CHAPTER **3**

Thermodynamics and Phase Diagrams

THERMODYNAMICS is a branch of physics and chemistry that covers a wide field, from the atomic to the macroscopic scale. In materials science, thermodynamics is a powerful tool for understanding and solving problems. Chemical thermodynamics is the part of thermodynamics that concerns the physical change of state of a chemical system following the laws of thermodynamics. The thermodynamic properties of individual phases can be used for evaluating their relative stability and heat evolution during phase transformations or reactions. Traditionally, one of the most common applications of chemical thermodynamics is for the construction and interpretation of phase diagrams.

The thermodynamic quantities that are most frequently used in materials science are the enthalpy, in the form of the heat content of a phase; the heat of formation of a phase, or the latent heat of a phase transformation; the heat capacity, which is the change of heat content with temperature; the Gibbs free energy, which determines whether or not a chemical reaction is possible; and the chemical potential or chemical activity, which describes the effect of compositional change in a solution phase on its energy. All of these thermodynamic quantities are part of the energy content of a system and are governed by the three laws of thermodynamics.

3.1 Three Laws of Thermodynamics

A physical system consists of a substance, or a group of substances, that is isolated from its surroundings, a concept used to facilitate study of the effects of conditions of state. Isolated means that there is no interchange of mass between the substance and its surroundings. The substances in alloy systems, for example, might be two metals, such as copper and zinc; a metal and a nonmetal, such as iron and carbon; a metal and an intermetallic compound, such as iron and cementite; or several metals, such as

aluminum, magnesium, and manganese. These substances constitute the components comprising the system. However, a system can also consist of a single component, such as an element or compound.

The sum of the kinetic energy (energy of motion) and potential energy (stored energy) of a system is called its internal energy, E. Internal energy is characterized solely by the state of the system. A thermodynamic system that undergoes no interchange of mass (material) with its surroundings is called a closed system. A closed system, however, can interchange energy with its surroundings.

First Law. The First Law of Thermodynamics, as stated by Julius von Mayer, James Joule, and Hermann von Helmholtz in the 1840s, states that energy can be neither created nor destroyed. Therefore, it is called the Law of Conservation of Energy. This law means that the total energy of an isolated system remains constant throughout any operations that are carried out on it; that is, for any quantity of energy in one form that disappears from the system, an equal quantity of another form (or other forms) will appear. For example, consider a closed gaseous system to which a quantity of heat energy, δQ, is added and a quantity of work, δW, is extracted. The First Law describes the change in internal energy, dE, of the system as:

$$dE = \delta Q - \delta W \qquad \text{(Eq 3.1)}$$

In the vast majority of industrial processes and material applications, the only work done by or on a system is limited to pressure/volume terms. Any energy contributions from electric, magnetic, or gravitational fields are neglected, except for electrowinning and electrorefining processes such as those used in the production of copper, aluminum, magnesium, the alkaline metals, and the alkaline earths. When these field effects are neglected, the work done by a system can be measured by summing the changes in volume, dV, times each pressure, P, causing a change. Therefore, when field effects are neglected, the First Law can be written:

$$dE = \delta Q - PdV \qquad \text{(Eq 3.2)}$$

Second Law. While the First Law establishes the relationship between the heat absorbed and the work performed by a system, it places no restriction on the source of the heat or its flow direction. This restriction, however, is set by the Second Law of Thermodynamics, which was advanced by Rudolf Clausius and William Thomson (Lord Kelvin). The Second Law states that the spontaneous flow of heat always is from the higher-temperature body to the lower-temperature body. In other words, all naturally occurring processes tend to take place spontaneously in the direction that will lead to equilibrium.

The entropy, S, represents the energy (per degree of absolute temperature, T) in a system that is not available for work. In terms of entropy, the Second Law states that all natural processes tend to occur only with an increase in entropy, and the direction of the process is always such as to lead to an increase in entropy. For processes taking place in a system in equilibrium with its surroundings, the change in entropy is defined as:

$$dS \equiv \frac{\delta Q}{T} \equiv \frac{dE + PdV}{T} \qquad \text{(Eq 3.3)}$$

Third Law. A principle advanced by Theodore Richards, Walter Nernst, Max Planck, and others, often called the Third Law of Thermodynamics, states that the entropy of all chemically homogeneous materials can be taken as zero at absolute zero temperature (0 K). This principle allows calculation of the absolute values of entropy of pure substances solely from their heat capacity.

3.2 Gibbs Free Energy

Josiah Willard Gibbs (1839–1903) was an American theoretical physicist, chemist, and mathematician. He devised much of the theoretical foundation for chemical thermodynamics and physical chemistry. Yale University awarded Gibbs the first American Ph.D. in engineering in 1863, and he spent his entire career at Yale. Between 1876 and 1878, Gibbs wrote a series of papers on the graphical analysis of multiphase chemical systems. These were eventually published together in a monograph titled *On the Equilibrium of Heterogeneous Substances*, his most renowned work. It is now deemed one of the greatest scientific achievements of the 19th century and one of the foundations of physical chemistry. In these papers Gibbs applied thermodynamics to interpret physicochemical phenomena, successfully explaining and interrelating what had previously been a mass of isolated facts.

For transformations that occur at constant temperature and pressure, the relative stability of the system is determined by its Gibbs free energy:

$$G \equiv H - TS \qquad \text{(Eq 3.4)}$$

where H is the enthalpy. Enthalpy is a measure of the heat content of the system and is given by:

$$H = E + PV \qquad \text{(Eq 3.5)}$$

The internal energy, E, is equal to the sum of the total kinetic and potential energy of the atoms in the system. Kinetic energy results from the

vibration of the atoms in solids or liquids, and the translational and rotational energies of the atoms and molecules within a liquid or gas. Potential energy results from the interactions or bonds between the atoms in the system. If a reaction or transformation occurs, the heat that is absorbed (endothermic) or given off (exothermic) depends on the change of the internal energy of the system. It also depends on the changes in the volume of the system which is accounted for by the term PV. At a constant pressure, the heat absorbed or given off is given by the change in H. When dealing with condensed phases (solids or liquids), the term PV is usually very small in comparison to E, and therefore $H \approx E$. Finally, the entropy, S, is a measure of the randomness of the system.

A system is considered to be in equilibrium when it is in its most stable state and has no desire to change with time. At a constant temperature and pressure, a system with a fixed mass and composition (a closed system) will be in a state of stable equilibrium if it has the lowest possible value of the Gibbs free energy:

$$dG = 0 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{(Eq 3.6)}$$

From this definition of free energy, the state with the highest stability will be the one with the lowest enthalpy and the highest entropy. Therefore, at low temperatures, solid phases are the most stable because they have the strongest atomic bonding and therefore the lowest enthalpy (internal energy). However, at high temperatures, the $-TS$ term dominates and the liquid and eventually the vapor phases becomes the most stable. In processes where pressure changes are important, phases with small volumes are most stable at high pressures.

The definition of equilibrium given in Eq 3.6 is illustrated graphically in Fig. 3.1. The various possible atomic configurations are represented by the points along the abscissa. The configuration with the lowest free energy, G, will be the stable equilibrium configuration. Therefore, configuration A would be the stable equilibrium configuration. There are other configurations, such as configuration B, which lie at a local minimum of free energy but do not have the lowest possible value of G. Such configurations are called metastable equilibrium states to distinguish them from the stable equilibrium state. The other configurations that lie between A and B are intermediate states for which $dG \neq 0$ and are unstable and will disappear at the first opportunity; that is, if a change in thermal fluctuations causes the atoms to be arranged into an unstable state, they will rapidly rearrange themselves into one with a free-energy minima. An example of a metastable configuration state is diamond. Given enough time, diamond will convert to graphite, the stable equilibrium configuration. However, as in diamond, metastable equilibrium can, for all practical instances, exist indefinitely.
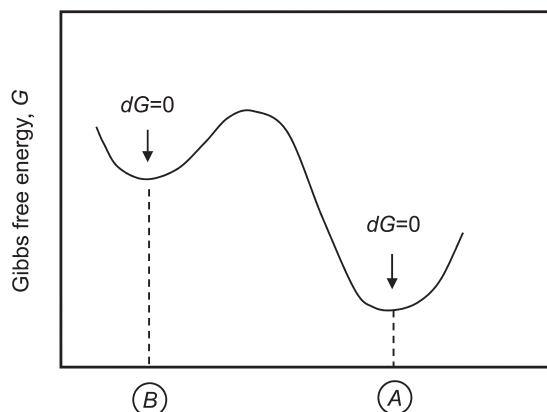
Fig. 3.1 Gibbs free energy for different atomic configurations in a system. Configuration *A* has the lowest free energy and therefore is the arrangement of stable equilibrium. Configuration *B* is in a state of metastable equilibrium. Adapted from Ref 3.1

Any transformation that results in a decrease in Gibbs free energy, *G*, is possible. Any reaction that results in an increase in *G* is impossible and will not occur. Therefore, the necessary criterion for any phase transformation is:

$$\Delta G = G_2 - G_1 < 0 \qquad\qquad\qquad\qquad \text{(Eq 3.7)}$$

where G_1 and G_2 are the free energies of the initial and final states, respectively. It is not necessary that the transformation immediately go to the stable equilibrium state. It may go through a whole series of intermediate metastable states.

Sometimes metastable states can be very short-lived, or at other times they can exist almost indefinitely. These are explained by the free-energy hump between the metastable and equilibrium states in Fig. 3.1. In general, higher free-energy humps, or energy barriers, lead to slower transformation rates.

Free Energy of Single-Component Systems

A single-component unary system is one containing a pure metal or one type of molecule that does not disassociate over the temperature range of interest. Consider the phase changes that occur with changes in temperature at a constant pressure of one atmosphere. To predict the phase changes that are stable, or mixtures that are equilibrium at different temperatures, it is necessary to be able to calculate the variation of *G* with *T*.

Specific heat is the quantity of heat required to raise the temperature of the substance by 1 K. At constant pressure, the specific heat, C_p, is given by:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad \text{(Eq 3.8)}$$

The specific heat of a substance varies with temperature in the manner shown in Fig. 3.2(a). Therefore, the variation of H with T can be obtained from the knowledge of the variation of C_p with T. The enthalpy, H, is usually measured by setting $H = 0$ for a pure element in its most stable state at room temperature (298 K, or 25 °C or 77 °F). The variation of H with T is then calculated by integrating Eq 3.8, that is:

$$H = \int_{298}^{T} C_p dT \qquad \text{(Eq 3.9)}$$

The slope of the H-T curve is C_p, as shown in Fig. 3.2(b).

The variation of entropy with temperature can also be derived from the specific heat, C_p. From thermodynamics:

$$\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p \qquad \text{(Eq 3.10)}$$

Because entropy is zero at 0 K, Eq 3.10 can be integrated to give:

$$S = \int_0^{T} \frac{C_p}{T} dT \qquad \text{(Eq 3.11)}$$

as shown in Fig. 3.2(c).

By combining Fig. 3.2(a) and (b) and using Eq 3.4, the variation of G with temperature shown in Fig. 3.3 is obtained. When temperature and pressure vary, the change in free energy, G, can be obtained for a system with fixed mass and composition from:
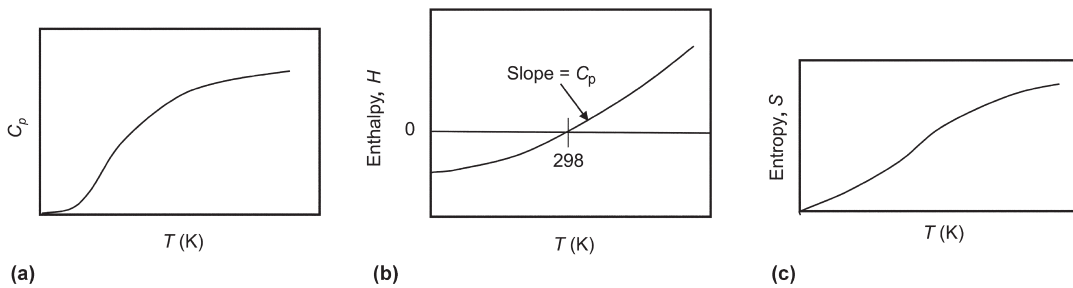

(a)   **(b)**   **(c)**

Fig. 3.2 (a) Variation of C_p with absolute temperature, T. (b) Variation of enthalpy, H, with absolute temperature for a pure metal. (c) Variation of entropy, S, with absolute temperature. Adapted from Ref 3.1
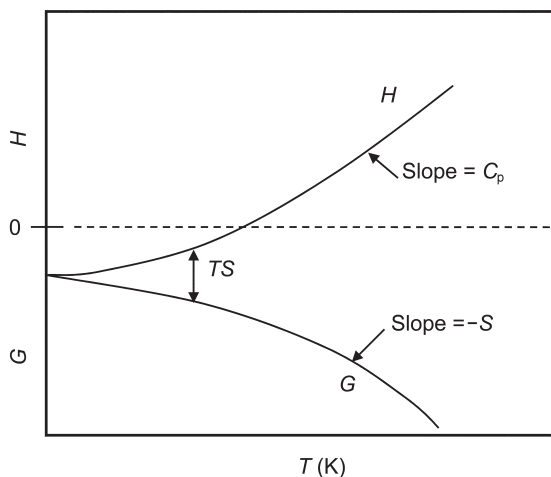
Fig. 3.3 Variation of Gibbs free energy with temperature. Adapted from Ref 3.1

$$dG = -SdT + VdP \qquad \text{(Eq 3.12)}$$

At constant pressure, $dP = 0$ and:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \text{(Eq 3.13)}$$

This equation shows that G decreases with increasing T at a rate given by $-S$. The relative positions of the free-energy curves of solid and liquid phases are shown in Fig. 3.4. At all temperatures, the liquid has a higher enthalpy (internal energy) than the solid phase. Therefore, at low temperatures, $G^L > G^S$. However, the liquid phase has a higher entropy than the solid phase and the Gibbs free energy of the liquid therefore decreases more rapidly with increasing temperature than that for the solid. For temperatures up to T_m, the solid phase has the lowest free energy and is therefore the equilibrium state of the system. At T_m, both phases have the same value of G and both the solid and liquid can coexist in equilibrium. Therefore, T_m is the equilibrium melting temperature at the pressure concerned.

If a pure component is heated from absolute zero, the heat supplied will raise the enthalpy at a rate determined by C_p (solid) along line ab in Fig. 3.4. Meanwhile, the free energy will decrease along line ae. At T_m, the heat supplied to the system will not raise its temperature but will be used to supply the latent heat of melting, L, that is required to convert the solid into a liquid (line bc in Fig. 3.4). Note that at T_m the specific heat appears to be infinite because the addition of heat does not appear as an increase in
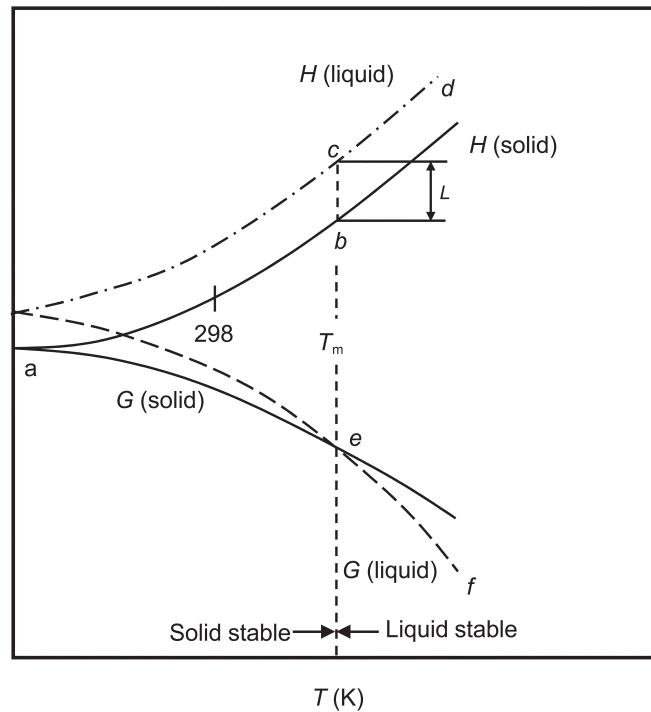
Fig. 3.4 Variation of enthalpy, *H*, and free energy, *G*, with temperature for the solid and liquid phases of a pure metal. *L*, latent heat of melting. *T*m, equilibrium melting temperature. Adapted from Ref 3.1

temperature. When all the solid has transformed into liquid, the enthalpy of the system follows the line *cd* while the free energy, *G*, decreases along line *ef*. At still higher temperatures than those shown in Fig. 3.4, the free energy of the gas phase at atmospheric pressure becomes lower than the liquid, and the liquid transforms in a gas.

The equilibrium temperatures discussed so far only apply at a specific pressure (1 atm). At other pressures, the equilibrium temperatures will differ. For example, the effect of pressure on the equilibrium temperatures for pure iron is shown in Fig. 3.5. Increasing pressure has the effect of depressing the α–γ equilibrium temperature and raising the equilibrium melting temperature. At very high pressures, hexagonal close-packed (hcp) ε–iron becomes stable. The reason for these changes can be explained by Eq 3.12. At constant temperature, the free energy of a phase increases with pressure such that:

$$\left(\frac{\partial G}{\partial T}\right)_T = V \tag{Eq 3.14}$$

If the two phases in equilibrium have different molar volumes, their respective free energies will not increase by the same amount at a given
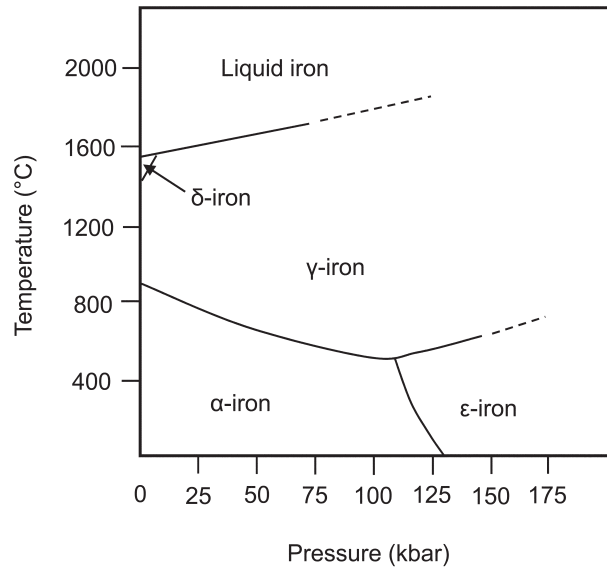
Fig. 3.5 Effect of pressure on the equilibrium phase diagram for pure iron. Adapted from Ref 3.1

temperature and equilibrium will be disturbed by changes in pressure. The only way to maintain equilibrium at different pressures is by varying the temperature.

If the two phases in equilibrium are α and β, the application of Eq 3.12 to 1 mol of both gives:

$$dG^{\alpha} = V_m^{\alpha} dP - S^{\alpha} dT$$
$$dG^{\beta} = V_m^{\beta} dP - S^{\beta} dT$$

(Eq 3.15)

If α and β are in equilibrium, $G_{\alpha} = G_{\beta}$, and therefore $dG_{\alpha} = dG_{\beta}$, and:

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^{\beta} - S^{\alpha}}{V_m^{\beta} - V_m^{\alpha}} = \frac{\Delta S}{\Delta V}$$

(Eq 3.16)

This equation gives the change in temperature, dT, required to maintain equilibrium between α and β if pressure is increased by dP. The equation can be simplified as follows. From Eq 3.4:

$$G_{\alpha} = H_{\alpha} - TS_{\alpha}$$
$$G_{\beta} = H_{\beta} - TS_{\beta}$$

Putting $\Delta G = G_{\beta} - G_{\alpha}$ gives:

$$\Delta G = \Delta H - T\Delta S$$

But because at equilibrium $G_\beta = G_\alpha$, $\Delta G = 0$ and:

$$\Delta H - T\Delta S = 0$$

As a result, Eq 3.16 becomes:

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T\Delta V} \qquad \text{(Eq 3.17)}$$

which is one form of the Clausius-Clapeyron equation. Because close-packed γ-iron has a smaller molar volume than α-iron, $\Delta V = V_{m\beta} - V_{m\alpha} < 0$, while $\Delta H = H_\gamma - H_\alpha < 0$ for the same reason a liquid has a higher enthalpy than a solid, so that dP/dT is negative; that is, an increase in pressure lowers the equilibrium transition temperature. On the other hand, the $\delta-L$ equilibrium temperature is raised with increasing pressure due to the larger molar volume of the liquid phase. The effect of increasing pressure is to increase the area of the phase diagram over which the phase with the smallest molar volume is stable (γ-iron in Fig. 3.5).

In dealing with phase transformations, it is important to be concerned with the difference in free energy between two phases at temperatures away from the equilibrium temperature. For example, if a liquid is undercooled by ΔT below the T_m before it solidifies, solidification will be accompanied by a decrease in free energy, ΔG, as shown in Fig. 3.6. This free-energy decrease provides the driving force for solidification. The magnitude of this change can be obtained as follows. The free energies of the liquid and solid at a temperature, T, are given by:

$$G^L = H^L - TS^L$$
$$G^S = H^S - TS^S$$

Therefore, at a temperature, T:

$$\Delta G = \Delta H - T\Delta S \qquad \text{(Eq 3.18)}$$

where:

$$\Delta H = H^L - H^S \text{ and } \Delta S = S^L - S^S$$

At the equilibrium melting temperature, T_m, the free energies of a solid and liquid are equal ($\Delta G = 0$). Therefore:

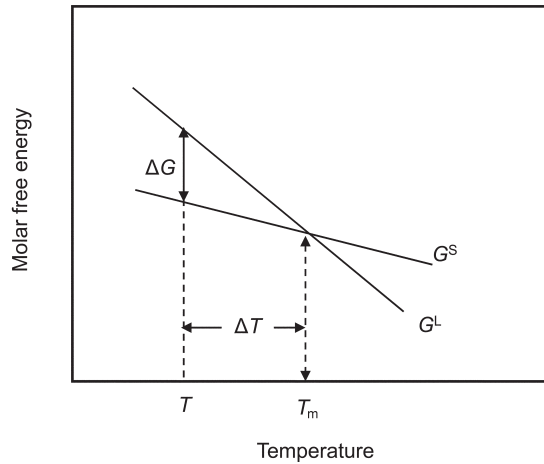$$\Delta G = \Delta H - T_m\Delta S = 0$$

and at T_m:

Fig. 3.6 Difference in free energy between liquid and solid close to the melting point. The curvature of G^S and G^L has been ignored. Adapted from Ref 3.1

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m}$$ (Eq 3.19)

This is known as the entropy of fusion. It is observed experimentally that the entropy of fusion is a constant $\approx R$ (8.4 Jmol^{-1}K^{-1}) for most metals per Richard's rule. This is not unexpected because metals with high bond strengths can be expected to have high values for both L and T_m.

For small undercoolings, ΔT, the difference in specific heats of the liquid and the solid ($C_p^L - C_p^S$) can be ignored. Both ΔH and ΔS are therefore independent of temperature. Combining Eq 3.18 and 3.19 gives:

$$\Delta G \cong L = T\frac{L}{T_m}$$

For a small ΔT:

$$\Delta G \cong \frac{L\Delta T}{T_m}$$ (Eq 3.20)

3.3 Binary Solutions

In single-component systems all phases have the same composition, and equilibrium only depends on pressure and temperature as variables. However, in alloys composition is also variable. Therefore, to understand phase changes in alloys requires the knowledge of how the Gibbs free energy of a given phase depends on composition as well as temperature and pres-

sure. Because the important phase transformations in metallurgy mainly occur at a fixed pressure of 1 atm, the focus is on changes in composition and temperature. In order to introduce some of the basic concepts of the thermodynamics of alloys, a simple physical model for binary solid solutions is presented.

3.3.1 Gibbs Free Energy of Binary Solutions

The Gibbs free energy of a binary solution of A and B atoms can be calculated from the free energies of pure A and pure B. It is assumed that A and B have the same crystal structures in their pure states and can be mixed in any proportions to make a solid solution with the same crystal structure. Consider the case where 1 mol of homogeneous solid solution is made by mixing together X_A mol of A and X_B mol of B. Because there is a total of 1 mol of solution:

$$X_A + X_B = 1 \qquad\qquad\qquad\qquad \text{(Eq 3.21)}$$

and X_A and X_B are the mole fractions of A and B, respectively, in the alloy. To calculate the free energy of the alloy, mixing can be made in two steps (Fig. 3.7):

1. Bring together X_A mol of pure A and X_B mol of pure B.
2. Allow the A and B atoms to mix together to make a homogeneous solid solution.

Before mixing   **After mixing**

Mix

X_A mol A X_B mol B

F.E.$X_A G_A$ F.E.$X_B G_B$

1 mol of solid solution

Total free energy =   Total free energy =

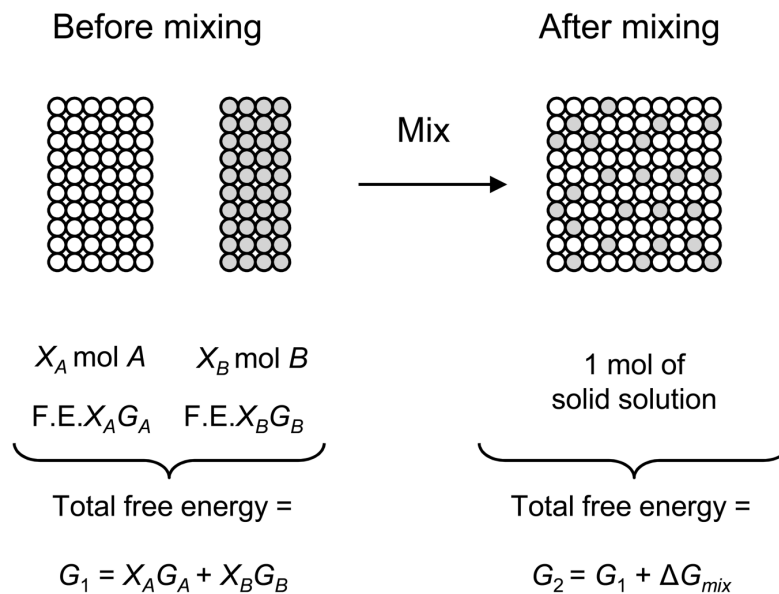$G_1 = X_A G_A + X_B G_B$ $G_2 = G_1 + \Delta G_{mix}$

Fig. 3.7   Free energy of mixing. Adapted from Ref 3.1

After step 1, the free energy of the system is given by:

$$G_1 = X_A G_A + X_B G_B \tag{Eq 3.22}$$

where G_A and G_B are the molar free energies of pure A and pure B at the temperature and pressure. G_1 can be most conveniently represented on a molar free-energy diagram (Fig. 3.8) in which molar free energy is plotted as a function of X_B or X_A. For all alloy compositions, G_1 lies on the straight line between G_A and G_B.

The free energy of the system will not remain constant during mixing of the A and B atoms, and after step 2, the free energy of the solid solution, G_2, can be expressed as:

$$G_2 = G_1 + \Delta G_{mix} \tag{Eq 3.23}$$

where ΔG_{mix} is the change in Gibbs free energy caused by the mixing.

Because:

$$G_1 = H_1 = TS_1$$

and:

$$G_2 = H_2 = TS_2$$

putting:

$$\Delta H_{mix} = H_2 - H_1$$

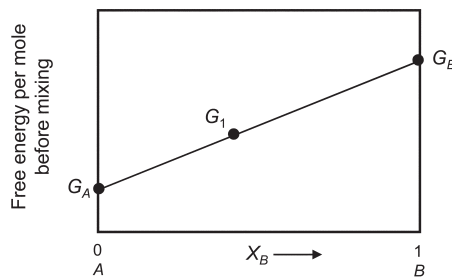and:

$$\Delta S_{mix} = S_2 - S_1$$

Fig. 3.8 Variation of G_1 (the free energy before mixing) with composition (X_A or X_B). Adapted from Ref 3.1

gives:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad \text{(Eq 3.24)}$$

where ΔH_{mix} is the heat absorbed or evolved during step 2;that is, it is the heat of solution and, ignoring volume changes during the process, it represents the difference in internal energy, E, before and after mixing. The difference in entropy between the mixed and unmixed states is ΔS_{mix}.

3.3.2 Ideal Solutions

The simplest type of mixing occurs in the ideal solution where $\Delta H_{mix} = 0$, and the free-energy change on mixing is therefore:

$$\Delta G_{mix} = -T\Delta S_{mix} \qquad \text{(Eq 3.25)}$$

In statistical thermodynamics, entropy is quantitatively related to randomness by the Boltzmann equation:

$$S = -k \ln \omega \qquad \text{(Eq 3.26)}$$

where k is Boltzmann's constant and ω is a measure of randomness. There are two contributions to the entropy of a solid solution: (1) a thermal contribution, S_{th}, and (2) a configurational contribution, S_{config}.

The measure of randomness (ω) is the number of ways in which the thermal energy of the solid can be divided among the atoms, that is, the total number of ways in which vibrations can be set up in the solid. In solutions, additional randomness exists due to the different ways in which the atoms can be arranged. This gives extra entropy, S_{config}, for which ω is the number of distinguishable ways of arranging the atoms in the solution.

If there is no volume change or heat change during mixing, then the only contribution to ΔS_{mix} is the change in configurational entropy. Before mixing, the A and B atoms are held separately in the system and there is only one distinguishable way in which the atoms can be arranged. Consequently, $S_1 = k \ln 1 = 0$, and therefore $\Delta S_{mix} = S_2$.

Assuming that A and B mix to form a substitutional solid solution and that all configurations of A and B atoms are equally probable, the number of distinguishable ways of arranging the atoms on the atom sites is:

$$\omega_{config} = \frac{\left(N_A + N_B\right)!}{N_A! N_B!} \qquad \text{(Eq 3.27)}$$

where N_A is the number of A atoms and N_B the number of B atoms.

Because this involves 1 mol of solution, that is, Avogadro's number of N_a atoms:

$$N_A = X_A N_a$$

and:

$$N_B = X_B N_b$$

Substituting into Eq 3.26 and 3.27, and using Stirling's approximation ($\ln N! \approx N \ln - N$) and the relationship $N_a k = R$, gives:

$$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_b) \tag{Eq 3.28}$$

Because X_A and X_B are less than unity, ΔS_{mix} is positive; that is, there is an increase in entropy on mixing, as expected. The free energy of mixing, ΔG_{mix}, is obtained from Eq 3.25 as:

$$\Delta G_{mix} = RT(X_A \ln X_A + X_B \ln X_b) \tag{Eq 3.29}$$

Figure 3.9 shows ΔG_{mix} as a function of composition and temperature. The actual free energy of the solution, G, will also depend on G_A and G_B. From Eq 3.22, 3.23, and 3.29:

$$G = G_2 = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_b) \tag{Eq 3.30}$$

This is shown schematically in Fig. 3.10. Note that, as the temperature increases, G_A and G_B decrease and the free-energy curves assume a greater
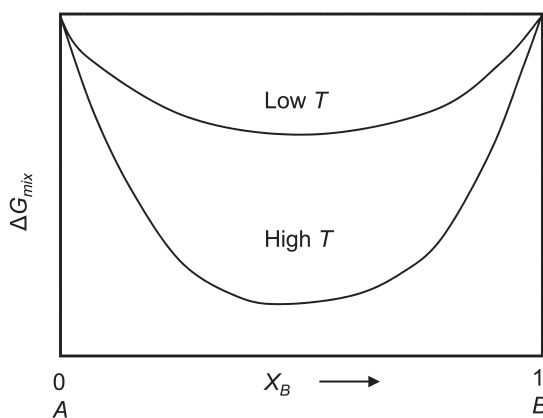

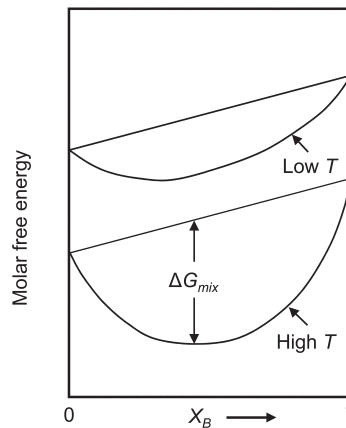**Fig. 3.9** Free energy of mixing for an ideal solution. Adapted from Ref 3.1

Fig. 3.10 A combination of Fig. 3.8 and 3.9: The molar free energy (free energy per mole of solution) for an ideal solution. Adapted from Ref 3.1

curvature. The decrease in G_A and G_B is due to the thermal entropy of both components and is given by Eq 3.13.

3.4 Chemical Potential

In alloys it is important to know how the free energy of a given phase will change when atoms are added or removed. If a small quantity of A, dn_A mol, is added to a large amount of a phase at constant temperature and pressure, the size of the system will increase by dn_A, and the total free energy of the system will also increase by a small amount, dG'. If dn_A is small enough, dG' will be proportional to the amount of A added. Then it can be written:

$$dG' = \mu_A dn_A \ (T, P, n_B \text{ constant}) \tag{Eq 3.31}$$

The proportionality constant, μ_A, is called the partial molar free energy of A, or alternatively, the chemical potential of A in the phase. The chemical potential, μ_A, depends on the composition of the phase, and therefore dn_A must be so small that the composition is not significantly altered. If Eq 3.31 is rewritten, it can be seen that a definition of the chemical potential of A is:

$$\mu_A = \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B} \tag{Eq 3.32}$$

The symbol G' has been used for the Gibbs free energy to emphasize the fact that it refers to the whole system. The usual symbol, G, will be

used to denote the molar free energy and is therefore independent of the size of the system.

Equations similar to Eq 3.31 and 3.32 can be written for the other components in the solution. For a binary solution at constant temperature and pressure, the separate contributions can be summed:

$$dG' = \mu_A dn_A + \mu_B dn_B \qquad \text{(Eq 3.33)}$$

This equation can be extended by adding further terms for solutions containing more than two components. If T and P changes are also allowed, Eq 3.12 must be added, giving the general equation:

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C = \dots$$

If 1 mol of the original phase contained X_A mol A and X_B mol B, the size of the system can be increased without altering its composition if A and B are added in the correct proportions; that is, such that $dn_A : dn_B = X_A : X_B$. For example, if the phase contains twice as many A as B atoms ($X_A = 2/3$, $X_B = 1/3$), the composition can be maintained constant by adding two A atoms for every one B atom ($dn_A : dn_B = 2$). In this way, the size of the system can be increased by 1 mol without changing μ_A and μ_B. To do this, X_A mol A and X_B mol B must be added and the free energy of the system will increase by the molar free energy, G. Therefore, from Eq 3.33:

$$G = \mu_A X_A + \mu_B X_B \qquad \text{(Eq 3.34)}$$

where G is a function of X_A and X_B, as in Fig. 3.10. For example, μ_A and μ_B can be obtained by extrapolating the tangent to the G curve to the sides of the molar free-energy diagram (Fig. 3.11). Remembering that $X_A + X_A$
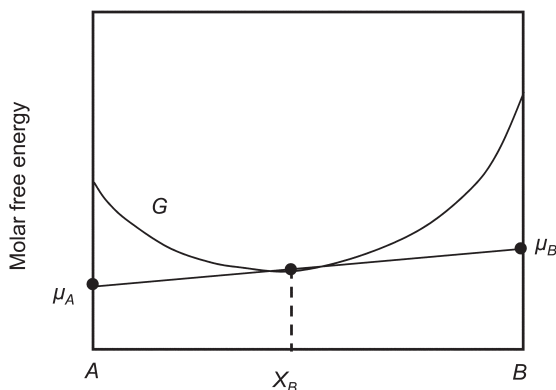

Fig. 3.11 The relationship between the free-energy curve for a solution and the chemical potentials of the components. Adapted from Ref 3.1

= 1; that is, $d\,X_A = -d\,X_B$, this result can be obtained from Eq 3.40 and 3.41. From Fig. 3.11, it is seen that μ_A and μ_A vary systematically with the composition of the phase.

Comparison of Eq 3.30 and 3.34 gives μ_A and μ_A for an ideal solution as:

$$\mu_A = G_A + RT \ln X_A$$
$$\mu_B = G_B + RT \ln X_B$$

(Eq 3.35)

which is a much simpler way of presenting Eq 3.30. These relationships are shown in Fig. 3.12. The distances ac and bd are $-RT \ln X_A$ and $-RT \ln X_B$.

3.5 Regular Solutions

Returning to the model of a solid solution, so far it has been assumed that $\Delta H_{mix} = 0$; however, this type of behavior is rare in practice and usually mixing is endothermic (heat absorbed) or exothermic (heat evolved). However, the model used for ideal solution can be extended to include the ΔH_{mix} term by using the so-called quasi-chemical approach.

In the quasi-chemical model, it is assumed that the heat of mixing ΔH_{mix} is only due to the bond energies between adjacent atoms. For this assumption to be valid, it is necessary that the volumes of pure A and B are equal and do not change during mixing so that the interatomic distances and bond energies are independent of composition.

The structure of a binary solid solution is shown schematically in Fig. 3.13. Three types of interatomic bonds are present:
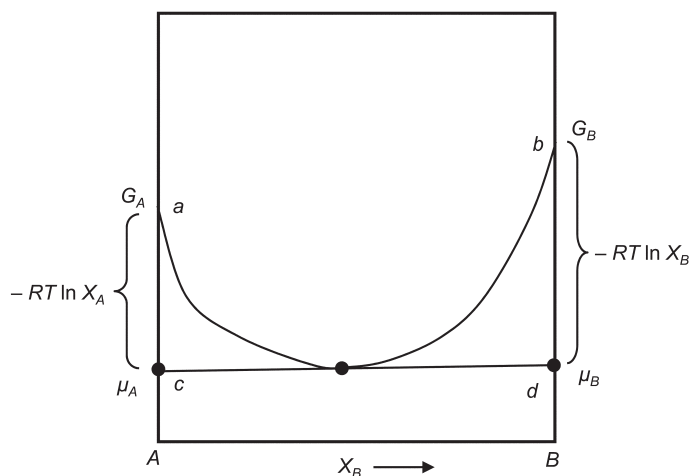

Fig. 3.12 The relationship between free energies and chemical potentials for an ideal solution. Adapted from Ref 3.1
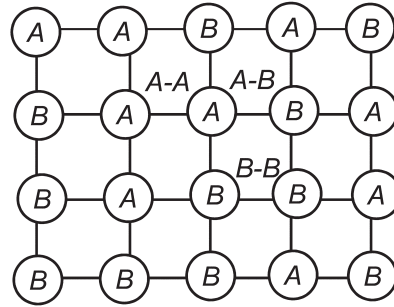
Fig. 3.13 The different types of interatomic bonds in a solid solution. Adapted from Ref 3.1

- A–A bonds, each with an energy ε_{AA}
- B–B bonds, each with an energy ε_{BB}
- A–B bonds, each with an energy ε_{AB}

By considering zero energy to be the state where the atoms are separated to infinity, ε_{AA}, ε_{BB}, and ε_{AB} are negative quantities and become increasingly more negative as the bonds become stronger. The internal energy of the solution, E, will depend on the number of bonds of each type—P_{AA}, P_{BB}, and P_{AB}—such that:

$$E = P_{AA}\varepsilon_{AA} + P_{BB}\varepsilon_{BB} + P_{AB}\varepsilon_{AB}$$

Before mixing, pure A and B contain only A–A and B–B bonds, respectively, and by considering the relationships between P_{AA}, P_{BB}, and P_{AB} in the solution, it can be shown that the change in internal energy on mixing is given by:

$$\Delta H_{mix} = P_{AB}\varepsilon \qquad\qquad\qquad \text{(Eq 3.36)}$$

where:

$$\varepsilon = \varepsilon_{AB} - \frac{1}{2}\left(\varepsilon_{AA} + \varepsilon_{BB}\right) \qquad\qquad\qquad \text{(Eq 3.37)}$$

That is, ε is the difference between the A–B bond energy and the average of the A–A and B–B bond energies.

If $\varepsilon = 0$, $\Delta H_{mix} = 0$ and the solution is ideal. In this case the atoms are completely randomly arranged and the entropy of mixing is given by Eq 3.28. In such a solution it can also be shown that:

$$P_{AB} = N_a z X_{AA} X_{BB} \qquad\qquad\qquad \text{(Eq 3.38)}$$

where N_a is Avogadro's number, and z is the number of bonds per atom.

If $\varepsilon < 0$, the atoms in the solution will prefer to be surrounded by atoms of the opposite type and this will increase P_{AB}, whereas, if $\varepsilon > 0$, P_{AB} will tend to be less than in a random solution. However, provided ε is not too different from zero, Eq 3.38 is still a good approximation, in which case:

$$\Delta H_{mix} = \Omega X_A X_B \tag{Eq 3.39}$$

where:

$$\Omega = N_a z \varepsilon \tag{Eq 3.40}$$

Real solutions that closely obey Eq 3.39 are known as regular solutions. The variation of ΔH_{mix} with composition is parabolic and is shown in Fig. 3.14 for $\Omega > 0$. Note that the tangents at $X_A = 0$ and 1 are related to Ω as shown.

The free-energy change on mixing a regular solution is given by Eq 3.24, 3.28, and 3.39 as:

$$\Delta G_{mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_b) \tag{Eq 3.41}$$

where $\Omega X_A X_B$ is ΔH_{mix}, and $RT(X_A \ln X_A + X_B \ln X_b)$ is $-T\Delta S_{mix}$.

This is shown in Fig. 3.15 for different values of Ω and temperature. For exothermic solutions, $\Delta H_{mix} < 0$, and mixing results in a free-energy decrease at all temperatures (Fig. 3.15a, b). When $\Delta H_{mix} > 0$, however, the situation is more complicated. At high temperatures, $T\Delta S_{mix}$ is greater than ΔH_{mix} for all compositions and the free-energy curve has a positive curvature at all points (Fig. 3.15c). On the other hand, at low temperatures, $T\Delta S_{mix}$ is smaller and ΔG_{mix} develops a negative curvature in the middle (Fig. 3.15d).
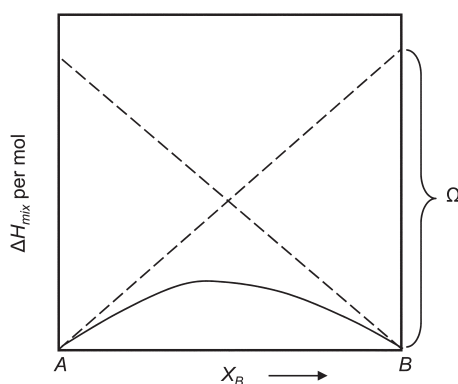

Fig. 3.14 The variation of ΔH_{mix} with composition for a regular solution. Adapted from Ref 3.1
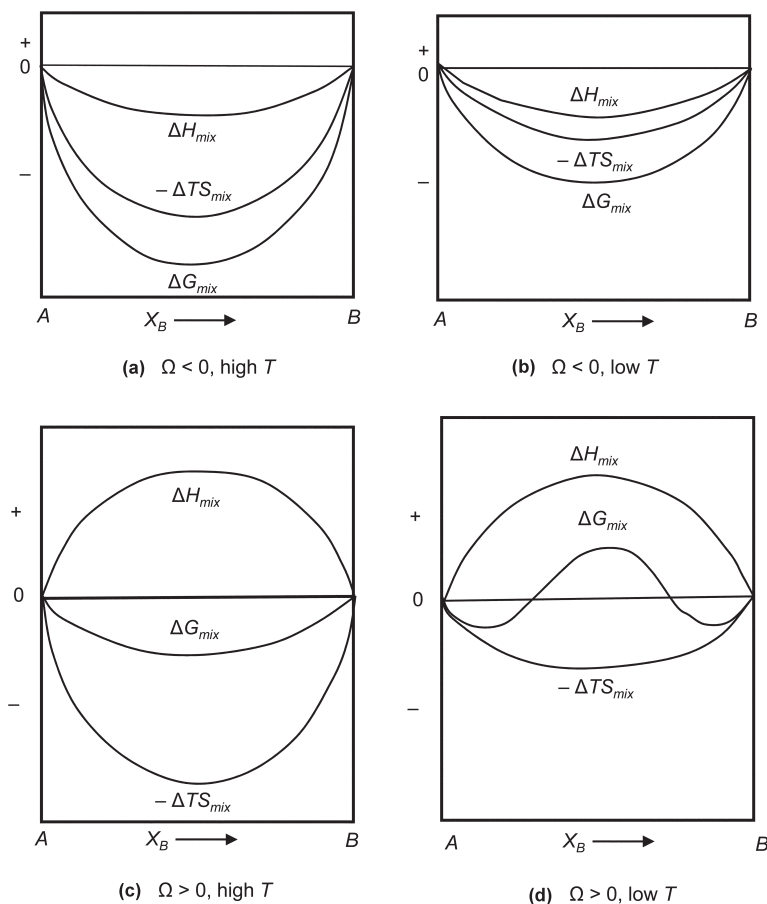
Fig. 3.15 The effect of ΔH_{mix} and T on ΔG_{mix}. Adapted from Ref 3.1

Differentiating Eq 3.28 shows that, as X_A or $X_A \to 0$, the $-T\Delta S_{mix}$ curve becomes vertical, while the slope of the ΔH_{mix} curve tends to a finite value, Ω (Fig. 3.14). This means that, except at absolute zero, ΔG_{mix} always decreases on the addition of a small amount of solute.

The actual free energy of the alloy depends on the values chosen for G_A and G_B and is given by Eq 3.22, 3.33, and 3.41 as:

$$G = X_A G_A = X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_b) \qquad \text{(Eq 3.42)}$$

This is shown in Fig. 3.16 along with the chemical potentials of A and B in the solution.

Using the relationship $X_A X_B = X_A^2 X_B + X_B^2 X_A$ and comparing Eq 3.34 and 3.42 shows that for a regular solution:
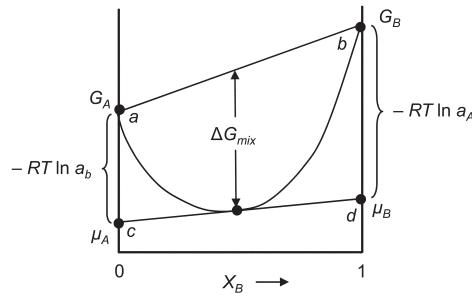
$$\mu_A = G_A + \Omega(1 - X_A)^2 + RT \ln X_A$$

Fig. 3.16 The relationship between molar free energy and activity. Adapted from Ref 3.1

and (Eq 3.43)

$$\mu_B = G_B + \Omega(1 - X_B)^2 + RT \ln X_B$$

3.5.1 Activity

The chemical potential of an ideal alloy is given by Eq 3.42. A similar expression for any solution is obtained by defining the activity of a component (μ_A) such that the distances *ac* and *bd* in Fig. 3.16 are $-RT \ln a_A$ and $-RT \ln a_B$. In this case:

$$\mu_A = G_A + RT \ln a_A$$
and (Eq 3.44)
$$\mu_B = G_B + RT \ln a_B$$

In general, a_A and a_B will be different from X_A and X_B, and the relationship between them will vary with the composition of the solution. For a regular solution, comparison of Eq 3.43 and 3.44 gives:

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}\left(1 - X_A\right)^2$$
and (Eq 3.45)
$$\ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}\left(1 - X_B\right)^2$$

The relationship between *a* and *X* for any solution can be represented graphically as illustrated in Fig. 3.17. Line 1 represents an ideal solution for which $a_A = X_A$ and $a_B = X_B$. If $\Delta H_{mix} < 0$, the activity of the components in solution will be less in an ideal solution (line 2) and vice versa when $\Delta H_{mix} > 0$ (line 3).

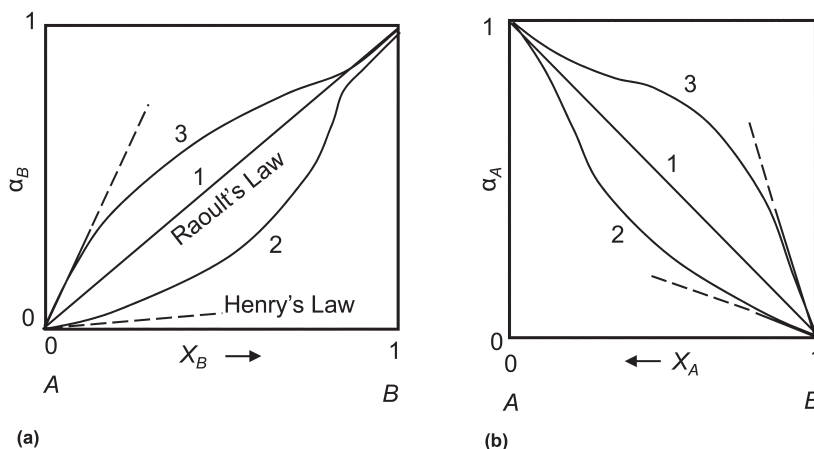The ratio (a_A / X_A) is usually referred to as γ_A, the activity coefficient of *A*, that is:

Fig. 3.17 The variation of activity with composition (a) α_B, and (b) α_B. Line 1: ideal solution (Raoult's law). Line 2: $\Delta H_{mix} < 0$. Line 3: $\Delta H_{mix} > 0$. Adapted from Ref 3.1

$$\gamma_A = \frac{a_A}{X_A} \qquad\qquad\qquad (Eq\ 3.46)$$

For a dilute solution of B in A, Eq 3.45 can be simplified by letting $X_B \to 0$, in which case:

$$\gamma_B = \frac{a_B}{X_B} = constant\ (Henry's\ Law) \qquad\qquad (Eq\ 3.47)$$

and:

$$\gamma_A = \frac{a_B}{X_B} = 1\ \ (Raoult's\ law) \qquad\qquad (Eq\ 3.48)$$

Equation 3.47 is known as Henry's law and Eq 3.46 as Raoult's law. Both apply to all solutions when the solutions are sufficiently dilute.

Because activity is related to chemical potential by Eq 3.44, the activity of a component is just another means of describing the state of the component in a solution. No extra information is supplied, and its use is simply a matter of convenience because it often leads to simpler mathematics.

Activity and chemical potential are a measure of the tendency of an atom to leave a solution. If the activity or chemical potential is low, the atoms are reluctant to leave the solution, which means, for example, that the vapor pressure of the component in equilibrium with the solution will be relatively low. The activity or chemical potential of a component is important when several condensed phases are in equilibrium.

3.6 Real Solutions

While the previous model provides a useful description of the effects of configurational entropy and interatomic bonding on the free energy of binary solutions, its practical use is rather limited. For many systems, the model is an oversimplification of reality and does not predict the correct dependence of ΔG_{mix} on composition and temperature.

As already indicated, in alloys where the enthalpy of mixing is not zero (ε and $\Omega \neq 0$), the assumption that a random arrangement of atoms is the equilibrium, or most stable arrangement, is not true, and the calculated value for ΔG_{mix} will not give the minimum free energy. The actual arrangement of atoms will be a compromise that gives the lowest internal energy consistent with sufficient entropy, or randomness, to achieve the minimum free energy. In systems with $\varepsilon < 0$, the internal energy of the system is reduced by increasing the number of A–B bonds, that is, by ordering the atoms as shown in Fig. 3.18(a). If $\varepsilon > 0$, the internal energy can be reduced by increasing the number of A–A and B–B bonds, that is, by the clustering of the atoms into A-rich and B-rich groups (Fig. 3.18b). However, the degree of ordering or clustering will decrease as temperature increases due to the increasing importance of entropy. In systems where there is a size difference between the atoms, the quasi-chemical model will underestimate the change in internal energy on mixing, because no account is taken of the elastic strain fields that introduce a strain-energy term into ΔH_{mix}. When the size difference is large, this effect can dominate over the chemical term. When the size difference between the atoms is very large, then interstitial solid solutions are energetically most favorable (Fig. 3.18c). In systems where there is strong chemical bonding between the atoms, there is a tendency for the formation of intermetallic phases. These are distinct from solutions based on the pure components because they have a different crystal structure and may also be highly ordered.
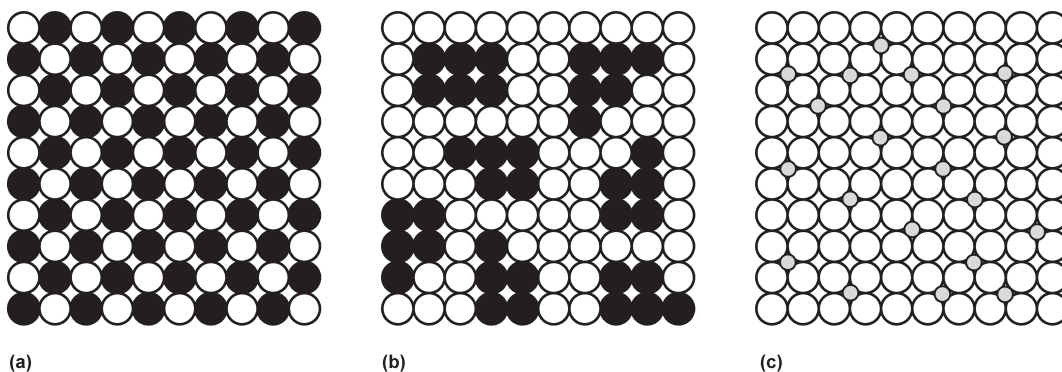

(a)   (b)   (c)

Fig. 3.18 Schematic representation of solid solutions. (a) Ordered substitutional. (b) Clustering. (c) Random interstitial. Adapted from Ref 3.1

3.6.1 Equilibrium in Heterogeneous Systems

Metals *A* and *B* usually do not have the same crystal structure when mixed into a solution. In such cases, two free-energy curves must be drawn, one for each structure. The stable forms of pure *A* and *B* at a given temperature (and pressure) can be denoted as α and β, respectively. For the sake of illustration, let α be face-centered cubic (fcc) and β be body-centered cubic (bcc). The molar free energies of fcc *A* and bcc *B* are shown in Fig. 3.19(a) as points *a* and *b*. The first step in drawing the free-energy curve of the fcc *A* phase is to convert the stable bcc arrangement of *B* atoms into an unstable fcc arrangement. This requires an increase in free energy, *be*. The free-energy curve for the α phase can now be constructed as before by mixing fcc *A* and fcc *B*, as shown in the figure. The distance *de* gives $-\Delta G_{mix}$ for α of composition *X*. A similar procedure produces the molar free-energy curve for the β phase (Fig. 3.19b). The distance *af* is now the difference in free energy between bcc *A* and fcc *A*.

It is clear from Fig. 3.19(b) that *A*-rich alloys will have the lowest free energy as a homogeneous α phase and *B*-rich alloys as β phase. For alloys with compositions near the crossover in the *G* curves, the situation is not so straightforward. In this case it can be shown that the total free energy can be minimized by the atoms separating into two phases.

It is first necessary to consider a general property of molar free-energy diagrams when phase mixtures are present. Suppose an alloy consists of two phases, α and β, each of which has a molar free energy given by G_α and G_β, respectively (Fig. 3.20). If the overall composition of the phase mixture is X_B^0, the lever rule gives the relative number of moles of α and β that must be present, and the molar free energy of the phase mixture, *G*, is given by the point on the straight line between α and β, as shown in the figure. This result can be proven most readily using the geometry of Fig. 3.20. The lengths *ad* and *cf* respectively represent the molar free energies of the α and β phases present in the alloy. Point *g* is obtained by the intersection of *be* and *dc* so that *bcg* and *acd*, as well as *deg* and *dfc*, form
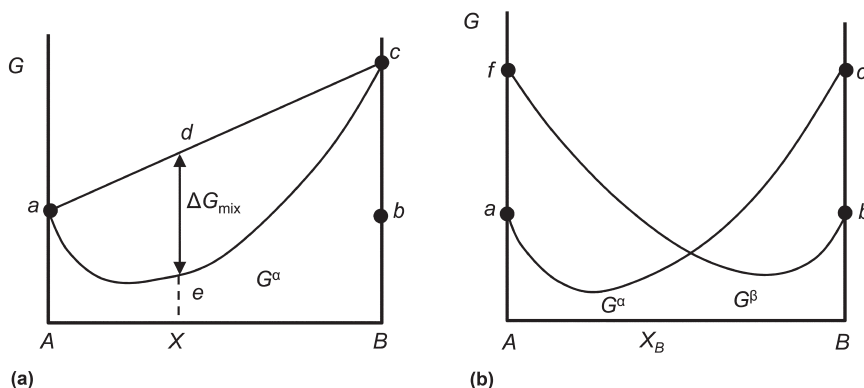

Fig. 3.19 (a) Molar free-energy curve for the α phase. (b) Molar free-energy curves for α and β. Adapted from Ref 3.1
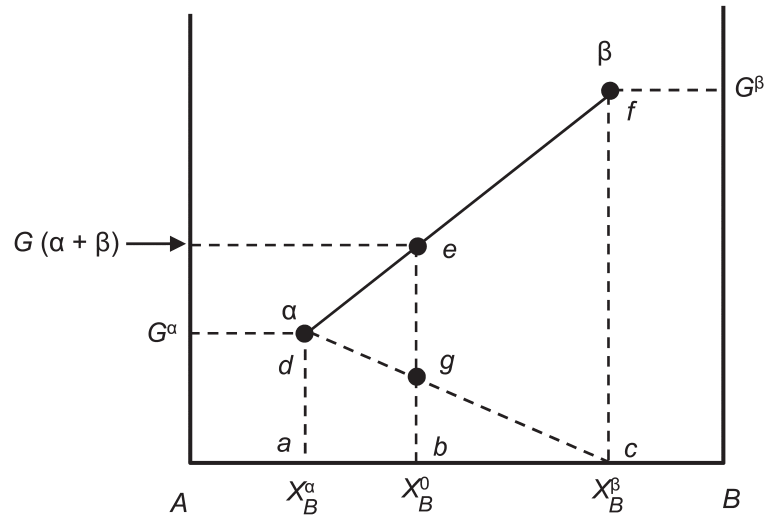
Fig. 3.20 Molar free energy of a two-phase mixture (α + β). Adapted from Ref 3.1

similar triangles. Therefore, $bg/ad = bc/ac$ and $ge/cf = ab/ac$. According to the lever rule, 1 mol of alloy will contain bc/ac mol of α and ab/ac mol of β. It follows that bg and ge represent the separate contributions from the α and β phases to the total free energy of 1 mol of alloy. Therefore, the length be represents the molar free energy of the phase mixture.

Consider now alloy X^o in Fig. 3.21(a). If the atoms are arranged as a homogeneous phase, the free energy will be lowest as α; that is, $G_{0\alpha}$ per mole. However, from the above it is clear that the system can lower its free energy if the atoms separate into two phases, with compositions α_1 and β_1, for example. The free energy of the system will then be reduced to G_1. Further reductions in free energy can be achieved if the A and B atoms interchange between the α and β phases until the compositions α_e and β_e are reached (Fig. 21b). The free energy of the system, G_e, is now a minimum and there is no desire for further change. Consequently, the system is in equilibrium and α_e and β_e are the equilibrium compositions of the α and β phases.

This result is quite general and applies to any alloy with an overall composition between α_e and β_e: Only the relative amounts of the two phases change, as given by the lever rule. When the alloy composition lies outside this range, however, the minimum free energy lies on the G_α or G_β curves and the equilibrium state of the alloy is a homogeneous single phase.

From Fig. 3.21 it can be seen that equilibrium between two phases requires that the tangents to each G curve at the equilibrium compositions lie on a common line. In other words, each component must have the same chemical potential in the two phases, that is, for heterogeneous equilibrium:
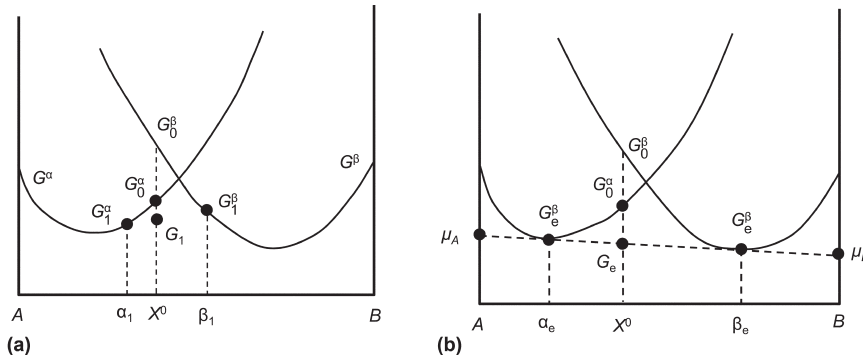
Fig. 3.21 (a) Alloy X^0 has a free energy, G_1, as a mixture of α and β. (b) At equilibrium, alloy X^0 has a minimum free energy, G_e, when it is a mixture αe and βe. Adapted from Ref 3.1

$$\mu_A^\alpha = \mu_A^\beta \ \text{and} \ \mu_B^\alpha = \mu_B^\beta \tag{Eq 3.49}$$

From Eq 3.49 it can be seen that the activities of the components must also be equal; that is:

$$a_A^\alpha = a_A^\beta \ \text{and} \ a_B^\alpha = a_B^\beta \tag{Eq 3.50}$$

It is easiest to plot the variation of activity with alloy composition, and this is shown schematically in Fig. 3.22. Between A and α_e and β_e and B, where single phases are stable, the activities (or chemical potentials) vary, and, for simplicity, ideal solutions have been assumed, in which case there is a straight line relationship between α_e and X. Between α_e and β_e the phase compositions in equilibrium do not change, and the activities are equal and given by points q and r.

3.6.2 Phase Diagrams

The previous section shows how the equilibrium state of an alloy can be obtained from the free-energy curves at a given temperature. The next step is to see how equilibrium is affected by temperature.

The shapes of liquidus, solidus, and solvus curves (or surfaces) in a phase diagram are determined by the Gibbs free energies of the relevant phases. In this instance, the free energy must include not only the energy of the constituent components, but also the energy of mixing of these components in the phase. Consider, for example, the situation of complete miscibility shown in Fig. 3.23. The two phases, liquid and solid, are in stable equilibrium in the two-phase field between the liquidus and solidus lines. The Gibbs free energies at various temperatures are calculated as a function of composition for ideal liquid solutions and for ideal solid solutions of the two components, A and B. The result is a series of plots similar to those shown in Fig. 3.24(a) to (e):
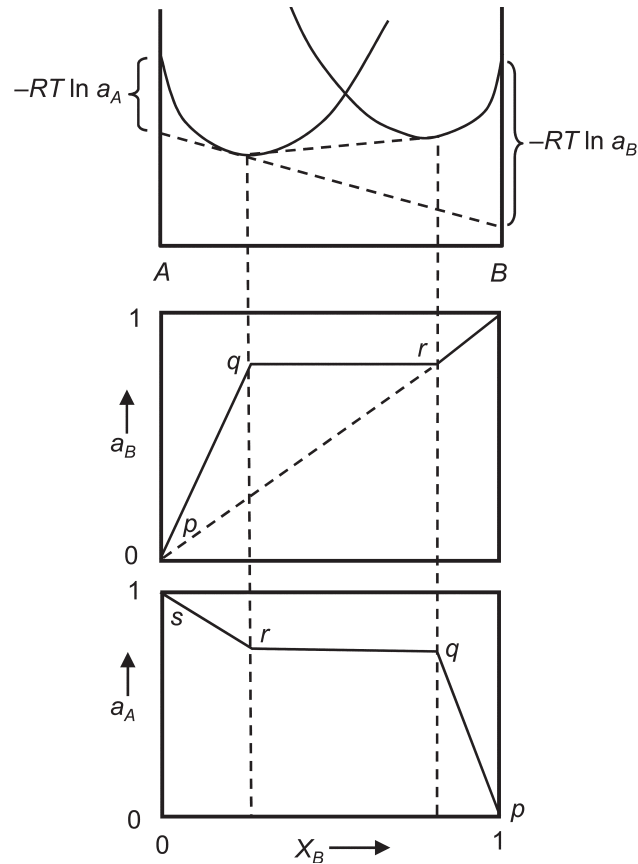
Fig. 3.22 The variation of a_A and a_B, with composition for a binary system containing two ideal solutions, α and β. Adapted from Ref 3.1

- At temperature T_1, the liquid solution has the lower Gibbs free energy and, therefore, is the more stable phase.
- At T_2, the melting temperature of A, the liquid and solid are equally stable only at a composition of pure A. The remainder of the solution is still liquid.
- At temperature T_3, between the melting temperatures of A and B, the Gibbs free-energy curves cross. Depending on the composition, there exist fields of liquid, liquid + solid α, and solid α.
- At temperature T_4, the melting temperature of B, pure B liquid and solid are equally stable. Except for pure B, the remainder of the solution is now solid α.
- At temperature T_5 and at all lower temperatures, the free-energy curve for solid α is below the curve for the liquid, and the whole solution is solid α.

Construction of the two-phase liquid-plus-solid field of the phase diagram in Fig. 3.24(f) is as follows. According to thermodynamic principles,
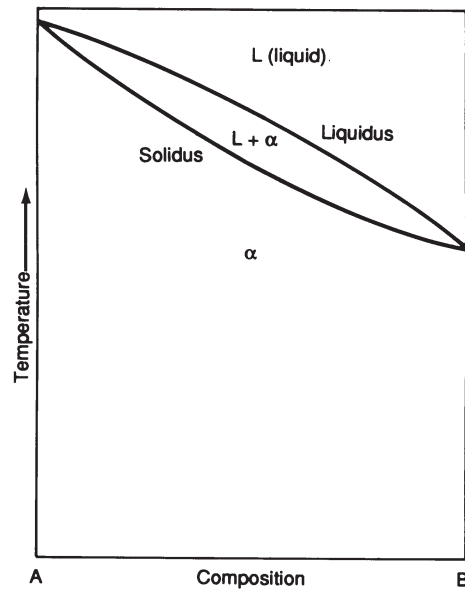
Fig. 3.23 Schematic binary phase diagram showing miscibility in both the liquid and solid states. Source: Ref 3.2

the compositions of the two phases in equilibrium with each other at temperature T_3 can be determined by constructing a straight line that is tangent to both curves in Fig. 3.24(c). The points of tangency, 1 and 2, are then transferred to the phase diagram as points on the solidus and liquidus, respectively. This is repeated at sufficient temperatures to determine the curves accurately.

If, at some temperature, the Gibbs free-energy curves for the liquid and the solid tangentially touch at some point, the resulting phase diagram will be similar to those shown in Fig. 3.25(a) and (b), where a maximum or minimum appears in the liquidus and solidus curves.

The two-phase field in Fig. 3.24(f) consists of a mixture of liquid and solid phases. As stated previously, the compositions of the two phases in equilibrium at temperature T_3 are C_1 and C_2. The horizontal isothermal line connecting points 1 and 2, where these compositions intersect temperature T_3, is the tie line. Similar tie lines connect the coexisting phases throughout all two-phase fields (areas) in binary systems, while tie triangles connect the coexisting phases throughout all three-phase regions (volumes) in ternary systems.

Eutectic phase diagrams, a feature of which is a field where there is a mixture of two solid phases, can also be constructed from Gibbs free-energy curves. Consider the temperatures indicated on the phase diagram in Fig. 3.26(f) and the Gibbs free-energy curves for these temperatures (Fig. 3.26a–e). When the points of tangency on the energy curves are trans-
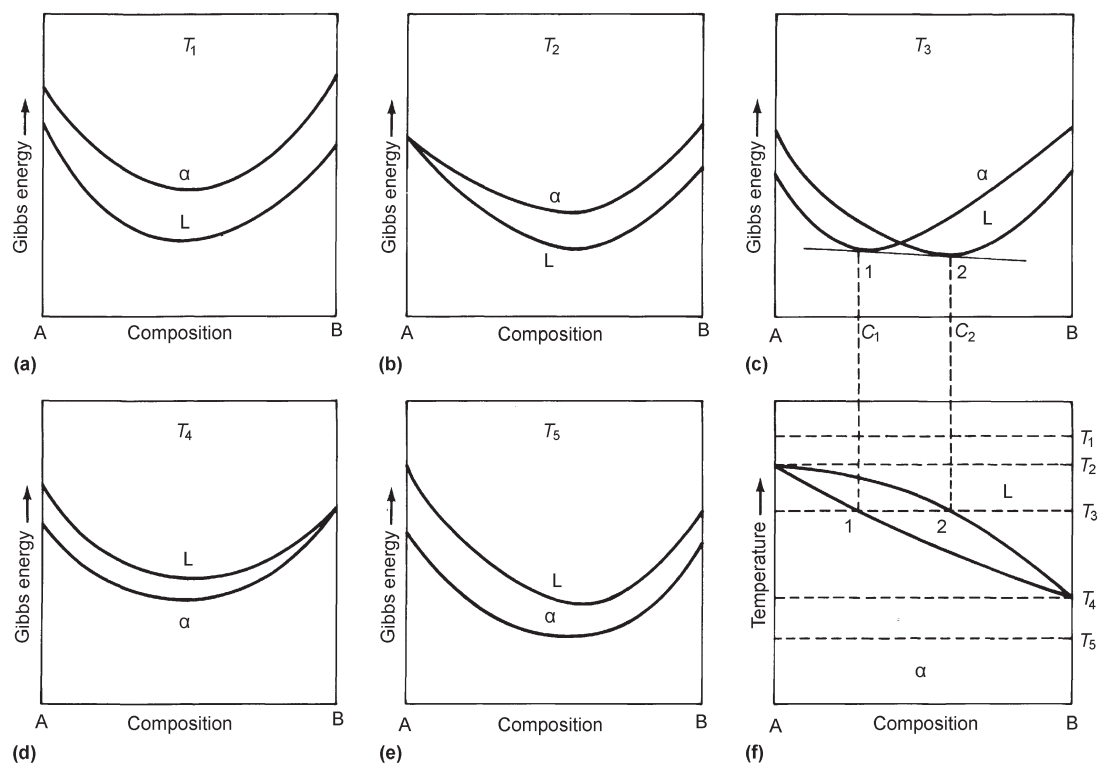
Fig. 3.24 Use of Gibbs energy curves to construct a binary phase diagram that shows miscibility in both the liquid and solid states. Source: Ref 3.3 as published in Ref 3.2
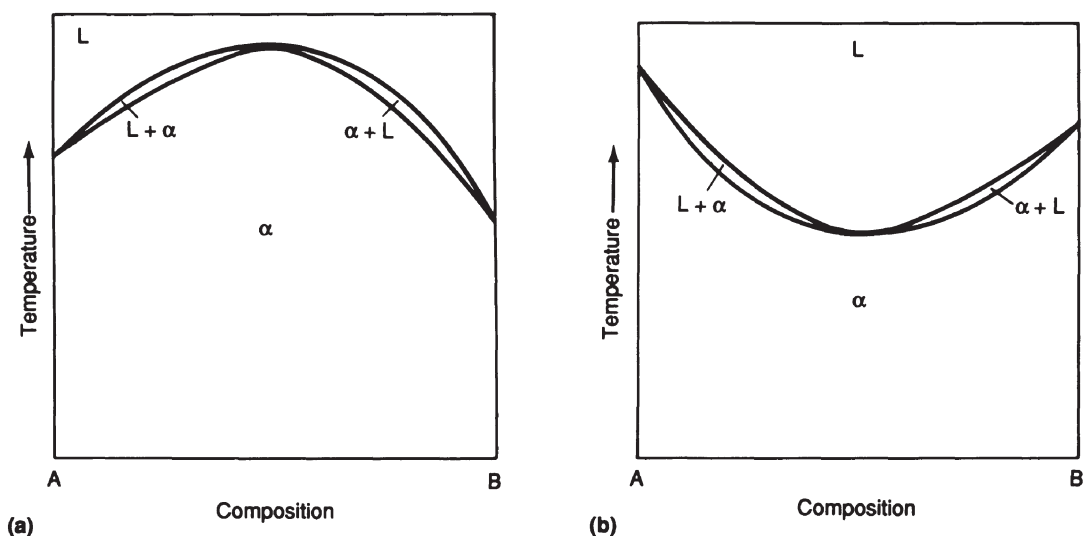

Fig. 3.25 Schematic binary phase diagrams with solid-state miscibility where the liquidus shows (a) a maximum and (b) a minimum. Source: Ref 3.2
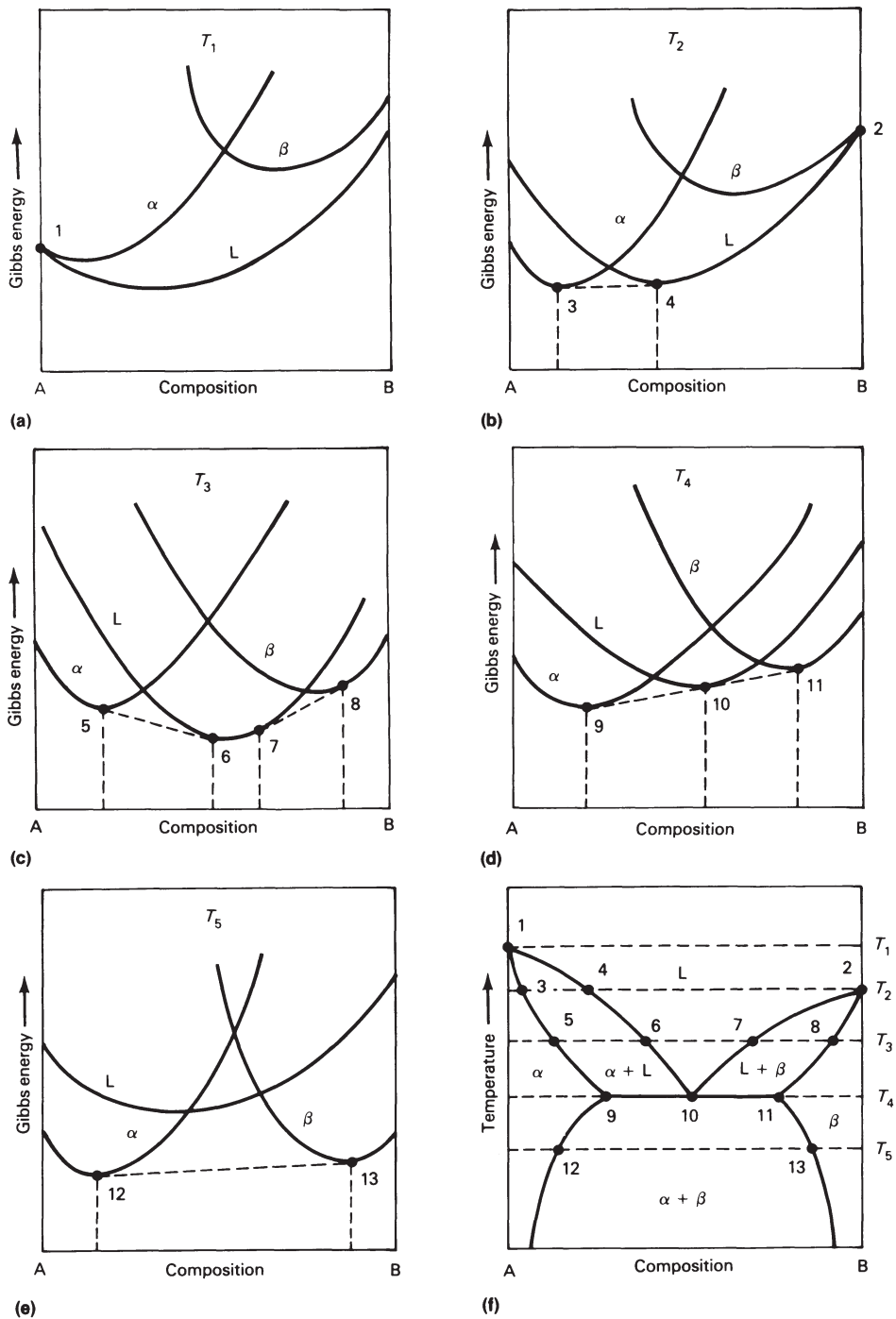
Fig. 3.26 Use of Gibbs energy curves to construct a binary phase diagram of the eutectic type. Source: Ref 3.4 as published in Ref 3.2

ferred to the diagram, the typical shape of a eutectic system results. The mixture of solid α and β that forms on cooling through the eutectic (Point 10 in Fig. 3.26f), has a special microstructure.

Binary phase diagrams that have three-phase reactions other than the eutectic reaction, as well as diagrams with multiple three-phase reactions, also can be constructed from appropriate Gibbs free-energy curves. Likewise, Gibbs free-energy surfaces and tangential planes can be used to construct ternary phase diagrams.

ACKNOWLEDGMENT

REFERENCES

3.1   D.A. Porter and K.E. Easterling, *Phase Transformations in Metals and Alloys*, Chapman and Hall, 1981

3.2   H. Baker, Introduction to Alloy Phase Diagrams, *Phase Diagrams*, Vol 3, *ASM Handbook*, ASM International, 1992, reprinted in *Desk Handbook: Phase Diagrams for Binary Alloys*, 2nd ed., H. Okamoto, Ed., ASM International, 2010

3.3   A. Prince, *Alloy Phase Equilibria*, Elsevier, 1966

3.4   P. Gordon, *Principles of Phase Diagrams in Materials Systems*, McGraw-Hill, 1968

SELECTED REFERENCES

- B.S. Bokstein, M.I. Mendelev, and D.J. Srolovitz, *Thermodynamics and Kinetics in Materials Science*, Oxford University Press, 2005
- R.T. DeHoff, *Thermodynamics in Materials Science*, McGraw-Hill, 1993
- D.R. Gaskell, *Introduction to the Chemical Thermodynamics of Materials*, 4th ed., Taylor & Francis, 2003
- H.-G. Lee, *Chemical Thermodynamics for Metals and Materials*, Imperial College Press, 1999
- S. Stolen, T. Grande, and N. Allan, *Chemical Thermodynamics of Materials*, John Wiley & Sons, 2004