1

Thermodynamics and Phase Diagrams

This chapter deals with some of the basic thermodynamic concepts that are required for a more fundamental appreciation of phase diagrams and phase transformations. It is assumed that the student is already acquainted with elementary thermodynamics and only a summary of the most important results as regards phase transformations will be given here. Fuller treatment can be found in the books listed in the bibliography at the end of this chapter.

The main use of thermodynamics in physical metallurgy is to allow the prediction of whether an alloy is in equilibrium. In considering phase transformations we are always concerned with changes towards equilibrium, and thermodynamics is therefore a very powerful tool. It should be noted, however, that the rate at which equilibrium is reached cannot be determined by thermodynamics alone, as will become apparent in later chapters.

1.1 Equilibrium

It is useful to begin this chapter on thermodynamics by defining a few of the terms that will be frequently used. In the study of phase transformations we will be dealing with the changes that can occur within a given *system*, e.g. an alloy that can exist as a mixture of one or more phases. A *phase* can be defined as a portion of the system whose properties and composition are homogeneous and which is physically distinct from other parts of the system. The *components* of a given system are the different elements or chemical compounds which make up the system, and the composition of a phase or the system can be described by giving the relative amounts of each component.

The study of phase transformations, as the name suggests, is concerned with how one or more phases in an alloy (the system) change into a new phase or mixture of phases. The reason why a transformation occurs at all is because the initial state of the alloy is unstable relative to the final state. But how is phase stability measured? The answer to this question is provided by thermodynamics. For transformations that occur at constant temperature and pressure the relative stability of a system is determined by its *Gibbs free energy* (G).

The Gibbs free energy of a system is defined by the equation

$$G = H - TS \tag{1.1}$$

where H is the enthalpy, T the absolute temperature, and S the entropy of the system. Enthalpy is a measure of the heat content of the system and is given by

$$H = E + PV \tag{1.2}$$

where E is the internal energy of the system, P the pressure, and V the volume. The internal energy arises from the total kinetic and potential energies of the atoms within the system. Kinetic energy can arise from atomic vibration in solids or liquids and from translational and rotational energies for the atoms and molecules within a liquid or gas; whereas potential energy arises from the interactions, or bonds, between the atoms within the system. If a transformation or reaction occurs the heat that is absorbed or evolved will depend on the change in the internal energy of the system. However it will also depend on changes in the volume of the system and the term PV takes this into account, so that at *constant pressure* the heat absorbed or evolved is given by the change in H. When dealing with condensed phases (solids and liquids) the PV term is usually very small in comparison to E, that is $H \simeq E$. This approximation will be made frequently in the treatments given in this book. The other function that appears in the expression for G is entropy (S) which is a measure of the randomness of the system.

A system is said to be in equilibrium when it is in the most stable state, i.e. shows no desire to change *ad infinitum*. An important consequence of the laws of classical thermodynamics is that at constant temperature and pressure a closed system (i.e. one of fixed mass and composition) will be in stable equilibrium if it has the lowest possible value of the Gibbs free energy, or in mathematical terms

$$\mathrm{d}G = 0 \tag{1.3}$$

It can be seen from the definition of G, Equation 1.1, that the state with the highest stability will be that with the best compromise between low enthalpy and high entropy. Thus at low temperatures solid phases are most stable since they have the strongest atomic binding and therefore the lowest internal energy (enthalpy). At high temperatures however the $-TS$ term dominates and phases with more freedom of atom movement, liquids and gases, become most stable. If pressure changes are considered it can be seen from Equation 1.2 that phases with small volumes are favoured by high pressures.

The definition of equilibrium given by Equation 1.3 can be illustrated graphically as follows. If it were possible to evaluate the free energy of a given system for all conceivable configurations the stable equilibrium configuration would be found to have the lowest free energy. This is illustrated in Fig. 1.1 where it is imagined that the various atomic configurations can be represented by points along the abscissa. Configuration A would be the stable equilibrium state. At this point small changes in the arrangement of atoms to a first approximation produce no change in G, i.e. Equation 1.3 applies. However there will always be other configurations, e.g. B, which lie at a local minimum in free energy and therefore also satisfy Equation 1.3, but which 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 intermediate states for which $\mathrm{d}G \neq 0$ are *unstable* and are only ever realized momentarily in practice. If, as the result of thermal fluctuations, the atoms become arranged in an intermediate state they will rapidly rearrange into one of the free energy minima. If by a change of temperature or pressure, for example, a system is moved from a stable to a metastable state it will, given time, transform to the new stable equilibrium state.

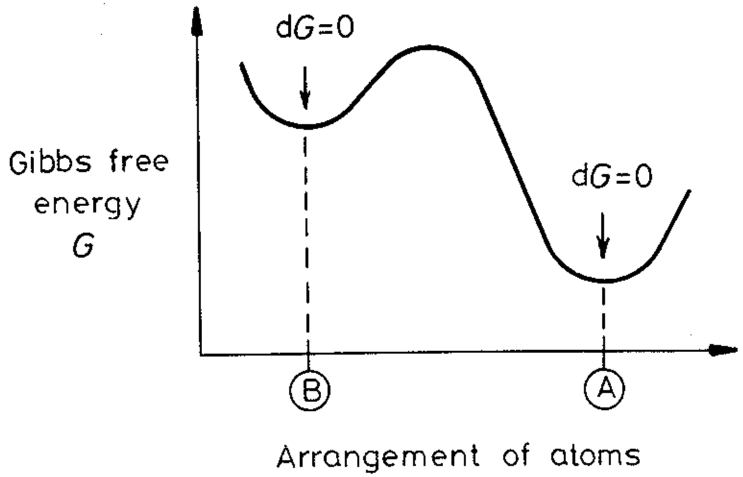


Fig. 1.1 A schematic variation of Gibbs free energy with the arrangement of atoms. Configuration 'A' has the lowest free energy and is therefore the arrangement when the system is at stable equilibrium. Configuration 'B' is a metastable equilibrium.

Graphite and diamond at room temperature and pressure are examples of stable and metastable equilibrium states. Given time, therefore, all diamond under these conditions will transform to graphite.

Any transformation that results in a decrease in Gibbs free energy is possible. Therefore a necessary criterion for any phase transformation is

$$\Delta G = G_2 - G_1 < 0 \tag{1.4}$$

where G_1 and G_2 are the free energies of the initial and final states respectively. The transformation need not go directly to the stable equilibrium state but can pass through a whole series of intermediate metastable states.

The answer to the question "How fast does a phase transformation occur?" is not provided by classical thermodynamics. Sometimes metastable states can be very short-lived; at other times they can exist almost indefinitely as in the case of diamond at room temperature and pressure. The reason for these differences is the presence of the free energy hump between the metastable and stable states in Fig. 1.1. The study of transformation rates in physical chemistry belongs to the realm of *kinetics*. In general, higher humps or energy barriers lead to slower transformation rates. Kinetics obviously plays a central role in the study of phase transformations and many examples of kinetic processes will be found throughout this book.

The different thermodynamic functions that have been mentioned in this section can be divided into two types called intensive and extensive properties. The *intensive* properties are those which are independent of the size of the system such as T and P, whereas the *extensive* properties are directly proportional to the quantity of material in the system, e.g. V, E, H, S and G. The usual way of measuring the size of the system is by the number of moles of material it contains. The extensive properties are then molar quantities, i.e. expressed in units *per mole*. The number of moles of a given component in the system is given by the mass of the component in grams divided by its atomic or molecular weight.

The number of atoms or molecules within 1 mol of material is given by Avogadro's number (N_a) and is 6.023×10^{23}.

1.2 Single Component Systems

Let us begin by dealing with the phase changes that can be induced in a single component by changes in temperature at a fixed pressure, say 1 atm. A single component system could be one containing a pure element or one type of molecule that does not dissociate over the range of temperature of interest. In order to predict the phases that are stable or mixtures that are in equilibrium at different temperatures it is necessary to be able to calculate the variation of G with T.

1.2.1 *Gibbs Free Energy as a Function of Temperature*

The specific heat of most substances is easily measured and readily available. In general it varies with temperature as shown in Fig. 1.2a. The specific heat is the quantity of heat (in joules) required to raise the temperature of the substance by one degree Kelvin. At constant pressure this is denoted by C_p and is given by

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.5}$$

Therefore the variation of H with T can be obtained from a knowledge of the variation of C_p with T. In considering phase transformations or chemical reactions it is only changes in thermodynamic functions that are of interest. Consequently H can be measured relative to any reference level which is usually done by defining $H = 0$ for a pure element in its most stable state at 298 K (25 °C). The variation of H with T can then be calculated by integrating

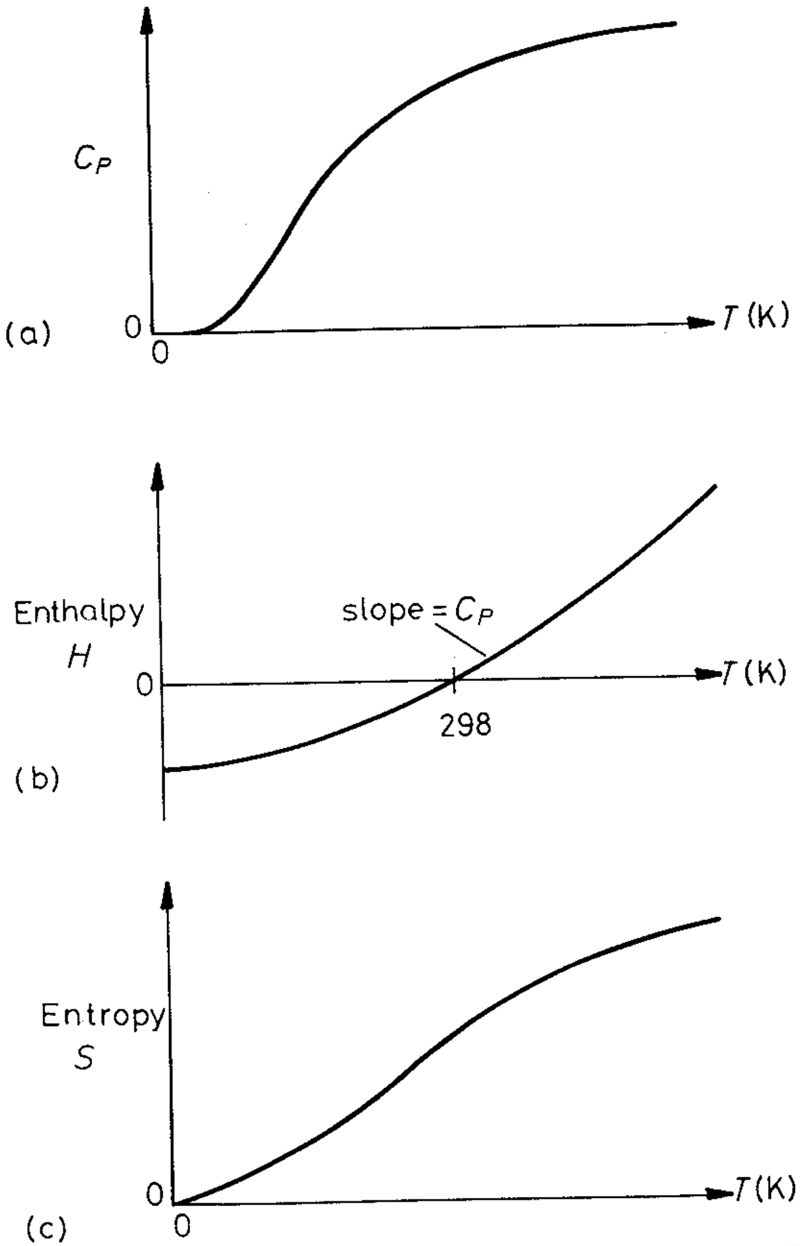


Fig. 1.2 (a) Variation of C_p with temperature, C_p tends to a limit of ~3R. (b) Variation of enthalpy (H) with absolute temperature for a pure metal. (c) Variation of entropy (S) with absolute temperature.

Equation 1.5, i.e.

$$H = \int_{298}^{T} C_p \mathrm{d}T \qquad (1.6)$$

The variation is shown schematically in Fig. 1.2b. The slope of the H–T curve is Cp.

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

$$\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_P \qquad (1.7)$$

Taking entropy at zero degrees Kelvin as zero, Equation 1.7 can be integrated to give

$$S = \int_0^T \frac{C_p}{T} \mathrm{d}T \qquad (1.8)$$

as shown in Fig. 1.2c.

Finally the variation of G with temperature shown in Fig. 1.3 is obtained by combining Fig. 1.2b and c using Equation 1.1. When temperature and pressure vary the change in Gibbs free energy can be obtained from the following result of classical thermodynamics: for a system of fixed mass and composition

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P \qquad (1.9)$$

At constant pressure $\mathrm{d}P = 0$ and

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad (1.10)$$

This means 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 illustrated in Fig. 1.4. At all temperatures the liquid has a higher enthalpy (internal energy) than the solid. Therefore at low temperatures $G^{\mathrm{L}} > G^{\mathrm{S}}$. 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 of the solid. For temperatures up to T_{m} the solid phase has the lowest free energy and is therefore the stable equilibrium phase, whereas above T_{m} the liquid phase is the equilibrium state of the system. At T_{m} both phases have the same value of G and both solid and liquid can exist in equilibrium. T_{m} is therefore 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 the line ab in Fig. 1.4. Meanwhile the free energy will *decrease* along ae. At T_{m} the heat supplied to the system will not raise its temperature but will be used in supplying the latent heat of melting (L) that is required to convert solid into liquid (bc in Fig. 1.4). Note that at T_{m} the specific heat appears to be infinite since the addition of heat does not appear as an increase in temperature. When all solid has transformed into liquid the enthalpy of the system will follow the line cd while the Gibbs free energy decreases along ef. At still higher temperatures than shown in Fig. 1.4 the free energy of the gas phase (at atmospheric pressure) becomes lower than that of the liquid and the liquid transforms to a gas. If the solid phase can exist in different crystal structures (allotropes or polymorphs) free energy curves can be constructed for each of these phases and the temperature at which they intersect will give the equilibrium temperature for the polymorphic transformation. For example at atmospheric pressure iron can exist as either bcc ferrite below 910 °C or fcc austenite above 910 °C, and at 910 °C both phases can exist in equilibrium.

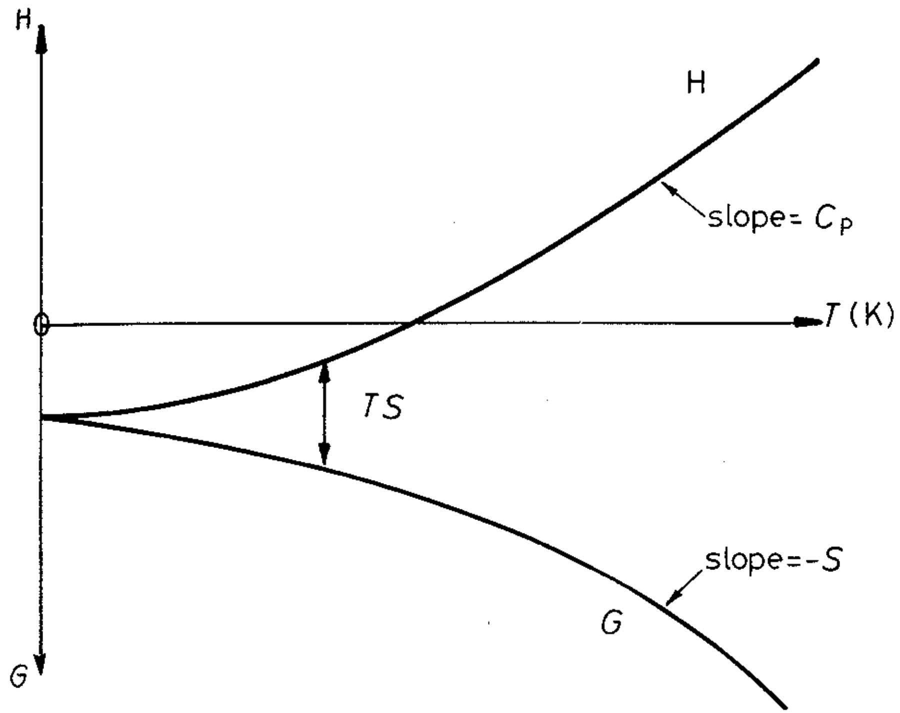


Fig. 1.3 Variation of Gibbs free energy with temperature.

1.2.2 *Pressure Effects*

The equilibrium temperatures discussed so far only apply at a specific pressure (1 atm, say). At other pressures the equilibrium temperatures will differ.

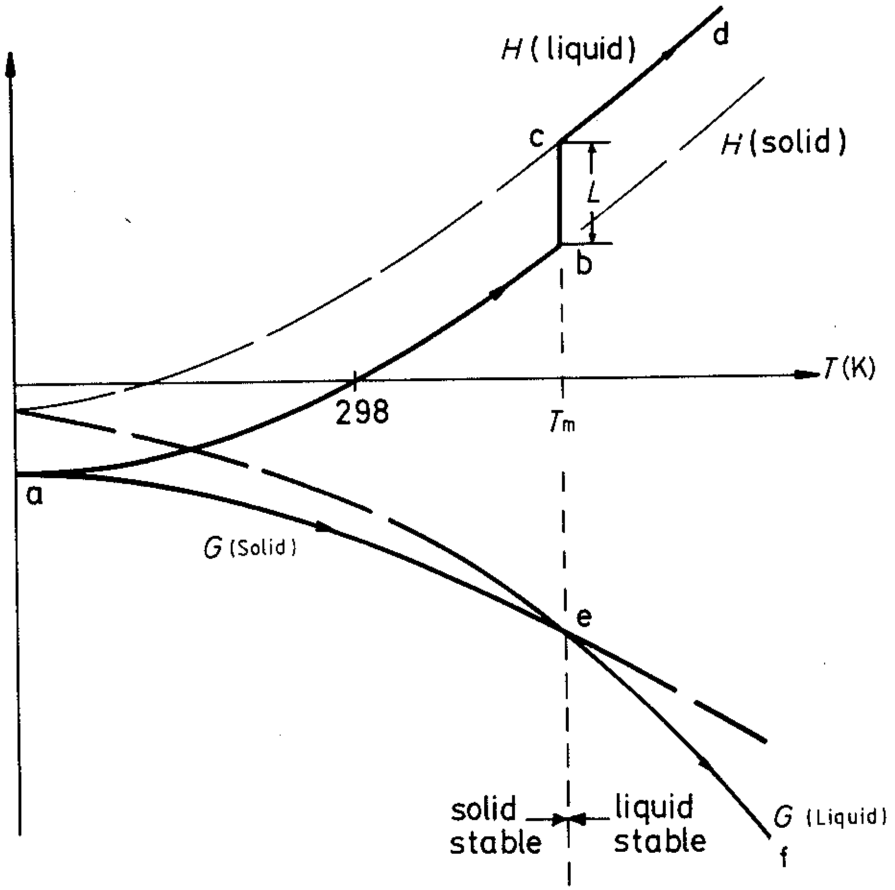


Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the solid and liquid phases of a pure metal. L is the latent heat of melting, T_m the equilibrium melting temperature.

For example Fig. 1.5 shows the effect of pressure on the equilibrium temperatures for pure iron. Increasing pressure has the effect of depressing the α/γ equilibrium temperature and raising the equilibrium melting temperature. At very high pressures hcp ε-Fe becomes stable. The reason for these changes derives from Equation 1.9. At constant temperature the free energy of a phase increases with pressure such that

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{1.11}$$

If the two phases in equilibrium have different molar volumes their respective free energies will not increase by the same amount at a given temperature and equilibrium will, therefore, be disturbed by changes in pressure. The only way to maintain equilibrium at different pressures is by varying the temperature.

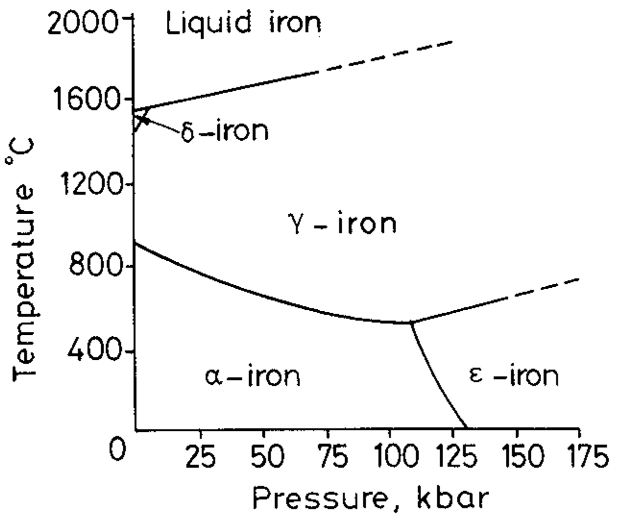


Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron.

If the two phases in equilibrium are α and β, application of Equation 1.9 to 1 mol of both gives

$$\begin{aligned} dG^\alpha &= V_m^\alpha dP - S^\alpha dT \\ dG^\beta &= V_m^\beta dP - S^\beta dT \end{aligned} \tag{1.12}$$

If α and β are in equilibrium $G^\alpha = G^\beta$ therefore $dG^\alpha = dG^\beta$ and

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^\beta - S^\alpha}{V_m^\beta - V_m^\alpha} = \frac{\Delta S}{\Delta V} \tag{1.13}$$

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 Equation 1.1

$$G^\alpha = H^\alpha - TS^\alpha$$
$$G^\beta = H^\beta - TS^\beta$$

Therefore, putting $\Delta G = G^\beta - G^\alpha$ etc. gives

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

But since at equilibrium $G^\beta = G^\alpha$, $\Delta G = 0$, and

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

Consequently Equation 1.13 becomes

$$\left(\frac{dP}{dT_{eq}}\right) = \frac{\Delta H}{T_{eq}\Delta V} \tag{1.14}$$

which is known as the Clausius–Clapeyron equation. Since close-packed γ-Fe has a smaller molar volume than α-Fe, $\Delta V = V_m^\gamma - V_m^\alpha < 0$ whereas $\Delta H = H^\gamma - H^\alpha > 0$ (for the same reason that a liquid has a higher enthalpy than a solid), so that (dP/dT) is negative, i.e. an increase in pressure lowers the equilibrium transition temperature. On the other hand the δ/L equilibrium temperature is raised with increasing pressure due to the larger molar volume of the liquid phase. It can be seen that 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-Fe in Fig. 1.5). It should also be noted that ε-Fe has the highest density of the three allotropes, consistent with the slopes of the phase boundaries in the Fe phase diagram.

1.2.3 *The Driving Force for Solidification*

In dealing with phase transformations we are often concerned with the difference in free energy between two phases at temperatures away from the equilibrium temperature. For example, if a liquid metal is undercooled by ΔT below T_m before it solidifies, solidification will be accompanied by a decrease in free energy ΔG (J mol^{-1}) as shown in Fig. 1.6. 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

$$\Delta G = \Delta H - T\Delta S \tag{1.15}$$

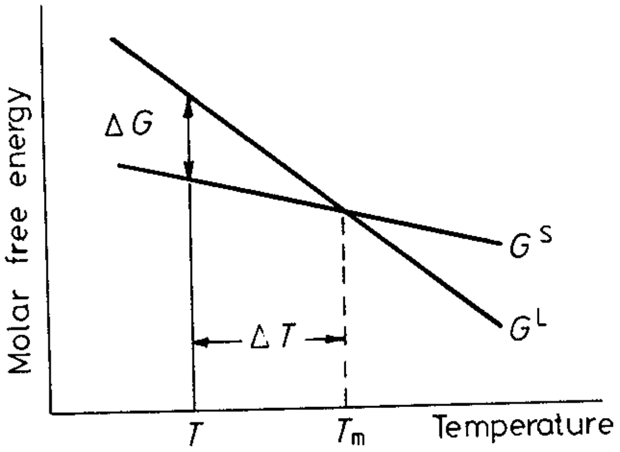


Fig. 1.6 Difference in free energy between liquid and solid close to the melting point. The curvature of the G^S and G^L lines has been ignored.

where

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

At the equilibrium melting temperature T_m the free energies of solid and liquid are equal, i.e. $\Delta G = 0$. Consequently

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

and therefore at T_m

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} \tag{1.16}$$

This is known as the entropy of fusion. It is observed experimentally that the entropy of fusion is a constant $\approx R$(8.3 J mol^{-1} K^{-1}) for most metals (Richard's rule). This is not unreasonable as 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 the specific heats of the liquid and solid ($C_p^L - C_p^S$) can be ignored. ΔH and ΔS are therefore approximately independent of temperature. Combining Equations 1.15 and 1.16 thus gives

$$\Delta G \simeq L - T\frac{L}{T_m}$$

i.e. for small ΔT

$$\Delta G \simeq \frac{L\Delta T}{T_m} \tag{1.17}$$

This is a very useful result which will frequently recur in subsequent chapters.

1.3 **Binary Solutions**

In single component systems all phases have the same composition, and equilibrium simply involves pressure and temperature as variables. In alloys, however, composition is also variable and to understand phase changes in alloys requires an appreciation of how the Gibbs free energy of a given phase depends on composition as well as temperature and pressure. Since the phase transformations described in this book mainly occur at a fixed pressure of 1 atm most attention will be given to 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 will be described.

1.3.1 *The 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 in the following way.

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. Imagine that 1 mol of homogeneous solid solution is made by mixing together X_A mol of A and X_B mol of B. Since there is a total of 1 mol of solution

$$X_A + X_B = 1 \tag{1.18}$$

and X_A and X_B are the *mole fractions* of A and B respectively in the alloy. In order to calculate the free energy of the alloy, the mixing can be made in two steps (see Fig. 1.7). These are:

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.

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

$$G_1 = X_A G_A + X_B G_B \quad \text{J mol}^{-1} \tag{1.19}$$

where G_A and G_B are the molar free energies of pure A and pure B at the temperature and pressure of the above experiment. G_1 can be most conveniently represented on a *molar free energy diagram* (Fig. 1.8) 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 the mixing of the A and B atoms and after step 2 the free energy of the solid solution G_2 can be expressed as

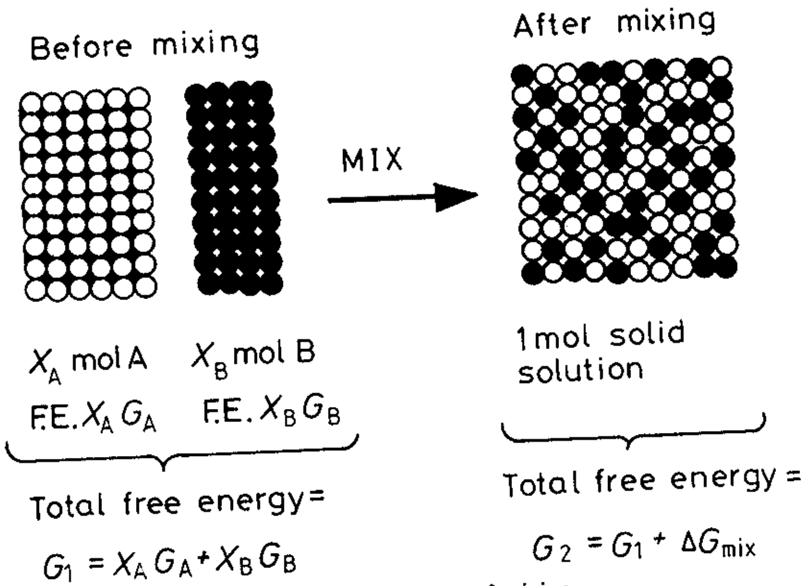


Fig. 1.7 Free energy of mixing.

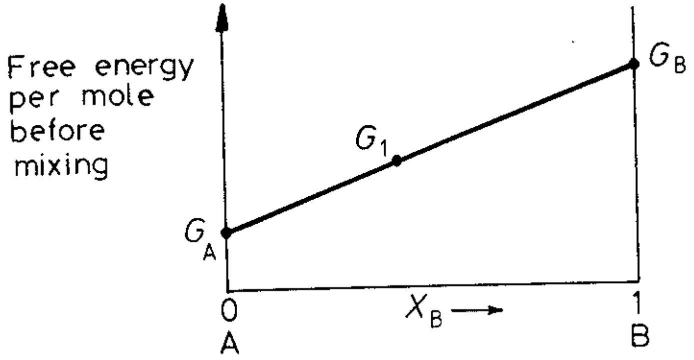


Fig. 1.8 Variation of G_1 (the free energy before mixing) with alloy composition (X_A or X_B).

$$G_2 = G_1 + \Delta G_{mix} \tag{1.20}$$

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

Since

$$G_1 = H_1 - TS_1$$

and

$$G_2 = H_2 - TS_2$$

putting

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

and

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

gives

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{1.21}$$

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

1.3.2 *Ideal Solutions*

The simplest type of mixing to treat first is when $\Delta H_{mix} = 0$, in which case the resultant solution is said to be *ideal* and the free energy change on mixing is only due to the change in entropy:

$$\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}} \tag{1.22}$$

In statistical thermodynamics, entropy is quantitatively related to randomness by the Boltzmann equation, i.e.

$$S = k \ln \omega \tag{1.23}$$

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

In the case of thermal entropy, 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 $\Delta S_{\text{mix}} = S_2$.

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

$$\omega_{\text{config}} = \frac{(N_A + N_B)!}{N_A!N_B!} \tag{1.24}$$

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

Since we are dealing with 1 mol of solution, i.e. N_a atoms (Avogadro's number),

$$N_A = X_A N_a$$

and

$$N_B = X_B N_a$$

By substituting into Equations 1.23 and 1.24, using Stirling's approximation ($\ln N! \simeq N \ln N - N$) and the relationship $N_a k = R$ (the universal gas constant) gives

$$\Delta S_{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B) \tag{1.25}$$

Note that, since X_A and X_B are less than unity, ΔS_{mix} is positive, i.e. there is an increase in entropy on mixing, as expected. The free energy of mixing, ΔG_{mix}, is obtained from Equation 1.22 as

$$\Delta G_{\text{mix}} = RT(X_A \ln X_A + X_B \ln X_B) \tag{1.26}$$

Figure 1.9 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 Equations 1.19, 1.20 and 1.26

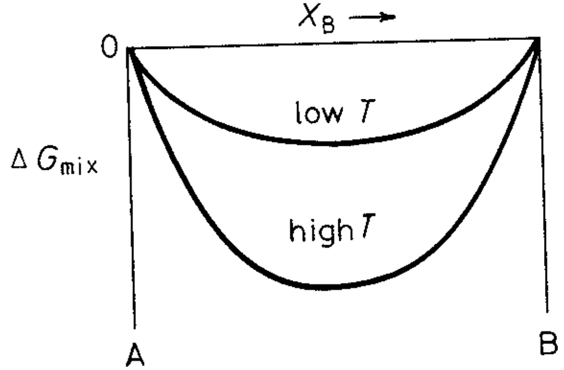


Fig. 1.9 Free energy of mixing for an ideal solution.

$$G = G_2 = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B) \tag{1.27}$$

This is shown schematically in Fig. 1.10. Note that, as the temperature increases, G_A and G_B decrease and the free energy curves assume a greater curvature. The decrease in G_A and G_B is due to the thermal entropy of both components and is given by Equation 1.10.

It should be noted that all of the free energy-composition diagrams in this book are essentially schematic; if properly plotted the free energy curves must end asymptotically at the vertical axes of the pure components, i.e. tangential to the vertical axes of the diagrams. This can be shown by differentiating Equation 1.26 or 1.27.

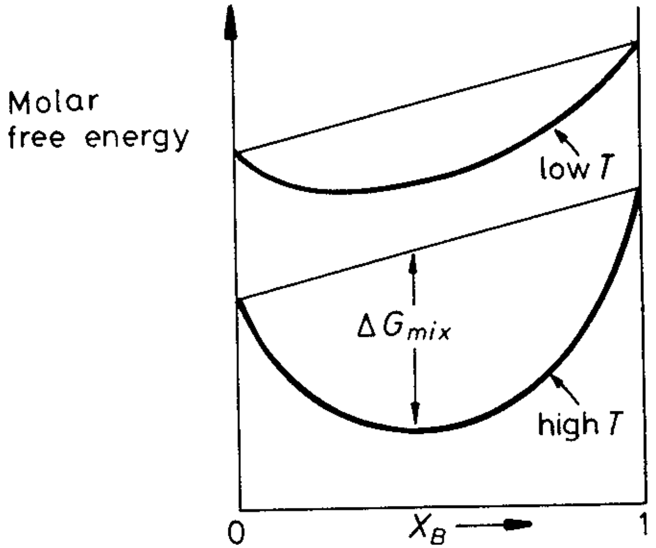


Fig. 1.10 The molar free energy (free energy per mole of solution) for an ideal solid solution. A combination of Figs. 1.8 and 1.9.

1.3.3 Chemical Potential

In alloys it is of interest 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 therefore 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. Thus we can write

$$dG' = \mu_A dn_A \qquad (T, P, n_B \text{ constant}) \tag{1.28}$$

The proportionality constant μ_A is called the *partial molar free energy* of A or alternatively the *chemical potential* of A in the phase. 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 Equation 1.28 is rewritten it can be seen that a definition of the chemical potential of A is

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P,n_B} \tag{1.29}$$

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 1.28 and 1.29 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:

$$dG' = \mu_A dn_A + \mu_B dn_B \tag{1.30}$$

This equation can be extended by adding further terms for solutions containing more than two components. If T and P changes are also allowed Equation 1.9 must be added giving the general equation

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

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, i.e. 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 Equation 1.30

$$G = \mu_A X_A + \mu_B X_B \quad \text{J mol}^{-1} \tag{1.31}$$

When G is known as a function of X_A and X_B, as in Fig. 1.10 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 as shown in Fig. 1.11. This can be obtained from Equations 1.30 and 1.31, remembering that $X_A + X_B = 1$, i.e. $dX_A = -dX_B$, and this is left as an exercise for the reader. It is clear from Fig. 1.11 that μ_A and μ_B vary systematically with the composition of the phase.

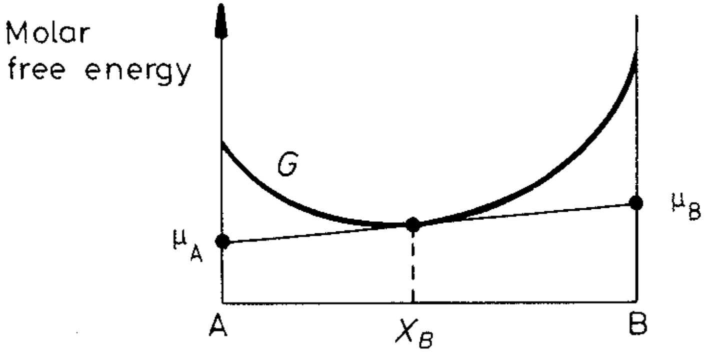


Fig. 1.11 The relationship between the free energy curve for a solution and the chemical potentials of the components.

Comparison of Equations 1.27 and 1.31 gives μ_A and μ_B for an ideal solution as

$$\begin{aligned} \mu_A &= G_A + RT \ln X_A \\ \mu_B &= G_B + RT \ln X_B \end{aligned} \tag{1.32}$$

which is a much simpler way of presenting Equation 1.27. These relationships are shown in Fig. 1.12. The distances ac and bd are simply $-RT \ln X_A$ and $-RT \ln X_B$.

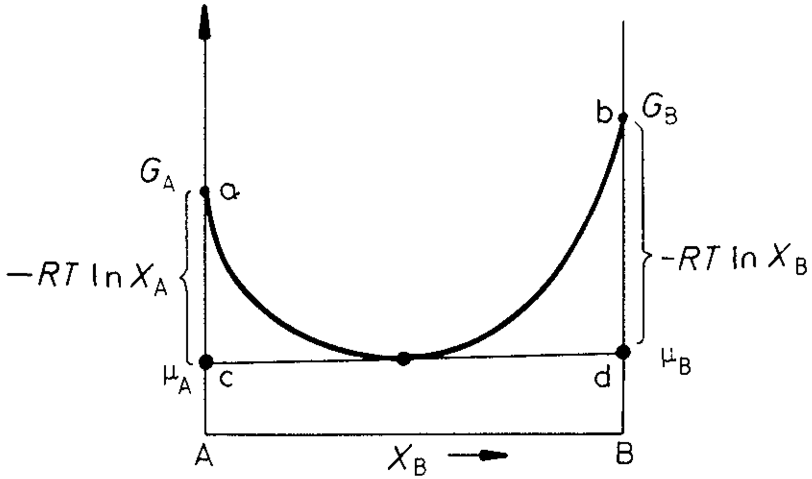


Fig. 1.12 The relationship between the free energy curve and chemical potentials for an ideal solution.

1.3.4 *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 behaviour is exceptional in practice and usually mixing is *endothermic* (heat absorbed) or *exothermic* (heat evolved). The simple model used for an ideal solution can, however, 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. 1.13. Three types of interatomic bonds are present:

1. A—A bonds each with an energy ε_{AA},
2. B—B bonds each with an energy ε_{BB},
3. 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[1] that the change in internal energy on mixing is given by

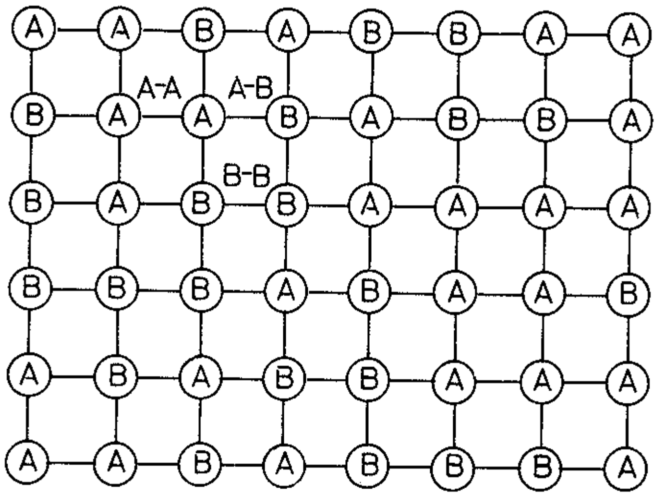


Fig. 1.13 The different types of interatomic bond in a solid solution.

$$\Delta H_{mix} = P_{AB}\varepsilon \tag{1.33}$$

where

$$\varepsilon = \varepsilon_{AB} - \tfrac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}) \tag{1.34}$$

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, as considered in Section 1.3.2. In this case the atoms are *completely randomly arranged* and the entropy of mixing is given by Equation 1.25. In such a solution it can also be shown[1] that

$$P_{AB} = N_a z X_A X_B \quad \text{bonds mol}^{-1} \tag{1.35}$$

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, Equation 1.35 is still a good approximation in which case

$$\Delta H_{mix} = \Omega X_A X_B \tag{1.36}$$

where

$$\Omega = N_a z \varepsilon \tag{1.37}$$

Real solutions that closely obey Equation 1.36 are known as *regular solutions*. The variation of ΔH_{mix} with composition is parabolic and is shown in Fig. 1.14 for $\Omega > 0$. Note that the tangents at $X_A = 0$ and 1 are related to Ω as shown.

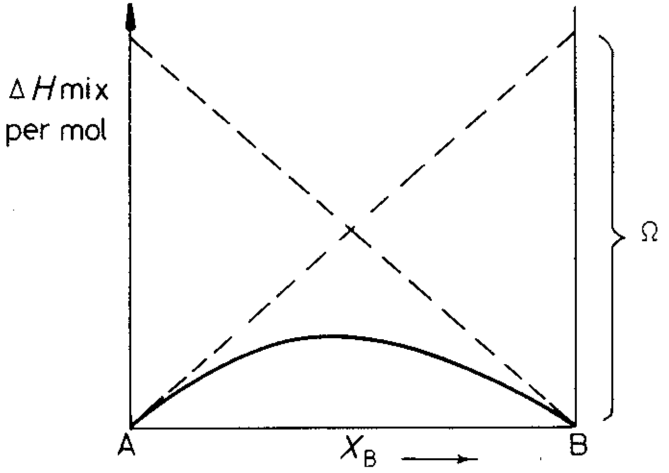


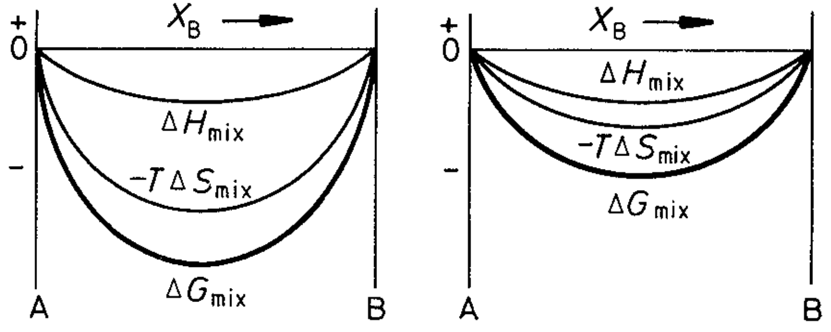
Fig. 1.14 The variation of ΔH_{mix} with composition for a regular solution.

The free energy change on mixing a regular solution is given by Equations 1.21, 1.25 and 1.36 as

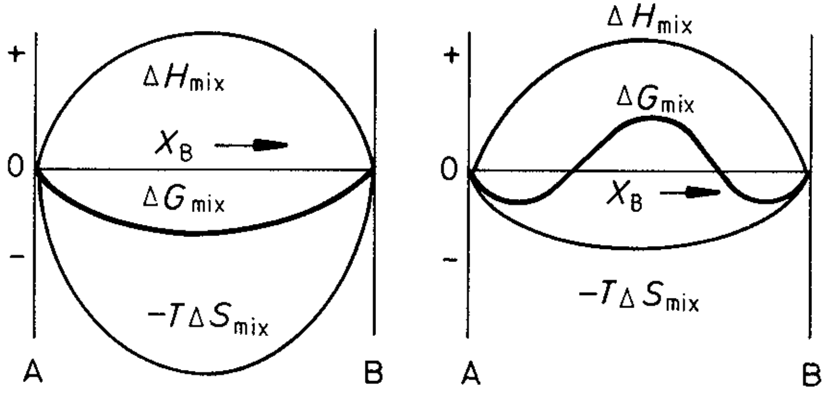
$$\Delta G_{\mathrm{mix}} = \underbrace{\Omega X_A X_B}_{\Delta H_{\mathrm{mix}}} + \underbrace{RT(X_A \ln X_A + X_B \ln X_B)}_{-T\Delta S_{\mathrm{mix}}} \tag{1.38}$$

This is shown in Fig. 1.15 for different values of Ω and temperature. For exothermic solutions $\Delta H_{\mathrm{mix}} < 0$ and mixing results in a free energy decrease at all temperatures (Fig. 1.15a and b). When $\Delta H_{\mathrm{mix}} > 0$, however, the situation is more complicated. At high temperatures $T\Delta S_{\mathrm{mix}}$ is greater than ΔH_{mix} for all compositions and the free energy curve has a positive curvature at all points (Fig. 1.15c). At low temperatures, on the other hand, $T\Delta S_{\mathrm{mix}}$ is smaller and ΔG_{mix} develops a negative curvature in the middle (Fig. 1.15d).

Differentiating Equation 1.25 shows that, as X_A or $X_B \to 0$, the $-T\Delta S_{\mathrm{mix}}$ curve becomes vertical whereas the slope of the ΔH_{mix} curve tends to a finite value Ω (Fig. 1.14). This means that, except at absolute zero, ΔG_{mix} always decreases on addition of a small amount of solute.



(a) $\Omega < 0$, high T (b) $\Omega < 0$, low T



(c) $\Omega > 0$, high T (d), $\Omega > 0$ low T

Fig. 1.15 The effect of ΔH_{mix} and T on ΔG_{mix}.

The actual free energy of the alloy depends on the values chosen for G_A and G_B and is given by Equations 1.19, 1.20 and 1.38 as

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B) \tag{1.39}$$

This is shown in Fig. 1.16 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 Equations 1.31 and 1.39 shows that for a regular solution

$$\mu_A = G_A + \Omega(1 - X_A)^2 + RT \ln X_A$$

and (1.40)

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

1.3.5 Activity

Expression 1.32 for the chemical potential of an ideal alloy was simple and it is convenient to retain a similar expression for any solution. This can be done by defining the *activity* of a component, a, such that the distances ac and bd in Fig. 1.16 are $-RT \ln a_A$ and $-RT \ln a_B$. In this case

$$\mu_A = G_A + RT \ln a_A$$

and (1.41)

$$\mu_B = G_B + RT \ln a_B$$

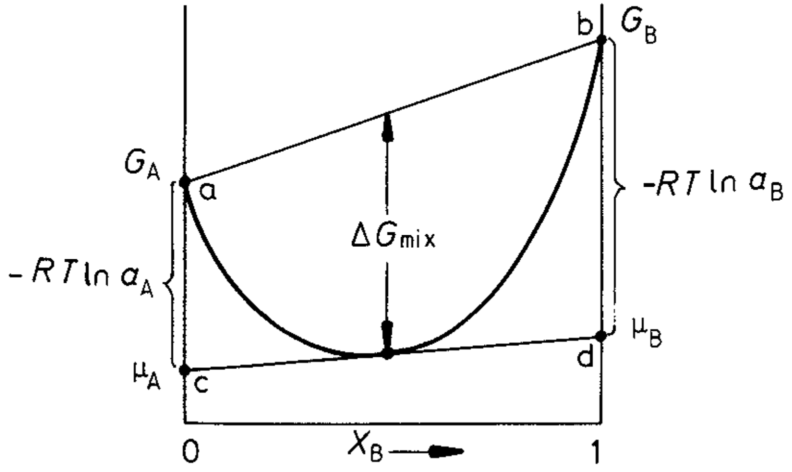


Fig. 1.16 The relationship between molar free energy and activity.

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 Equations 1.40 and 1.41 gives

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1 - X_A)^2$$

and (1.42)

$$\ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1 - X_B)^2$$

Assuming pure A and pure B have the same crystal structure, the relationship between a and X for any solution can be represented graphically as illustrated in Fig. 1.17. 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

$$\gamma_A = a_A/X_A \tag{1.43}$$

For a dilute solution of B in A, Equation 1.42 can be simplified by letting $X_B \to 0$ in which case

$$\gamma_B = \frac{a_B}{X_B} \simeq \text{constant} \quad \text{(Henry's law)} \tag{1.44}$$

and

$$\gamma_A = \frac{a_A}{X_A} \simeq 1 \quad \text{(Raoult's law)} \tag{1.45}$$

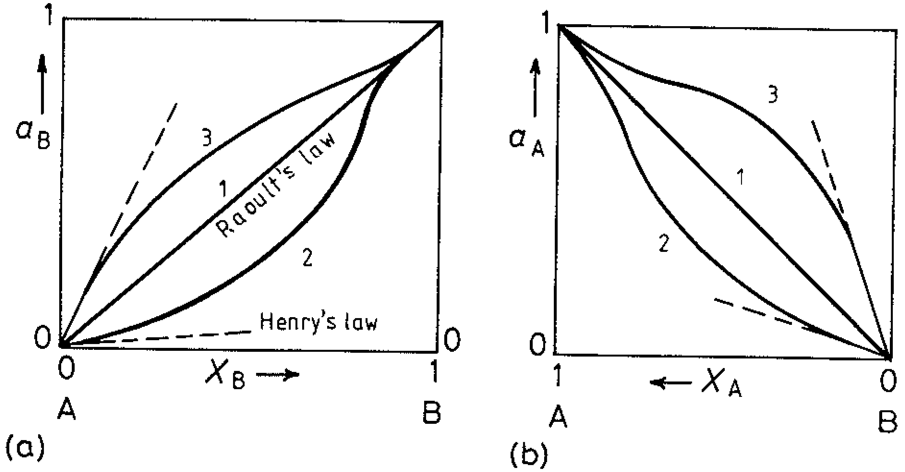


Fig. 1.17 The variation of activity with composition (a) a_B (b) a_A. Line 1: ideal solution (Raoult's law). Line 2: $\Delta H_{mix} < 0$. Line 3: $\Delta H_{mix} > 0$.

Equation 1.44 is known as Henry's law and 1.45 as Raoult's law; they apply to all solutions when sufficiently dilute.

Since activity is simply related to chemical potential via Equation 1.41 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 as it often leads to simpler mathematics.

Activity and chemical potential are simply 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 vapour pressure of the component in equilibrium with the solution will be relatively low. It will also be apparent later that the activity or chemical potential of a component is important when several condensed phases are in equilibrium.

1.3.6 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, i.e. by ordering the atoms as shown in Fig. 1.18a. If $\varepsilon > 0$ the internal energy can be reduced by increasing the number of A—A and B—B bonds, i.e. by the clustering of the atoms into A-rich and B-rich groups, Fig. 1.18b. However, the degree of ordering or

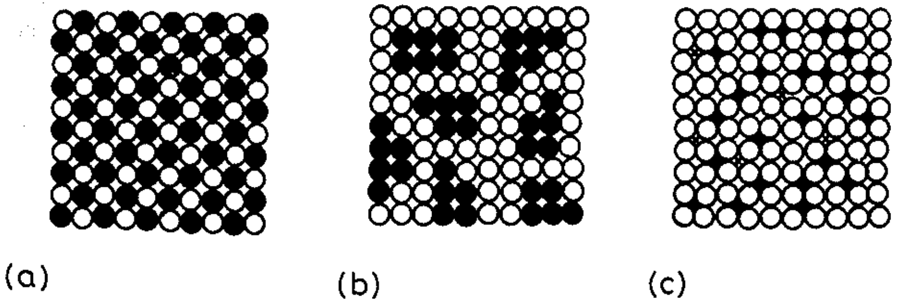


Fig. 1.18 Schematic representation of solid solutions: (a) ordered substitutional, (b) clustering, (c) random interstitial.

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 since no account is taken of the elastic strain fields which 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 favourable, Fig. 1.18c. New mathematical models are needed to describe these solutions.

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 since they have a different crystal structure and may also be highly ordered. Intermediate phases and ordered phases are discussed further in the next two sections.

1.3.7 *Ordered Phases*

If the atoms in a substitutional solid solution are completely randomly arranged each atom position is equivalent and the probability that any given site in the lattice will contain an A atom will be equal to the fraction of A atoms in the solution X_A, similarly X_B for the B atoms. In such solutions P_{AB}, the number of A—B bonds, is given by Equation 1.35. If $\Omega < 0$ and the number of A—B bonds is greater than this, the solution is said to contain short-range order (SRO). The degree of ordering can be quantified by defining a SRO parameter s such that

$$s = \frac{P_{AB} - P_{AB}(\text{random})}{P_{AB}(\text{max}) - P_{AB}(\text{random})}$$

where $P_{AB}(\text{max})$ and $P_{AB}(\text{random})$ refer to the maximum number of bonds possible and the number of bonds for a random solution, respectively. Figure 1.19 illustrates the difference between random and short-range ordered solutions.

In solutions with compositions that are close to a simple ratio of A : B atoms another type of order can be found as shown schematically in Fig. 1.18a. This is known as long-range order. Now the atom sites are no longer equivalent but can be labelled as A-sites and B-sites. Such a solution can be considered to be a different (ordered) phase separate from the random or nearly random solution.

Consider Cu-Au alloys as a specific example. Cu and Au are both fcc and totally miscible. At high temperatures Cu or Au atoms can occupy any site and the lattice can be considered as fcc with a 'random' atom at each lattice point as shown in Fig. 1.20a. At low temperatures, however, solutions with $X_{Cu} = X_{Au} = 0.5$, i.e. a 50/50 Cu/Au mixture, form an ordered structure in which the Cu and Au atoms are arranged in alternate layers, Fig. 1.20b. Each atom position is no longer equivalent and the lattice is described as a CuAu *superlattice*. In alloys with the composition Cu_3Au another superlattice is found, Fig. 1.20c.

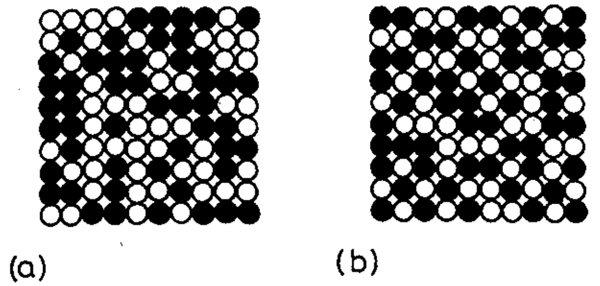


Fig. 1.19 (a) Random A–B solution with a total of 100 atoms and $X_A = X_B = 0.5$, $P_{AB} \sim 100$, $S = 0$. (b) Same alloy with short-range order $P_{AB} = 132$, $P_{AB(\text{max})} \sim 200$, $S = (132 - 100)/(200 - 100) = 0.32$.

The entropy of mixing of structures with long-range order is extremely small and with increasing temperature the degree of order decreases until above some critical temperature there is no long-range order at all. This temperature is a maximum when the composition is the ideal required for the superlattice. However, long-range order can still be obtained when the composition deviates from the ideal if some of the atom sites are left vacant or if some atoms sit on wrong sites. In such cases it can be easier to disrupt the order with increasing temperature and the critical temperature is lower, see Fig. 1.21.

The most common ordered lattices in other systems are summarized in Fig. 1.22 along with their *Structurbericht* notation and examples of alloys in which they are found. Finally, note that the critical temperature for loss of long-range order increases with increasing Ω, or ΔH_{mix}, and in many systems the ordered phase is stable up to the melting point.

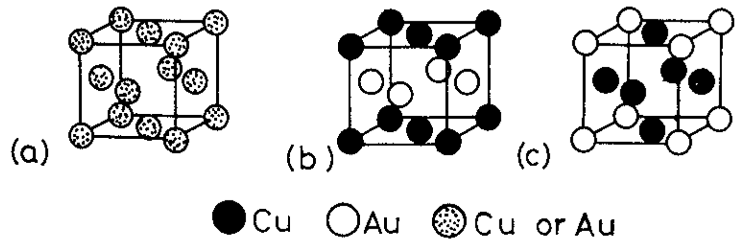


Fig. 1.20 Ordered substitutional structures in the Cu–Au system: (a) high-temperature disordered structure, (b) CuAu superlattice, (c) Cu_3Au superlattice.

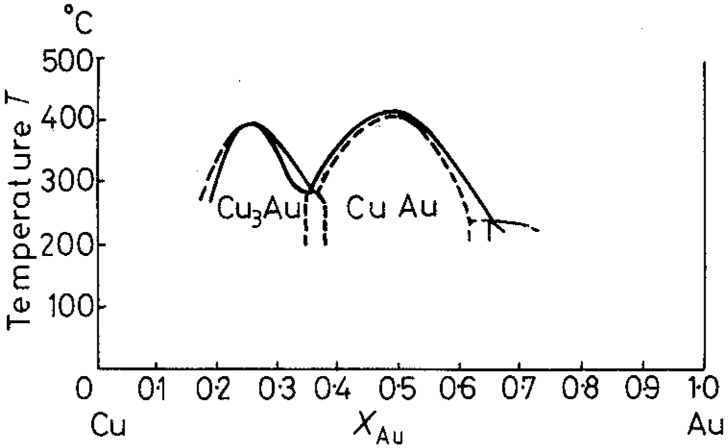


Fig. 1.21 Part of the Cu–Au phase diagram showing the regions where the Cu_3Au and CuAu superlattices are stable.

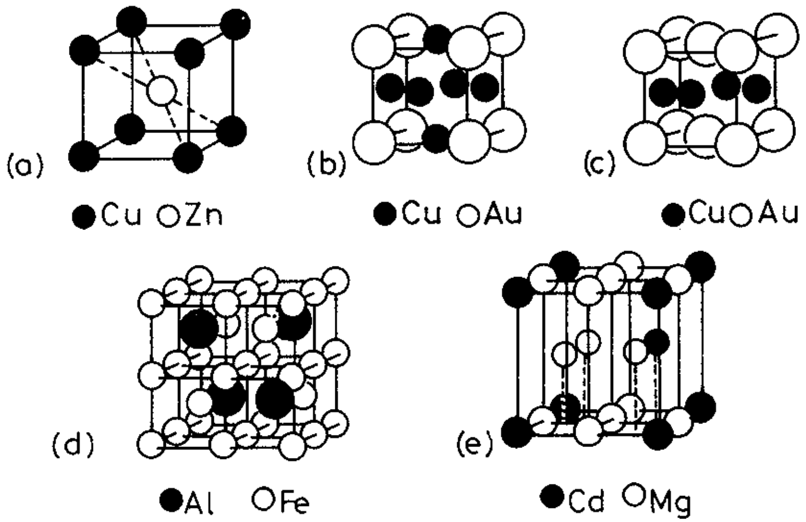


Fig. 1.22 The five common ordered lattices, examples of which are: (a) $L2_0$: CuZn, FeCo, NiAl, FeAl, AgMg; (b) $L1_2$: Cu_3Au, Au_3Cu, Ni_3Mn, Ni_3Fe, Ni_3Al, Pt_3Fe; (c) $L1_0$: CuAu, CoPt, FePt; (d) $D0_3$: Fe_3Al, Fe_3Si, Fe_3Be, Cu_3Al; (e) $D0_{19}$: Mg_3Cd, Cd_3Mg, Ti_3Al, Ni_3Sn. (After R.E. Smallman, *Modern Physical Metallurgy, 3rd edition*, Butterworths, London, 1970.)

1.3.8 *Intermediate Phases*

Often the configuration of atoms that has the minimum free energy after mixing does not have the same crystal structure as either of the pure components. In such cases the new structure is known as an *intermediate phase*.

Intermediate phases are often based on an ideal atom ratio that results in a minimum Gibbs free energy. For compositions that deviate from the ideal, the free energy is higher giving a characteristic 'U' shape to the G curve, as in Fig. 1.23. The range of compositions over which the free energy curve has a meaningful existence depends on the structure of the phase and the type of interatomic bonding—metallic, covalent or ionic. When small composition deviations cause a rapid rise in G the phase is referred to as an *intermetallic compound* and is usually stoichiometric, i.e. has a formula A_mB_n where m and n are integers, Fig. 1.23a. In other structures fluctuations in composition can be tolerated by some atoms occupying 'wrong' positions or by atom sites being left vacant, and in these cases the curvature of the G curve is much less, Fig. 1.23b.

Some intermediate phases can undergo order-disorder transformations in which an almost random arrangement of the atoms is stable at high temperatures and an ordered structure is stable below some critical temperature. Such a transformation occurs in the β phase in the Cu–Zn system for example (see Section 5.10).

The structure of intermediate phases is determined by three main factors: relative atomic size, valency and electronegativity. When the component atoms differ in size by a factor of about 1.1–1.6 it is possible for the atoms to fill space most efficiently if the atoms order themselves into one of the so-called Laves phases based on $MgCu_2$, $MgZn_2$ and $MgNi_2$, Fig 1.24. Another example where atomic size determines the structure is in the formation of the *interstitial compounds* MX, M_2X, MX_2 and M_6X where M can be Zr, Ti, V, Cr, etc. and X can be H, B, C and N. In this case the M atoms form a cubic or hexagonal close-packed arrangement and the X atoms are small enough to fit into the interstices between them.

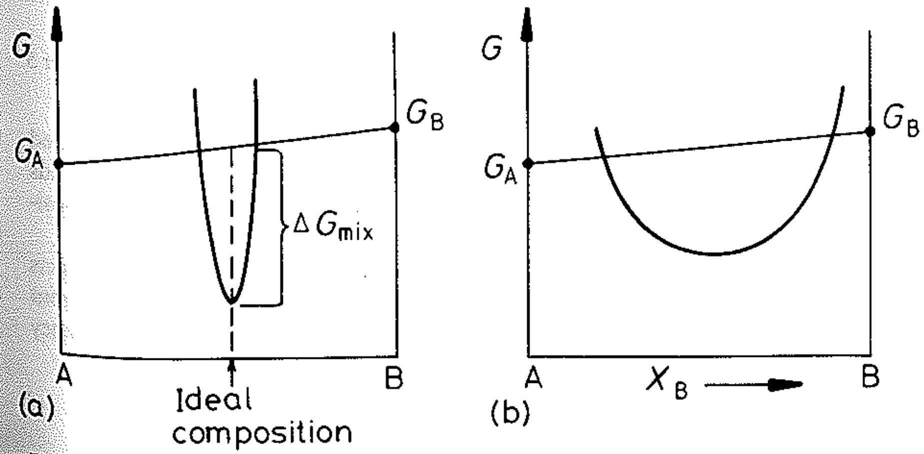


Fig. 1.23 Free energy curves for intermediate phases: (a) for an intermetallic compound with a very narrow stability range, (b) for an intermediate phase with a wide stability range.

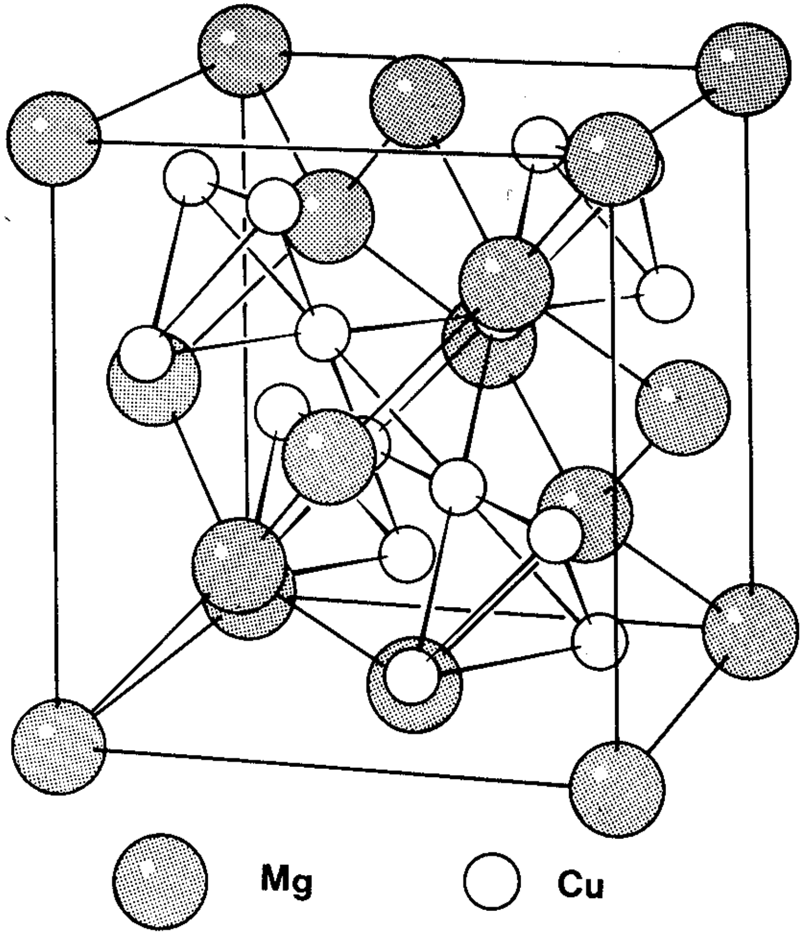


Fig. 1.24 The structure of $MgCu_2$ (A Laves phase). (From J.H. Wernick, chapter 5 in *Physical Metallurgy*, 2nd edn., R.W. Cahn (Ed.) North Holland, 1974.)

The relative valency of the atoms becomes important in the so-called *electron phases*, e.g. α and β brasses. The free energy of these phases depends on the number of valency electrons per unit cell, and this varies with composition due to the valency difference.

The electronegativity of an atom is a measure of how strongly it attracts electrons and in systems where the two components have very different electronegativities ionic bonds can be formed producing normal valency compounds, e.g. Mg^{2+} and Sn^{4-} are ionically bonded in Mg_2Sn.[2]

1.4 Equilibrium in Heterogeneous Systems

It is usually the case that A and B do not have the same crystal structure in their pure states at a given temperature. 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 fcc and β bcc. The molar free energies of fcc A and bcc B are shown in Fig. 1.25a as points a and b. The first step in drawing the free energy curve of the fcc α phase is, therefore, to convert the stable bcc arrangement of B atoms into an unstable fcc arrangement. This requires an increase in free energy, bc. 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. $-\Delta G_{mix}$ for α of composition X is given by the distance de as usual.

A similar procedure produces the molar free energy curve for the β phase, Fig. 1.25b. The distance af is now the difference in free energy between bcc A and fcc A.

It is clear from Fig. 1.25b 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

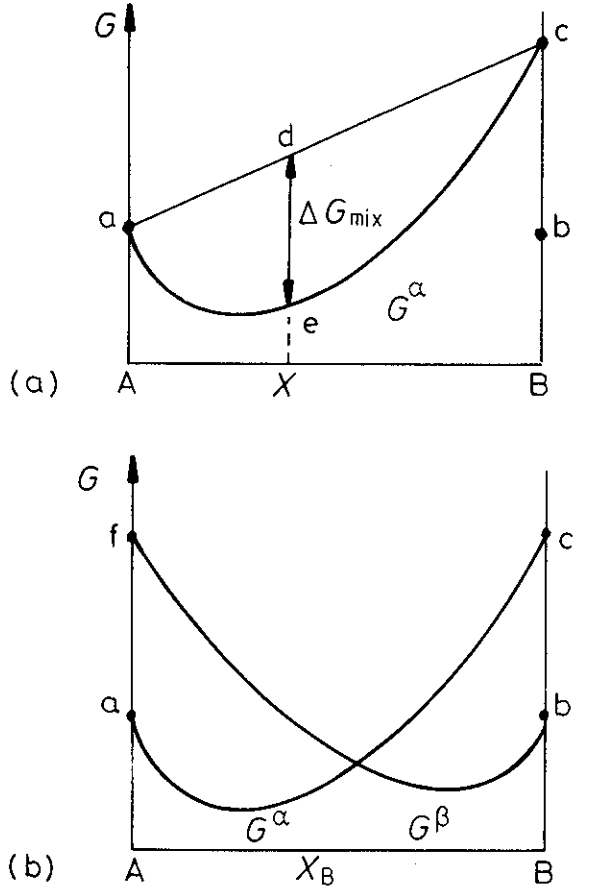


Fig. 1.25 (a) The molar free energy curve for the α phase. (b) Molar free energy curves for α and β phases.

compositions near the cross-over 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, Fig. 1.26. 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. 1.26. 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 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^0 in Fig. 1.27a. If the atoms are arranged as a homogeneous phase, the free energy will be lowest as α, i.e. G_0^α 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. 1.27b. 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,

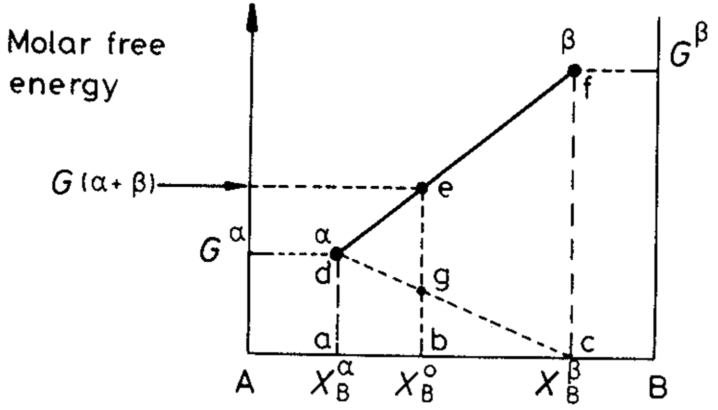


Fig. 1.26 The molar free energy of a two-phase mixture (α + β).

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. 1.27 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, i.e. for heterogeneous equilibrium:

$$\mu_A^\alpha = \mu_A^\beta, \qquad \mu_B^\alpha = \mu_B^\beta \tag{1.46}$$

The condition for equilibrium in a heterogeneous system containing

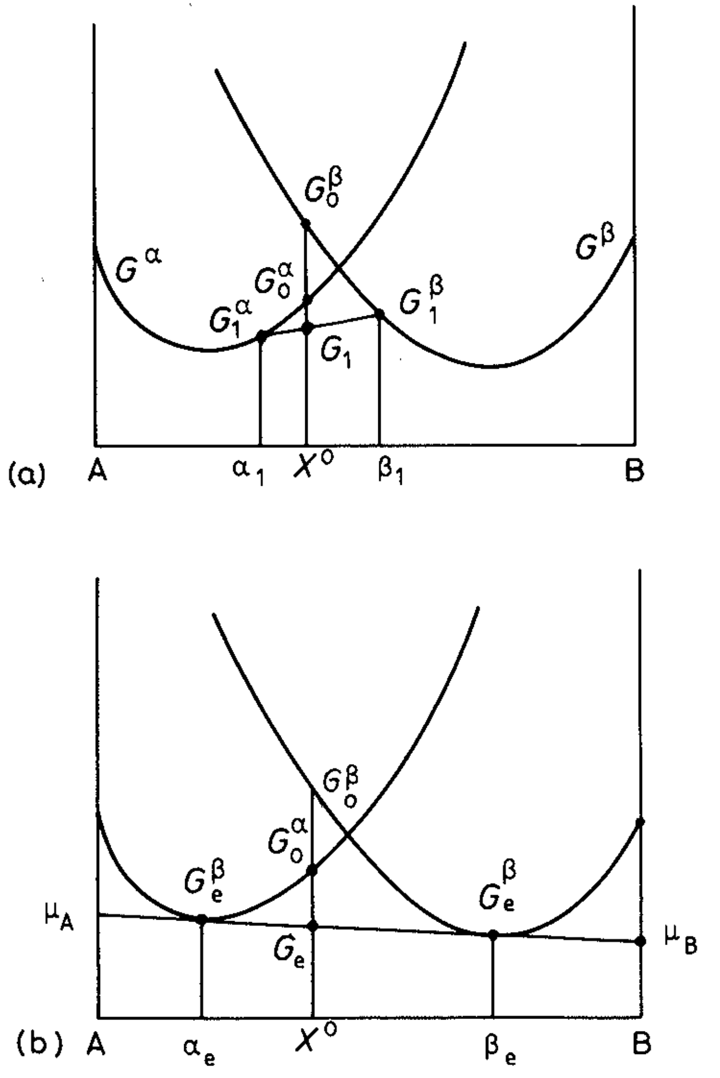


Fig. 1.27 (a) Alloy X^0 has a free energy G_1 as a mixture of $\alpha_1 + \beta_1$. (b) At equilibrium, alloy X^0 has a minimum free energy G_e when it is a mixture of $\alpha_e + \beta_e$.

two phases can also be expressed using the activity concept defined for homogeneous systems in Fig. 1.16. In heterogeneous systems containing more than one phase the pure components can, at least theoretically, exist in different crystal structures. The most stable state, with the lowest free energy, is usually defined as the state in which the pure component has unit activity. In the present example this would correspond to defining the activity of A in pure α − A as unity, i.e. when $X_A = 1$, $a_A^\alpha = 1$. Similarly when $X_B = 1$, $a_B^\beta = 1$. This definition of activity is shown graphically in Fig. 1.28a; Fig. 1.28b and c show how the activities of B and A vary with the composition of the α and β phases. 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 a 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. In other words, when two phases exist in equilibrium, the activities of the components in the system must be equal in the two phases, i.e.

$$a_A^\alpha = a_A^\beta, \qquad a_B^\alpha = a_B^\beta \tag{1.47}$$

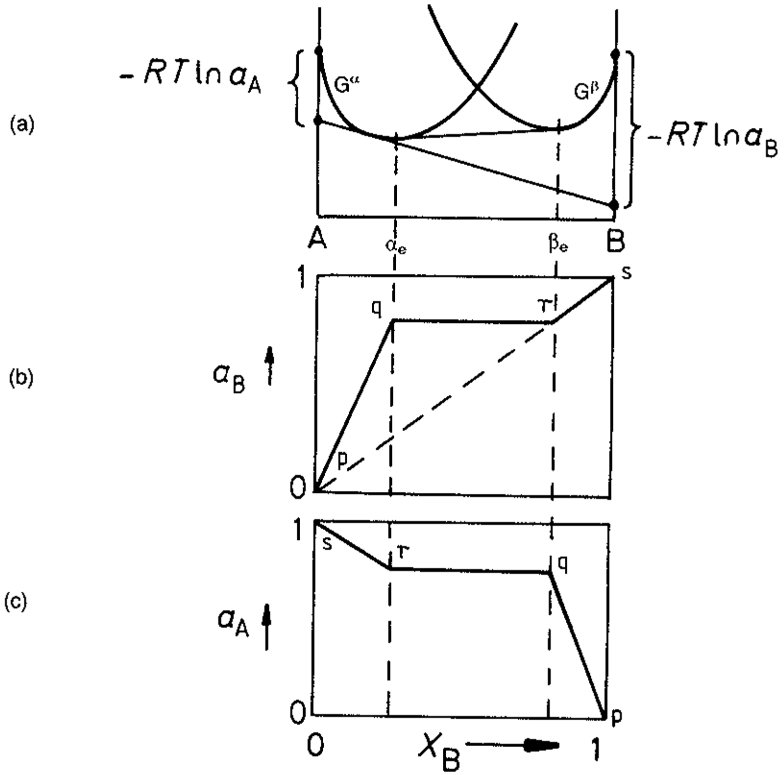


Fig. 1.28 The variation of a_A and a_B with composition for a binary system containing two ideal solutions, α and β.

1.5 Binary Phase Diagrams

In the previous section it has been shown 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.

1.5.1 A Simple Phase Diagram

The simplest case to start with is when A and B are completely miscible in both the solid and liquid states and both are ideal solutions. The free energy of pure A and pure B will vary with temperature as shown schematically in Fig. 1.4. The equilibrium melting temperatures of the pure components occur when $G^S = G^L$, i.e. at $T_m(A)$ and $T_m(B)$. The free energy of both phases decreases as temperature increases. These variations are important for A–B alloys also since they determine the relative positions of G_A^S, G_A^L, G_B^S and G_B^L on the molar free energy diagrams of the alloy at different temperatures, Fig. 1.29.

At a high temperature $T_1 > T_m(A) > T_m(B)$ the liquid will be the stable phase for pure A and pure B, and for the simple case we are considering the liquid also has a lower free energy than the solid at all the intermediate compositions as shown in Fig. 1.29a.

Decreasing the temperature will have two effects: firstly G_A^L and G_B^L will increase more rapidly than G_A^S and G_B^S, secondly the curvature of the G curves will be reduced due to the smaller contribution of $-T\Delta S_{mix}$ to the free energy.

At $T_m(A)$, Fig. 1.29b, $G_A^S = G_A^L$, and this corresponds to point a on the A–B phase diagram, Fig. 1.29f. At a lower temperature T_2 the free energy curves cross, Fig. 1.29c, and the common tangent construction indicates that alloys between A and b are solid at equilibrium, between c and B they are liquid, and between b and c equilibrium consists of a two-phase mixture (S + L) with compositions b and c. These points are plotted on the equilibrium phase diagram at T_2.

Between T_2 and $T_m(B)$ G^L continues to rise faster than G^S so that points b and c in Fig. 1.29c will both move to the right tracing out the solidus and liquidus lines in the phase diagram. Eventually at $T_m(B)$ b and c will meet at a single point, d in Fig. 1.29f. Below $T_m(B)$ the free energy of the solid phase is everywhere below that of the liquid and all alloys are stable as a single phase solid.

1.5.2 Systems with a Miscibility Gap

Figure 1.30 shows the free energy curves for a system in which the liquid phase is approximately ideal, but for the solid phase $\Delta H_{mix} > 0$, i.e. the A and B atoms 'dislike' each other. Therefore at low temperatures (T_3) the free energy curve for the solid assumes a negative curvature in the middle,