc. such as (100) and (110) in x-ray diffraction images of Cu-25at. % Au solid solution. He declared that the cause is the ordered configuration of Cu atoms and Au atoms (Ref 1).

Similar ordering can also be observed in bcc solid solution of Cu-Zn system and hcp solid solution of Mg-Cd system (Fig. 7.2) and is generally called an ordered phase.

### 7.1.2 Short-Range Ordering

Ordering of atomic configuration has been analyzed by two kinds of ordering models, the long-range ordering model and the short-range ordering model.

The former is called the Bragg-Williams-Gorsky (B-W-G) model, in which crystal lattices are regarded as compound lattices of some sublattices as shown in Fig. 7.3(b) and the order parameter ( $\phi$ ) is determined by the number of A (or B) atoms on each of the sublattices. This model is considered in detail in Sections 7.2 to 7.4; the short-range ordering is discussed here.

In order to analyze the short-range ordering, the order parameter is defined as follows, noticing the number of A-B bonds ( $P_{AB}$ ).

Short-range order parameter: 
$$\varphi^* = \frac{P_{AB} - (P_{AB})_0}{(P_{AB})_1 - (P_{AB})_0}$$
 (Eq 7.1)

Here  $(P_{AB})_1$  and  $(P_{AB})_0$  are the numbers of A-B bonds in case of  $\phi^* = 1$ and  $\phi^* = 0$ .

In the case of a solid solution of A:B = 1:1, if the total of atoms is N, and the number of the nearest neighbors to each atom is z, then the total



Fig. 7.2 Alloys showing typical ordering phases

of bonds is zN/2. Because all of A and B atoms are configured alternately in a completely ordered state,  $(P_{AB})_1 = zN/2$ . Because only half of the bonds are A-B bonds in a completely disordered state,  $(P_{AB})_0 = zN/4$ . Therefore, the relation between the number of each bond and  $\varphi^*$  is:

$$\phi^* = \frac{P_{AB} - zN/4}{zN/2 - zN/4} = \frac{P_{AB}}{zN/4} - 1,$$

$$P_{AB} = \frac{zN}{4} (1 + \phi^*), \ P_{AA} = P_{BB} = \frac{zN}{8} (1 - \phi^*)$$
(Eq 7.2)

For example, in the case of the two-dimensional lattice in Fig. 7.3(a), the number of A-B bonds is 35, while the total of bonds is 60. Therefore, the order parameter is  $\varphi^* = {}^{35}\!/_{30} - 1 = {}^{1}\!/_{6}$ .

Both the white and gray domains in Fig. 7.3(a) are ordered, but they have an antiphase to each other, so a boundary shown by the dotted lines is called an antiphase boundary (APB). The more disordered this APB is, the smaller the number of A-B bonds is and the smaller  $\phi^*$  is. However, it can be said that the phenomenon of domain growth by rearrangement of APBs is ordering.

If it is assumed that "each bond is independent and does not interfere mutually" to analyze the aforementioned ordering thermodynamically, then the enthalpy *H* can be approximated by a linear function of the order parameter ( $\varphi$ \*):\*

\*Bonds usually interact strongly with each other in a solid phase. The assumption that "each bond is independent" is correct only when the arrangement of atoms is almost completely in disorder, or in the state of a solid solution in the region of high temperature.



**Fig. 7.3** The two-dimensional model of short-range and long-range ordering ( $\circ$ , A;  $\bullet$ , B). In the short-range model (a), note the number of A-B bonds ( $P_{AB}$ ). On the other hand, in the long-range model (b), the order parameter is to be determined by noting the arrangement on the sublattice (for example,  $B_{II}$ )

$$H \approx \varepsilon_{AA} P_{AA} + \varepsilon_{BB} P_{BB} + \varepsilon_{AB} P_{AB}$$
$$= \frac{zN}{8} (\varepsilon_{AA} + \varepsilon_{BB} + 2\varepsilon_{AB}) + \frac{\Omega_{AB}}{4} \phi^* \qquad (Eq \ 7.3)$$

Here  $\varepsilon_{AA}$ ,  $\varepsilon_{BB}$ , and  $\varepsilon_{AB}$  are the energies per bond pair of each,  $\Omega_{AB} = zN$ [ $\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2$ ] is the parameter indicating the interactions between atoms, and  $\Omega_{AB} < 0$  in an alloy system where ordering occurs (see Eq 3.11).

On the other hand, the entropy *S* can be approximated by substitution into Boltzmann's relation (Eq 2.34) of all the combination of distributing zN/2 bonds to  $P_{AA}$ ,  $P_{BB}$ , and  $P_{AB}$ .

$$S \approx k_{\rm B} \ln W = k_{\rm B} \ln \left[ \frac{(zN/2)!}{P_{\rm AA}! P_{\rm BB}! P_{\rm AB}!} \right]$$
$$\approx (3/_4) zR \ln 2 - (zR/4) [(1 + \phi^*) \ln (1 + \phi^*) + (1 - \phi^*) \ln (1 - \phi^*)]$$
(Eq 7.4)

Here Stirling's approximation,  $\ln (n!) \approx n \ln n - n$ , and the relationship when the total atoms *N* is 1 mole,  $Nk_{\rm B} = R$  (the gas constant), are used.

By Eq 7.3 and 7.4, the free-energy change according to the short-range ordering ( $\Delta G_{\rm T}^*$ ) ordering and the equilibrium order parameter  $\varphi^*_{\rm e}$ , which satisfies the extreme value condition  $\partial (\Delta G^*)/\partial \varphi^* = 0$ , can be obtained:

$$(\Delta G^*) \text{ ordering} = \frac{\Omega_{AB}}{4} \phi^* + \frac{zRT}{4} [(1 + \phi^*) \ln (1 + \phi^*) + (1 - \phi^*) \ln (1 - \phi^*)]$$
(Eq 7.5)

$$\varphi_{\rm e}^* = \frac{1 - \exp\left[-(2/z)T_{\rm C}/T\right]}{1 + \exp\left[-(2/z)T_{\rm C}/T\right]}$$
(Eq 7.6)

Here  $T_{\rm C} = -\Omega_{\rm AB}/2R$  is the critical temperature of the long-range ordering considered in the next section.

The short-range order parameter  $\phi^*_e$  calculated by Eq 7.6 decreases largely in the low-temperature region as shown by the thin dashed lines in Fig. 7.4(b). On the other hand, the decrease is mild in the high-temperature region, and it never reaches  $\phi^*_e = 0$  even at a high temperature near the melting point.

By the way, did the aforementioned analysis elucidate the true characteristics of ordering?

"Ordering" is essentially one of the cooperative phenomena and has the feature that once an ordered arrangement appears locally, it spreads to surroundings and promotes ordering of an entire crystal. Therefore, the order parameter ought to change greatly in the neighborhood of a specific critical temperature ( $T_c$ ), and it can be thought that the aforementioned short-range ordering corresponds to small-scale ordering ( $\phi_e^* \ll 1$ ) in the high-temperature region.

Ordinary large-scale ordering was, as explained in the following section, elucidated by the long-range ordering model of Bragg and Williams (1934) and Gorsky (1928), in short, the B-W-G model (Ref 2, 3).

The short-range ordering and the long-range ordering are complementary ideas, and models to combine them were presented by Bethe (Ref 4), Fowler (Ref 5), Takagi (Ref 6), Kikuchi (Ref 7), and others. Refer to Ref 8 to 11 for explanations about them.



**Fig. 7.4** The short-range ordering in bcc solid solution (A:B = 1:1, z = 8). (a) The relationship between the free energy at  $T_1$  to  $T_4$  and the short-range order parameter (Eq 7.5). (b) Comparison of the short-range order parameter and the long-range order parameter

### 7.2 Analysis of CuZn Ordering by B-W-G Model

A typical example for order-disorder transformation is the CuZn ordering in the  $\beta$  phase (bcc) of the Cu-Zn system (see Fig. 7.2). This type of ordering by the B-W-G model is analyzed in this section.

### 7.2.1 Sublattice and Order Parameter

As shown in Fig. 7.5(a, upper), let a bcc lattice be divided into the sublattice I consisting of the corners, and the sublattice II of the body centers, and the order parameter to be defined by noticing the number of the B atoms on the II sublattice ( $B_{II}$ ) ( $A_{I}$ ,  $A_{II}$ , and  $B_{I}$  may be chosen instead of  $B_{II}$ ):

Long-range order parameter: 
$$\varphi = \frac{B_{\mathrm{II}} - (B_{\mathrm{II}})_0}{(B_{\mathrm{II}})_1 - (B_{\mathrm{II}})_0}$$
 (Eq 7.7)

Here  $(B_{\rm II})_1$  and  $(B_{\rm II})_0$  are the numbers of  $B_{\rm II}$  when  $\varphi = 1$  and  $\varphi = 0$ , respectively.

Since the lattice points of corners and body centers in a bcc lattice are quite equivalent to each other, both the numbers of lattice points in I and II are N/2. The half of sublattice points are occupied by the B atoms in the completely disordered state,  $\varphi = 0$ . Therefore, the following relationship is appropriate.

$$A_{\rm I} + B_{\rm I} = A_{\rm II} + B_{\rm II} = \frac{N}{2}, \ (B_{\rm II})_1 = \frac{N}{2}, \ (B_{\rm II})_0 = \frac{N}{4}$$
 (Eq 7.8)



**Fig. 7.5** Analysis of CuZn ordering by B-W-G model

Rearranging Eq 7.7 and 7.8, the numbers of A and B atoms on the sublattices can be obtained:

$$A_{\rm I} = B_{\rm II} = \frac{N}{4}(1+\phi), \ A_{\rm II} = B_{\rm I} = \frac{N}{4}(1-\phi)$$
 (Eq 7.9)

# 7.2.2 Change in Enthalpy and Entropy According to Ordering

First, if the energies per nearest-neighbor pair of atoms are expressed as  $\varepsilon_{AA}$ ,  $\varepsilon_{BB}$ , and  $\varepsilon_{AB}$ , the enthalpy can be approximated by

$$H = \varepsilon_{AA} \cdot P_{AA} + \varepsilon_{BB} \cdot P_{BB} + \varepsilon_{AB} \cdot P_{AB}$$
 (Eq 7.10)

Here  $P_{AA}$ ,  $P_{BB}$ , and  $P_{AB}$ , are the totals of atomic pairs, and, for example, the total of A-A pairs can be approximated by the following equation on the assumption of random distribution (the probability that the neighboring atom to an A atom on the I sublattice is A is equal to the mean fraction of A component on the II sublattice).\*

$$P_{\rm AA} \approx A_1 \cdot z \left(\frac{A_{\rm II}}{N/2}\right) = \frac{zN}{8}(1 - \varphi^2)$$
 (Eq 7.11)

The totals of B-B and A-B pairs can be expressed in the same manner.

$$P_{BB} \approx B_{I} \cdot z[B_{II}/(N/2)] = (zN/8)(1 - \varphi^{2})$$

$$P_{AB} \approx A_{I} \cdot z[B_{II}/(N/2)] + A_{II} \cdot z[B_{I}/(N/2)] = (zN/4)(1 + \varphi^{2})$$
(Eq 7.11a)

By rearranging the Eq 7.10 and 7.11, the approximation of the enthalpy H can be obtained:

$$H = (H)_{\varphi=0} + \frac{\Omega_{AB}}{4} \varphi^2$$
 (Eq 7.12)

Here  $(H)_{\phi=0} = (zN/8)(\varepsilon_{AA} + \varepsilon_{BB} + 2\varepsilon_{AB})$  is the enthalpy in the disordered state ( $\phi = 0$ ).  $\Omega_{AB} = zN[\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2]$  is the interaction

<sup>\*</sup>Though B atoms tend to gather in the neighbor of an A atom in an alloy where ordering occurs, B-W-G model ignores this tendency and assumes the random distribution. Because this kind of approximation was invented by P. Weiss (1907) to analyze ferromagnetic phenomena, it is called Weiss approximation, or the mean-field approximation.

parameter between A and B atoms (Eq 3.11), and, as a matter of course,  $\Omega_{AB} < 0$ . Therefore, the enthalpy reduces in proportion to  $\phi^2$  according to the long-range ordering.

Next, the change in entropy by ordering can be approximated using the Boltzmann's relation (Eq 2.34) and Eq 7.9.

$$S = k_{\rm B} \ln W = k_{\rm B} \ln \left[ \frac{(N/2)!}{A_{\rm I}! \cdot B_{\rm I}!} \right] \left[ \frac{(N/2)!}{A_{\rm II}! \cdot B_{\rm II}!} \right]$$
$$= (S)_{\phi=0} - (R/2)[(1+\phi) \ln (1+\phi) + (1-\phi) \ln (1-\phi)] \qquad (\text{Eq 7.13})$$

Here  $(S)_{\phi=0}$  (=  $R \ln 2$ ) is the entropy in the disordered state, and R (=  $k_{\rm B}N$ ) becomes the gas constant if N is Avogadro's number.

#### 7.2.3 Equilibrium Order Parameter

An equilibrium state of matter is determined by the condition of  $G = \min$ . Then, if the free energy of ordering and the minimal condition are calculated from Eq 7.12 and 7.13, two equations can be obtained:

$$(\Delta G)_{\text{ordering}} = (\Delta H)_{\text{ordering}} - T(\Delta S)_{\text{ordering}}$$
$$= (\Omega_{\text{AB}}/4)\varphi^2 + (RT/2)[(1+\varphi) \ln (1+\varphi) + (1-\varphi) \ln (1-\varphi)]$$
(Eq 7.14)

$$\left[\frac{\partial(\Delta G)_{\text{ordering}}}{\partial\phi}\right]_{\phi=\phi_e} = \frac{\Omega_{AB}}{2}\phi_e + \frac{RT}{2}\ln\left(\frac{1+\phi_e}{1-\phi_e}\right) = 0 \quad (\text{Eq 7.15})$$

Figures 7.5(a) and (b) correspond to Eq 7.14 and 7.15, respectively, and in particular Fig. 7.5(a) clearly indicates the feature of the long-range ordering (ordering occurs rapidly in the temperature region near the critical temperature,  $T_{\rm C}$ ). The critical point can be obtained according to the condition that  $\varphi = 0$  at a point of inflection (data point  $\times$ ) in Fig. 7.5(b).

$$T_{\rm C} = -\Omega_{\rm AB}/2R \tag{Eq 7.16}$$

**[Exercise 7.1]** Find out the heat capacity (specific heat) of a solid solution with A:B = 1:1 according to CuZn type of ordering by the B-W-G model.

**[Answer]** Because the heat capacity is the differential of the enthalpy *H* by the temperature *T*, it can be expressed according to Eq 7.12 and 7.16.

$$(\Delta C)_{\text{ordering}} = \frac{d(\Delta H)_{\text{ordering}}}{dT} = \frac{\Omega_{\text{AB}}}{2} \varphi_{\text{e}} \left(\frac{d\varphi_{\text{e}}}{dT}\right) = -RT_{\text{c}} \varphi_{\text{e}} \left(\frac{d\varphi_{\text{e}}}{dT}\right) \quad \text{(Eq 7.17)}$$

 $\varphi_e(d\varphi_e/dT)$  in Eq 7.17 can be rewritten by differentiating Eq 7.15 with respect to *T*.

$$\varphi_{\rm e}\left(\frac{d\varphi_{\rm e}}{dT}\right) = \frac{\varphi_{\rm e}^2(1-\varphi_{\rm e}^2)}{(1-\varphi_{\rm e}^2)-(T/T_{\rm c})}\left(\frac{1}{T}\right)$$
(Eq 7.18)

Therefore, the heat capacity can be approximated by

$$(\Delta C)_{\text{ordering}} = R \frac{\phi_e^2 (1 - \phi_e^2)}{(T/T_c) - (1 - \phi_e^2)} \left(\frac{T_c}{T}\right)$$
(Eq 7.19)

Figure 7.6 shows the calculated values of  $(\Delta G)_{\text{ordering}}$  and  $(\Delta C)_{\text{ordering}}$ by substituting the temperatures at each points of to in Fig. 7.5 and the value of equilibrium order parameter  $\varphi_e$  into Eq 7.14 and 7.19, and the heat capacity curve is called the  $\lambda$ -type heat capacity because it looks like the Greek letter  $\lambda$ . (See Section 2.4 "Thermodynamics of Magnetic Transition" for  $\lambda$ -type heat capacity.)

In order to obtain the value of heat capacity at the critical temperature  $T_c$ , First approximate Eq 7.15 by Taylor expansion:  $\ln (1 + x) \approx x - x^2/2 + x^3/3$ :

$$\frac{T_{\rm c}}{T} = \frac{1}{2\varphi_{\rm e}} \ln\left(\frac{1+\varphi_{\rm e}}{1-\varphi_{\rm e}}\right) \approx 1+\varphi_{\rm e}^2/3 \quad (\varphi_{\rm e} \ll 1) \tag{Eq 7.20}$$

From Eq 7.20 and Eq 7.19, the critical value of  $\lambda$ -type heat capacity can be obtained:

$$\left[ (\Delta C)_{\text{ordering}} \right]_{T \to T_c} = R \frac{\phi_e^2 (1 - \phi_e)^2}{(2/3)\phi_e^2} (1 + \phi_e^2/3) = \frac{3}{2}R \qquad (\text{Eq 7.21})$$



**Fig. 7.6** Change in free energy and the  $\lambda$ -type heat capacity due to CuZn ordering

**[Exercise 7.2]** Analyze the CuZn ordering in a bcc solid solution with A:B $\neq$ 1:1 by the B-W-G model, and find out the critical temperature  $T_c$  and the heat capacity  $[(\Delta C)_{\text{ordering}}]_{T_c}$  at which the order parameter becomes zero.

**[Answer]** Let  $x_B$  denote the fraction of B component in the solid solution, and there will be the following relationship in the numbers of A and B atoms that belong to the I sublattice (the corners) and the II sublattice (the body centers).

$$A_{\rm I} + A_{\rm II} = N(1 - x_{\rm B}), B_{\rm I} + B_{\rm II} = Nx_{\rm B}, A_{\rm I} + B_{\rm I} = A_{\rm II} + B_{\rm II} = N/2$$
 (Eq 7.22)

Because  $(B_{I})_0 = (B_{II})_0 = Nx_B/2$  for a completely disordered state, and  $(B_{II})_1 = Nx_B$  for a completely ordered state, the long-range order parameter is determined by

$$\varphi = \frac{B_{\rm II} - (B_{\rm II})_0}{(B_{\rm II})_1 - (B_{\rm II})_0} = \frac{B_{\rm II} - Nx_{\rm B}/2}{Nx_{\rm B}/2}$$
(Eq 7.23)

From Eq 7.22 and 7.23, the relationship between the numbers of A and B atoms on the I and II sublattices and the order parameter becomes:

$$A_{\rm I} = \frac{N}{2} [1 - x_{\rm B}(1 - \phi)], \ A_{\rm II} = \frac{N}{2} [1 - x_{\rm B}(1 + \phi)],$$
  
$$B_{\rm I} = \frac{N}{2} x_{\rm B}(1 - \phi), \ B_{\rm II} = \frac{N}{2} x_{\rm B}(1 + \phi)$$
(Eq 7.24)

The change in the enthalpy according to ordering can be obtained by the random distribution assumption:

$$(\Delta H)_{\text{ordering}} = \Omega_{\text{AB}} x_{\text{B}}^2 \phi^2 \qquad (\text{Eq 7.25})$$

On the other hand, the change in the entropy according to ordering is

$$(\Delta S)_{\text{ordering}} = \left\{ \begin{array}{l} [1 - x_{\text{B}}(1 - \phi)] \ln [1 - x_{\text{B}}(1 - \phi)] + [x_{\text{B}}(1 - \phi)] \ln [x_{\text{B}}(1 - \phi)] \\ + [1 - x_{\text{B}}(1 + \phi)] \ln [1 - x_{\text{B}}(1 + \phi)] + [x_{\text{B}}(1 + \phi)] \ln [x_{\text{B}}(1 + \phi)] \\ - 2[(1 - x_{\text{B}}) \ln (1 - x_{\text{B}}) + x_{\text{B}} \ln x_{\text{B}}] \end{array} \right\}$$
(Eq 7.26)

Moreover, according to the equilibrium condition:  $(\Delta G)_{\text{ordering}} = \min$ , the relationship between the equilibrium order parameter and the temperature can be expressed as:

$$-\frac{4\Omega_{AB}}{RT}x_{B}\phi_{e} = \ln\left\{\left(\frac{1+\phi_{e}}{1-\phi_{e}}\right)\left[\frac{1-x_{B}(1-\phi_{e})}{1-x_{B}(1+\phi_{e})}\right]\right\}$$
(Eq 7.27)

In order to obtain the temperature  $T_c$  for  $\phi_e \rightarrow 0$ , the right-hand side of Eq 7.27 is first approximated:

$$\begin{cases} \ln (1 + \varphi_{e}) - \ln (1 - \varphi_{e}) \approx 2\varphi_{e} + (2/3)\varphi_{e}^{3} \\ \ln [1 - x_{B}(1 - \varphi_{e})] - \ln [1 - x_{B}(1 + \varphi_{e})] \\ \approx 2\varphi_{e}x_{B}/(1 - x_{B}) + (2/3)[\varphi_{e}x_{B}(1 - x_{B})]^{3} \end{cases}$$
 (Eq 7.28)

By this approximation, Eq 7.27 can be simplified:

$$-\frac{\Omega_{AB}}{RT} \approx \frac{1}{2x_{B}(1-x_{B})} + \left[\frac{x_{B}^{3} + (1-x_{B})^{3}}{12x_{B}(1-x_{B})^{3}}\right] \varphi_{e}^{2}$$
(Eq 7.29)

Since the second term is vanished at the critical temperature,  $T_c$  can be shown as the equation of parabola (Fig. 7.7a).

$$T_{\rm C} = (-2\Omega_{\rm AB}/R)x_{\rm B}(1-x_{\rm B})$$
 (Eq 7.30)

Also, the heat capacity in accordance with ordering is as below by Eq 7.25.

$$(\Delta C)_{\text{ordering}} = \frac{d(\Delta H)_{\text{ordering}}}{dT} = 2\Omega_{\text{AB}} x_{\text{B}}^2 \varphi_{\text{e}} \left(\frac{d\varphi_{\text{e}}}{dT}\right)$$
(Eq 7.31)

The value of the last term of Eq 7.31,  $\varphi_e (d\varphi_e/dT)$ , can be expressed by differentiating both sides of Eq 7.29 with respect to *T*.

$$\varphi_{\rm e}\left(\frac{d\varphi_{\rm e}}{dT}\right) = \frac{3\Omega_{\rm AB}}{RT} \left[ \left(\frac{x_{\rm B}(1-x_{\rm B})^3}{x_{\rm B}^3 + (1-x_{\rm B})^3}\right) \right]$$
(Eq 7.32)

Rearranging Eq 7.30 to 7.32 and letting  $T \rightarrow T_c$ , the heat capacity of ordering at the critical temperature can be obtained:

$$\left[ (\Delta C)_{\text{ordering}} \right]_{T_c} = \frac{3}{2} R \left[ \frac{x_B (1 - x_B)}{x_B^3 + (1 - x_B)^3} \right]$$
(Eq 7.33)

As shown in Fig. 7.7(b), Eq 7.33 shows a nearly isosceles triangle with its vertex at A:B = 1:1.

# 7.3 Analysis of Cu<sub>3</sub>Au Ordering by B-W-G Model

Another typical ordering is the type of  $Cu_3Au$  in a fcc solid solution (Fig. 7.2). When a fcc lattice is divided into two sublattices, one of



Fig. 7.7 Generation region of CuZn ordering phase and the critical value of  $\lambda$ -type heat capacity in a solid solution of A-B system

which consists of face centers (data points  $\circ$  in Fig. 7.8(a, upper)) and the other consists of corners (data points  $\bullet$ ), one can analyze this kind of ordering by the B-W-G model if the total of lattice points on the sublattice I is 3N/4 and that on the sublattice II is N/4. Only four of the twelve lattice points neighboring to a I sublattice point are II sublattice points, and the other eight are I sublattice points. Thus, inequality between the sublattices I and II causes a peculiar "discontinuous ordering."

### 7.3.1 Degree of Order and Number of Atomic Pairs

If the numbers of A and B atoms on the sublattices I and II are written as  $A_{I}$ ,  $A_{II}$ ,  $B_{I}$ , and  $B_{II}$ , the following relationship will hold.

$$A_{\rm I} + A_{\rm II} = A_{\rm I} + B_{\rm I} = 3N/4, \ B_{\rm I} + B_{\rm II} = A_{\rm II} + B_{\rm II} = N/4$$
 (Eq 7.34)

The order parameter  $\varphi$  can be defined according to Eq 7.7:

Long-range order parameter: 
$$\varphi = \frac{B_{II} - (B_{II})_0}{(B_{II})_1 - (B_{II})_0} = \frac{B_{II} - N/16}{3N/16}$$
 (Eq 7.35)

Here  $(B_{\rm II})_1 = N/4$  and  $(B_{\rm II})_0 = N/16$  are the numbers of  $B_{\rm II}$  when  $\varphi = 1$  and  $\varphi = 0$ , and if this  $\varphi$  is used, then the total of A and B atoms on the sublattices I and II can be described:

$$A_{\rm I} = (3N/16)(3+\phi), \ A_{\rm II} = B_{\rm I} = (3N/16)(1-\phi), \ B_{\rm II} = (N/16)(1+3\phi)$$
  
(Eq 7.36)



Fig. 7.8 Analysis of Cu<sub>3</sub>Au ordering by B-W-G model

Moreover, the number of the nearest-neighbor pairs of atoms can be approximated according to the random distribution assumption.

$$P_{AA} = A_{II} \cdot 12 \cdot [A_{I}/(3N/4)] + (A_{I}/2) \cdot 8 \cdot [A_{I}/(3N/4)] = (3N/8)(9 - \phi^{2})$$

$$P_{BB} = B_{II} \cdot 12 \cdot [B_{I}/(3N/4)] + (B_{I}/2) \cdot 8 \cdot [B_{I}/(3N/4)] = (3N/8)(1 - \phi^{2})$$

$$P_{AB} = A_{II} \cdot 12 \cdot [B_{I}/(3N/4)] + B_{II} \cdot 12 \cdot [A_{I}/(3N/4)] + A_{I} \cdot 8 \cdot [B_{I}/(3N/4)]$$

$$= (3N/4)(3 + \phi^{2})$$
(Eq 7.37)

## 7.3.2 Change in Free Energy According to Ordering

Enthalpy *H* varies in proportion to  $\varphi^2$  according to Eq 7.37:

$$H = \varepsilon_{AA}P_{AA} + \varepsilon_{BB}P_{BB} + \varepsilon_{AB}P_{AB} = (H)_{\phi=0} + (\Omega_{AB}/16)\phi^2 \qquad (\text{Eq 7.38})$$

Here  $(H)_{\phi=0} = (3N/8)(9\epsilon_{AA} + \epsilon_{BB} + 6\epsilon_{AB})$  is the enthalpy in a disordered state, and  $\Omega_{AB} = 12N[\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2]$  is the interaction parameter.

On the other hand, entropy S can be obtained in the same way as derivation of Eq 7.13.

$$S = (S)_{\phi=0} - \frac{R}{16} \left[ 9 \left( 1 + \frac{\phi}{3} \right) \ln \left( 1 + \frac{\phi}{3} \right) + 6(1 - \phi) \ln (1 - \phi) + (1 + 3\phi) \ln (1 + 3\phi) \right]$$
(Eq 7.39)

From Eq 7.39, the change in free energy in accordance with ordering can be approximated by

$$(\Delta G)_{\text{ordering}} = \frac{\Omega_{\text{AB}}}{16} \phi^2 + \frac{R}{16} \left[ 9 \left( 1 + \frac{\phi}{3} \right) \ln \left( 1 + \frac{\phi}{3} \right) + 6(1 - \phi) \ln (1 - \phi) + (1 + 3\phi) \ln (1 + 3\phi) \right]$$
(Eq 7.40)

### 7.3.3 Discontinuous Change in Equilibrium Order Parameter

The equation of relationship between the equilibrium order parameter  $\phi_e$  and the temperature can be obtained by  $\partial (\Delta G)_{ordering} / \partial \phi = 0$ .

$$-\frac{2\Omega_{AB}}{3RT}\phi_{e} = \ln\left[\frac{(1+\phi_{e}/3)(1+3\phi_{e})}{(1-\phi_{e})^{2}}\right]$$
(Eq 7.41)

As shown in Fig. 7.8(a, lower), Eq 7.41 has two solutions (2 and 2', ① and ①') at the temperature of  $T_2$  to  $T_0$ . However, seeing the relationship between  $(\Delta G)_{\text{ordering}}$  and the order parameter  $\varphi$  (Fig. 7.8b), 2' and ①' are the maximum points, and  $(\Delta G)_{\text{ordering}} > 0$  at the temperature of  $T_1$  to  $T_0$ . Therefore, the true critical temperature  $T_c$  is  $T_1$ , and the order parameter  $\varphi_e$  varies discontinuously from ① of the data point • to ①'' of the data point  $\blacktriangle$ , that is,  $\varphi_e = 0$ . The temperature of 1 and the order parameter can be calculated:

> Critical temperature:  $T_c = T_1 = -\Omega_{AB}/7.3R$ Critical order parameter:  $(\phi_e)_{Tc} = 0.46$

The following exercise, shows how to arrange the aforementioned analysis.

**[Exercise 7.3]** Compare the change in free energy according to the allotropic transformation of Ti  $[\alpha(hcp) \stackrel{1156K}{\rightleftharpoons} \beta(bcc)]$  and the change in free energy according to the CuZn ordering, and consider the reason that the former is called the phase transition of First order and the latter is called the phase transition of second order. In addition, investigate the Cu<sub>3</sub>Au ordering from a similar view point.

**[Answer]** (i) The change in free energy according to the allotropic transformation is proportional to  $\Delta T$  in the region of small supercooling ( $\Delta T$ ):

$$\Delta G^{\beta \to \alpha} \approx \left[ \frac{d(G^{\alpha} - G^{\beta})}{dT} \right]_{T_{c}} \cdot \Delta T = -\left( \frac{\Delta H^{\alpha/\beta}}{T_{c}} \right) \cdot \Delta T \qquad (\text{Eq 7.42})$$

Here  $\Delta H^{\alpha/\beta}$  is the enthalpy change (the latent heat) according to the transformation, and  $\Delta H_{\text{Ti}}^{\beta/\alpha} = 4.1$  kJ/mol for the allotropic transformation of Ti. Therefore, the coefficient of  $\Delta T$  is  $\Delta H_{\text{Ti}}^{\alpha/\beta}/\text{Tc} = 3.55$  J/mol • K = 0.43 R. (ii) The change in free energy according to the CuZn ordering can be described by Eq 7.14.

$$(\Delta G)_{\text{CuZn}} = \frac{\Omega_{\text{CuZn}}}{4} \phi^2 + \frac{RT}{2} [(1+\phi) \ln (1+\phi) + (1-\phi) \ln (1-\phi)]$$

If this equation is rewritten by Taylor expansion  $\ln (1 + x) \approx x - x^2/2$  and Eq 7.16:  $\Omega_{AB} = -2RT_c$ , then the following equation can be obtained.

$$(\Delta G)_{\rm CuZn} \approx -(R/2)(T_{\rm c}-T)\varphi^2 = -(R/2)\Delta T \cdot \varphi^2$$

Also, if the relationship between the order parameter  $\varphi$  and the temperature *T*, Eq 7.15, is rearranged by the Taylor expansion, then the relationship between  $\varphi$  and  $\Delta T$  can be obtained:

$$-\frac{\Omega_{\text{CuZn}}}{2}\phi = \frac{RT}{2} \ln\left(\frac{(1+\phi)}{(1-\phi)}\right) \rightarrow \phi^2 \approx 3\frac{T_{\text{c}}-T}{T} = 3\frac{\Delta T}{T}$$

Therefore, the change in free energy according to the CuZn ordering is proportional to  $(\Delta T)^2$  in the neighborhood of the critical temperature  $T_c$  as shown by

$$(\Delta G)_{\rm CuZn} \approx -\frac{3R}{2T_{\rm c}} (\Delta T)^2$$
 (Eq 7.43)

From Eq 7.43, because the change in free energy according to the allotropic transformation is proportional to  $\Delta T$  and the change in free energy according to the CuZn ordering is proportional to  $(\Delta T)^2$ , each change is classified as a phase transition of first order or second order, respectively.

(iii) In the Cu<sub>3</sub>Au ordering, the order parameter  $\varphi$  varies  $0 \rightarrow 0.46$  discontinuously at the critical temperature  $T_{\rm C}$ , and the enthalpy change described (that is, production of the latent heat) occurs:

$$(\Delta H)_{\rm Cu_3Au} = \frac{\Omega_{\rm CuAu}}{16} \varphi^2 = -7.3 \frac{RT_{\rm c}}{16} (0.46)^2 = 0.096 RT_{\rm c}$$

However, in the ordering where  $\varphi$  changes 0.46  $\rightarrow$  1,  $\varphi$  will vary continuously in the same way as the type of CuZn. Consequently, the Cu<sub>3</sub>Au ordering can be regarded as a combined transformation of First and Second order because the free-energy change includes both the First and Second order of  $\Delta T$ . Figure 7.9 shows the changes in enthalpy and free energy according to these phase transformations in a comparable way.



Fig. 7.9 The change in enthalpy and free energy in accordance with first-order and second-order phase change

# 7.4 Phase Separation due to Ordering

### 7.4.1 Symbiosis of Ordering and Phase Separation

In the 1970s, it was discovered that both ordering and phase separation occur in such alloys as Fe-Al system (Ref 12, 13) and Cu-Zn system (Ref 14).

As mentioned in Section 4.4 the phase separation can usually be observed when A and B are repulsive, or in an alloy system with  $\Omega_{AB} > 0$ . On the other hand, ordering generally occurs in an alloy system where A and B are attractive, or when  $\Omega_{AB} < 0$ . Therefore, it was thought impossible in the beginning that ordering and phase separation occurred in the same alloy. However, as a result of close examination, it was recognized that ordering and phase separation are conflicting phenomena, but it is rather natural in some conditions that both of them live together.

The next section considers phase separation caused in CuZn ordering (i) when the interaction between the second nearest neighbor atoms is strong and (ii) when the third element is added.

# 7.4.2 Analysis on Ordering by B-W-G Model Considering Second Nearest Neighbor Atoms

Interactions of Atoms on Sublattices. In A-B system where ordered phase is formed, the interaction parameter between the nearestneighbor atoms is  $\Omega_{AB} \ll 0$ . However, it might be too hasty to infer that the interaction parameter between the second nearest neighbors (hereinafter, written as  $\Omega'_{AB}$ ) is similarly negative. The reason is, in order for the sublattices I and II of the AB ordered phase to be occupied by A atoms or B atoms as shown in Fig. 7.10(a), it is desirable that A and B atoms should exclude each other, or  $\Omega'_{AB} \gg 0$ .

If  $\Omega'_{AB} \gg 0$  and the composition is A:B  $\neq$  1:1, then light and shade ought to be caused on the sublattices as shown in Fig. 7.10(b), and as a result, in spite of  $\Omega_{AB} \ll 0$ , the phase separation of  $\alpha$  phase with a primary element of A from the AB ordered phase will occur.

On the contrary, if  $\Omega'_{AB} \ll 0$ , then ordered arrangement will occur on the sublattices, and an ordered phase with such a complicated structure as, for example, the type of Fe<sub>3</sub>Al (Fig. 7.14b described later) will be formed.

As described previously, the interaction between atoms on the sublattices will provide the structure of solid solution with variegated change.

**Enthalpy and Entropy in Consideration of Second Nearest Neighbors.** The enthalpy for bcc solid solution of A-B system can be approximated by adding the term of the second nearest neighbor pair of atoms to the enthalpy of the nearest neighbor pair of atoms (Eq 7.10).

$$H = \varepsilon_{AA} \cdot P_{AA} + \varepsilon_{BB} \cdot P_{BB} + \varepsilon_{AB} \cdot P_{AB} + \varepsilon'_{AA} \cdot P'_{AA} + \varepsilon'_{BB} \cdot P'_{BB} + \varepsilon'_{AB} \cdot P'_{AB}$$
(Eq 7.44)

Here  $\varepsilon'_{AA}$  (and so on) is the energy of atomic pairs on the sublattices,  $P'_{AA}$  (and so on) is the total of atomic pairs on the sublattice, which can be approximated by the random distribution assumption as.



**Fig. 7.10** Phase separation due to CuZn ordering. (a) A:B = 1:1. (b) A:B = 3:1. Solid lines indicate the nearest-neighboring bond ( $\Omega'_{AB} \ll 0$ ). Broken lines are the second nearest neighboring bond ( $\Omega'_{AB} \gg 0$ ).

$$P'_{AA} = (1/2)[A_{I}z'A_{I}/(N/2) + A_{II}z'A_{II}/(N/2)] = z'(A_{I}^{2} + A_{II}^{2})/N$$

$$P'_{BB} = (1/2)[B_{I}z'B_{I}/(N/2) + B_{II}z'B_{II}/(N/2)] = z'(B_{I}^{2} + B_{II}^{2})/N$$

$$P'_{AB} = A_{I}z'B_{I}/(N/2) + A_{II}z'B_{II}/(N/2) = 2z'(A_{I}B_{I} + A_{II}B_{II})/N$$
(Eq 7.45)

Here z' is the number of the nearest-neighbor atoms on the sublattices I and II, and z' = 6 because the sublattice of CuZn ordered phase is a simple cubic.

The analytical method below is quite similar to Exercise 7.2, and the order parameter and the numbers of A and B atoms on each of the sublattices in the A-B system consisting of B component with the mean fraction of  $x_{\rm B}$  ( $\leq \frac{1}{2}$ ) are

$$\varphi = \frac{B_{\rm II} - (B_{\rm II})_0}{(B_{\rm II})_1 - (B_{\rm II})_0} = \frac{B_{\rm II} - Nx_{\rm B}/2}{Nx_{\rm B}/2} A_1 = \frac{N}{2} [1 - x_{\rm B}(1 - \varphi)], \ A_{\rm II} = \frac{N}{2} [1 - x_{\rm B}(1 + \varphi)], B_{\rm I} = \frac{N}{2} x_{\rm B}(1 - \varphi), \ B_{\rm II} = \frac{N}{2} x_{\rm B}(1 + \varphi)$$
 (Eq 7.46)

By rearranging Eq 7.44 to 7.46, the enthalpy in a disordered state  $(H)_{\phi=0}$  and the change in enthalpy in accordance with ordering  $(\Delta H)_{\text{ordering}}$  can be obtained:

$$(H)_{\varphi=0} = H_{\rm A}(1-x_{\rm B}) + H_{\rm B}x_{\rm B} + (\Omega_{\rm AB} + \Omega'_{\rm AB})x_{\rm B}(1-x_{\rm B})$$
(Eq 7.47)

$$(\Delta H)_{\text{ordering}} = (\Omega_{\text{AB}} - \Omega'_{\text{AB}}) x_{\text{B}}^2 \phi^2 \qquad (\text{Eq 7.48})$$

Here  $\Omega_{AB} = zN[\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2]$  is the interaction parameter between the nearest-neighbor atoms,  $\Omega'_{AB} = z'N[\varepsilon'_{AB} - (\varepsilon'_{AA} + \varepsilon'_{BB})/2]$ is the interaction parameter in the sublattice, and  $H_A = N(z\varepsilon_{AA} + z'\varepsilon'_{AA})/2$  and  $H_B = N(z\varepsilon_{BB} + z'\varepsilon'_{BB})/2$  are the enthalpies of A component and B component when energies of the nearest bonds and the second nearest bonds are synthesized.

Comparing both Eq 7.47 and 7.48, the coefficient of mixing enthalpy in a disordered solid solution is  $(\Omega_{AB} + \Omega'_{AB})$ . On the other hand, the coefficient of enthalpy change according to ordering is  $(\Omega_{AB} - \Omega'_{AB})$ , and this difference will cause the phase separation.

Next, the entropy can be also approximated in quite the same manner as Exercise 7.2 as

$$(S)_{\varphi=0} = -R[(1 - x_{\rm B}) \ln (1 - x_{\rm B}) + x_{\rm B} \ln x_{\rm B}]$$
 (Eq 7.49)

$$(\Delta S)_{\text{ordering}} = -(R/2) \begin{cases} [1 - x_{\text{B}}(1 - \phi)] \ln [1 - x_{\text{B}}(1 - \phi)] \\ + x_{\text{B}}(1 - \phi) \ln [x_{\text{B}}(1 - \phi)] \\ + [1 - x_{\text{B}}(1 + \phi)] \ln [1 - x_{\text{B}}(1 + \phi)] \\ + x_{\text{B}}(1 + \phi) \ln [x_{\text{B}}(1 + \phi)] \\ - 2[(1 - x_{\text{B}}) \ln (1 - x_{\text{B}}) + x_{\text{B}} \ln x_{\text{B}}] \end{cases}$$
(Eq 7.50)

**Critical Temperature of Ordering.** When the change in free energy according to ordering  $(\Delta G)_{\text{ordering}}$  is calculated from Eq. 7.48 and 7.50, and the conditional equation  $(\Delta G)_{\text{ordering}} = \min$  is solved, the following equation, which defines the equilibrium order parameter  $\varphi_{e}$ , can be obtained.

$$-\frac{4(\Omega_{AB} - \Omega'_{AB})}{RT} x_B \varphi_e = \ln \left\{ \left( \frac{1 + \varphi_e}{1 - \varphi_e} \right) \left[ \frac{1 - x_B(1 - \varphi_e)}{1 - x_B(1 + \varphi)} \right] \right\}$$
(Eq 7.51)

Because Eq 7.51 is quite the same type as Eq 7.27, it can be seen that the critical temperature of ordering  $T_c$  is expressed by the following equation of a parabola.

$$T_{\rm c} = \left[\frac{-2(\Omega_{\rm AB} - \Omega'_{\rm AB})}{R}\right] x_{\rm B}(1 - x_{\rm B})$$
(Eq 7.52)

Figure 7.11 (lower) shows the phase diagrams when the values of  $\Omega_{AB}$  and  $\Omega'_{AB}$  are modified so that the term [ ] in Eq 7.52 is +8000 K, and the dotted lines indicate the critical temperature of ordering.

**Phase Separation into Ordered Phase (** $\alpha_0$ **) and Disordered Phase (** $\alpha$ **).** If the combinations of the composition ( $x_B$ ) and the equilibrium order parameter ( $\phi_e$ ) at a temperature *T* are calculated by Eq 7.51, and these values of  $T - x_B - \phi_e$  are substituted into Eq 7.47 to 7.50, then the free-energy curve at each temperature can be obtained. Figure 7.11 (upper) shows the samples of calculation, all of the free-energy curves for the three cases (a), (b), and (c) are concave in the composition region of 1 to 2, and the phase will be separated into an ordered phase ( $\alpha_0$ ) and a disordered phase ( $\alpha$ ).

While an ordinary binodal curve is domelike, "the binodal curve according to ordering" looks like a mountain with an edge on the top, and the vertex ③ is called the edge-critical point. The edge-critical point is also called "the tricritical point," but the former is used here in order not to be confused with the triple point where a gas, a liquid, and a solid phase of a pure substance coexist. See Ref 15 and 16 for details.

Point ④ in Fig. 7.11(a) is the edge-critical point of the inverted type, and the transition point from the two-phase of the ordered phases  $(\alpha_0 + \alpha'_0)$  to the two-phase of the ordered phase  $(\alpha'_0)$  + the disordered phase  $(\alpha)$ . This sort of complicated phase separation is observed in an ordered structure of such an alloy as Fe-Al system (Ref 12, 13).



**Fig. 7.11** Examples of calculation of phase separation due to ordering. Upper, free-energy diagram; lower, equilibrium phase diagrams. Because each is symmetric, the region of  $x_{\rm R} > 0.5$  is omitted.

### 7.4.3 Miscibility Gap Island in Consideration of Ordering

If B-C bonds are far stronger than A-B and A-C bonds in A-B-C solid solution, then the two-phase region is formed,  $\alpha'$  solid solution with primary elements of B and C and  $\alpha$  solid solution with a primary element of A (Fig. 7.12a.) This two-phase separation phenomenon called "the miscibility gap island" has already been investigated using the ordinary regular solution model in Exercise 4.12.

However, it is certain that the phase equilibrium will be influenced remarkably by ordering in a solid solution where B-C bonds are strong. So, the influence by the B-W-G model with ordering taken into account is reviewed.

**[Exercise 7.4]** Show that there will appear a miscibility gap island that has such an edge as shown in Fig. 7.12(b), in a bcc solid solution of A-B-C system where CuZn ordering is formed in B-C system. Let the interaction parameters between the nearest-neighbor atoms be  $\Omega_{BC} = -8000 R$ ,  $\Omega_{AB} = \Omega_{AC} = 0$ , and the interaction parameters between the second nearest neighbor atoms be  $\Omega'_{AB} = \Omega'_{AC} = 0$ .

**[Answer]** Here, analysis of A-BC pseudobinary system is described. As for the whole aspect of a ternary system, see Ref 17.



Fig. 7.12 The miscibility gap island in A-B-C ternary system (see Fig. 4.18). (a) In a disordered solid solution. (b) When ordering is considered

In a way similar to Exercise 4.12, the composition scale *y* on the line of A-BC is defined as

$$y = 1 - x_{\rm A} = 2x_{\rm B} = 2x_{\rm C}$$
 (Eq 7.53)

The total of C atoms locating at the body centers of bcc (II sublattice),  $C_{\text{II}}$  is equal to the average,  $(N/2)x_{\text{C}} = (N/4)y$ , in a disordered state. On the other hand, because all of C atoms locate on the II sublattice in a completely ordered state,  $(C_{\text{II}})_1 = N \cdot x_{\text{c}} = (N/2)y$ . Therefore, the order parameter  $\varphi$  can be defined by

$$\varphi = \frac{C_{\rm II} - (C_{\rm II})_0}{(C_{\rm II})_1 - (C_{\rm II})_0} = \frac{C_{\rm II} - (N/4)y}{(N/4)y}$$
(Eq 7.54)

Consequently, the number of each atoms on the I sublattice and the II sublattice can be expressed as

$$A_{\rm I} = N(1-y)/2, \ B_{\rm I} = Ny(1+\phi)/4, \ C_{\rm I} = Ny(1-\phi)/4 \\ A_{\rm II} = N(1-y)/2, \ B_{\rm II} = Ny(1-\phi)/4, \ C_{\rm II} = Ny(1+\phi)/4$$
 (Eq 7.55)

Next, the number of atomic pairs, for example the C-C pairs and the B-C pairs, are as follows by the random assumption.

$$P_{CC} = C_{I}ZC_{II}(N/2) = (zN/8)y^{2}(1 - \varphi^{2})$$

$$P_{BC} = B_{I}ZC_{II}(N/2) + B_{II}ZC_{I}/(N/2) = (zN/4)y^{2}(1 + \varphi^{2})$$
(Eq 7.56)

From the above, the enthalpy H is

$$H = \varepsilon_{AA}P_{AA} + \varepsilon_{BB}P_{BB} + \varepsilon_{CC}P_{CC} + \varepsilon_{AB}P_{AB} + \varepsilon_{AC}P_{AC} + \varepsilon_{BC}P_{BC}$$
$$= H^{\alpha} + (\Omega_{AB}/4)y^{2}\phi^{2}$$
(Eq 7.57)

Here  $H^{\alpha}$  is the enthalpy of the disordered  $\alpha$  solid solution and can be approximated by

$$H^{\alpha} = (zN/2)[\varepsilon_{AA}(1-y) + \varepsilon_{BB}(y/2) + \varepsilon_{CC}(y/2)] + \Omega_{BC}(y/2)^2$$

Moreover, the entropy S is

$$S = k_{\rm B} \cdot \ln (N!/A_{\rm I}! \cdot A_{\rm II}! \cdot B_{\rm I}! \cdot B_{\rm I}! \cdot C_{\rm I}! \cdot C_{\rm I}!)$$
  
=  $S^{\alpha} - (R/2)y[(1+\phi) \ln (1+\phi) + (1-\phi) \ln (1-\phi)]$  (Eq 7.58)

Here,  $S^{\alpha}$  is the entropy of the disordered  $\alpha$  solid solution and can be approximated by

$$S^{\alpha} = R[y \ln 2 - (1 - y) \ln (1 - y) - y \ln y]$$

The equilibrium order parameter  $\varphi_e$  is prescribed by the condition of  $G = H - TS = \min$ , or:

$$\frac{1}{y} \left( \frac{\partial G}{\partial \varphi} \right)_{\varphi_{e}} = \left( \frac{\Omega_{\rm BC}}{2} y \right) \varphi_{e} + \frac{RT}{2} \ln \left( \frac{1 + \varphi_{e}}{1 - \varphi_{e}} \right) = 0 \quad (\text{Eq 7.59})$$

If Eq 7.59 is compared with Eq 7.15, then it can be seen that the critical temperature of ordering  $T_c$  is proportional to y as shown:

$$T_{\rm c} = -\frac{\Omega_{\rm BC}}{2R} y =^{\circ} T_{\rm c} \cdot y \tag{Eq 7.60}$$

Here  ${}^{\circ}T_{\rm c} (= -\Omega_{\rm BC} / 2R)$  is the vertex of the critical temperature of the B-C system.

If the combinations of the composition (y) and the equilibrium order parameter  $(\phi_e)$  obtained from Eq 7.59 are substituted into Eq 7.57 and 7.58, then the free energy curve at each temperature can be obtained. Figure 7.13(a) is the analysis when T = 1500 K and the tangent  $\bigcirc$  ...  $\oslash$ indicates the two-phase equilibrium between the disordered phase  $(\alpha)$  and the ordered phase  $(\alpha_0)$ , that is, the miscibility gap.



**Fig. 7.13** The analysis of the miscibility gap island extended by ordering (see Fig. 4.18). (a) Free energy of A-BC system (T = 1500 K). (b) Phase diagram of A-BC system. (c) Phase diagram of A-B-C system

The phase separation obtained in Exercise 4.12 is the case in a disordered state, and the vertex of the domelike miscibility gap island  $T_s$  was 1000 K. On the other hand, the miscibility gap in consideration of ordering looks like a mountain with edges, and the temperature at the vertex of edges (tricritical point)  $T_t$  increases to 2400 K. According to this, the composition width of phase separation region will be expanded remarkably.

#### EXERCISES

**7.5** Examine the antiphase boundary in an ordered structure and the domain wall in a ferromagnetic material, and consider their common features and different points.

**7.6** Analyze the CuAu(L1<sub>0</sub>) ordering (Fig. 7.14a) by the B-W-G model with only the interaction between the nearest-neighbor atoms taken into account, and show that the critical temperature is expressed as  $T_{\rm c} = -\Omega_{\rm AB}^{\rm fcc}/6R$ .

7.7 Show that the critical temperature of transition of a bcc solid solution with a composition of A:B = 3:1 from an ordered phase of the CuZn (B2) type to an ordered phase of the Fe<sub>3</sub>Al(D0<sub>3</sub>) type can be expressed as  $T_{\rm c} = -\Omega'_{\rm AB}/2R$  according to the B-W-G model. Here  $\Omega'_{\rm AB}$  is the interaction parameter between the second nearest neighbor atoms (Fig. 7.14b).


Fig. 7.14 CuAu ordering and Fe<sub>3</sub>Al ordering

**7.8** Show the enthalpy and the entropy for a solid solution of a binary system with a ferromagnetic metal M and a paramagnetic metal Y can be approximated according to Ising model (see Section 2.4.3).

$$H^{\alpha} = H^{\alpha}_{\text{para}} + \Delta H^{\alpha}_{\text{mag}}, \ \Delta H^{\alpha}_{\text{mag}} \approx -(zN\varepsilon/2)[(1-y)X]^2$$
(Eq 7.61)

$$S^{\alpha} = S^{\alpha}_{\text{para}} + \Delta S^{\alpha}_{\text{mag}}$$
$$\Delta S^{\alpha}_{\text{mag}} \approx -R(1-y) \left[ \frac{1+X}{2} \ln \left( \frac{1+X}{2} \right) + \frac{1-X}{2} \ln \left( \frac{1-X}{2} \right) \right] \quad \text{(Eq 7.62)}$$

Also, show that the relationship between  $X_e$  and T satisfying the minimum condition of free energy,  $[\partial G^{\alpha} / \partial X] = 0$ , can be expressed by

$$T_{\text{mag}}(1-y)X_{\text{e}} = (T/2) \ln \left[ (1+X_{\text{e}})/(1-X_{\text{e}}) \right]$$
 (Eq 7.63)

Here  $\varepsilon$  is the energy of spin pairs,  $X = (N_+ - N_-)/(N_+ + N_-)$  is the ferromagnetic parameter, y is the molar fraction of Y atoms, and  $T_{\text{mag}}$  is the Curie temperature of M.

In addition, substitute the values of  $X_e$  and T obtained from Eq 7.63 into Eq 7.61 and 7.62 and draw the phase diagram of the M-Y alloy.

*Hint*: Figure 7.15 is a calculated example on the assumption that the interaction parameter of the paramagnetic solid solution is  $\Omega^{\alpha}_{MY} = RT_{mag}$ . See Ref 18 and 19 for details.



Fig. 7.15 The phase separation due to magnetic transition. Source: Ref 18 and 19



**Fig. 7.16** (a) Precipitated structure by ordinary phase separation. (b) Precipitated structure of inversion type by edge-critical separation. (c) Microstructure of a Fe-Cr-Co magnetic alloy aged in magnetic field. Photograph by M. Okada, M. Homma, H. Kaneko, and G. Thomas

# Appendix: Effect of the Inversion Type of Phase Separation

Precipitated alloys are usually produced by aging at temperature  $T_3$  in the two-phase region of a supersaturated solid solution rapidly cooled from temperature  $T_1$  in the single-phase region, and nucleation and growth of subphase  $\alpha_2$  in the main phase c.

However, the inversion structure in which a main phase is dispersed in a subphase often demonstrates a special effect in such an alloy as is produced by an order-disorder transition or a magnetic transition. The typical one is a Fe-Cr-Co magnet developed by Kaneko et al. (Ref 20); use is made of inclination of the two-phase separation region according to magnetic transformation toward the side of Fe-Co, and the main phase, a ferromagnetic  $\alpha_f$  (Fe-Co) is precipitated in a paramagnetic  $\alpha_p$ with a primary component of Cr as a substrate phase that ought to be a subphase naturally. See Fig 7.16.

Particularly, if the step aging is carried out in a magnetic field, the  $\alpha_f$  phase of a single magnetic domain size forms a structure oriented to the easy-magnetization direction  $\langle 100 \rangle_{bcc}$ , and the performance of the magnet will improve remarkably.

Alnico alloys, the king of magnets until the 1980s, are also two-phase alloys of inversion type in which a ferromagnetic  $\alpha_f$  phase is precipitated in a paramagnetic NiAl ordered phase as a substrate (Ref 21).

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CHAPTER **E** 

# Thermodynamics of Nucleation

"Nucleation" is an absolutely necessary process for the birth of microscopic structure, and various studies on it have been attempted since olden times. However, "a nucleus" is not only extremely small (around  $10^{-9}$  m), but also extremely ephemeral ( $10^{-3}$  to  $10^{-13}$  s). Therefore, it is most difficult to grasp the realities of "a nucleus," and a lot of unsolved problems have been carried over to the 21st century. This chapter discusses the fundamental ideas of "classical nucleation theory" established by our predecessors and its application examples, and classical means not old-fashioned but orthodox here. Do not misunderstand it!

# 8.1 Basic Subjects of Nucleation

# 8.1.1 Small Droplets Experiment

In the 1940s and 1950s, skillful experiments called "the droplet method" were carried out by Turnbull et al., and the study of nucleation progressed remarkably (Ref 1–3). In order to understand the principle of this experimental method, think of the following easy problem.

**[Exercise 8.1]** If a substance in which fine particles disperse is divided into cubic cells of side 1  $\mu$ m, then how many particles will be included in a cell? Here, a dispersion particle is presumed to be a cube of side 10 nm and the volume fraction of total amount is  $10^{-6}$ .

**[Answer]** If the total volume of the substance is presumed to be  $1 \text{ m}^3$ , then the total volume of dispersion particles is  $10^{-6}\text{m}^3$ . Because the volume of a particle is  $(10 \text{ nm})^3 = 10^{-24}\text{m}^3$ , the total of particles is  $10^{-6}/10^{-24} = 10^{18}$ . On the other hand, because the total of divided cells is also  $1 \text{ m}^3/(10^{-6}\text{m})^3 = 10^{18}$ , the average number of particles in a cell is one (Fig. 8.1a).



**Fig. 8.1** Experiment on the spontaneous nucleation by the droplet method. (a) Principle of droplet method. (b) Observation with an optical microscope. (c) Observation of volume change. Source: Ref 1–3

Even a pure substance usually contains impurities of around 1 point per million (ppm). However, the above calculation implies that if it is divided into droplets of diameter less than 1 µm, then some of them do not include any impurity particles at all. Then, high-purified water droplets were floated in the interface between two liquid phases A of lighter specific gravity than water and B of heavier as shown in Fig. 8.1(b); they were observed with microscopy during cooling, and the maximum supercooling was estimated as  $\Delta T_{\text{max}} \approx 40$  K. On the other hand, as is shown in (C), high-purified Pb droplets were isolated from each other by an organic liquid of high-melting-point C, the temperature at which volume shrinkage occurred according to solidification was measured, and it was estimated that  $\Delta T_{\text{max}} \approx 80$  K.

This small droplets experiment was performed on the basis of a hypothesis that solidification starting point is not "an atom" but "a group of atoms (critical nucleus)," and solidification is caused by impurity particles (if it is caused by impurity atoms, then it is necessary to make fine droplets of less than 30 nm, and it is impossible to make an experiment).

This "critical nucleus theory" was presented by Volmer and A. Weber (1926) (Ref 4) and Becker and Döring (1935), (Ref 5) about 20 years before the small droplets experiment by Turnbull et al. (Ref 2). This is called VWBD theory. The gist of it is considered after the next section.

## 8.1.2 Homogeneous Nucleation (Spontaneous Nucleation)

First, think about nucleation in a pure substance without any impurity particles at all. This is called the homogeneous nucleation (or the spontaneous nucleation).



Fig. 8.2 The process and the energy change of spontaneous nucleation (homogeneous nucleation)

**Embryo and Critical Nucleus.** If a globular particle of a new phase (a liquid phase or a solid phase) is produced in a supercooled phase (a gas phase or a liquid phase), the change in free energy per particle can be expressed by

$$\Delta g = -(\Delta G/V) \cdot (4\pi/3)r^3 + \sigma \cdot 4\pi r^2$$
Volume energy Interface energy (Eq 8.1)

Here  $\Delta G$  is the change in free energy according to the transformation, V is the molar volume,  $\sigma$  is the interface energy, and the value of  $\Delta g$  reaches the maximum  $\Delta g_c$  at the following radius  $r_c$  as shown in Fig. 8.2.

$$(\partial \Delta g/\partial r)r_{\rm c} = 0 \rightarrow r_{\rm c} = 2\sigma V/\Delta G, \ \Delta g_{\rm c} = (4\pi/3)r_{\rm c}^2\sigma$$
 (Eq 8.2)

Because the change in free energy is upward while the radius is less than  $r_c$ , the new phase particle is metastable and it will be annihilated immediately after it is generated. The new phase particle in such a state is called an embryo. However, because once the radius goes beyond  $r_c$ the change in free energy becomes downward, the new phase particles will go on growing.

This  $r_c$  is called the critical radius, and a new phase particle of radius  $r_c$  is called the critical nucleus.

In general, the free energy of transformation  $\Delta G$  is proportional to the degree of supercooling  $\Delta T$ :\*

<sup>\*</sup>For example, the change in free energy of a gas phase  $\rightarrow$  a liquid phase is  $\Delta G = (\Delta H_b/T_b) \cdot \Delta T$ (Eq 5.14).

$$\Delta G = (\Delta H/T_{\rm e}) \cdot \Delta T \tag{Eq 8.3}$$

Here  $T_e$  is the transformation point, and  $\Delta H$  is the latent heat of transformation. Therefore, if the degree of supercooling  $\Delta T$  is measured, then  $r_c$  and  $\Delta g_c$  can be estimated by the following equations.

$$r_{\rm c} = \frac{2\sigma V}{\Delta G} = \left(\frac{2VT_{\rm e}}{\Delta H}\right) \cdot \frac{\sigma}{\Delta T}, \quad \Delta g_{\rm c} = \frac{4\pi}{3}r_{\rm c}^2\sigma = \left(\frac{16\pi V^2T_{\rm c}^2}{3\Delta H^2}\right) \cdot \frac{\sigma^3}{\Delta T^2} \quad ({\rm Eq} \ 8.4)$$

**[Exercise 8.2]** Small droplet experiments were made on pure water and Cu, and the maximum supercoolings were measured as 40 K for water, and 236 K for Cu. Find out  $r_c$  and  $\Delta g_c$  according to the values shown in Table 8.1.

**[Answer]** If the case of water  $\rightarrow$  ice is explained, because the latent heat of fusion is  $\Delta H_{\rm m} = 6000 \,\text{J/mol}$ , the interface energy is  $\sigma^{\rm ice/water} = 0.025 \,\text{J/mol}^2$ , the following values can be obtained from Eq 8.4.

$$r_{\rm c} = \frac{2 \times 18 \times 10^{-6} \times 273 \times 0.025}{6000 \times 40} = 1.02 \times 10^{-9} \,\mathrm{m}$$
$$\Delta g_{\rm c} = \frac{4\pi}{3} (1.02 \times 10^{-9})^2 \times 0.025 = 1.09 \times 10^{-19} \,\mathrm{J}$$

Table 8.1 Calculated values for parameters regarding solidification and for the critical nuclei of water and Cu

		Latent heat		Maximum degree of			
Substance	Melting point $(T_m)$ , K	of fusion $(\Delta H_m)$ , kJ/mol	Molar volume (V), m <sup>3</sup> /mol	$\begin{array}{c} Interface \\ energy \ (\sigma), \ J/m^2 \end{array}$	supercooling $(\Delta T_{\text{max}})$ , K	Critical radius ( <i>r</i> <sub>c</sub> ), m	Critical nucleus energy $(\Delta g_c)$ , J
H <sub>2</sub> O Cu	273 1356	6.0 13.1	$\begin{array}{c} 18 \times 10^{-6} \\ 7.9 \times 10^{-6} \end{array}$	0.025 0.18	40 236	$\substack{1.02\times10^{-9}\\1.25\times10^{-9}}$	$\substack{1.09\times10^{-19}\\1.17\times10^{-18}}$



**Fig. 8.3** The number of atoms and the ratio of atoms on the outermost layer forming a closepacked cluster. (The number of atoms on the outermost layer exceeds 50% of the total composing atoms in a smaller cluster than the type of a regular icosahedron of i = 6.)

Thus, the radius of a critical nucleus is usually  $r_c \approx 1 \text{ nm.*}$ 

**Equilibrium Distribution Density of Critical Nuclei.** Consider how much density the above critical nuclei exist with in the following exercise.

**[Exercise 8.3]** Show that the number of critical nuclei existent in 1 mole of a supercooled liquid phase can be approximated by:

$$N_{\rm c} = N \exp\left(-\Delta g_{\rm c}/k_{\rm B}T\right) \tag{Eq 8.5}$$

Here N is Avogadro's constant, and  $k_{\rm B}$  is the Boltzmann constant.

**[Answer]** Let *n* denote the number of atoms forming a critical nucleus. Approximate a liquid phase by a lattice model (the total of lattice points is *N*) analogous to a crystal. The total of random configuration of  $N_c$  critical nuclei  $W_{\text{config}}$  can be expressed by the following equation in consideration that *n* lattice points are occupied as each critical nucleus is arranged.

$$W_{\text{config}} = \frac{N \cdot (N - n) \cdot (N - 2n) \cdots [N - (N_{\text{c}} - 1)n]}{N_{\text{c}}!}$$
$$= \frac{N_{\text{n}}!}{(N_{\text{n}} - N_{\text{c}})!N_{\text{c}}!} \cdot n^{N_{\text{c}}}$$
(Eq 8.6)

Here  $N_n = N/n$  is the number of lattice points per critical nucleus.

Therefore, the entropy of configuration can be obtained by the Boltzmann equation (Eq 2.34).

$$\Delta S_{\text{config}} = k_B \ln W_{\text{config}}$$
$$= k_B \left[ \ln \left( \frac{N_c}{N_n} \right) + (N_n - N_c) \ln \left( 1 - \frac{N_c}{N_n} \right) - N_c \ln n \right] \quad (\text{Eq 8.7})$$

\*If it is assumed that a crystal nucleus has a close-packed structure, the number of atoms or molecules n forming a critical nucleus of radius  $r_c$  can be roughly estimated by:

$(4\pi/3)r_{\rm c}^3$	$\times$	0.74	=	$(4\pi/3)r_{a}^{3}$	Х	n
Volume		Packing		Volume		Number of
of a		factor		of an		composing
critical				atom		atoms
nucleus						

In the case of Cu in Table 8.1, n = 690 because the atomic radius is  $r_a = 0.128$  nm. In the case of ice, n = 100 because the volume of a molecule is  $3 \times 10^{-29}$ m<sup>3</sup>, and the volume of a critical nucleus is  $4.4 \times 10^{-27}$ m<sup>3</sup>. According to the model shown in Fig. 8.3, the critical nucleus of Cu is a regular icosahedron with six layers on each face. That of ice is nearly three or four layered cluster.

Because the formation energy of one critical nucleus is  $\Delta g_c$ , the change in free energy in accordance with the formation of  $N_c$  critical nuclei is

$$\Delta G = \Delta g_{c} \cdot N_{c} - T \cdot \Delta S_{config}$$
  
=  $\Delta g_{c} \cdot N_{c} + k_{B}T \left[ N_{c} \ln \left( \frac{N_{c}}{N_{n}} \right) + (N_{n} - N) \ln \left( 1 - \frac{N_{c}}{N_{n}} \right) - N_{c} \ln n \right]$   
(Eq 8.8)

The condition for  $\Delta G = \min$  is as below.

$$O = \partial \Delta G / \partial N_{\rm c} = \Delta g_{\rm c} + k_{\rm B} T \ln\{(N_{\rm c}/N_{\rm n})/n[1 - (N_{\rm c}/N_{\rm n})]\}$$
(Eq 8.9)

Rearranging Eq 8.9 in consideration of  $N_c/N_n \ll 1$ , Eq 8.5 in question can be obtained.

In the case of Cu shown in Table 8.1, because  $T = T_{\rm m} - \Delta T_{\rm max} = 1120 \,\text{K}$  and  $\Delta g_{\rm c} = 1.17 \times 10^{-18} \,\text{J}$ ,

$$N_{\rm c} = 6 \times 10^{23} \exp(-1.17 \times 10^{-18} / 1.38 \times 10^{-23} \times 1120) = 8 \times 10^{-10} \text{mol}^{-1}$$

If the above is converted into the value per unit volume, then  $N_c/V = 8 \times 10^{-10}/7.8 \times 10^{-6} = 10^{-4} \text{m}^{-3}$ , and the equilibrium density of critical nuclei is extremely small.

**Nucleation Rate.** Because nucleation is a dynamic process, it must be considered not "how many nuclei exist in a unit volume," but "how many nuclei are created in a unit time." This is called the nucleation rate, and it can be expressed by the product of the density of critical nuclei and the transition rate of embryos into critical nuclei as

$$I$$
(nucleation rate) =  $(N_c/V) \times v_c$  (transition rate) (Eq 8.10)

As was mentioned previously, a critical nucleus becomes a crystal if only one atom is added or, becomes an embryo if only one atom breaks away. Therefore, the value of  $v_c$  is, as in the following equation, equal to the product of the number of atoms on the surface of a critical nucleus  $n_s$ and the times of atomic transition in a unit time  $v_+$ .

$$v_c \approx n_s \cdot v_+$$
 (Eq 8.11)

Moreover, because the value of  $n_s$  is approximated by the number of squares with side of an atomic diameter  $2r_a$ , which is necessary for covering the surface, and  $v_+$  can be estimated from the diffusion coefficient of a liquid phase  $D^L$  and the jumping distance  $\lambda = 2 r_a$  according to the

fundamental equation about the diffusion coefficient,  $D = v_+ \cdot \lambda^2$  (Eq 6.8),  $v_c$  can be obtained by

$$v_{\rm c} \approx \frac{4\pi r_{\rm c}^2}{(2r_{\rm a})^2} \cdot \frac{D^{\rm L}}{(2r_{\rm a})^2} = \frac{\pi r_{\rm c}^2}{4r_{\rm a}^4} D^{\rm L}$$
 (Eq 8.12)

**[Exercise 8.4]** Estimate the homogeneous nucleation rate in solidification of pure Cu by the values in Table 8.1. The diffusion coefficient of the liquid phase is presumed as  $D^{\rm L} \approx 10^{-9} {\rm m}^2/{\rm s}$  according to Fig. 6.14.

**[Answer]** The transition rate from an embryo to a critical nucleus is extremely large as shown.

$$v_{\rm c} \approx \frac{\pi \cdot (1.25 \times 10^{-9})^2}{4 \cdot (0.128 \times 10^{-9})^4} \times 10^{-9} = 4.6 \times 10^{12} {\rm s}^{-1}$$

On the other hand, because the density of critical nuclei is extremely small,  $N_c/V = 10^{-4} \text{m}^{-3}$ , the nucleation rate is

$$I(\Delta T = 236 \text{ K}) = 4.6 \times 10^8 \text{ m}^{-3}/\text{s} = 0.46 \text{ mm}^{-3}/\text{s}$$

That is, if a supercooled liquid phase of volume  $1 \text{ mm}^3$  is noticed, one nucleus is created nearly every 2 s. As shown in Fig. 8.4(b, lower), when the degree of supercooling increases by only 10 K (4% of  $\Delta T_{\text{max}}$ ) the nucleation rate will increase by several hundred times.



Fig. 8.4 Frequency of spontaneous nucleation. (a) Schematic representation. (b) Calculated values of nucleation energy and rate for solidification of pure Cu

### 8.1.3 Heterogeneous Nucleation (Interface Nucleation)

Actual nucleation is not such a spontaneous nucleation as mentioned previously, but often occurs on the surface of a substrate.\* This is called the heterogeneous nucleation (or the interface nucleation), and it has been analyzed by the lens model or the disk model (also called the pillbox model).

**Lenticular Critical Nucleus Model.** When nucleation of a liquid phase (II) is generated in the interface between a supercooled gas phase or liquid phase (I) and a substrate (III), the following relationship between each interface energy is approved according to an approximation of the critical nuclei by the lens model.

$$\sigma^{I/III} - \sigma^{II/III} = \sigma^{I/II} \cos \theta \text{ [T.Youngs equation (1805)]}$$
(Eq 8.13)

Here  $\theta$  is called a contact angle or a wetting angle, and the better the wettability of the product phase and the substrate is, the smaller the value of  $\theta$  is.

The change in free energy according to this generation of lenticular nuclei can be approximated:\*\*

Volume energy Energy of Energy of (Eq 8.14)  

$$\Delta g^* = -(\Delta G/V)\upsilon_{II} + \sigma_{a_{I/II}}^{I/II} + (\sigma^{II/II} - \sigma^{I/II})_{a_{II/III}}$$

$$= f(\theta) \cdot \left[ -(\Delta G/V)(4\pi/3)\rho^3 + \sigma^{I/II} \cdot 4\pi\rho^2 \right]$$
(Eq 8.14a)

\*U. Nakaya (1936) succeeded in an experiment on nucleation of artificial snow with rabbit fur used as a substrate.

\*\*The volume of the lens and the area of the basal plain and the convex can be obtained:

$$V_{\rm II} = \int_0^h \pi (r^*)^2 dh = f(\theta) \cdot (4\pi/3)\rho^3, \quad a_{\rm II/III} = \pi (r^*)^2 = \pi \rho^2 (1 - \cos^2 \theta) \\ a_{\rm I/II} = \int_0^h 2\pi r^* / \sin \theta ) dh = 2\pi \rho^2 (1 - \cos \theta)$$
(Eq 8.15)

 $\rho$  in Eq 8.15 is the radius of curvature of the convex, and Eq 8.14a can be obtained if they are substituted into Eq 8.14 and rearranged using Eq 8.13.

Here  $f(\theta)$  is the volume ratio of the lens to a sphere of the same radius of curvature, and it can be calculated by

$$f(\theta) = \left(\frac{\text{Lens}}{\text{Sphere}}\right) = \frac{(1 - \cos\theta)^2(2 + \cos\theta)}{4} \approx \frac{\theta^4}{16}(3 - \theta^2) \quad [\theta < \pi/4]$$
(Eq 8.14b)

What is noticed is that the term of [ ] in Eq 8.14a is similar to Eq 8.1 about the aforementioned spontaneous nucleation, and therefore the critical value of radius of curvature of the lens  $\rho_c$  is equal to the critical radius for spontaneous nucleation  $r_c$  as shown in the following equation.

On the other hand, the energy of formation for lenticular nucleus is:

$$(\partial \Delta g^* / \partial \rho)_{\rho_c} = 0 \rightarrow \rho_c = r_c = 2\sigma^{I/II} V / \Delta G$$
 (Eq 8.16)

$$\Delta g_{\rm c}^* = f(\theta) \cdot \Delta g^* = f(\theta) \cdot (4\pi/3)\rho_{\rm c}^2 \sigma^{\rm I/II}$$
 (Eq 8.17)

As is shown in Fig. 8.5(b), if the contact angle is small, for example  $\theta = \pi/4$ , then  $f(\theta) \approx 0.06$  and  $\Delta g_c^* \ll \Delta g_c$ . Therefore, in a comparison using the same degree of supercooling  $\Delta T$ , the generation rate of lenticular



Fig. 8.5 The lens model for interface nucleation (heterogeneous nucleation). (a) Critical nucleus of interface nucleation. (b) Energy of critical nucleus. (c) Change in free energy according to nucleation.

critical nuclei on the interface of the substrate is far larger than that of globular spontaneous nuclei.

**Disklike Critical Nucleus Model.** When a solid phase (II) nucleates on the surface of a substrate (III), the disk model is more realistic than the aforementioned lens model. Four kinds of interface energies  $(\sigma_F^{I/II}, \sigma_E^{I/II}, \sigma^{I/III}, \text{ and } \sigma^{II/III})$  are used in this model (Fig. 8.6), but they can be summed up to only two kinds of basic parameters in consideration of the stability of shape as shown in the following exercise.

**[Exercise 8.5]** Induce the stable size ratio  $(\delta/r^D)$  of a disklike nucleus (radius  $r^D$ , thickness  $\delta$ ) according to the idea of "the conditional minimum problem" with a constant volume.

**[Answer]** The volume of disklike nucleus and the increase in the interface energy according to the generation of this nucleus are

Volume of disk:  $v_D = \pi (r^D)^2 \delta$ 

Interface energy:

$$[\Delta g^{\rm D}]_{\rm interface} = \pi (r^{\rm D})^2 \Big[ \sigma_{\rm F}^{\rm I/II} + \sigma^{\rm II/III} - \sigma^{\rm I/II} \Big] + 2\pi r^{\rm D} \delta \cdot \sigma_{\rm E}^{\rm I/II}$$

Therefore, the size ratio where the interface energy is minimum while the volume is constant can be obtained using Lagrange's undetermined coefficient  $\lambda$ :

$$\frac{\partial [\Delta g^{\mathrm{D}}]_{\mathrm{interface}}/\partial r^{\mathrm{D}} = \lambda \cdot \partial \upsilon_{\mathrm{D}}/\partial r^{\mathrm{D}}}{\partial [\Delta g^{\mathrm{D}}]_{\mathrm{interface}}/\partial \delta = \lambda \cdot \partial \upsilon_{\mathrm{D}}/\partial \delta)} \right\} \rightarrow \frac{\delta}{r^{\mathrm{D}}} = \frac{\Delta \sigma}{\sigma_{\mathrm{E}}^{\mathrm{I/II}}}$$
(Eq 8.18)

Here  $\Delta\sigma = \sigma_F^{I/II} + \sigma^{II/III} - \sigma^{I/III}$  is the increase in energy of disk plane, and  $\sigma_E^{I/II}$  is the energy of side face of disk.

According to the above consideration, the critical radius  $(r_C^D)$ , the critical thickness  $(\delta_C)$ , and the nucleation energy  $(\Delta g_C^D)$  of the disk is obtained.

First, the change in free energy in accordance with the generation of disklike nuclei is

Volume energy Energy of disk plane Energy of disk side face  

$$\Delta g^{\rm D} = -(\Delta G/V)\pi (r^{\rm D})^2 \delta + \pi (r^{\rm D})^2 \cdot \Delta \sigma + 2\pi r^{\rm D} \delta \cdot \sigma_{\rm E}^{\rm I/II}$$

$$= -(\Delta G/V)(\Delta \sigma/\sigma_{\rm E}^{\rm I/I})\pi (r^{\rm D})^3 + 3\Delta \sigma \cdot \pi (r^{\rm D})^2$$
(Eq. 8.19)



Fig. 8.6 The disk model for interface nucleation (heterogeneous nucleation)

	Sphere	Lens	Disk
Basic parameter	$\sigma^{I/II}$	$\sigma^{I/II} \\ \theta(\text{contact angle})$	$\begin{split} \Delta \sigma &= \sigma_{F}^{I/II} + \sigma^{II/III} - \sigma^{I/III} \\ \sigma_{E}^{I/II} (\text{Side face energy}) \end{split}$
Size of critical nucleus	$r_{\rm c} = \frac{2\sigma^{\rm I/II}V}{\Delta G}$	$r_{\rm c}^* = \left(rac{2\sigma^{{ m I}/{ m II}}V}{\Delta G} ight)\sin heta$	$r_{\rm c}^{\rm D} = rac{2\sigma_{\rm E}^{ m I/II}V}{\Delta G}$
		$h_{\rm c}^* = \left(\frac{2\sigma^{\rm I/II}V}{\Delta G}\right)(1-\cos\theta)$	$\delta_{ m c} = rac{2\Delta\sigma V}{\Delta G}$
Energy of formation	$\Delta g_{\rm c} = \frac{4}{3}\pi r_{\rm c}^2 \cdot \sigma^{\rm I/II}$	$\Delta g_{\rm c}^* = f(\theta) \cdot \frac{4}{3} \pi \rho_{\rm c}^2 \cdot \sigma^{\rm I/II}$	$\Delta g_{\mathrm{c}}^{\mathrm{D}} = \pi \left( r_{\mathrm{c}}^{\mathrm{D}}  ight)^2  \cdot  \Delta \sigma$

Table 8.2 Comparison of the models for critical nuclei

Here the variables are rearranged to only  $r^{D}$  using Eq 8.18.

From Eq 8.19, the critical values for the radius and thickness of disklike nucleus can be obtained:

$$\begin{array}{l} (\partial \Delta g^{\mathrm{D}} / \partial r^{\mathrm{D}})_{r_{\mathrm{c}}^{\mathrm{D}}} = 0 \rightarrow r_{\mathrm{c}}^{\mathrm{D}} = 2\sigma_{\mathrm{E}}^{\mathrm{I}/\mathrm{II}} V / \Delta G \\ \\ \delta_{\mathrm{c}} = (\Delta \sigma / \sigma_{\mathrm{E}}^{\mathrm{I}/\mathrm{II}}) r_{\mathrm{c}}^{\mathrm{D}} = 2\Delta \sigma V / \Delta G \end{array} \right\}$$

$$(\mathrm{Eq} \ 8.20)$$

The nucleation energy of critical nuclei is also obtained by Eq 8.19 and 8.20:

$$\Delta g_{\rm c}^{\rm D} = \pi (r_{\rm c}^{\rm D})^2 \cdot \Delta \sigma \tag{Eq 8.21}$$

In summary, Table 8.2 shows the basic parameters in spontaneous nucleation and interface nucleation, and the sizes and the generation energies of the critical nuclei.

# 8.2 Spontaneous Nucleation in Solution

### 8.2.1 Fluctuation in Concentration of Solution

Analysis of nucleation in a solution becomes more complicated than in the case of pure substances in the former section because not only the change in structure but also the change in composition should be taken into account. Before entering the main subject, consider a rudimentary exercise about "fluctuation in concentration."

**[Exercise 8.6]** When A and B atoms are mixed with the fractions of  $x_A$  and  $x_B$  in a solid, find out the probability that a very small ensemble composed of *m* A atoms and *n* B atoms will be generated in the solution by accident.

**[Answer]** The probability to be obtained is synonymous with the value of the probability that when (m + n) balls are picked up at random from the box with balls of A and B mixed in it, *m* balls of A and *n* balls

of B will be in sequence, multiplied by the permutation of them, and can be calculated by

$$P_{m+n} = x_{\mathbf{A}}^{m} \cdot x_{\mathbf{B}}^{n} \cdot (m+n)!/(m! \cdot n!)$$
 (Eq 8.22)

For example, the probability that an ensemble of A:B = 1:1 (m = n = 10) will be generated in a solution with  $x_B = 0.01$  is

$$P_{10+10} = (0.99)^{10} \cdot (0.01)^{10} \cdot 20!/(10!)^2 = 2 \times 10^{-15}$$

and the probability is extremely small.

However, the aforementioned calculation is for when the numbers of A and B atoms forming the very small ensemble are limited to m = n = 10, and it would be better to think both *m* and *n* have the permissible degree of around  $10 \pm 3$  if the nature of "fluctuation" is considered. The probability of existence for such a very small ensemble becomes

$$P_{(10\pm3)+(10\pm3)} = \sum_{m,n=7}^{13} (0.99)^m \cdot (0.01)^n \cdot (m+n)! / (m! \cdot n!) \approx 2 \times 10^{-9}$$

and it increases by  $10^6$  times the aforementioned calculation value.

Because the total of atoms is around  $10^{20}$  in the solution of volume  $1 \text{ mm}^3$ ,  $2 \times 10^{11}$  atoms per 1 mm<sup>3</sup> exist in the very small ensemble with the ratio of A:B about 1:1. If it is converted into dimension, the atoms exist at intervals of about 0.2 µm. What is more, each of the atoms makes the Brownian motion by violent thermal vibration of around  $10^{13}$  cycles per second, and very small ensembles might meet and part each other in any part of the solution. Borelius (Ref 6) developed thermodynamics of nucleation in a solution by assuming the existence of the aforementioned very small ensemble with the same composition as the product phase (hereafter called "the compatible assembly").

#### 8.2.2 Driving Force of Nucleation in a Solution

The driving force by which a nucleus of  $\theta$  phase  $(A_m B_n)$  is generated from a solution of A-B system (concentration of B,  $x_B^L$ ) is neither  $\Delta G_1$ nor  $\Delta G_2$  shown in Fig. 8.7(c).  $\Delta G_1 (2 \rightarrow 4)$  is the energy for promoting the dissolution process of the supersaturated liquid phase 2 into the equilibrium liquid phase 1 and  $\theta$  phase 3, that is, crystallization of  $\theta$  phase after nucleation, and  $\Delta G_2 (5 \rightarrow 3)$  is the one for promoting the transformation process of the liquid phase 5 with the same composition as  $\theta$ phase into  $\theta$  phase, that is, the solidification.

The driving force of nucleation in consideration in this section is the change in free energy when "compatible assemblies" existent in



**Fig. 8.7** The driving force in case of the nucleation of the compound  $(A_m B_n)$  from the supersaturated solution of A-B system. Numbered circles are explained in text. (a) The nucleation of a compound. (b) The phase diagram. (c) Driving force (erroneous). (d) Driving force (correct)

the liquid phase @ transit to  $\theta$  phase, and it corresponds to  $\Delta G^{L \to \theta}$  ( $\textcircled{i} \to \textcircled{3}$ ) in Fig. 8.7(d). The reason can be understood using a general idea of chemical potential (Section 3.4).

Because the free energies possessed by A and B atoms in A-B system solution @, or the chemical potentials  $\mu_A^L$  and  $\mu_B^L$  are indicated as the intersections where the tangent of the free energy curve at @ meets A and B axes (@ and @), the free energy of a compatible assembly (A:B = *m*:*n*) formed in the solution is @, and the driving force to promote nucleation is  $@ \rightarrow @$ . Therefore, both can be described by

Free energy of compatible assembly:

$$[G^{L}]_{\theta} = (m/m + n)\mu_{A}^{L} + (n/m + n)\mu_{B}^{L}$$
 (Eq 8.23)

Driving force of nucleation:

$$\Delta G^{L \to \theta} = [G^{L}]_{\theta} - G^{\theta} / (m+n)$$
  
=  $(m/m+n)(\mu_{\rm A}^{\rm L} - \mu_{\rm B}^{{\rm L}/\theta}) + (n/m+n)(\mu_{\rm B}^{\rm L} - \mu_{\rm B}^{{\rm L}/\theta})$  (Eq 8.24)

**[Exercise 8.7]** Show that the driving force by which  $\theta$  phase  $(A_m B_n)$  nucleates in A-B system solution of low density can be approximated

by the following equation. Here  $x_{\rm B}^{{\rm L}/\theta}$  is the equilibrium solubility of  $\theta$  phase to the liquid phase.

Driving force of nucleation: 
$$\Delta G^{L \to \theta} \approx (n/m + n)RT \cdot \ln (x_B^L/x_B^{L/\theta})$$
 (Eq 8.25)

**[Answer]** In case of  $x_B^L \ll 1$ , because  $\mathcal{O}$  and  $\circledast$  in Fig. 8.7(d) are close to each other, the first term of Eq 8.24 can be omitted.  $\mu_B^L$  and  $\mu_B^{L/\theta}$  in the second term can be approximated according to the regular solution model:

$$\mu_{\rm B}^{\rm L}\approx^{\circ}\!\!G_{\rm B}^{\rm L}+\Omega_{\rm AB}^{\rm L}+RT\ln x_{\rm B}^{\rm L},\ \mu_{\rm B}^{\rm L/\theta}\approx^{\circ}\!\!G_{\rm B}^{\rm L}+\Omega_{\rm AB}^{\rm L}+RT\ln x_{\rm B}^{\rm L/\theta}$$

When these are substituted into Eq 8.24, Eq 8.25 in question can be obtained.

In addition, the solubility curve can usually be approximated by (see Eq 4.33):

$$x_{\rm B}^{\rm L/\theta} \approx K_{\rm \theta}^{\rm L} \exp\left(-Q_{\rm \theta}/RT\right), \text{ or } \ln x_{\rm B}^{\rm L/\theta} \approx \ln K_{\rm \theta}^{\rm L} - Q_{\rm \theta}RT$$
 (Eq 8.26)

Therefore, Eq 8.25 can be also described as

Driving force of nucleation:

$$\Delta G^{\mathcal{L}\to\theta} \approx (n/m+n)(Q_{\theta}/T^*) \ \Delta T \tag{Eq 8.27}$$

Here  $T^*$  is the temperature of primary crystallization line  $\mathbb{O}^*$ , and  $\Delta T = T^* - T$  is the degree of supercooling.

# 8.2.3 Radius and Generation Rate of Critical Nucleus in a Solution

The change in free energy per particle when a globular  $\theta$  phase  $(A_m B_n)$  of radius *r* is generated in a supersaturated solution of A-B system can be expressed in the same way as in Eq 8.1:

$$\Delta g^{\theta} = -\left(\Delta G^{\mathbf{L} \to \theta} / V_{\theta}\right) \cdot (4\pi/3)r^3 + \sigma^{\theta/\mathbf{L}} \cdot 4\pi r^2 \qquad (\text{Eq 8.28})$$

Here  $V_{\theta}$  is the atomic volume of  $\theta$  phase, and  $\sigma^{\theta/L}$  is the interface energy between the solution and  $\theta$  phase.

The values of the radius  $r_c^{\hat{\theta}}$  and the generation energy  $\Delta g_c^{\theta}$  of a critical nucleus of  $\theta$  phase are as follows by the extreme value condition Eq 8.28:

$$(\partial \Delta g^{\theta} / \partial r) = 0 \to r_{\rm c}^{\theta} = 2\sigma^{\theta/L} V_{\theta} / \Delta G^{L \to \theta}, \ \Delta g_{\rm c}^{\theta} = (4\pi/3)\sigma^{\theta/L} (r_{\rm c}^{\theta})^2 \quad (\text{Eq 8.29})$$

Equation 8.29 is rearranged using Eq 8.26 and 8.27 to obtain.

$$r_{\rm c}^{\theta} = \frac{2(m+n)\sigma^{\theta/\rm L}V_{\theta}}{nRT \cdot \ln\left(x_{\rm B}^{\rm L}/x_{\rm B}^{\rm L/\theta}\right)} \approx \frac{2(m+n)\sigma^{\theta/\rm L}V_{\theta}}{nQ_{\theta}} \cdot \left(\frac{T^{*}}{\Delta T}\right)$$
(Eq 8.30)

**[Exercise 8.8]** Estimate the radius and the generation energy of a critical nucleus of Cu crystal that is generated when Pb-1at.%Cu alloy is rapidly cooled from the liquid phase down to a temperature 60 K lower than the primary crystallization line. Here, let the interface energy between Cu crystal and liquid Pb be  $\sigma^{cu/LPb} = 0.22 \text{ J/m}^2$ , and the solubility of Cu into liquid Pb be

$$x_{\rm Cu}^{\rm L} \approx 20 \exp\left(-47,000/RT\right)$$
 (Eq 8.31)

(see the phase diagram in Fig. 8.8).

**[Answer]** It is estimated that the primary crystallization temperature at which the crystallization of Cu begins is  $T_{Cu}^* = 744$  K according to Eq 8.31 in question when Pb-1at.%Cu alloy is slowly cooled. Therefore, the radius and the generation energy of a critical nucleus generated when the alloy is rapidly cooled down to  $T = T^* - 60 = 684$  K are as below according to Eqs 8.29 and 8.30.

$$r_{\rm c}^{\rm Cu} = 2 \times 0.22 \times 7.1 \times 10^{-6} \times 744/47,000 \times 60 = 0.824 \times 10^{-9} \text{ m}$$
  
$$\Delta g_{\rm c}^{\rm Cu} = (4\pi/3) \times 0.22 \times (0.824 \times 10^{-9})^2 = 6.25 \times 10^{-9} \text{ J}$$

Here the molar volume of Cu is presumed to be  $V_{\text{Cu}} = 7.1 \times 10^{-6} \text{m}^3/\text{mol}$ .



Fig. 8.8 The nucleation rate for crystallization of Cu phase from a liquid phase of Pb-Cu system ( $x_{Cu} = 0.01$ )

As mentioned previously, if the values of the radius and the generation energy of a critical nucleus are estimated, the equilibrium density and the generation rate of critical nuclei can be calculated in the same way of thinking as the analysis on the nucleation of a pure substance in the foregoing section.

First, the equilibrium density of critical nuclei can be approximated similarly to Eq 8.5:

$$N_{\rm c}^{\rm \theta} \approx N_{\rm B} \exp\left(-\Delta g_{\rm c}^{\rm \theta}/k_{\rm B}T\right)$$
 (Eq 8.32)

Here  $N_{\rm B}$  is the total of B atoms existent in 1 mole of the solution.

Next, the transition rate of embryos of  $\theta$  phase into critical nuclei  $v_c^{\theta}$  can be approximated by the following equation, which can be obtained from multiplying Eq 8.12 concerning a pure substance by the fraction of B atoms existent around the critical nuclei  $(x_B^{\text{B}})$ .

$$v_{\rm c}^{\theta} \approx (\pi r_{\rm c}^2 / 4 r_{\rm a}^4) D_{\rm B}^{\rm L} \cdot x_{\rm B}^{\rm L} \tag{Eq 8.33}$$

Finally, the nucleation rate of  $\theta$  phase can be calculated by

Nucleation rate: 
$$I_{\theta} \approx (N_{c}^{\theta}/V^{L}) \cdot v_{c}^{\theta}$$
 (Eq 8.34)

Here  $V^L$  is the molar volume of the solution phase.

If the above equations are applied to Pb-1at. % Cu alloy of Exercise 8.8, then

(i) The equilibrium density of critical nuclei of Cu crystal is

$$N_{\rm c}^{\rm Cu} \approx 6 \times 10^{23} \times 0.01 \exp\left(-\frac{6.25 \times 10^{-19}}{1.38 \times 10^{-23} \times 684}\right) = 1.05 \times 10^{-7} {\rm mol}^{-1}$$

(ii) The equilibrium density per unit volume is, if the molar volume of liquid Pb is assumed to be  $V_{Pb}^{L} = 1.94 \times 10^{-5} \text{m}^{3}/\text{mol}$ ,

$$N_{\rm c}^{
m Cu}/V_{
m Pb}^{
m L} pprox 1.05 imes 10^{-7}/1.94 imes 10^{-5} = 5.4 imes 10^{-3} {
m m}^{-3}$$

(iii) The transition rate of embryos into critical nuclei is, if it is assumed that  $D_{\rm L}^{\rm Cu} \approx 3 \times 10^{-9} {\rm m}^2/{\rm s}$ ,

$$\nu_{c}^{Cu} = \left[\pi (8.24 \times 10^{-10})^{2} / 4 (1.28 \times 10^{-10})^{4}\right] \times 3 \times 10^{-9} \times 0.01 = 6 \times 10^{10} \text{s}^{-1}$$

(iv) From the above, the nucleation rate of Cu crystal in Pb-1 at. %Cu solution at a supercooling 60 K is

$$I_{Cu} \approx 5.4 \times 10^{-3} \times 6 \times 10^{10} \approx 3 \times 10^8 \, \text{m}^{-3}/\text{s} = 0.3 \, \text{mm}^{-3}/\text{s}$$

As shown in Fig. 8.8(c), when the supercooling exceeds 60 K, the nucleation rate increases abruptly.

# 8.3 Nucleation by Inoculation

In the past, when microcrystals of silver iodide (AgI) or lead iodide (PbI<sub>2</sub>) were aerially applied in a dry season, supercooled water vapor in the air nucleated heterogeneously and coagulated, and the welcome rain was made to fall.\* Such a technique of promoting coagulation or solidification by nucleators is called "inoculation." Controlling solidification structure by inoculation according to thermodynamic analyses of the previous sections are considered in this section.

# 8.3.1 Morphological Control of Primary Crystal by Inoculation

First, consider an exercise about refinement of primary crystals in a eutectic alloy.

**[Exercise 8.9]** Coarse primary crystals of diameter about  $100 \,\mu\text{m}$  Si can be observed in solidification structure of a hypereutectic silumin alloy (Al-16%Si) as shown in Fig. 8.9(a, upper). However, if small amount of P is added, the primary crystals Si are remarkably refined as shown in Fig. 8.9(a, lower). Investigate this phenomenon by thermodynamics of nucleation.

[Answer] (i) Generation of coarse primary crystals Si in Al-Si system

Al-Si system is eutectic as shown in Fig. 8.10(b), and the solubility of Si into liquid Al can be approximated by

$$x_{\rm Si}^{\rm L} \approx 6.4 \exp{(-28,000/RT)}$$

Therefore, the primary crystallization temperature of 16% Si alloy is  $T_{\text{Si}}^* \approx 915 \text{ K}$ . The degree of supercooling when rapidly cooled down to the eutectic temperature is  $\Delta T \approx 65 \text{ K}$ , and the driving force to generate the primary crystals Si is

$$\Delta G^{L \to \mathrm{Si}} \approx Q_{\mathrm{Si}} \left( \Delta T / T_{\mathrm{Si}}^* \right) \approx 28,000 \times 65/915 \approx 2.0 \,\mathrm{kJ/mol}$$

Because Si is a covalent crystal and its interface energy with liquid Al ought to be larger than those values of metal/metal (0.1 to  $0.3 \text{ J/m}^2$ ), the radius of a critical nucleus  $r_c$  is seven times as large as the aforementioned case of Pb-Cu system as shown in Table 8.3 if it is assumed that  $\sigma^{\text{Si/Al}} \approx 0.5 \text{ J/m}^2$ . The nucleation rate is  $I \approx 0$ .

\*Both AgI and PbI<sub>2</sub> are hexagonal crystals; they have a very similar structure to ice crystal, and the interface nucleation of ice crystal is caused by a very small degree of supercooling ( $\Delta T \approx 5$  K).



**Fig. 8.9** Control of solidification structure by inoculation. (a, upper) The solidification structure of Al-16%Si alloy; (a, lower) the refinement of primary crystal Si by inoculation of P (Ref 7, 8). (b, upper) The cast structure of 17Cr stainless steel; (b, lower) the equiaxialization and refinement by inoculation of Ti (Ref 9)



**Fig. 8.10** Nucleation of silcon. (a), (b) Primary crystal Si of Al-Si system cannot nucleate spontaneously. (c) Primary crystal AIP nucleates spontaneously in Al-Si-P system. (d), (e) Because Si crystal and AIP crystal have a good compatibility, Si (the secondary nucleus) nucleates on the surface of AIP (the primary nucleus)

Therefore, the primary crystals of Si in Al-Si alloy Si are not formed by spontaneous nucleation but by heterogeneous nucleation on surface of impurities (MgO or  $Al_2O_3$ ) floating in a melt, and then they will grow coarsely.

Alloys	Primary crystal	Degree of supercooling $(\Delta T)$ , K	Driving force(ΔG), J/mol	Critical nucleus radius (r <sub>c</sub> ), nm	Nucleation rate (I), $mm^{-3}/s$	Style of nucleation
Pb-1%Cu	Cu	60	3.8	0.82	0.3	Spontaneous nucleation
Al-16%Si	Si	65	2.0	5.9		Interface nucleation
Al-0.01%P	AlP	350	20.3	0.58	5.6	Spontaneous nucleation

Table 8.3 Nucleation of primary crystals in binary alloys

(ii) Spontaneous nucleation of AlP in case of adding small amount of P to Al-Si

There exists AIP among AI-P system. This compound has a high melting point ( $T_{\rm m} \approx 2770 \,\text{K}$ ) and its solubility to liquid Al is uncertain, but it can be approximated in a low-density region.

$$x_{\rm P}^{\rm L} \approx 1.2 \times 10^2 \exp{(-150,000/RT)}$$

Assuming that the solubility of AlP into Al-16%Si is similar, because the primary crystallization temperature is  $T_{AIP}^* \approx 1290$  K for 0.01 at.%P, the degree of supercooling caused by inoculation of P is  $\Delta T \approx 350$  K. The driving force of generating AlP can be estimated according to Eq 8.27.

$$\Delta G^{L \to AIP} \approx (Q_{AIP}/2) (\Delta T/T^*_{AIP}) \approx (150,000/2) (350/1290) \approx 20.3 \text{ kJ/mol}$$

If the interface energy of AlP/Al is assumed to be the same as the value of Si/Al  $(0.5 \text{ J/m}^2)$  because AlP is a semiconductor of ZnS (*B*3) structure and it has similar physical properties to Si, the value of the radius and generation rate of the nucleus is rather close to that of the aforementioned Pb-Cu system as shown in Table 8.3. Therefore, for inoculation of 0.01 at. %P into Al-16%Si, it is supposed that AlP nucleates spontaneously.\* (iii) Interface nucleation of Si on AlP as a substrate

Because the crystal structure of AlP is not only the same type of Si but its lattice constant is also almost equal to Si as shown in Fig. 8.10(d) and (e), the primary crystal Si is generated by interface nucleation on AlP as a substrate when AlP nucleates spontaneously. In the same way as mentioned previously in the case of hypereutectic alloys of Al-Ge system, AlAs (ZnS type, a = 0.562 nm) is generated by primary nucleation according to inoculation of very small amount of As, and the primary crystal Ge (diamond type, a = 0.565 nm) is generated by interface nucleation on it as a substrate. It has been confirmed that, as a result, the primary crystal Ge can be remarkably refined (Ref 8).

<sup>\*</sup>Cu-P mother alloys are usually used for inoculation of P to Al alloys. The yield of P in that case is about  $\frac{1}{5}$  (Ref 7).

### 8.3.2 Refinement of Solidification Structure by Inoculation

Solidification structure is usually composed of (i) the chill zone of fine crystal grains generated on a mold face, (ii) the equiaxed crystal zone at the central part generated at the final stage of solidification, and (iii) the columnar crystal zone of intermediate part growing along heat flow.

Figure 8.9(b, upper) shows a macroscopic structure on a vertical section of a continuously cast steel sheet, and in this case equiaxialization and refinement by "inoculation" (Fig. 8.9(b, lower) is desirable because the columnar crystal zone consists of coarse grains and that may cause rolling cracks. Consider the mechanism of inoculation in such a case.

**[Exercise 8.11]** Describe properties required for inoculators to equiaxialize and refine solidification structure.

**[Answer]** In order to obtain fine equiaxed structure, generate primary nuclei ( $\theta$ ) in a liquid by homogeneous nucleation and form a solidifying phase (S) on them as substrates by interface nucleation. In such a case, the following conditions must be satisfied:

- (i) The driving force of generating  $\theta$  phase  $\Delta G^{L \to \theta}$  is large.
- (ii) The interface energy with liquid phase  $\sigma^{\theta/L}$  is small.
- (iii) The interface energy with solidifying phase  $\sigma^{\theta/S}$  is smaller than  $\sigma^{\theta/L}$ .

However, because an inoculator rarely exists that satisfies conditions (i) to (iii), refinement of structure is usually realized by three stages of processes (primary nuclei  $\rightarrow$  substrate phase  $\rightarrow$  solidification) as shown in Fig. 8.11(a, lower).

For example, Al alloys can be equiaxed and refined when Ti-B of about 0.15 mass%Ti-0.001mass%B is added, and it is determined that Al<sub>3</sub>Ti plays a role of substrate phase for Al crystal in such a case (Ref 10). However, because the driving force for crystallization of Al<sub>3</sub>Ti phase  $\Delta G^{L\to Al_3Ti}$  is not very large, a metastable compound of Ti-B system; TiB\*(NaCl type, a = 0.424 nm) (Ref 11), probably, nucleates spontaneously at first and Al<sub>3</sub>Ti is generated by secondary nucleation on the surface of the TiB\*. Next, Al crystal is supposed to be generated by interface nucleation on Al<sub>3</sub>Ti as a substrate (Fig. 8.12)\*.

<sup>\*</sup>There is also a theory that the primary nucleus is regarded as  $TiB_2$ , or  $(Ti, Al)B_2$  which has the highest melting point in Al-Ti-B system when Ti-B is inoculated into Al. However,  $TiB_2$  is, as shown in Fig. 8.12(c), a compound with Ti atoms at the centers of honeycomb cells of B atoms, and it has poor wettability with Al. On the other hand,  $TiB^*$  is a metastable phase (a stable phase is TiB of FeB type), but it is a metallic compound such as TiC and TiN, and it can be presumed that the compound is the most suitable for the primary nucleus because it has good wettability with Al and is in good conformity with  $Al_3$ Ti crystal.



Fig. 8.11 The process of formation of solid nucleus due to inoculation. The formation of solid nucleus by (a, upper) the single process and (a, lower) the sequential processes. (b) The condition of interface energy between solid nucleus (S) and the substrate (C)



Fig. 8.12 The compound phase related to refinement of solidification structure of Al alloy by inoculation of Ti-B

## 8.4 Nucleation in Solid

Various kinds of nucleation phenomena can be observed in a solid. Figure 8.13 shows summarization of typical examples of nucleation in iron and steel. Because, among them, the driving forces of A<sub>3</sub> transformation ( $\gamma Fe \rightarrow \alpha Fe$ ), pearlite transformation ( $\gamma \rightarrow \alpha + Fe_3C$ ) and recrystallization ( $\Delta G$ ) are less than 1 kJ/mol, nucleation is usually commenced by interface nucleation on the grain boundary of crystal. On the other hand, most precipitation of  $\varepsilon$  carbides or Cu particles according to aging is started by spontaneous nucleation in crystal grains because  $\Delta G$  is large.

Before entering the main subject, consider an exercise about strain energy according to nucleation.

**[Exercise 8.11]** Estimate the strain energy if solute atoms of different atomic radius from that of solvent atoms form globular precipitation particles.

**[Answer]** When the atomic radii of a matrix and a solute are assumed to be *r* and  $r \pm \Delta r$ , the volume increase by formation of globular aggregates will become  $\Delta \upsilon / \upsilon = \left[ (r \pm \Delta r)^3 - r^3 \right] / r^3 \approx \pm 3(\Delta r/r)$ .

On the other hand, the energy required for compressing or expanding a globe of volume  $v + \Delta v$  to v is  $\Delta u_{globe} = (\frac{1}{2})B(\Delta v/v)^2(J/m^3)$  if the bulk modulus is assumed to be B  $(J/m^3)$ .

Therefore, the change in energy according to formation of 1 mole of a globular aggregate will become

$$\Delta G_{\text{globe}} = \Delta u_{\text{globe}} \cdot V \approx (\%) (\Delta r/r)^2 BV (\text{J/mol})$$
(Eq 8.35)

Here  $V (m^3/mol)$  is the molar volume of the matrix.



Fig. 8.13 The driving force on nucleation during structure change of iron and steel (the solid lines indicate spontaneous nucleations, and the dot and dash lines indicate interface nucleations)

For example, because  $B \approx 0.8 \times 10^{11} \text{ J/m}^3$ , and  $V \approx 10^{-5} \text{m}^3/\text{mol}$  for Al alloys, it can be estimated that  $\Delta G_{\text{globe}} \approx 36 \text{ kJ/mol}$  if the difference of atomic radii is  $\Delta r/r = 0.1$ . Because this value is the energy equal to the driving force of precipitation, it is difficult to form globular particles. However, if the difference of atomic radii is  $\Delta r/r < 0.03$ , the strain energy will become 1/10 of the aforementioned value and it is possible to form globular particles. Figure 8.14(a) is the typical example, the atomic radii of Al and Ag are almost equal, 0.143 and 0.144 nm, respectively, and globular particles (Guinier-Preston zone) are formed by aging (Ref 12, 13).

On the other hand, if disklike particles are formed, the strain energy is much smaller, as shown by the Nabarro curve (Ref 14) in Fig. 8.14(b). Therefore, if an alloy with the difference of the atomic radii  $\Delta r/r > 0.03$  (for example, Al-Cu system,  $\Delta r/r = 0.1$ ) is aged, disklike Guinier-Preston zone is generated.

### 8.4.1 Formation of Precipitation Nuclei and Clusters

**[Exercise 8.12]** Investigate the homogeneous nucleation if a fcc solid solution of Cu-2at.%Co system is aged at 700 to 1050 K. Here, let the fundamental parameters be the values:

Solubility of Co into Cu (atomic fraction):  $x_{Co} = 20.2 \exp(-63,890/RT)$ 

(Eq 8.36)

Diffusion coefficient of Co in Cu: (Eq. 8.37)

$$D_{\rm Co}^{\alpha} = 1.93 \times 10^{-4} \exp\left(-226,000/RT\right)({\rm m}^2/{\rm s})$$



**Fig. 8.14** The strain energy according to the precipitation of particles. (a) Electron microscope image of the structure of Al-5.5at.%Ag alloy thin film after aged at 433 K (Ref 12). Globular particles dispersed in the matrix indicate Guinier-Preston zone. Thick straight lines mean sections of the hexagonal disklike compound phase (AlAg<sub>2</sub>, hexagonal crystal), and the GP zone annihilates according to the growth of this compound. (b) Nabarro curve that shows the relation between the shape factor (*c/a*) and the strain energy of a precipitation phase (Ref 14)

Interface energy between  $\alpha$  phase on Cu side and  $\alpha'$  phase on Co side:

$$\sigma^{\alpha'/\alpha} = 0.22 \text{ J/m}^2$$

Molar volume of  $\alpha$  phase and  $\alpha'$  phase; $V = 7 \times 10^{-6} \text{m}^3/\text{mol}$ 

**[Answer]** In Cu-Co system (Fig. 8.15a), both  $\alpha$  phase and  $\alpha'$  phase are fcc, and the atomic radii of both components are almost equal (0.128 nm for Cu, 0.125 nm for Co). From this reason, it has been estimated the energy of coherent interface between both phases is  $0.22 \text{ J/m}^2$ , smaller than that of random grain boundary (0.5 and  $0.8 \text{ J/m}^2$ , for Cu and Co, respectively) (Ref 15). What is more, because the strain energy caused by precipitation is also small, the analytical equations in Section 8.2 "Spontaneous Nucleation in Solution" can be adopted without any modification.

First, the temperature ① at which the equilibrium solubility becomes 2% is  $T_1 = 1110$  K according to Eq 8.36 in question. If this solid solution is supercooled to, for example,  $T_2 = 1023$  K (the degree of supercooling is  $\Delta T = 87$  K), then the driving force of precipitation will become as follows according to Eq 8.27:



$$\Delta G^{\alpha \to \alpha'} = (Q_{\rm Co}/T_1) \Delta T = (63, 890/1110) \cdot 87 \approx 5.0 \text{ kJ/mol}$$

**Fig. 8.15** The formation of precipitation nuclei or clusters of Cu-Co system by aging treatment. See text for details of process. (a) Phase diagram. (b) Free-energy diagram  $(T = T_2)$ . (c) Critical radius  $(r_c)$  and the nucleation rate (l). (d) Generation of precipitation nuclei and clusters. The values in the figure are rounded numbers of atoms forming a critical nucleus.

The radius and the formation energy of a critical nucleus are as follows according to Eq 8.29:

$$r_{\rm c}^{\rm Co} = 2\sigma^{\alpha'/\alpha} V / \Delta G^{\alpha'/\alpha} = 2 \times 0.22 \times 7 \times 10^{-6} / 5000 \approx 0.62 \times 10^{-9} {\rm m}$$
$$\Delta g_{\rm c}^{\rm Co} = (4\pi/3)\sigma^{\alpha'/\alpha} \cdot (r_{\rm c}^{\rm Co})^2 = (4\pi/3)0.22 \cdot (0.62 \times 10^{-9})^2 \approx 3.5 \times 10^{-19} {\rm J}$$

The equilibrium density per unit volume of critical nuclei is as follows according to Eq 8.32:

$$\frac{N_{\rm c}^{\rm Co}}{V} = \frac{N_{x_1}}{V} \exp\left(-\frac{\Delta g_{\rm c}^{\rm Co}}{k_{\rm B}T_2}\right) = \frac{6 \times 10^{23} \times 0.02}{7 \times 10^{-6}}$$
$$\exp\left(-\frac{3.5 \times 10^{-19}}{1.38 \times 10^{-23} \times 1023}\right) \approx 2.9 \ \mu {\rm m}^{-3}$$

The diffusion coefficient of Co atoms in Cu is as follows according to Eq 8.37 in question:

$$D_{C_0}^{\alpha} = 1.93 \times 10^{-4} \exp{(-226,000/R \cdot 1023)} \approx 5.6 \times 10^{-16} \text{ m}^2/\text{s}$$

Therefore, the frequency of transition from embryos to critical nuclei is as follows according to Eq 8.33:

$$v_{\rm c}^{\rm Co} = \left[\pi (r_{\rm c}^{\rm Co})^2 / 4 (r_{\rm a}^{\rm Co})^4\right] D_{\rm Co}^{\alpha} X_{\rm Co} \approx 1.4 \times 10^4 \ {\rm s}^{-1}$$

From the above, we can estimate the generation frequency of critical nuclei of Co phase to be precipitated:

$$I_{\rm Co} = (N_{\rm c}^{\rm Co}/V) \cdot v_{\rm c}^{\rm Co} = 2.9 \times 1.4 \times 10^4 \approx 4.1 \times 10^4 \mu {\rm m}^{-3}/{\rm s}$$

Figure 8.15(c) shows the results from similar calculations at each temperature 700 to 1050 K. As written in the figure, when the aging temperature is below  $T^* = 950$  K, the number of atoms forming a critical nucleus is less than 10. In addition, the activation energy for nucleation ( $\Delta g_c$ ) is remarkably small, and it can reach no more than about  $\frac{1}{10}$  of the activation energy for diffusion of atoms  $226 \text{ kJ/mol} \approx 3.8 \times 10^{-19} \text{ J/atom}$ ) (Fig. 8.15d). Such a transition process should not be regarded any longer as one of nucleation phenomena but as one of formation phenomena of atomic clusters (Ref 16).

### 8.4.2 Formation of Guinier-Preston Zone

The nucleation in Cu-Co system mentioned in the previous subsection is a single process where nuclei with the same structure (fcc) as a matrix are generated, and the relationship between the nucleation rate (I) and the aging temperature (T) can be expressed by one reverse C-curve. However, in most cases of alloys with different structures between a solute and a matrix, first, nuclei with the same structure as a matrix, Guinier-Preston (GP) zone, are generated; next, metastable transition phases are formed; and finally, stable precipitation phases are nucleated (Ref 17). The typical example is precipitation in an Al-Cu alloy (Duralumin), and Guinier-Preston zone of Cu atoms along (100) surface of the matrix is formed before appearance of a stable precipitation phase (Al<sub>2</sub>Cu, tetragonal).

The following exercise is a model of nucleation in this Al-Cu system, and let the solubility and the diffusion coefficient of Cu be close values to the reality. However, both Guinier-Preston zone and a stable precipitation phase are assumed to form globular critical nuclei in order to simplify the analysis.

**[Exercise 8.13]** Calculate the nucleation rate of  $A_2B$  ( $\theta$  phase) after aging  $\alpha$  phase ( $x_B = 0.02$ ) in A-B system, which has such a phase diagram as shown in Fig. 8.16(a). Also estimate the formation rate of Guinier-Preston zone on the assumption that A atoms and B atoms are repulsive and a metastable binodal curve exists as shown by the dashed curve in the figure.

Here, let the fundamental parameters be the values described below.

Solid solubility of  $\theta$  phase into  $\alpha$  phase:  $x_{\rm B} = 18 \exp(-45,000/RT)$ 



**Fig. 8.16** The nucleation of the equilibrium phase ( $\theta$ ) and the GP zone ( $\alpha'$  by aging treatment). (a) The phase diagram. (b) The free-energy diagram ( $T = T_2$ ). (c) The nucleation rates of  $\theta$  phase and the GP zone. The values in the figure are rounded numbers of atoms forming a critical nucleus.

Density of the metastable binodal curve:  $x'_{\rm B} = 10 \exp(-25,000/RT)$ 

Diffusion coefficient of B atoms in  $\alpha$  phase:

 $D_{\rm B}^{\alpha} = 1.5 \times 10^{-5} \exp{(-12,600/RT)} \ ({\rm m}^2/{\rm s})$ 

Interface energies of  $\theta/\alpha$  and  $\alpha'/\alpha$  interfaces:

$$\sigma^{\theta/\alpha} = 0.18 \, \text{J/m}^2, \ \sigma^{\alpha'/\alpha} = 0.10 \, \text{J/m}^2$$

Molar volume of  $\alpha$  and  $\alpha'$  phases:  $V = 10^{-5} \text{m}^3/\text{mol}$ 

**[Answer]** Because the procedure of calculation is almost same as the case of Cu-Co system described previously, only the calculated results are shown in Fig. 8.16(c) by a solid curve ( $\theta$  phase) and a dashed curve (Guinier-Preston zone).

What should be noticed is that the driving force of precipitation decreases to  $\frac{1}{3}$  as the following equation because  $\theta$  phase has the composition of A<sub>2</sub>B.

 $\Delta G^{\alpha \to \theta} = (n/m + n)(Q/T_1)\Delta T = (1/3)(45,000/796)\Delta T \approx 18.8\Delta T \text{ (J/mol)}$ 

For this reason, a large degree of supercooling is required for generating  $\theta$  phase, and the supercooling reaches  $\Delta T_{\text{max}} \approx 400 \text{ K} (\Delta T_{\text{max}} \approx 200 \text{ K} \text{ for Cu} - \text{Co system})$  in order to maximize the nucleation rate.

On the other hand, Guinier-Preston zone is metastable, it requires larger degree of supercooling than  $\theta$  phase, so it can nucleate only in a low-temperature region. However, because its interface energy is small, its nucleation rate is by far larger than that of  $\theta$  phase.

In addition, because the critical nucleus radius of Guinier-Preston zone is less than 0.6 nm and the number of component atoms is less than 60, it should be better to regard it as "a cluster" rather than "a precipitated nucleus."

As mentioned previously, the nucleation rates of Guinier-Preston zone and compound phase could be calculated by similar analysis to the one used for "nucleation in a supersaturated solution." However, if the period required for precipitation is estimated by these calculated values, it does not agree with the period required of the reality at all as shown in the following exercise.

**[Exercise 8.14]** Estimate the incubation period of precipitation according to the nucleation rate obtained in the previous question.

**[Answer]** The time required for precipitation can be estimated by the following Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation (see Sec. 9.1).

$$X_{P} = 1 - \exp\left(-k_{pt}^{'5/2}\right)$$

$$k_{p}^{'} = \left(16\sqrt{2\pi}/15\right)\left[(x_{0} - x_{e})(x_{p} - x_{e})\right] \cdot I \cdot D^{3/2}$$
(Eq. 8.38)

Here  $X_P$  is the rate of progress in precipitation,  $x_o$  and  $x_e$  are the initial and equilibrium values for concentration of B in  $\alpha$  phase, and  $x_P$  is the concentration of B in the precipitation phase.

The thin solid line ( $\theta$  phase) and dashed line (GP) in Fig. 8.17(a) are the results of calculation using Eq 8.38 considering the time until which the rate of progress in precipitation reaches  $X_P = 0.05(t_{0.05})$  is an incubation period, and, for example,  $t_{0.05} \approx 10^9 \text{s}(\sim 30 \text{ years})$  at T = 300 K. However, the incubation period of Guinier-Preston zone for Al-4 mass %Cu alloy is about  $10^4$  s at 300 K, and they do not agree at all.

This contradiction was elucidated by taking the promotion effect by "excess vacancies" on diffusion into consideration (Ref 17, 18).

Precipitated alloys are always treated with heat into "solution" before aging treatment. Though this treatment aims to dissolve solute atoms in a solid solution, it generates a lot of lattice vacancies (about 0.01 at.%) secondarily. These are called excess vacancies or frozen vacancies (see Exercises 2.9 and 6.2).

Frozen vacancies move around in a crystal during aging treatment, promote diffusion of solute atoms remarkably, and, as a result, increase



Fig. 8.17 The promotion of nucleation by "excess vacancies" generated during solution heat treatment

the nucleation rate (I) greatly. The thick solid line and dashed line in Fig. 8.17 indicate the modified values considering promotion of nucleation by frozen vacancies as described previously.

Frozen vacancies will be absorbed into dislocations in a crystal or crystal boundaries and annihilate gradually. Because the higher the temperature is, the faster the frequency of annihilation is, the influence of frozen vacancies seldom appears if the aging temperature is as high as the case of Cu-Co system considered in the previous section.

#### EXERCISES

**8.15** Show that the critical radius of a waterdrop can be approximated by the following equation if waterdrops are formed from water vapor by increasing pressure from the saturated pressure  $P_e$  to  $P_1$  without any change in temperature.

$$r_{\rm c} = 2\sigma V/RT \ln\left(\mathrm{P}_{\rm 1}/\mathrm{P}_{\rm e}\right) \tag{Eq 8.39}$$

*Hint:* Because the change in the free energy of a liquid phase by increasing pressure is small, if only the change in the free energy of a gas phase is considered, then the driving force of forming waterdrops can be obtained (Fig. 8.18):

$$\Delta G^{\text{vapor} \to \text{water}} \approx \int_{P_e}^{P_1} V dP = \int_{P_e}^{P_1} (RT/P) dP = RT \ln \left( P_1/P_e \right)$$

For example, if pressure is increased to  $P_1/P_e = 2$  at T = 273 K,  $\Delta G \approx 1570$  J/mol. The surface tension of water is  $\sigma = 0.07$  J/m<sup>2</sup>. The molar volume is  $V = 1.8 \times 10^{-5}$ m<sup>3</sup>/mol. Therefore, the critical radius of a waterdrop is  $r_c^{\text{water}} \approx 1.6$  nm.

**8.16** Show that the critical radius of  $\theta$  phase (BC) that is crystallized from a liquid of A-B-C system (L) with a primary component of A can be approximated by

$$r_{\rm c} = 2\sigma V/R[(\alpha_1 \ln 10)/2] \cdot (\Delta T/T_0)$$
 (Eq 8.40)

Here  $T_0$  is the equilibrium temperature at which  $\theta$  phase is crystallized, and  $\alpha_1$  is the coefficient of the following solubility product.

$$\log [B\%][C\%] = -\alpha_1/T + \alpha_2$$
 (Eq 8.41)

*Hint:* First, convert Eq 8.41 expressed in mass% into an equation of the atomic fractions ( $x_B$ ,  $x_C$ ) and ln.

$$\ln (x_{\rm B} \cdot x_{\rm C}) = -\alpha_1 \cdot \ln 10/T + \alpha_2' \qquad ({\rm Eq} \ 8.41a)$$



Fig. 8.18 The G-P diagrams for a gas phase and a liquid phase

Next, convert the solubility curved surface of A-B-C ternary system into the solubility curve of A-BC pseudobinary system. For this, introduce a new variable,  $z = 2(x_B \cdot x_C)^{1/2}$ , which becomes z = 1 when  $x_B = x_C = \frac{1}{2}$ , and Eq 8.41a will be converted as follows (Fig. 8.19):

$$\ln z = -\alpha_1 \cdot \ln 10/2T + \alpha_2''$$
 (Eq 8.41b)

The driving force so that  $\theta$  phase (BC) can be crystallized is as follows by Eq 8.25 in Exercise 8.7:

$$\Delta G^{\mathbf{L} \to \theta} = RT \cdot \ln (z_0/z_e) = R[(\alpha_1 \ln 10)/2](\Delta T/T_0)$$

For example, in the case of the critical nucleus of TiN generated when molten steel of Fe-0.1%Ti-0.006%N is solidified, because  $T_0 = 1800 \text{ K}$  if the equation of solubility product, log [Ti%][N%] = -19,800/T + 7.78 is used,

 $\Delta G^{L \rightarrow TiN} \approx 4200 \,\text{J/mol}$  for the degree of supercooling  $\Delta T = 40 \,\text{K}$ 

The interface energy between TiN and LFe is  $\sigma^{\text{TiN/LFe}} \approx 0.3 \text{ J/m}^2$ . The molar volume of molten steel is  $V \approx 8 \times 10^{-6} \text{m}^3/\text{mol}$ . Therefore, the critical radius is  $r_c^{\text{TiN}} \approx 1.1 \text{ nm}$ .

**8.17** The degree of supercooling during allotropic transformation  $(\alpha \Leftrightarrow \beta)$  is by far smaller in the case of nucleation on crystal grain boundaries than in case of nucleation in crystal grains (Fig. 8.20). Consider the reason for it.

**8.18** When a supersaturated solid solution of A-B system ( $\alpha$ ) is heated at the temperature of (3) in Fig. 8.21 after Guinier-Preston zone is generated by aging treatment of the solution at the temperature of (2), it will



Fig. 8.19 The driving force for crystallization of  $\theta$  phase (BC) from a solution of A-B-C system (L)



Fig. 8.20 The nucleation in a grain and a grain boundary

return in the state of a supersaturated solid solution before aging. This is called reversion. Consider why it returns to structure of the single phase  $\alpha$  before aging though the two phase of  $\alpha + \theta$  is stable at 3 here.

# **Appendix: True Colors of Guinier-Preston Zone**

A. Guinier of the University of Paris and G.D. Preston of the National Physical Laboratory discovered in 1938 that the Laue diffraction image



Fig. 8.21 The reversion phenomenon by heating after aging



**Fig. 8.22** (a, upper) The Laue diffraction image of Al-4%Cu alloy photographed by Preston (Ref 20, 22). (a, lower) the image of Guinier-Preston zone in the Al-Cu alloy from high-resolution electron microscopy (Ref 23). (b, upper) The phase diagram and the free-energy diagram of a precipitated alloy. (b, lower) A model for Guinier-Preston zone by Gerold (Ref 21) (sheet GP is formed in an Al-Cu alloy)

of a single crystal of Al-Cu alloy after aging showed such singular streaks as shown in Fig. 8.22 (a, upper) and advocated that the age hardening of this alloy is according to generation of sheet aggregates of Cu atoms along (100) surface (Ref 17, 20, 21).
Compared with the images from recent high-resolution electron microscopy (Fig. 8a, lower), their model makes one marvel at its exactness. True colors of this cluster, named Guinier-Preston zone in commemoration of the discoverers, have had analyzed not only its shape but also the arrangement of each component atoms (Ref 21); the nucleation theory, which was once kept at a respectful distance as "a story at age of gods," will become a reality at last.

However, if it is seen from a viewpoint of controlling structure of materials, quantitative investigation on the nucleation process is insufficient. In particular, it may be indispensable to make progress in thermodynamic analysis on generation of Guinier-Preston zone by developing the idea of "phase separation due to ordering" explained in Chapter 7 of this book.

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# Thermodynamics of Microstructure Change

Microstructure science made remarkable progress in 20th century. In recent years, computers have enabled such detailed simulations that these results can be confused with reality. However, mere surfacial simulations may have the danger of bringing us useless virtual images. Significant analysis and applications based on an accurate understanding of the mechanism of microstructure changes should be expected.

## 9.1 Outline of Microstructure Change

#### 9.1.1 Types of Microstructure Change

There are various types of microstructure changes, and attempts have been made on systematization of every kind. Table 9.1 shows the classification by Christian (Ref 1), and its keywords are described in this section:

**Nucleation Type or Non-nucleation Type?** Usual transformations and precipitations begin and progress from "nucleation" of a product phase ( $\beta$ ) in a parent phase ( $\alpha$ ). In recrystallization, a region where the strain existent in a deformed structure can be easily removed becomes "a nucleus" and grows, swallowing up the surrounding deformed structures. This sort of microstructure change has an "incubation period," and the relationship between the rate of change and the time can be shown by a sigmoidal curve (Fig. 9.1a).

On the other hand, in order-disorder transition, A and B atoms in an ordered solid solution ( $\alpha$ ) that have been arranged in a perfect order gradually become without order as the temperature rises, and the solution becomes a disordered solid solution ( $\alpha''$ ). On the other hand, in the grain growth observed when a fine structure of grains is heated, the grains in the entire structure will gradually become coarse. These microstructure

Growth	Thermally activ					
Initial process process	Interface control	Diffusion control	Diffusionless type			
Non-nucleation type	Grain growth	Ostwald ripening Order-disorder transition Spinodal decomposition Recovery of deformed structure	Glass transition			
Nucleation type	Solidification and transformation of pure substance Recrystallization of deformed structure Abnormal grain growth	Crystallization and precipitation Eutectic and eutectoid transformation	Martensitic transformation			
	(Interface + diffusion) Pearlite transformation Discontinuous precipit					

 Table 9.1
 The classification of structure change



Fig. 9.1 The structure change of the nucleation type (sigmoidal curve) and the nonnucleation type (asymptotic curve)

changes have nothing to do with "nucleation" or "incubation periods," and the relationship between the rate of change and the time can be shown by an asymptotic curve (Fig. 9.1b).

**Diffusion Control or Interface Control?** The phenomenon that  $\beta$  phase mainly composed of B atoms is precipitated from  $\alpha$  solid solution of A-B system is controlled by the diffusion velocity of B atoms in the  $\alpha$  phase. On the other hand, the allotropic transformation (I  $\rightarrow$  II) is controlled by the transition velocity of atoms crossing the I/II interface, that is, the velocity of the interface migration. The former is called the microstructure change by "diffusion control" and the latter by "interface control."

By the way, eutectic solidification is under "diffusion control." However, the pearlite transformation  $(\gamma \rightarrow \alpha Fe + Fe_3C)$  is thought to be a combined microstructure change of interface control and diffusion control because the diffusion of C atoms and the transition of Fe atoms require the same level of energy.

**Thermally Activated Type or Diffusionless Type?** Ordinary microstructure change proceeds according to a chain of elementary processes that individual atoms are activated thermally, cut off the bonds to the side of the parent phase, and transit to the lattice points on the side of the product phase (Fig. 9.2a). Because this pattern is analogous to the diffusion in a crystal, it is sometimes called "the diffusional type," but "the thermally activated type" is used here to avoid confusion with the aforementioned "diffusion control."

On the other hand, when steel or ceramics are rapidly cooled from a high temperature, the change in crystal structures may occur according to displacement of atoms as a group. This is called the "diffusionless type," or the "martensitic type" of phase transformation in commemoration of a metallurgist who played an active part in the 19th and 20th centuries, A. Martens (1850–1914).

Amorphous formation in rapid cooling of such alloys as Fe-B, Au-Si, and so on, or such a liquid phase as silicates is also "diffusionless type," but it is a unique phase transformation without any stages of nucleation, different from the martensitic transformation.

#### 9.1.2 Rate of Structure Change

The rate of structure change (X) in thermally activated type is generally described by

Nucleation type: 
$$X = 1 - \exp(-kt^n)$$
 (Eq 9.1)

Non-nucleation type: 
$$X = 1 - (1 + k't)^{-1/m}$$
 (Eq 9.2)

Equation 9.1 is the well-known Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation. It will be investigated in the next section, so think of an introductory exercise on Eq 9.2 here.



Fig. 9.2 Phase change of the thermally activated type (a) and the diffusionless type (b)

**[Exercise 9.1]** Find out the equation for the rate of grain growth (Eq 9.4) according to the following rule of grain growth.

Grain growth law: 
$$\bar{R}^2 - \bar{R}_0^2 = k_{gb} \cdot t$$
 [similar form to Eq 5.73] (Eq 9.3)

Rate of grain growth: 
$$X = 1 - [1 + (k_{gb}/\bar{R}_0)t]^{-1/2}$$
 (Eq 9.4)

Here  $\overline{R}$  is the mean radius of grains and  $\overline{R}_0$  is its initial value.

**[Answer]** A polycrystalline material, whose mean radius of grains is  $\overline{R}$ , possesses more free energy than a single crystal. The value of it can be expressed by (see Section 5.2 "Gibbs-Thomson Effect"):

$$\Delta G^{\rm gb} = 2\sigma V/\bar{R} \ (\rm J/mol) \tag{Eq 9.5}$$

Here  $\sigma$  is the grain-boundary energy, and V is the molar volume.

Because the growth of grains is regarded as a phenomenon in which this energy gradually decreases, its rate of change can be approximated by

$$X = \frac{\Delta G_0^{\rm gb} - \Delta G^{\rm gb}}{\Delta G_0^{\rm gb}} = 1 - \frac{G^{\rm gb}}{\Delta G_0^{\rm gb}} = 1 - \frac{\bar{R}_0}{\bar{R}}$$
(Eq 9.6)

Substituting  $\overline{R}$  of Eq 9.3 into Eq 9.6 and rearranging it, Eq 9.4 in question can be obtained. Figure 9.3 shows the calculated results about the rate of grain growth in pure iron.



**Fig. 9.3** The rate of grain growth of pure iron. The parameters such as the grain-boundary diffusion coefficient the are same as in Exercise 5.16.

Structure change	Equation of phenomena (basic parameters)	Rate of change									
Recovery	$\frac{1}{\rho} - \frac{1}{\rho_0} = k_d \cdot t(\rho; \text{ dislocation density})$	$X = 1 - (1 + k_{\rm d} \rho_0 \cdot t)^{-1}$									
Grain growth	$\bar{R}^2 - \bar{R}_0^2 = k_{\rm gb} \cdot t(\bar{R}; \text{ radius of grains})$	$X = 1 - \left[1 + (k_{\rm gb}/\bar{R}_0^2) \cdot t\right]^{-1/2}$									
Ostwald ripening(a)	$(\bar{r})^3 - (\bar{r}_0)^3 = k_{\text{ost}} \cdot t(\bar{r}; \text{ particle radius})$	$X = 1 - \left[1 + \left(k_{\text{ost}}/(\bar{r}_0)^3\right) \cdot t\right]^{-1/3}$									
(a) The particle on the grain dislocation line is by the fift	(a) The particle on the grain boundary is described by the fourth power law $(\tilde{c})^4 - (\tilde{r}_0)^4 = k'_{ost} \cdot t)$ , and the particle on the dislocation line is by the fifth power law $(\tilde{c})^5 \tilde{c} \tilde{c}^5 - \tilde{c}_0)^5 = k'_{ost} \cdot t$ (see Exercise 9.3).										

Table 9.2The equation of phenomena and the rate of structure change of thenon-nucleation type

Table 9.2 shows the summarization of the rates of change obtained from the recovery equation of deformed structure and Ostwald ripening equation for dispersed particles.

### 9.2 Johnson-Mehl-Avrami-Kolmogorov (JMAK) Equation

#### 9.2.1 Extended Volume of Product Phase

In 1939, Johnson, Mehl, and Avrami advocated that the relationship between the rate of phase change (X) of "nucleation type" and the elapsed time (t) can be described by (Ref 2, 3):

$$X = 1 - \exp(-kt^{n})$$
 [same as Eq 9.1]

However, it was later found that Kolmogorov had also published an equation of the same content in 1937 (Ref 4), and it is called Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation today.

In order to understand the content of Eq 9.1, one must first learn the concept of extended volume.

**[Exercise 9.2]** When a phase change proceeds, product phases will impinge upon each other. If it is assumed that this "impingement" is ignored and they grow freely, the virtual volume is called "an extended volume." Let  $V_{\text{ex}}$  denote the total volume and show that the rate of phase change (X) can be approximated by

$$X = 1 - \exp\left(-V_{\rm ex}/V_0\right)$$
 (Eq 9.7)

Here  $V_0$  is the volume of the entire material. The nuclei of product phase are assumed to distribute at random.

**[Answer]** Let *z* be product phases generated till time *t*, and each of them have an extended volume of  $v_i$  where  $i = 1, \ldots, z$ . Both when they are generated all at once and when they are sequentially generated in order of 1, 2, ..., and *z*, the ratio of unchanged region (1 - X) can be considered equal to the probability that an arbitrarily chosen area does not belong to any product phases, so it can be expressed by

$$1 - X = \left(\frac{V_0 - \upsilon_1}{V_0}\right) \cdot \left(\frac{V_0 - \upsilon_2}{V_0}\right) \dots \left(\frac{V_0 - \upsilon_z}{V_0}\right)$$
$$= \left(1 - \frac{\upsilon_1}{V_0}\right) \cdot \left(1 - \frac{\upsilon_2}{V_0}\right) \dots \left(1 - \frac{\upsilon_z}{V_0}\right)$$
(Eq 9.8)

The logarithm of multiplication is equal to the addition of the logarithm of each term. Therefore, Eq 9.8 can be rewritten as

$$\ln (1 - X) = \ln [1 - (\upsilon_1/V_0)] + \ln [1 - (\upsilon_2/V_0)] + \dots + \ln [1 - (\upsilon_z/V_0)]$$
(Eq 9.9)

Because an individual product phase is extremely small compared to the entire material, Eq 9.9 can be rearranged by an approximation,  $\ln (1 + x) \approx x$ , and Eq 9.7 can be obtained:

$$\ln (1 - X) \approx -(\upsilon_1 + \upsilon_2 + \ldots + \upsilon_z)/V_0 \rightarrow X \approx 1 - \exp(-V_{\text{ex}}/V_0)$$

Figure 9.4(a) illustrates the state of "impingement" when four product phases are generated in order of I  $\rightarrow$  IV, and they grow at a constant rate. Figure 9.4(b) is the illustration of Eq 9.7, and it can be seen that the total of extended volumes  $V_{\text{ex}}$  reaches about three times the total volume of the material  $V_0$  at a time of X = 0.95 when phase change is almost completed.

If such a general idea of an extended volume is used, the JMAK equation can be easily derived.



**Fig. 9.4** (a) The impingement of product phases. (b) The relation between the extended volume and the rate of change. The extended volume  $(V_{ex})$  ignoring "impingement" reaches about three times the total volume of the material  $(V_0)$  at the end of the phase transition

**[Exercise 9.3]** Find out JMAK equations for two cases of phase change:

- (i) When  $n_0$  nuclei are generated all at once in a unit volume at t = 0 (simultaneous nucleation)
- (ii) When nuclei are generated one after another at a constant rate  $I (m^{-3}/s)$  (constant nucleation rate)

Here it is assumed that a product phase grows spherically at a constant linear velocity  $\dot{r}$  (m/s).

**[Answer (i)]**  $V_0 n_0$  nuclei generated in the volume  $V_0$  of the material grow up to spheres with a radius  $r = \dot{r}t$  at the time *t*, and the total of extended volumes becomes  $V_{\text{ex}} = V_0 n_0 (4\pi/3)(\dot{r}t)^3$ . Therefore, the JMAK equation will become

$$X = 1 - \exp[-(4\pi/3)n_0\dot{r}^3 \cdot t^3]$$
 (Eq 9.10)

**[Answer (ii)]** The number of nuclei generated between the time  $\tau$  and  $\tau + d\tau$  is  $V_0 I d\tau$ . The extended volume of these nuclei at the time *t* is  $(4\pi/3)[\dot{r}(t-\tau)]^3$ . Therefore, the total extended volume at time *t* is:

$$V_{\rm ex} = (4\pi/3)V_0 I \dot{r}^3 \int_0^t (t-\tau)^3 d\tau = (\pi/3)V_0 I \dot{r}^3 t^4$$
 (Eq 9.11)

From Eq 9.11 and Eq 9.7, the JMAK equation can be obtained:

$$X = 1 - \exp[-(\pi/3)I\dot{r}^3 \cdot t^4]$$
 (Eq 9.12)

The equation Johnson and Mehl presented first was this equation for n = 4.

As shown in Fig. 9.5, the JMAK equation is a sigmoidal curve; the larger the index n is, the narrower the time width of phase change becomes, and the curve will become a vertically elongated "S".

#### 9.2.2 JMAK Equation for Precipitation

If a globular precipitate grows under diffusion control, its radius can be approximated by the following equation according to the analysis in Section 6.2.

$$r = [2D(x_0 - x_e)/(x_0 - x_e)]^{1/2} \cdot t^{1/2} \text{ [see Eq 6.27]}$$
(Eq 9.13)

Here D is the diffusion coefficient of solute atoms,  $x_0$  is the concentration of a solute in a supersaturated solution,  $x_e$  is the equilibrium solid



Fig. 9.5 The change of JMAK curve according to its coefficient k and exponent n



Fig. 9.6 The extended volume of the territory of a precipitate

solubility at the aging temperature, and  $x_{\theta}$  is the concentration of a solute in a precipitation phase.

According to Eq 9.13, precipitates can continue growing unlimitedly. However, because precipitates grow by absorbing solute atoms, "a territory" where the solute concentration is decreased should be formed around each particle, and the growth of particles ought to become dull by impingement of these territories (Fig. 9.6).

Therefore, Eq 9.13 is a growth equation about an extended radius  $(r_{ex})$  ignoring impingement of territories. Bearing this in mind, think about the following exercise.

**[Exercise 9.4]** Find JMAK equations for globular precipitates generated (i) by simultaneous nucleation and (ii) at a constant nucleation rate.

**[Answer (i)]** When  $n_0$  particles nucleate simultaneously in a unit volume, the total of extended volumes can be expressed using Eq 9.13 if the volume of the entire material is denoted by  $V_0$ :

$$(V_{\rm P})_{\rm ex} = V_0 n_0 (4\pi/3) r_{\rm ex}^3$$
  
=  $V_0 n_0 (4\pi/3) [2D(x_0 - x_{\rm e})/(x_{\rm \theta} - x_{\rm e})]^{3/2} \cdot t^{3/2}$  (Eq 9.14)

The total volume at the end of precipitation, according to the balance beam rules in Fig. 9.6(a) is

$$(V_{\rm P})_0 = V_0 \cdot f_{\theta} = V_0 (x_0 - x_{\rm e}) / (x_{\theta} - x_{\rm e})$$
 (Eq 9.15)

Therefore, the JMAK equation can be obtained, and the index for rate of change is n = 3/2:

$$X_{\rm P} = 1 - \exp[-(V_{\rm P})_{\rm ex}/(V_{\rm P})_0] = 1 - \exp(-k_{\rm p} \cdot t^{3/2})$$
  

$$k_{\rm p} = (8\sqrt{2}\pi/3)n_0 D^{3/2} f_{\theta}^{1/2}$$
(Eq 9.16)

**[Answer (ii)]** When precipitation nuclei are generated at a rate of  $I(m^{-3}/s)$ , the number of particles that nucleate between the time  $\tau$  and  $\tau + d\tau$  is  $V_0I d\tau$ . The extended volume for these particles at the time *t*, according to Eq 9.13 is

$$(4\pi/3)r_{\rm ex}^3 = (4\pi/3)(2Df_{\theta})^{3/2} \cdot (t-\tau)^{3/2}$$
 (Eq 9.17)

Therefore, the total extended volume of particles at the time t becomes

$$(V_{\rm P})'_{\rm ex} = \int_0^t (4\pi/3) r_{\rm ex}^3 \cdot V_0 I d\tau = (8\pi/15) V_0 I (2Df_{\theta})^{3/2} \cdot t^{5/2} \qquad ({\rm Eq} \ 9.18)$$

Therefore, the JMAK equation can be obtained, and the index for rate of change is n = 5/2:

$$X'_{\rm p} = 1 - \exp\left(-k'_{\rm p} \cdot t^{5/2}\right) \\ k'_{\rm p} = (16\sqrt{2}\pi/15)ID^{3/2}f_{\theta}^{1/2}$$
 (Eq 9.19)

Figure 9.7 shows examples of calculation for the rate of change in precipitation ( $X_P$ ) and the particle radius (r) by Eq 9.16 for simultaneous nucleation of  $n_0$  particles.

#### 9.2.3 JMAK Equation for $\gamma \rightarrow \alpha$ Transformation of Steel

If Fe or Fe-C alloy is cooled from the temperature region of  $\gamma$  phase (fcc),  $\alpha$  phase (bcc) is formed. Control of this  $\gamma \rightarrow \alpha$  transformation is a principal subject in heat treatment of steel, and various studies on it



Fig. 9.7 Analysis by JMAK equation for precipitation by simultaneous nucleation

have been carried out. In the following two exercises, consider the transformation by JMAK equation using the simplest model. Refer to the technical books (Ref 5–7) for details.

**[Exercise 9.5]** Analyze the  $\gamma \rightarrow \alpha$  transformation of a pure iron by JMAK equation, and complete the T-T-T diagram expressing the relationship of time (*t*)-temperature(*T*)-transformation. Here, let the mean radius of grains in  $\gamma$  phase be  $\bar{R} = 25 \,\mu\text{m}$ , and the nuclei of  $\alpha$  phase nucleate simultaneously at all the corners of grain boundaries of  $\gamma$  phase. Moreover, the driving force of  $\gamma \rightarrow \alpha$  transformation ( $\Delta G_{\text{Fe}}^{\gamma \rightarrow \alpha}$ ) is assumed to be the value (Ref 8) shown in Fig. 9.8(a, upper).

**[Answer]** If the transformation rate of pure iron is consider proportional to the driving force in the same way as the case of solidification of a pure metal (Eq 5.64), the growth rate for extended radius of  $\alpha$  phase  $(\dot{r}_{\alpha})_{ex}$  can be calculated by

Growth rate Interfacial  

$$(\dot{r}_{\alpha})_{\text{ex}} = M^{\alpha/\gamma} \times \Delta G_{\text{Fe}}^{\gamma \to \alpha} = (D_{\text{Fe}}^{\alpha/\gamma} / \delta RT) \cdot \Delta G_{\text{Fe}}^{\gamma \to \alpha}$$
 (Eq 9.20)

Here  $\delta$  is the thickness of  $\alpha/\gamma$  interface and assumed to be three-atom width (0.75 × 10<sup>-9</sup> m).  $D_{\text{Fe}}^{\alpha/\gamma}$  is the coefficient of diffusion across  $\alpha/\gamma$  interface, and if it is approximated by the coefficient of grain-boundary diffusion for pure iron, then it can be estimated by (Ref 9):

$$D_{\rm Fe}^{\alpha/\gamma} \approx D_{\rm Fe}^{\rm gb} = 8.8 \times 10^{-4} \exp{(-167,000/RT)}$$



Fig. 9.8 The T-T-T diagram for  $\gamma \rightarrow \alpha$  transformation of steel (the isothermal transformation diagram). The transformation of pure iron is interface control. The transformation of Fe-C alloys is diffusion control of C atoms.

For example, at T = 1050 K,  $D_{\text{Fe}}^{\alpha/\gamma} \approx 4.3 \times 10^{-12} \text{ m}^2/\text{s}$ , and  $\Delta G^{\gamma \to \alpha} \approx 180 \text{ J/mol}$ . Therefore, the growth rate of extended radius can be estimated as  $(\dot{r}_{\alpha})_{\text{ex}} \approx 88 \,\mu\text{m/s}$ .

On the other hand, because each corner is owned jointly by four grains, if a grain of  $\gamma$  phase is approximated by the tetrakaidecahedron (14-hedron) model (Fig. 9.8, upper), the number of corners per grain is 24/4 = 6. Therefore, the number of nuclei of  $n_0 = 6/(4\pi/3)\bar{R}^3 = 9.2 \times 10^{13} (\text{m}^{-3})$ .

If these nuclei are generated all at once and grow up spherically at a constant rate, the JMAK equation becomes

$$X(\gamma \text{Fe} \to \alpha \text{Fe})$$
  

$$\approx 1 - \exp\left\{-(4\pi/3)n_0 \cdot \left[(\dot{r}_{\alpha})_{\text{ex}}\right]^3 \cdot t^3\right\} \text{ (see Eq 9.10)} \qquad \text{(Eq 9.21)}$$

The T-T-T diagram calculated by Eq 9.21 is shown by the long-dashed/ short-dashed line in Fig. 9.8(b, lower).

**[Exercise 9.6]** Estimate the T-T-T diagram for  $\gamma \rightarrow \alpha$  transformation of Fe-0.22mass%C (atomic fraction:  $x_0 = 0.01$ ). Here, the nucleation of  $\alpha$  phase is assumed simultaneously at the corners of grain boundaries of  $\gamma$  crystal in the same way as Exercise 9.5.

**[Answer]** Nuclei of  $\alpha$  phase generated at the grain-boundary corners of  $\gamma$  phase of Fe-C system grow by excluding C atoms (Fig. 9.8b, upper).

Therefore, the extended radius of  $\alpha$  phase can be approximated similarly to the equation for diffusion-controlled precipitation (Eq 9.13).

$$(r_{\alpha})_{\rm ex} = \left[2D_{\rm C}^{\gamma {\rm Fe}}(x_{\gamma} - x_0)/(x_{\gamma} - x_{\alpha})\right]^{1/2} \cdot t^{1/2}$$
 (Eq 9.22)

Here  $x_{\gamma}$  is the equilibrium composition of  $\gamma$  phase at the transformation temperature, and, for example,  $x_{\gamma} = 0.02$  at T = 1050 K.  $x_{\alpha} \approx 0$  is the equilibrium composition of  $\alpha$  phase.

Therefore, the JMAK equation for  $\gamma \rightarrow \alpha$  transformation in question can be approximated similarly to Eq 9.16 by

$$X(\gamma \text{Fe-C} \to \alpha \text{Fe}) = 1 - \exp\left(-k_{\text{Fe-C}} \cdot t^{3/2}\right) \\ k_{\text{Fe-C}} = (8\sqrt{2}\pi/3)n_0 \left(D_{\text{C}}^{\gamma \text{Fe}}\right)^{3/2} \left[(x_{\gamma} - x_0)/(x_{\gamma} - x_{\alpha})\right]^{1/2}$$
 (Eq 9.23)

 $n_0$  in Eq 9.23 has the same value  $(9.2 \times 10^{13})$  as in Exercise 9.5. The diffusion coefficient can be estimated by (Ref 10):

$$D_{\rm C}^{\gamma \rm Fe} = 4.7 \times 10^{-5} \exp\left(-155,000/RT\right)$$

As shown by the solid curves in Fig. 9.8(b, lower),  $\gamma \rightarrow \alpha$  transformation of Fe-C system is considerably slower than  $\gamma \rightarrow \alpha$  transformation of pure iron.

# 9.3 Thermodynamics of Eutectic Solidification and Eutectoid Transformation

If an alloy at its eutectic (or eutectoid) composition undergoes controlled cooling, a lamellar structure is formed with two kinds of platelike crystals alternately laminated in the same way as Al-Al<sub>2</sub>Cu system shown in Fig. 9.9(b)\*.

Because this lamellar structure is formed by diffusion of solute atoms, the interval of layers ( $\lambda$ ) was thought to depend on the diffusion coefficient (*D*). However, Zener (1946) made it clear by his unique thermodynamic analysis that  $\lambda$  is not dependent on *D* but is inversely proportional to  $\Delta T$ , the degree of supercooling from the eutectic point (or the

<sup>\*</sup>Ordinary eutectic or eutectoid structure is lamellar, but it often becomes a rodlike eutectic crystal such as Al-Al<sub>3</sub>Ni system in Fig. 9.9(c) if the volume fraction of one phase is f < 0.25 (Ref 11, 12) (Exercise 9.5). Lamella faults as shown in Fig. 9.9(b, lower) are often formed at a low solidification rate of about 1 µm/s.



Fig. 9.9 Optical microscopic images of the vertical and the cross section of the unidirectional eutectic solidification structure. (a) Phase diagrams. (b) Lamellar eutectic structure. (c) Rodlike eutectic structure. Courtesy of Y. Kawahara

eutectoid point) (Ref 13). This section explains the gist of Zener's analytical method.

## 9.3.1 Effective Driving Force on Eutectic-Eutectoid Transformation

The driving force to promote phase transformation  $(\Delta G_T)$  can be expressed in general by

Total driving force of transformation:  $\Delta G = (\Delta H/T_E) \cdot \Delta T$  (Eq 9.24)

Here  $\Delta H$  is the enthalpy change during transformation,  $T_{\rm E}$  is the transformation temperature, and  $\Delta T$  is the degree of supercooling.

However, in case of eutectic-eutectoid transformation, the driving force will decrease because  $\alpha/\beta$  interface is formed according to transformation. Consider how much this decrease is in the following exercise.

**[Exercise 9.7]** Show that the energy required for formation of  $\alpha/\beta$  laminated interface can be approximated by

Energy of interface formation; 
$$\Delta G^{\alpha/\beta} = 2\sigma^{\alpha/\beta}V/\lambda$$
 (Eq 9.25)

Here  $\sigma^{\alpha/\beta}$  is the interface energy of  $\alpha/\beta$ , *V* is the molar volume of  $\alpha + \beta$  structure, and  $\lambda = \lambda_{\alpha} + \lambda_{\beta}$  is the thickness per unit of the laminated structure.

**[Answer]** Because  $V \cdot \lambda^{-1}$  layers of  $\alpha$  and  $\beta$  exist in a rectangular prism of volume V as shown in Fig. 9.10(a), and every unit of  $\alpha + \beta$  layer has two  $\alpha/\beta$  interfaces, the total area of interfaces is  $A^{\alpha/\beta} = 2V \cdot \lambda^{-1}$ , and the total amount of energy can be expressed by Eq 9.25 in question.

**[Another answer]** In each layer of  $\alpha$  and  $\beta$ , the pressures of  $\Delta P_{\alpha} = \sigma^{\alpha/\beta} \cdot \lambda_{\alpha}^{-1}$  and  $\Delta P_{\beta} = \sigma^{\alpha/\beta} \cdot \lambda_{\beta}^{-1}$  are caused by the Gibbs-Thomson effect (Section 5.2) of interface tension, respectively.\* These pressures act negatively on the growth of both  $\alpha$  and  $\beta$  phases and reduce the driving force. The amount of reduction agrees with Eq 9.25 in question according to the relation  $\Delta G = \Delta P \cdot V$ :

$$\Delta G^{\alpha/\beta} = \Delta P_{\alpha} \cdot f_{\alpha} V + \Delta P_{\beta} \cdot f_{\beta} V = \sigma^{\alpha/\beta} V \left( f_{\alpha} \cdot \lambda_{\alpha}^{-1} + f_{\beta} \cdot \lambda_{\beta}^{-1} \right)$$
$$= 2\sigma^{\alpha/\beta} V \cdot \lambda^{-1}$$
(Eq 9.26)

Here  $f_{\alpha} = \lambda_{\alpha} \cdot \lambda^{-1}$  and  $f_{\beta} = \lambda_{\beta} \cdot \lambda^{-1}$  are the volume fractions of both phases.



Fig. 9.10 The formation energy of interface during eutectic or eutectoid transformation  $\Delta G^{\alpha/\beta}$ 

\*A thin plate has two faces, the front and the back, and the pressure inside it is  $\Delta P = 2\sigma \cdot \lambda^{-1}$  (Exercise 5.3). On the other hand, lamellar structure has one interface per layer, and the internal pressure is  $\Delta P = \sigma \cdot \lambda^{-1}$ .

The effective driving force obtained by subtraction of the aforementioned  $\Delta G^{\alpha/\beta}$  from the total driving force  $\Delta G$  can be expressed by

Effective driving force: 
$$\Delta G_{\text{eff}} = \Delta G - 2\sigma^{\alpha/\beta} V/\lambda$$
 (Eq 9.27)

This effective driving force is, as discussed in the following sections, no more than  $\frac{1}{2}$  of  $\Delta G$  for eutectic solidification or  $\frac{1}{2}$  of  $\Delta G$  for eutectoid transformation.

## **9.3.2 Rate Equation of Eutectic Solidification** (Volume Diffusion Model)

Transformation from liquid phase (L) to eutectic  $(\alpha + \beta)$  is promoted by diffusion of A and B atoms in a liquid phase in front of an eutectic. Here, to make consideration easy, a simple eutectic shown in Fig. 9.11(a) is explained on the assumption that the molar volume of each phases, L,  $\alpha$ , and  $\beta$  satisfies  $V_L = V_{\alpha} = V_{\beta}$ .

**Driving Force for Diffusion in Liquid Phase.** If B atom in a liquid phase is noticed, B atoms exhausted from the front ① of  $\alpha$  phase diffuse toward the front ② of  $\beta$  phase and they are absorbed into  $\beta$  phase (Fig 9.11). The drop of chemical potential promoting this diffusion from  $\bigcirc \rightarrow \oslash$  can be approximated according to the illustration of the free-energy diagram shown in Fig. 9.11(b) by



**Fig. 9.11** The driving force on diffusion during eutectic solidification  $\Delta G_{\text{eff.}}$  (a) The phase diagram for eutectic system. (b) The free energy diagram ( $T = T_1$ ). (c) The diffusion of component atoms

$$\Delta \mu_{\rm B}^{\rm L} \ (\mbox{$\mathbbmm$$$ $\longrightarrow$ $$}\ ) \approx \Delta G_{\rm eff} / x_{\rm B}^{\rm L} \tag{Eq 9.28}$$

Similarly, the drop of chemical potential promoting the diffusion of A atoms becomes:

$$\Delta \mu_{\rm A}^{\rm L} \ (@ \to @) \approx \Delta G_{\rm eff} / (1 - x_{\rm B}^{\rm L}) \tag{Eq 9.28a}$$

**Diffusion Flow Rate in Liquid Phase.** The diffusion flow rates of A and B atoms by the aforementioned driving force can be expressed as

Flow rate Mobility Potential  
gradient 
$$v_{\rm B}^{\rm L}(\mathbb{O} \to \mathbb{O}) = (D_{\rm A-B}^{\rm L}/RT_{\rm E}) \cdot [\Delta \mu_{\rm B}^{\rm L}/(\lambda/2)]$$
 (Eq 9.29)

$$v_{\rm A}^{\rm L} (\mathcal{D} \to \mathbb{O}) = \left( D_{\rm A-B}^{\rm L} / RT_{\rm E} \right) \cdot \left[ \Delta \mu_{\rm A}^{\rm L} / (\lambda/2) \right]$$
 (Eq 9.29a)

Equation for Growth Rate of Eutectic. The necessary supply of B atoms is  $(1 - x_B^L)v$  for  $\beta$  phase with  $x_B^\beta = 1$  in a liquid phase where the concentration of B is  $x_B^L$  as a parent phase to grow at a rate of v. In the same way,  $(1 - x_A^L)v$  of A atoms must be supplied in order for  $\alpha$  phase with  $x_A^\alpha = 1$  to grow at a rate of v. Therefore, it is necessary that the following relationship holds among  $v_B^L$ ,  $v_A^L$ , and v.

$$v_{\rm B}^{\rm L} = (1 - x_{\rm B}^{\rm L})v, \ v_{\rm A}^{\rm L} = (1 - x_{\rm A}^{\rm L})v = x_{\rm B}^{\rm L}v$$
 (Eq 9.30)

When Eq 9.27 to 9.30 are rearranged, the rate equation can be obtained:

Growth rate Rate Effective  
equation of eutectic: 
$$\begin{array}{c} \text{Rate} & \text{Effective} \\ \text{coefficient} & \text{driving force} \\ v = \left(\frac{k_{\text{E}}}{\lambda}\right) & \bullet & \left(\Delta G - \frac{2\sigma^{\alpha/\beta}V}{\lambda}\right) \\ k_{\text{E}} = 2D_{\text{A-B}}^{\text{L}}/RT_{\text{E}}x_{\text{B}}^{\text{L}}(1 - x_{\text{B}}^{\text{L}}) \end{array}\right)$$
(Eq 9.31)

**Optimum Condition for Eutectic Solidification.** The rate equation (Eq 9.31) involves three variables (growth rate v, layer interval  $\lambda$ , and driving force  $\Delta G$ ), and as it is the relations among variables that cannot be understood. However, if it is rearranged, the breakdown of energy consumption during eutectic solidification can be understood:

Total driving force Interface energy Diffusion energy  

$$\Delta G(L \to \alpha + \beta) = \frac{2\sigma^{\alpha/\beta}V}{\lambda} + \frac{\lambda}{k_{\rm E}V}$$
(Eq 9.32)

Here the second term on the right-hand side is the effective driving force  $(\Delta G_{\text{eff}})$  to promote the growth of eutectic, and it corresponds to the energy consumed by diffusion of A and B atoms in a liquid phase in front of eutectic.

**[Exercise 9.8]** Show that the total driving force  $(\Delta G)$  is minimized at the layer interval  $(\lambda_0)$  to maximize the growth rate of eutectic in eutectic solidification  $(\mathbf{L} \rightarrow \alpha + \beta)$ . In this case, also show that the energy consumed by formation of interface  $(\Delta G^{\alpha/\beta})$  and the one consumed by diffusion  $(\Delta G_{\text{eff}})$  are equal.

**[Answer]** Partially differentiating Eq 9.31 and 9.32 with respect to  $\lambda$ , and finding out the extreme value conditions, then the following relations can be obtained.

Maximum growth rate:  $(\partial v / \partial \lambda) = 0 \rightarrow \Delta G_{\min} = 4\sigma^{\alpha/\beta} V / \lambda_0$  (Eq 9.33)

Minimum total driving force: 
$$(\partial \Delta G / \partial \lambda) = 0 \rightarrow v_0 \cdot \lambda_0^2$$
  
=  $2\sigma^{\alpha/\beta}Vk_{\rm F}$  (Eq 9.34)

As shown in Fig. 9.12(a),  $\Delta G$  is minimized and v is maximized at  $\lambda = \lambda_0$ . On the other hand,  $\Delta G^{\alpha/\beta} = \Delta G_{\text{eff}} = \Delta G/2$  at  $\lambda = \lambda_0$ .

Zener called these the optimum conditions, and he advocated that the interval of layers in an actual eutectic structure corresponds to  $\lambda_0$ . Actually, if the experimental results (Ref 11, 12) and the calculated values of Eq 9.34 are compared, they agree very well, as shown in Fig. 9.12(b).



**Fig. 9.12** (a) The relation of  $v - \lambda - \Delta T$  obtained from the optimum conditions. (b) The example of experiment on  $v \cdot \lambda^2 = \text{const}$ 

Rearranging Eq 9.24 and Eq 9.33 and 9.34, the relations between the lamellar spacing and growth rate of eutectic structure and the degree of supercooling ( $\Delta T$ ) can be obtained:

Lamellar spacing: 
$$\lambda_0 = k_1 / \Delta T$$
, where  $k_1 = 4\sigma^{\alpha/\beta} V T_E / \Delta H$  (Eq 9.35)

Growth rate: 
$$v_0 = k_2 \cdot (\Delta T)^2$$
, where  $k_2 = 2\sigma^{\alpha/\beta} V k_E / k_1^2$  (Eq 9.36)

This indicates that the lamellar spacing  $\lambda$  has nothing to do with the diffusion coefficient *D*, and it is in inverse proportion to the degree of supercooling  $\Delta T$ .

## **9.3.3 Rate Equation of Eutectoid Transformation** (Interface Diffusion Model)

Volume diffusion in a solid phase is generally by far slower than diffusion in a liquid phase. Therefore, if the growth rate of eutectoid phase is evaluated considering that eutectoid transformation proceeds by a mechanism similar to that of eutectic solidification, then it becomes about  $10^{-9}$  m/s and does not agree with the actual eutectoid rate (about  $10^{-6}$  m/s) at all.

So, Turnbull et al. (Ref 14, 15) advocated the eutectoid transformation model according to diffusion along the interface between a parent phase ( $\gamma$ ) and an eutectoid phase ( $\alpha + \beta$ ) (see Section 6, 4, 3 for interface diffusion). In the following analysis, it is assumed that a product phase ( $\alpha$ ,  $\beta$ ) is pure A, B phase, the molar volumes of each phases  $\alpha$ ,  $\beta$ , and  $\gamma$  are  $V_{\alpha} = V_{\beta} = V_{\gamma}$ , and the concentration of B at the interface between  $\alpha + \beta$  and  $\gamma$  is equivalent to that in a parent phase  $\gamma$  (that is,  $x_{\rm B}^{\rm i} = x_{\beta}^{\rm a}$ ).

**Comparison of Interface Diffusion Model and Volume Diffusion Model—[Exercise 9.9].** Show that the ratio of the growth rate of eutectoid by interface diffusion  $v^*$  to the growth rate of eutectoid by volume diffusion v can be approximated using

$$\frac{v^{*}(\text{interface diffusion})}{v(\text{volume diffusion})} \approx \frac{D_{B}^{i} \cdot \delta}{D_{B}^{p} \cdot \lambda/2}$$
(Eq 9.37)

Here  $D_{\rm B}^{\rm i}$  is the interface diffusion coefficient of B atoms,  $D_{\rm B}^{\gamma}$  is the volume diffusion coefficient in  $\gamma$  phase,  $\delta$  is the thickness of the interface, and  $\lambda$  is the lamellar spacing.

**[Answer]** First, consider the relation between the interface diffusion rate of B atoms  $v_{\rm B}^{\rm i}$  and the growth rate of eutectoid  $v^*$ .

As shown in Fig. 9.13(a), the flow rate (per unit time) of B atoms transferring from the front of  $\alpha$  phase O \* to the front of  $\beta$  phase O \* is  $j_{\rm B}^{\rm i} \approx x_{\rm B}^{\gamma} \cdot \delta \cdot \upsilon_{\rm B}^{\rm i}$ . Moreover, because the necessary supply of B atoms in



**Fig. 9.13** The interface diffusion model for eutectoid transformation and the relation of  $v^* - \lambda^* - \Delta T$ . (a) Movement of B atoms. (b) Mutual relationship among  $\lambda$ ,  $\Delta G$ , degree of supercooling, and growth rate

order for  $\beta$  phase to grow at a rate of  $v^*$  is  $j_B^{i \to \beta} \approx (1 - x_B^{\gamma}) \cdot (\lambda_{\beta}/2) \cdot v^*$ and  $j_B^i = j_B^{i \to \beta}$  in a stationary state, the following equation can be obtained.

$$v^* = [\delta/(\lambda/2)(1-x_{\rm B}^{\gamma})]v_{\rm B}^{\rm i}$$
 (Eq 9.38)

Here the relation of  $\lambda_{\beta} = \lambda \cdot x_{B}^{\gamma}$  is used.

Next, when returning back to the rate equation to obtain the relation between  $v_{\rm B}^{\rm i}$  and the driving force, the following equation can be obtained.

Flow rate Mobility Potential gradient  

$$v_{\rm B}^{\rm i}(\mathbb{O}^* \to \mathbb{O}^*) = (D_{\rm B}^{\rm i}/RT) \cdot [\Delta \mu_{\rm B}^{\rm i}(\mathbb{O}^* \to \mathbb{O}^*)(\lambda/2)]$$
(Eq 9.39)

It can be thought that  $\Delta \mu_B^i$  ( $\mathbb{O}^* \rightarrow \mathbb{Q}^*$ ) in Eq 9.39 is equal to the drop of chemical potential on the side of  $\gamma$  phase;  $\Delta \mu_B^{\gamma}$  ( $\mathbb{O} \rightarrow \mathbb{Q}$ ) according to the principle of local equilibrium. Therefore, rearranging Eq 9.27 and 9.28 and Eq 9.38 and 9.39, the rate equation by the interface diffusion model can be obtained:

Rate coefficient Effective driving force

Growth rate equation of eutectoid: 
$$v^* = \left(\frac{k_{\rm E}^*}{\lambda^2}\right) \cdot \left(\Delta G - \frac{2\sigma^{\alpha/\beta}V}{\lambda}\right)$$
  
 $k_{\rm E}^* = 4D_{\rm B}^{\rm i}\delta/RTx_{\rm B}^{\gamma}(1-x_{\rm B}^{\gamma})$ 
(Eq 9.40)

If the ratio of Eq 40 to the growth rate equation by the volume diffusion model (Eq 9.31) is found out, Eq 9.37 in question can be obtained.

Substituting ordinary values:  $D_{\rm B}^{\gamma} = 10^{-15} \text{ m}^2/\text{s}$ ,  $D_{\rm B}^{\rm i} = 10^{-10} \text{ m}^2/\text{s}$ ,  $\lambda = 0.05 \,\mu\text{m}$ , and  $\gamma = 0.75 \,\text{nm}$  into each parameter in the equation, the rate by the interface diffusion model is markedly faster.

$$\frac{v^*(\text{interface diffusion})}{v \text{ (lattice diffusion)}} \approx \frac{10^{-10} \cdot 0.75 \times 10^{-9}}{10^{-15} \cdot 0.025 \times 10^{-6}} \approx 3000$$

**Optimum Condition for Eutectoid Transformation**—[Exercise 9.10] Derive the mutual relationship among the growth rate ( $v^*$ ), the lamellar spacing ( $\lambda$ ), the driving force ( $\Delta G$ ), and the degree of supercooling ( $\Delta T$ ) of eutectoid by the interface diffusion model from Zener's idea of optimum conditions.

**[Answer]** Rewrite the growth rate equation of eutectoid (Eq 9.40) into the equation of energy distribution form.

Breakdown of energy consumption:

Total driving force	Interface energy	Diffusion energy	(Ea 9.41)
$\Delta G(\gamma \rightarrow \alpha + \beta) =$	$rac{2\sigma^{lpha/eta}V}{\lambda}$ -	+ $\frac{\lambda^2}{k_{\rm E}^*}v^*$	(24,711)

Next, if Eq 9.40 and 9.41 are partially differentiated and extreme values are found out, the following relations can be obtained.

Maximum growth rate:  $(\partial v^* / \partial \lambda) = 0 \rightarrow \Delta G^*_{\min} = 3\sigma^{\alpha/\beta} V / \lambda_0^*$  (Eq 9.42) Minimum total driving force:  $(\partial \Delta G / \partial \lambda) = 0 \rightarrow v_0^* (\lambda_0^*)^3 = \sigma^{\alpha/\beta} \bar{V} k_E^*$  (Eq 9.43)

As illustrated in Fig. 9.13(b),  $\Delta G^*$  is minimized and  $v^*$  is maximized at  $\lambda^* = \lambda_0^*$ . In addition, the following relations can also be obtained.

Lamellar spacing:  $\lambda_0^* = k_1^* / \Delta T$ , where  $k_1^* = 3\sigma^{\alpha/\beta} V T_E / \Delta H$  (Eq 9.44)

Growth rate: 
$$v_0^* = k_2^* \cdot (\Delta T)^3$$
, where  $k_2^* = \sigma^{\alpha/\beta} V k_E^* / (k_1^*)^3$  (Eq 9.45)

Breakdown of energy consumption:  $\Delta G_{eff}^* = \Delta G^{\alpha/\beta}/2 = \Delta G^*/3$  (Eq 9.46)

## 9.3.4 Rate Equation of Pearlite (Interface Diffusion and Interface Migration Model)

Pearlite of the Fe-C system is the most widely known eutectoid structure. However, because C atoms are interstitial atoms, in spite of

eutectoid transformation, it grows at an unusual rate equal to that of eutectic (Fig. 9.14b).\* Therefore, the aforementioned interface diffusion model is insufficient for analysis on pearlite transformation, and a combined model of interface migration and interface diffusion should be adopted. The detailed investigation can be found in Ref 16 to 19, and only the points of the analysis are explained here.

Is the Diffusion of C Atoms During Pearlite Transformation a Volume Diffusion or an Interface Diffusion? The coefficient  $(D_C^{\gamma Fe})$  for interstitial volume diffusion of C atoms in  $\gamma Fe$  is about 10<sup>9</sup> times the self-diffusion coefficient of Fe atoms  $(D_{Fe}^{\gamma})$  (Fig. 9.15a). On the other hand, if the coefficient of diffusion along  $\alpha + \theta/\gamma$  interface in front of pearlite  $(D_C^i)$  is assumed five times the coefficient of interstitial volume diffusion in  $\alpha Fe$   $(D_C^{\alpha Fe})$  because its value has not been determined, yet, the relative ratio of growth rate of pearlite by interface diffusion to that by volume diffusion can be estimated about 13 times according to the Eq 9.37.



**Fig. 9.14** (a) The electron micrograph image of Fe-C pearlite replica. (b) Comparison of  $\lambda$  and v of Fe-C pearlite and ordinary eutectic or eutectoid

\*Because  $v \cdot \lambda^2$  of an eutectic is in proportion to the diffusion coefficient *D* according to Eq 9.34, it is not precisely constant. However, the degree of supercooling ( $\Delta T$ ) is around 1 K, the variation of the value *D* is very small, so it can be actually considered that  $v \cdot \lambda^2 \approx \text{const.}$  On the other hand, because  $\Delta T$  is 10 to 200 K for pearlite transformation, the value of  $v \cdot \lambda^3$  varies according to  $\Delta T$ , and in particular the deviation is remarkable at  $\Delta T > 100$  K.



Fig. 9.15 (a) The diffusion coefficient of Fe-C system. (b) The mechanism of pearlite transformation of Fe-C system and the breakdown of energy consumption

$$\frac{v^{*}(\text{interface diffusion})}{v \text{ (volume diffusion)}} \approx \frac{D_{\rm C}^{\rm i} \cdot \delta}{D_{\rm C}^{\gamma \text{Fe}} \cdot (\lambda/2)} \approx \frac{1.2 \times 10^{-10} \cdot 0.75 \times 10^{-9}}{2.3 \times 10^{-13} \cdot 0.03 \times 10^{-6}} \approx 13$$
(transformation temperature: 900K)

If rearranging the experimental values for the lamellar spacing ( $\lambda$ ) and the growth rate (v) of pearlite, then they are closer to those of interface diffusion ( $v^*\lambda^3 = \text{const.}$ ) than those of volume diffusion ( $v^*\lambda^2 = \text{const.}$ ) as shown in Fig. 9.14(b).

What is more, the interface diffusion model is by far more advantageous in analysis of pearlite transformation of Fe-C-M system containing an alloying element M.

Thus, the diffusion style of C atoms during pearlite transformation can be decided as interface diffusion.

Is Pearlite Transformation Controlled by Diffusion or Interface? In order for pearlite to grow, other than the interface diffusion of C atoms, transfer of Fe atoms across the interface—that is, the interface migration—is necessary (Fig. 9.15b, the upper). The energy required for this interface migration ( $\Delta G_m$ ) can be estimated by

Rate equation of interface migration:

Rate Interfacial mobility Driving force

 $v = (D_{\rm Fe}^{\rm i}/\delta RT) \times \Delta G_{\rm m}$  (see Eq 9.20) (Eq 9.47)

For example, the growth rate of pearlite whose transformation temperature is 900 K is  $v \approx 40 \,\mu\text{m/s}^{-1}$  (measured value). If the diffusion coefficient of Fe atoms transferring across the interface is presumed to be  $D_{\text{Fe}}^{\text{i}} = 2 \times 10^{-12} \text{m}^2/\text{s}$ , the energy required for interface transport can be estimated as  $\Delta G_{\text{m}} \approx 110 \,\text{J/mol}$  by Eq 9.47. This value of energy corresponds to about 24% of the total driving force of pearlite transformation at 900 K ( $\Delta G \approx 460 \,\text{J/mol}$ ).

Clearly from this example of calculation, the driving force should be considered by dividing it into three terms described below for analysis of pearlite transformation.

The	breakdown	of	energy	consumption:
-----	-----------	----	--------	--------------

Total				
driving	Interface		Interface	
force	formation	Diffusion	migration	
$\Delta G(\gamma \to \alpha + \theta) =$	$\Delta G^{lpha/ heta}$ +	- $\Delta G_{ m d}$ +	$\Delta G_{ m m}$	(Eq 9.48)

As shown in Fig. 9.15(b, lower), almost all the energy is consumed only by formation of  $\alpha/\theta$  interface and interface diffusion of C atoms in the temperature region where the degree of supercooling  $\Delta T$  is small. On the other hand, the energy consumed by interface transport  $\Delta G_{\rm m}$ becomes larger than  $\Delta G_{\rm d}$  in the temperature region of large  $\Delta T$ .

Therefore, pearlite transformation immediately below the transformation point is controlled by diffusion of C atoms, but pearlite transformation with large degree of supercooling should be considered a combined transformation of interface control and diffusion control (see Table 9.1).

#### EXERCISES

**9.11** Show that JMAK equation will be expressed by the following equation if disklike precipitates with a constant thickness ( $\delta$ ) nucleate simultaneously at the concentration of  $n_0$  particles per unit volume.

$$X_{\rm P} = 1 - \exp\left(-2\pi\delta n_0 D f_{\theta} \cdot t\right) \tag{Eq 9.49}$$

*Hint:* Application of Eq 9.16.

**9.12** The density of dislocation decreases by coalescence of dislocations of the opposite signs during the recovery process according to annealing. Show that the relation between the density of dislocation ( $\rho$ ) and annealing time (t) can be approximated by

 $1/\rho - 1/\rho_0 = kt$  (k is a constant including the diffusion coefficient) (Eq 9.50)

*Hint:* Because an attractive force in inverse proportion to the distance acts between dislocations of the opposite signs, they will coalesce and annihilate by annealing, and the mean distance between dislocations  $(\bar{z})$  will increase. The rate equation of this process is  $d\bar{z}/dt =$  mobility  $(M) \times$  driving force  $(k_1/\bar{z})$ . If it is integrated,  $(\bar{z})^2 - (\bar{z}_0)^2 = 2Mk_1 \cdot t$ . Because  $(\bar{z})^2 = 1/\rho$ , Eq 9.50 can be obtained (Ref 20).

**9.13** When a structure with globular  $\theta$  particles dispersed in it is heated, Ostwald ripening will occur by the Gibbs-Thomson effect according to the energy of  $\alpha/\theta$  interface. Show that the rule of this growth can be approximated using:

Lattice diffusion control:  $(\bar{r})^{3} - (\bar{r}_{0})^{3} = k_{ost} \cdot t$ Grain-boundary diffusion control  $(\bar{r})^{4} - (\bar{r}_{0})^{4} = k'_{ost} \cdot t$  (Eq 9.51) Dislocation diffusion control  $(\bar{r})^{5} - (\bar{r}_{0})^{5} = k''_{ost} \cdot t$ 

*Hint:* Coarsening at grain boundaries can be described by (see also Fig. 9.16):

Coarsening Area Mobility Concentration Driving  
rate of inlet of atoms gradient 
$$\left(\frac{d}{3}\pi r^3\right) = (2\pi r\delta) \cdot \left(\frac{D_B^a}{RT}\right) \cdot \left(\frac{x_B^a}{RT}\right) \cdot \left(\frac{x_B^a}{r}\right) \cdot \frac{2\sigma V}{r} \to r^3\left(\frac{dr}{dt}\right) = k$$

(Eq 9.52)

**9.14** Show that the rate of martensitic transformation in such a system as Fe-C-Ni  $(X_M)$  can be approximated using.

$$X_{\rm M} \approx 1 - \exp\left[-3\left(\frac{M_{\rm s}-T}{M_{\rm s}-M_{\rm f}}\right)\right]$$

Here  $M_s$  is the start temperature of martensitic transformation, and  $M_f$  is the finish temperature.

Hint: Application of Eq 9.7 (see Fig 9.17).

**9.15** If the composition at eutectic point inclines to one side, such an alloy tends to generate rodlike eutectics rather than lamellar eutectics. Consider the reason for it.



Fig. 9.16 Coarsening of particles on the grain boundary, with thickness,  $\delta$ 



Fig. 9.17 The rate of transformation of lenticular martensite



Fig. 9.18 The eutectic structures of lamellar type and rodlike type along with their phase diagrams

*Hint:* If  $\beta$  phases such as square bar with a thickness *a* arrange at an interval of  $\lambda$ , the total area of  $\alpha/\beta$  interfaces is  $(A^{\alpha/\beta})_{\text{bar}} = 4aV/\lambda^2 = 4V\sqrt{f_{\beta}}/\lambda$  when the volume fraction of  $\beta$  phase is denoted by  $f_{\beta}$ .

On the other hand, the total area of  $\alpha/\beta$  interfaces of lamellar structure is  $(A^{\alpha/\beta})_{\text{lamellar}} = 2V/\lambda$ . If both of them are compared,  $(A^{\alpha/\beta})_{\text{bar}} < (A^{\alpha/\beta})_{\text{lamellar}}$  for  $f_{\beta} < 0.25$  (Fig. 9.18). **9.16** When Mn (about 1%) or Mo (about 0.3%) is added to Fe-C system, the growth of pearlite will become remarkably slower and the steel will become easier to "quench." Consider the function of Mn and Mo in this case.

*Hint:* Because  $\gamma$ Fe phase is stabilized if Mn is dissolved into a solid solution, the equilibrium temperature of pearlite transformation (A<sub>1</sub> point) becomes lower and the total driving force of the transformation ( $\Delta G$ ) becomes smaller than  $\alpha$ Fe phase.

On the other hand, Mo segregates at pearlite/ $\gamma$  interface, and it makes interface transport slower by the solute drag effect (see Section 5.5.2).

### **Appendix: Carburized Pearlite**

Pearlite was discovered by a founder of steel metallography, H.C. Sorby (1863), and it is a monumental eutectoid structure named for its pearly constituent. Because wires and rods (such as piano wires) produced by drawing show such excellent strength as no other kinds of materials can so easily attain, they have been adopted as cables of long suspension bridges whose spans exceed 800 m and so on. In recent years, attention has been attracted to the mechanism of forced solid solution of Fe<sub>3</sub>C in case of ultramachining of piano wires.

Another topic is carburized pearlite (Fig. 9.19). If  $\alpha$ Fe alloy with V or Cr, which has a strong tendency of forming carbides is carburized, eutectoid



**Fig. 9.19** Pearlitic structure caused by carburization. The carburized structures of (a, upper) Fe-18Cr alloy and (b, upper) Fe-18Cr-0.8Si alloy at 1273 K. Magnification:  $300 \times$ . (a, lower) The isothermal phase diagram for Fe-M-C system. (b, lower) The relation between the lamellar spacing ( $\lambda$ ) and the growth rate ( $\nu$ )

structure analogous to pearlite is formed by a reaction of  $\alpha \rightarrow \gamma +$  carbides as illustrated in Fig. 9.19(a, lower). Because  $\gamma$  phase transforms to martensite if this is quenched, outstanding wear resistance can be obtained.

Because the growth of this eutectoid structure is controlled by volume diffusion of C atoms from surface to reaction front, it resembles the growth mechanism of eutectic rather than pearlite transformation of Fe-C system. For example, in an alloy of Fe-Cr with small amount of Si added to it, the reaction front changes to "cellular" as shown in Fig. 9.19(b, upper) (Ref 21).

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# **Reference Information**

#### **Physical Constants**

Avogadro's constant	$N_0$	$6.022\times10^{23}\text{mol}^{-1}$	Charge on electron	е	$1.602 \times 10^{-19} A \cdot s$
Boltzmann constant	$k_{\rm B}$	$1.38\times 10^{-23} J/K$	Magnetic permeability	$\mu_0$	$1.257 \times 10^{-6} \text{J/A} \cdot \text{m}$
Plank constant	h	$6.626\times 10^{-34} J$ · s	Standard acceleration	g	$9.807 \text{m/s}^2$
Molar gas constant	R	8.314 J/mol • K	ado to gravity		

#### **Unit Symbols**

A = Ampere	°F = degree Fahrenheit	m = meter
Å = angström	ft = foot	min = minute
atm = atmosphere	g = gram	mol = mole
bar = (bar) unit of pressure	h = hour	N = newton
°C = degree Celsius	in. = inch	Pa = pascal
cal = calorie	J = joule	psi = pound per square inch
dyn = dyne	K = Kelvin	s = second
eV = electron volt	$lb_f = pound force$	torr = (Torr) unit of preesure
erg = (cgs) unit of energy	$lb_m = pound mass$	W = watt

#### **SI Prefixes**

Symbol	Prefix	Exponential expression	Symbol	Prefix	Exponential expression				
Т	tera	1012	m	milli	$10^{-3}$				
G	giga	109	μ	micro	$10^{-6}$				
М	mega	10 <sup>6</sup>	n	nano	$10^{-9}$				
k	kilo	$10^{3}$	р	pico	$10^{-12}$				

#### **Greek Alphabet**

Upper and lower cases	Name	Upper and lower cases	Name	Upper and lower cases	Name	Upper and lower cases	Name	
Αα	Alpha	Нη	Eta	Νv	Nu	Ττ	Tau	
Ββ	Beta	Θθφ	Theta	Ξξ	Xi	Υυ	Upsilon	
Γγ	Gamma	Iι	Iota	0 0	Omicron	Φφφ	Phi	
Δδ∂	Delta	Кк	Kappa	Ππ	Pi	Xχ	Chi	
Eε	Epsilon	Λλ	Lambda	Ρρ	Rho	ΨΨ	Psi	
Zζ	Zeta	Μμ	Mu	Σσς	Sigma	Ωω	Omega	

#### Unit Conversion Table

Length [SI base unit: m]									
$ \begin{array}{l} 1 \hspace{0.1cm} \mathring{A} = 10^{-10} \hspace{0.1cm} m \\ 1 \hspace{0.1cm} pm = 10^{-12} \hspace{0.1cm} m \\ 1 \hspace{0.1cm} nm = 10^{-9} \hspace{0.1cm} m \\ 1 \hspace{0.1cm} \mu m = 10^{-6} \hspace{0.1cm} m \end{array} $	$\begin{array}{l} 1 \mbox{ mm} = 10^{-3} \mbox{ m} \\ 1 \mbox{ km} = 10^{3} \mbox{ m} \\ 1 \mbox{ in.} = 0.025 \mbox{ m} \\ 1 \mbox{ ft} = 0.305 \mbox{ m} \end{array}$								
Mass [SI base unit: kg]									
$\begin{array}{l} 1 \ g = 10^{-3} \ kg \\ 1 \ Mg = 10^{3} \ kg \end{array}$	$1\ lb=0.454\ kg$								
Mass density [SI unit: kg/m <sup>3</sup> ]									
$\begin{array}{l} 1 \ g \ / \ cm^3 = 10^3 \ kg/m^3 \\ 1 \ lb/ft^3 = 16.02 \ kg/m^3 \\ 1 \ lb/in.^3 = 27.7 \times 10^3 \ kg/m^3 \end{array}$									
Time [SI base unit: s]									
$1 \min = 60 s$	$1\ h=3.6\ ks$								
Force [SI unit: $N = kg \cdot m/s^2$ ]									
$1 \text{ dyn} = 10^{-5} \text{ N}$ 1 kgf = 9.807 N	1 lbf = 4.448 N								
Pressure, stress [SI unit: Pa = N/	m <sup>2</sup> ]								
1 kgf/mm <sup>2</sup> = 9.807 × 10 <sup>6</sup> Pa 1 kgf/mm <sup>2</sup> = 9.807 × 10 <sup>6</sup> Pa 1 bar = 10 <sup>5</sup> Pa 1 torr = 1 mmHg = 133.3 Pa 1 atm = 760 torr = $1.013 \times 10^5$ Pa 1 psi = 1 lb/in. <sup>2</sup> = $6.89 \times 10^3$ Pa									
Energy, work [SI unit: $J=N \ \cdot$	m]								
$ \begin{array}{c} 1 \ \text{erg} = 10^{-7} \ \text{J} \\ 1 \ \text{eV} = 1.602 \times 10^{-19} \ \text{J} \\ 1 \ \text{cal} = 4.184 \ \text{J} \end{array} $	$1 \text{ kgf} \cdot \text{m} = 9.807 \text{ J}$ 1 ft $\cdot$ 1bf = 1.356 J								

Molar energy [SI unit: J/mol]
1 cal/mol = 4.184 J/mol 1 erg/atom = $6.022 \times 10^{16}$ J/mol 1 eV/atom = $9.648 \times 10^{4}$ J/mol
Energy per unit area [SI unit: J/m <sup>2</sup> ]
$1 \text{ erg/cm}^2 = 10^{-3} \text{ J/m}^2$
Force per unit length [SI unit: N/m]
$1 \text{ dyn/cm} = 10^{-3} \text{ N/m}$
Temperature [SI base unit: K]
$\begin{array}{l} T(^{\circ}C) = T(K) \; -273 \\ T(^{\circ}F) = (9/5) \; [T(K) \; - \; 273] \; + \; 32 \end{array}$
Specific heat capacity, specific entropy [SI unit: $J/kg \cdot K$ ]
1 cal/g · °C = 4.184 kJ/kg · K
Diffusion coefficient [SI unit: m <sup>2</sup> /s]
$1cm^2/s = 10^{-4}m^2/s$
$\frac{\text{Viscosity [SI unit: Pa \cdot s]}}{1 \text{ P (poise)} = 1 \text{ dyn} \cdot \text{ cm}^{-2} \cdot \text{s} = 10^{-1} \text{ Pa} \cdot \text{s}}$

## Note for Periodic Table of Elements

Over the years, various conventions have been used to identify each group in the periodic table. A system adopted by the International Union of Pure and Applied Chemistry (IUPAC) in 1970 in which the left-side and right-side elements in periods 1 through 7 are distinguished by the addition of the letters "A" and "B" with the Roman numerals rather than Arabic numerals used in this book and by many others. In contrast to the 1970 IUPAC system, which was commonly used in Europe, the Chemical Abstracts Service (CAS) of the American Chemical Society and many other U.S. chemists applied the "B" to the additional groups (groups 3 through 12) in periods 4 through 7 and "A" to the rest. In this book, "0" is used instead of VIIIA or VIIIB to identify group 18. The most recent (1988) IUPAC recommendation is to eliminate both practices and to use Arabic numerals 1 through 18 (left to right) instead.

													_									_			
	0	2	4.0026	10	Ne	20.183	18	Ar	39.948	36	Kr	83.80	54	Xe	131.30	88	Rn	(227)		11	Lu	174.97	103	Ŀ	(257)
			7B	6	4	18.998	17	5	35.453	35	Br	79.91	53	I	127.90	85	At	(210)		70	γp	173.04	102	No	(254)
			6B	8	0	15.999	16	s	32.064	34	Se	78.96	52	Te	127.60	84	Po	(210)		69	Tn	168.93	101	PW	(256)
			5B	7	N	14.007	15	Ρ	30.974	33	As	74.922	51	Sb	121.75	83	Bi	208.98		89	Br	167.26	100	Fm	(253)
			4B	9	0	12.011	14	Si	28.086	32	g	72.59	50	Sn	118.69	82	Pb	207.19		29	Ho	164.93	66	Es	(254)
			3B	5	B	10.811	13	N	26.982	31	Ga	69.72	49	Ч	114.82	81	F	204.37		99	D	162.50	98	ç	(249)
									2B	30	Zn	65.37	48	РО	112.40	80	Hg	200.59		65	£	158.92	26	Bk	(247)
			al			tal	Im		1B	29	Cu	63.54	47	Ag	107.87	79	Au	196.97		64	В	157.25	96	CB	(247)
	etal		onmet			mime				28	N	58.71	46	Pd	106.4	78	Pt	195.09		63	Eu	151.96	95	Am	(243)
	Me		ž		7	Se	5	1	8	27	ပိ	58.933	45	Rh	102.91	11	Γ	192.2		62	Sm	150.35	94	Pu	(242)
_							/			26	Fe	55.847	#	Ru	101.07	76	ő	190.2		61	Pm	(145)	93	Np	(237)
		mic	loda	innic	6				7A	25	Mn	54.938	43	Τc	(66)	75	Re	186.2		09	PN	144.24	92	D	238.03
		Ato	Syn	+ Ato					6A	24	ç	51.996	42	Mo	95.94	74	M	183.85		59	Pr	140.91	16	Pa	(231)
	N. T.	P6←	Fet	55.847				3	5A	23	>	50.942	41	đ	92.91	73	Ta	180.95		58	ഠ്	140.12	90	Ł	232.04
		1							44	22	F	47.90	40	Zr	91.22	72	Ηf	178.49		57	La	138.91	89	Ac	(227)
									3A	21	s	44.956	39	Y	88.91		19	FI	Ac - Lr	:	nides			Pes -	
			2A	4	Be	9.0122	12	Mg	24.312	20	Ca	40.08	38	Sr	87.62	56	Ba	137.34	88 Ra (226)		anthar			Actinic	
	IA	- 5	1.0080	3	Li	6.939	11	Na	22.990	19	K	39.102	37	Rb	85.47	55	പ	132.91	87 Fr (223)	,	Ë			-	•

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