Phase Diagrams and Alloy Theory

2.1 Introduction
Phase diagrams present the range of composition and temperature over which various phases are stable. A typical example is shown in Figure 2.14 for the solution of zinc in copper where it can be seen that an addition of up to ~40 wt% Zn produces a single-phase alloy usually termed the α-phase. A knowledge and understanding of these diagrams are important for the development of alloys and their properties. The diagrams represent the equilibrium state and, while much of metallurgical practice leads to non-equilibrium conditions, they are nevertheless important in indicating the structural state of the alloy and its approach to equilibrium.

2.2 The concept of a phase
The term ‘phase’ refers to a separate and identifiable state of matter in which a given substance may exist. Being applicable to both crystalline and non-crystalline materials, its use provides a convenient way of expressing a material’s structure. Thus, in addition to the three crystalline forms mentioned in Section 1.8.1, the element iron may exist as a liquid or vapour, giving five phases overall. Under certain conditions, it is possible for two or more different phases to coexist.

When referring to a particular phase in the structure of a material, we imply a region comprising a large number of atoms (or ions or molecules) and the existence of a bounding surface which separates it from contiguous phases. Local structural defects and imperfections are disregarded. Thus, a pure metal or solid solution is each described, by convention, as single-phase structures even though they may contain grain boundaries, concentration gradients (coring) and microdefects, such as vacancies, dislocations and voids (Chapters 4 and 6). Industrial practice understandably favours relatively rapid cooling rates, frequently causing phases to exist in a metastable condition. Some form of ‘triggering’ process, such as thermal activation, is needed before a metastable phase can adopt the stable, or equilibrium, state of lowest energy (e.g. annealing of metals and alloys). These two features, structural heterogeneity on a microscale and non-equilibrium, do not give rise to any untoward scientific difficulty.
2.3 The Phase Rule

For a given metallic material, there is a theoretical condition of equilibrium in which each constituent phase is in a reference state of lowest energy. The independent variables determining this energy state, which are manipulated by scientists and technologists, are composition, temperature and pressure.

The Phase Rule derived by Willard Gibbs from complex thermodynamical theory provides a device for testing multi-phase (heterogeneous) equilibria and deciding the number of variables (degrees of freedom) necessary to define the energy state of a system. Its basic equation, \( P + F = C + 2 \), relates the number of phases present at equilibrium \( P \) and the number of degrees of freedom \( F \) to the number of components \( C \), which is the smallest number of substances of independently variable composition making up the system. For metallic systems, the components are metallic elements, and for ceramics, the components are frequently oxides (e.g. MgO, SiO₂).

Consider Figure 2.1, which is a single-component ( unary) diagram representing the phase relations for a typical pure metal. Transitions such as melting, sublimation and vaporization occur as boundaries between the three single-phase fields are crossed. Suppose that conditions are such that three phases of a pure metal coexist simultaneously, a unique condition represented by the triple-point \( T \).

Applying the Phase Rule: \( P = 3 \), \( C = 1 \) and \( F = 0 \). This system is said to be invariant with no degrees of freedom. Having stated that 'three phases coexist', the energy state is fully defined and it is unnecessary to specify values for variables. One or two phases could be caused to disappear, but this would require temperature and/or pressure to be changed. Similarly, at a melting point on the line between single-phase fields, a solid phase and a liquid phase may coexist (i.e. \( P = 2 \), \( C = 1 \) and \( F = 1 \)). Specification of one variable (either temperature or pressure) will suffice to define the energy state of a particular two-phase equilibrium. A point within one of the single-phase fields represents a system that is bivariant (\( F = 2 \)). Both temperature and pressure must be specified if its state is to be fully defined.

Let us consider some practical implications of Figure 2.1. The line for the solid/liquid transition is shown with a slight inclination to the right in this schematic diagram because, theoretically, one may reason from Le Chatelier's principle that a pressure increase on a typical melt, from \( P_1 \) to \( P_2 \), will favour a constraint-removing contraction and therefore lead to freezing. (Bismuth and gallium are exceptions: like water, they expand on freezing and the solid/liquid line has an opposite slope.)

The pressure at the critical point \( C \), beyond which liquid and vapour are indistinguishable, is usually extremely high and considerably greater than 1 atm. The diagram refers to an enclosed system. For instance, if molten metal is in a vacuum system, and the pressure is reduced isothermally from \( P_1 \) to \( P_2 \), then vaporization will be favoured.

For most metals, the pressure value at the triple point is far below 1 atm (1 atm = 101.325 kN/m² = 1 bar). For copper and lead, it is in the order of \( 10^{-8} \) atm. The pressures associated with the solid/vapour line are obviously even lower. Thus, for most metals, vapour pressure is disregarded and it is customary to use isobaric (constant pressure) phase diagrams in which the composition (concentration) of component metals is plotted against temperature. As a consequence of this practice, metallurgists use a modified form of the Phase Rule equation i.e. \( P + F = C + 1 \).

Nevertheless, it is possible for vapour pressure to be a highly significant factor in alloy systems formed by volatile components such as mercury, zinc, cadmium and magnesium: in such cases, it is advisable to take advantage of full pressure—temperature diagrams. Furthermore, the partial pressures of certain gases in a contacting atmosphere can be highly significant and at elevated temperatures can contribute to serious corrosion of metals (e.g. Cu). Again, the pressure variable must be taken into account.

2.4 Stability of phases

2.4.1 The concept of free energy

Every material in a given state has a characteristic heat content or enthalpy, \( H \), and the rate of change of heat content with temperature is equal to the specific heat of the material measured at constant pressure, \( C_P = \frac{dH}{dT} \). A knowledge of the quantity \( H \) is clearly important to understand reactions but it does not provide a criterion for equilibrium, nor does it determine when a phase change occurs, as shown by the occurrence of both exothermic and endothermic reactions. To provide this criterion it is necessary to consider a second important property of state known as the entropy, \( S \). In statistical terms \( S \) may be regarded as a measure of the state of disorder of the structure, but from classical thermodynamics it may be shown that for any material passing through a complete cycle of events

\[
\int \frac{dQ}{T} = 0
\]

where \( dQ \) is the heat exchanged between the system and its surroundings during each infinitesimal step and \( T \) is the temperature at which the transfer takes place.
It is then convenient to define a quantity \( S \) such that \( dS = dQ/T \) so that \( \oint dS = 0 \); entropy so defined is then a state property. At constant pressure, \( dQ = dH \) and consequently
\[
\frac{dS}{T} = C_v \frac{dT}{T}
\]
(2.1)
which by integration gives
\[
S = S_0 + \int_{T_0}^T (C_v/T) dT = S_0 + \int_{T_0}^T C_p \delta \ln(T)
\]
where \( S \) is the entropy at \( T \) kelvin usually measured in joules per kelvin. The integration constant \( S_0 \) represents the entropy at absolute zero, which for an ordered crystalline substance is taken to be zero; this is often quoted as the third law of thermodynamics. Clearly, any reaction or transformation within a system will be associated with a characteristic entropy change given by
\[
\Delta S = S_f - S_i
\]
where \( \Delta S \) is the entropy of transformation and \( S_f \) and \( S_i \) are the entropy values of the new phase \( \beta \) and the old phase \( \alpha \), respectively. It is a consequence of this that any irreversible change which takes place in a system (e.g., the combustion of a metal) must be accompanied by an increase in the total entropy of the system. This is commonly known as the second law of thermodynamics.

The quantity entropy could be used for deciding the equilibrium state of a system, but it is much more convenient to work in terms of energy. Accordingly, it is usual to deal with the quantity \( TS \), which has the units of energy, rather than just \( S \), and to separate the total energy of the system \( H \) into two components according to the relation
\[
H = G + TS
\]
where \( G \) is that part of the energy of the system which causes the process to occur and \( TS \) is the energy requirement resulting from the change involved. The term \( G \) is known as Gibbs' free energy and is defined by the equation
\[
G = H - TS
\]
(2.2)

Every material in a given state will have a characteristic value of \( G \). The change of free energy accompanying a change represents the 'driving force' of the change and is given by the expression
\[
dG = dH - T dS = dE + P dV - T dS
\]

All spontaneous changes in a system must be accompanied by a reduction of the total free energy of that system, and thus for a change to occur the free energy change \( \Delta G \) must be negative. It also follows that the equilibrium condition of a reaction will correspond to the state where \( dG = 0 \), i.e. zero driving force.

For solids and liquids at atmospheric pressure the volume change accompanying changes of state is very small and hence \( P dV \) is also very small. It is therefore reasonable to neglect this term in the free energy equation and use as the criterion of equilibrium \( dE - T dS = 0 \). This is equivalent to defining the quantity \( (E - TS) \) to be a minimum in the equilibrium state, for by differentiation
\[
\frac{d(E - TS)}{dT} = \frac{dE}{dT} - T \frac{dS}{dT} - S \frac{dT}{dT} = 0
\]
(since \( T \) is constant)
for the equilibrium state

The quantity \( (E - TS) \) thus defines the equilibrium state at constant temperature and volume, and is given the symbol \( F \), the Helmholtz free energy \( (F = E - TS) \), to distinguish it from the Gibbs free energy \( (G = H - TS) \). In considering changes in the solid state it is thus a reasonable approximation to use \( F \) in place of \( G \). The enthalpy \( H \) is the sum of the internal and external energies which reduces to \( H \approx E \) when the external energy \( PV \) is neglected.

2.4.2 Free energy and temperature

If a metal undergoes a structural change from phase \( \alpha \) to phase \( \beta \) at a temperature \( T_f \) then it does so because above this temperature the free energy of the \( \beta \) phase, \( G_{\beta} \), becomes lower than the free energy of the \( \alpha \) phase, \( G_{\alpha} \). For this to occur the free energy curves must vary with temperature in the manner shown in Figure 2.2(a). It can be seen that at \( T_f \) the free energy of the \( \alpha \)-phase is equal to that of the \( \beta \)-phase so that \( \Delta G = 0 \); \( T_f \) is, therefore, the equilibrium transformation point.

Figure 2.2(a) also shows that successive transformations occur in a given temperature range. The way in which the absolute value of the free energy of a crystal varies with temperature is shown in Figure 2.2(b), where \( H \) and \( -TS \) are plotted as a function of temperature. At the transformation temperature, \( T_f \), the change in heat content \( \Delta H \) is equal to the latent heat \( L \), while the entropy change

\[\text{Figure 2.2} \]
Free energy-temperature curves for \( \alpha \), \( \beta \), and liquid phases.
\[ S = k \ln W \]

where \( k \) is Boltzmann's constant. From this equation it can be seen that entropy is a property which measures the probability of a configuration, and that the greater the probability, the greater is the entropy. Substituting for \( W \) in the statistical equation of entropy and using Stirling's approximation\(^1\) we obtain

\[ S = k \ln [N/n((N-n)!)] = k[N \ln N - n \ln n - (N-n) \ln(N-n)] \]

for the entropy of disorder, or mixing. The form of this entropy is shown in Figure 2.3(a), where \( c = n/N \) is the atomic concentration of A in the solution. It is of particular interest to note the sharp increase in entropy for the addition of only a small amount of solute. This fact accounts for the difficulty of producing really pure metals, since the entropy factor, \(-T \Delta S\), associated with impurity addition, usually outweighs the energy term, \( dH \), so that the free energy of the material is almost certainly lowered by contamination.

While Figure 2.3(a) shows the change in entropy with composition the corresponding free energy versus composition curve is of the form shown in Figure 2.3(b), c or d depending on whether the solid solution is ideal or deviates from ideal behaviour. The variation of enthalpy with composition, or heat of mixing, is linear for an ideal solid solution, but if A atoms prefer to be in the vicinity of B atoms rather than A atoms, and B atoms behave similarly, the enthalpy will be lowered by alloying (Figure 2.3(c)). A positive deviation occurs when A and B atoms prefer like atoms as neighbours and the free energy curve takes the form shown in Figure 2.3(d). In Figure 2.3(b) and c) the curvature \( d^2G/dc^2 \) is everywhere positive, whereas in Figure 2.3(d) there are two minima and a region of negative curvature between points of inflection\(^2\) given by \( d^2G/dc^2 = 0 \). A free energy curve for which \( d^2G/dc^2 \) is positive, i.e. simple U-shaped, gives rise to a homogeneous solution. When a region of negative curvature exists, the stable state is a phase mixture rather than a homogeneous solid solution, as shown in Figure 2.4(a). An alloy of composition \( c \) has a lower free energy \( G \) when it exists as a mixture of A-rich phase (\( \alpha_1 \)) of composition \( c_\alpha \) and B-rich phase (\( \alpha_2 \)) of composition \( c_\beta \) in the proportions given by the Lever Rule, i.e. \( c_\alpha/c_\beta = (c_\beta - c)/(c - c_\alpha) \). Alloys with composition \( c < c_\alpha \) or \( c > c_\beta \) exist as homogenous solid solutions and are denoted by phases \( \alpha_1 \) and \( \alpha_2 \), respectively. Partial miscibility in the solid state can also occur when the crystal structures of the component metals are different. The free energy curve then takes the form shown in Figure 2.4(b), the phases being denoted by \( \alpha \) and \( \beta \).

\(^1\)Stirling's theorem states that if \( N \) is large

\[ \ln N = N - N/N \]

\(^2\)The composition \( c \) at which \( d^2G/dc^2 = 0 \) varies with temperature and the corresponding temperature-composition curves are called spinodal lines.
2.5 The mechanism of phase changes

2.5.1 Kinetic considerations

Changes of phase in the solid state involve a redistribution of the atoms in that solid and the kinetics of the change necessarily depend upon the rate of atomic migration. The transport of atoms through the crystal is more generally termed diffusion, and is dealt with in Chapter 7. This can occur more easily with the aid of vacancies, since the basic act of diffusion is the movement of an atom to an empty adjacent atomic site.

Let us consider that during a phase change an atom is moved from an α-phase lattice site to a more favourable β-phase lattice site. The energy of the atom should vary with distance as shown in Figure 2.5, where the potential barrier which has to be overcome arises from the interatomic forces between the moving atom and the group of atoms which adjoin it and the new site. Only those atoms (α) with an energy greater than Q are able to make the jump, where Q = Hα − Hβ and Q = Hα − Hβ are the activation enthalpies for heating and cooling, respectively. The probability of an atom having sufficient energy to jump the barrier is given, from the Maxwell–Boltzmann distribution law, as proportional to exp [−Q/kT] where k is Boltzmann’s constant, T is the temperature and Q is usually expressed as the energy per atom in electron volts.

The rate of reaction is given by

\[ \text{Rate} = A \exp \left( \frac{-Q}{kT} \right) \]  \hspace{1cm} (2.6)

where \( A \) is a constant involving \( n \) and \( v \), the frequency of vibration. To determine \( Q \) experimentally, the reaction velocity is measured at different temperatures and, since

\[ \ln \text{Rate} = \ln A - \frac{Q}{kT} \]  \hspace{1cm} (2.7)

the slope of the ln(rate) versus 1/T curve gives \( Q/k \).

\( Q \) may also be given as the energy in joules per mole in which case the rate equation becomes

\[ \text{Rate of reaction} = A \exp \left( \frac{-Q}{RT} \right) \]

where \( R = \text{kcal} \) is the gas constant, i.e. 8.314 J moll \(^{-1}\) K \(^{-1}\).

Figure 2.5

Energy barrier separating structural states.

In deriving Eq. (2.6), usually called an Arrhenius equation after the Swedish chemist who first studied reaction kinetics, no account is taken of the entropy of activation, i.e. the change in entropy as a result of the transition. In considering a general reaction the probability expression should be written in the terms of the free energy of activation per atom \( F \) or \( G \) rather than just the internal energy or enthalpy. The rate equation then becomes

\[ \text{Rate} = A \exp \left[ \frac{-F}{kT} \right] = A \exp \left[ \frac{S}{k} \right] \exp \left[ \frac{-E}{kT} \right] \]  \hspace{1cm} (2.8)

The slope of the ln(rate) versus 1/T curve then gives the temperature dependence of the reaction rate, which is governed by the activation energy or enthalpy, and the magnitude of the intercept on the ln(rate) axis depends on the temperature-independent terms and includes the frequency factor and the entropy term.

During the transformation it is not necessary for the entire system to go from α to β at one jump and, in fact, if this were necessary, phase changes would practically never occur. Instead, most phase changes occur by a process of nucleation and growth. Chance thermal fluctuations provide a small number of atoms with sufficient activation energy to break away from the matrix (the old structure) and form a small nucleus of the new phase as shown in Figure 2.6(a), which then grows at the expense of the matrix until the whole structure is transformed. By this mechanism, the amount of material in the intermediate configuration of higher free energy is kept to a minimum, as it is localized into atomically thin layers at the interface between the phases. Because of this mechanism of transformation, the factors which determine the rate of phase change are (i) the rate of nucleation, \( N \) (i.e. the number of nuclei formed in unit volume in unit time) and (ii) the rate of growth, \( G \) (i.e. the rate of increase in radius with time). Both processes require activation energies, which in general are not equal, but the values are much smaller than that needed to change the whole structure from α to β in one operation.

Even with such an economical process as nucleation and growth transformation, difficulties occur and it is common to find that the transformation temperature, even under the best experimental conditions, is slightly higher on heating than on cooling. This sluggishness of the transformation is known as hysteresis, and is attributed to the difficulties of nucleation, since diffusion, which controls the growth process, is usually high at temperatures near the transformation temperature and is, therefore, not rate controlling. Perhaps the simplest phase change to indicate this is the solidification of a liquid metal.
2.5 The mechanism of phase changes

2.5.2 Nucleation in solids

When the transformation takes place in the solid state, i.e. between two solid phases, a second factor giving rise to hysteresis operates. The new phase usually has a different parameter and crystal structure from the old so that the transformation is accompanied by dimensional changes. However, the changes in volume and shape cannot occur freely because of the rigidity of the surrounding matrix, and elastic strains are induced. The strain energy and surface energy created by the nuclei of the new phase are positive contributions to the free energy and so tend to oppose the transition.

The total free energy change is

$$\Delta G = V \Delta G_s + A \gamma + V \Delta G_i$$

where $A$ is the area of interface between the two phases, $\gamma$ the interfacial energy per unit area and $\Delta G_i (>0)$ the misfit strain energy per unit volume of new phase. For a spherical nucleus of the second phase

$$\Delta G = \frac{4}{3} \pi r^3 (\Delta G_s + \Delta G_i) + 4 \pi r^2 \gamma$$

and since $\Delta G_s > 0$ while $\Delta G_i < 0$, the misfit strain energy reduces the effective driving force for the transformation. When the nucleus is small the positive surface energy term predominates, while when it is large the negative volume term predominates, so that the change in free energy as a function of nucleus size is as shown in Figure 2.6(b). This indicates that a critical nucleus size $r_c$ exists below which the free energy increases as the nucleus grows, and above which further growth can proceed with a lowering of free energy; $\Delta G_{\text{min}}$ may be considered as the energy or work of nucleation $W$. The critical nucleus size arises when $4\Delta G_i r_c^2 = 4\pi r_c^3 (\Delta G_s + \Delta G_i) + 8\pi \gamma r_c = 0$, giving

$$r_c = -2\gamma/(\Delta G_s + \Delta G_i) \quad \text{and} \quad W = 16\pi \gamma^2 / (3(\Delta G_s + \Delta G_i)^2)$$

The value of $\gamma$ can vary widely from a few millijoule per square metre to several hundred millijoule per square metre depending on the coherency of the interface. A coherent interface is formed when the two crystals have a good ‘match’ and the two lattices are continuous across the interface. This happens when the interfacial plane has the same atomic configuration in both phases, e.g. (1 1 1) in fcc and (0 0 1) in cph. When the ‘match’ at the interface is not perfect it is still possible to maintain coherency by straining one or both lattices, as shown in Figure 2.7(a). These coherency strains increase the energy, and for large misfits it becomes energetically more favourable to form a semi-coherent interface (Figure 2.7(b)) in which the mismatch is periodically taken up by misfit
dislocations. The coherency strains can then be relieved by a cross-grid of dislocations in the interface plane, the spacing of which depends on the Burgers vector b of the dislocation and the misfit ε, i.e. \(\text{hkl}\). The interfacial energy for semi-coherent interfaces arises from the change in composition across the interface or chemical contribution as for fully coherent interfaces, plus the energy of the dislocations (see Chapter 4). The energy of a semi-coherent interface is \(200-500\ \text{mJ m}^{-2}\) and increases with decreasing dislocation spacing until the dislocation strain fields overlap. When this occurs, the discrete nature of the dislocations is lost and the interface becomes incoherent. The incoherent interface is somewhat similar to a high-angle grain boundary (see Chapter 10) with its energy of \(0.5-1\ \text{J m}^{-2}\) relatively independent of the orientation.

The surface and strain energy effects discussed above play an important role in phase separation. When there is coherency in the atomic structure across the interface between precipitate and matrix the surface energy term is small, and it is the strain energy factor which controls the shape of the particle. A plate-shaped particle is associated with the least strain energy, while a spherical-shaped particle is associated with maximum strain energy but the minimum surface energy. On the other hand, surface energy determines the crystallographic plane of the matrix on which a plate-like precipitate forms. Thus, the habit plane is the one which allows the planes at the interface to fit together with the minimum of disregistry; the frequent occurrence of the Widmannstätten structures may be explained on this basis. It is also observed that precipitation occurs most readily in regions of the structure which are somewhat disarranged, e.g. at grain boundaries, inclusions, dislocations or other positions of high residual stress caused by plastic deformation. Such regions have an unusually high free energy and necessarily are the first areas to become unstable during the transformation. Also, new phases can form there with a minimum increase in surface energy. This behaviour is considered again in Chapter 10.

\[ A \gamma_{\alpha \beta} + 3 \pi r^2 \Delta G_i \]

\[ \Delta G = -A \gamma_{\alpha \beta} + 4\pi r^2 \gamma_{\alpha \beta} + 4\pi r^2 \Delta G_i \]

\[ \frac{d(\Delta G)}{dr} = -2\pi r \gamma_{\alpha \beta} + 8\pi r^2 \gamma_{\alpha \beta} + 4\pi r^2 \Delta G_i = 0 \]

\[ r_c = \frac{-2\pi r^2 \gamma_{\alpha \beta}}{2\Delta G_i} \]

For homogeneous nucleation, \(r_c\) is given by the above formula with \(\gamma_{\alpha \beta} = 0\) (Eq. 2.11), so

\[ r_c (\text{heterogeneous}) = \frac{4r^2 \gamma_{\alpha \beta}}{2\Delta G_i} = \frac{4\pi r^2 \gamma_{\alpha \beta}}{4\pi r^2 \Delta G_i} = 1000 - 500 = 500 \]

\[ r_c (\text{homogeneous}) = \frac{2r^2 \gamma_{\alpha \beta}}{2\Delta G_i} = \frac{2\pi r^2 \gamma_{\alpha \beta}}{4\pi r^2 \Delta G_i} = \frac{1000}{2} = 500 \]

So,\( r_c (\text{heterogeneous}) = (1/2)r_c (\text{homogeneous})\).

2.6 Two-phase equilibria

Solid solubility is a feature of many metallic and ceramic systems, being favoured when the components have similarities in crystal structure and atomic (ionic) diameter. Such solubility may be either extended (continuous) or limited. The former case is illustrated by the binary phase diagram for the nickel–copper system (Figure 2.8) in which the solid solution (α) extends from component to component. In contrast to the abrupt (congruent) melting points of the pure metals, the intervening alloys freeze, or fuse, over a range of temperatures which is associated with a uniaxial two-phase (α + liquid) field. This "paste" zone is located between two lines known as the liquidus and solidus.

Let us consider the very slow (equilibrating) solidification of a 70Ni–30Cu alloy. A commercial version of this alloy, Monel, also contains small amounts of iron and manganese. It is strong, ductile and resists corrosion at all forms of water, including sea water (e.g. chemical and food processing, water treatment). An ordinate is erected from its average composition on the base line. Freezing starts at a temperature \(T_f\). A horizontal tie-line is drawn to show that the first crystals of solid solution to
form have a composition $\alpha_1$. When the temperature reaches $T_3$, crystals of composition $\alpha_2$ are in equilibrium with liquid of composition $L_2$. Ultimately, at temperature $T_2$, solidification is completed as the composition $\alpha_2$ of the crystals coincides with the average composition of the alloy. It will be seen that the compositions of the $\alpha$-phase and liquid have moved down the solidus and liquidus, respectively, during freezing.

Each tie-line joins two points which represent two phase compositions. One might visualize that a two-phase region in a binary diagram is made up of an infinite number of horizontal (isothermal) tie-lines. Using the average alloy composition as a fulcrum ($x$) and applying the lever rule, it is quickly possible to derive mass ratios and fractions. For instance, for equilibrium at temperature $T_2$ in Figure 2.8, the mass ratio of solid solution crystals to liquid is $\frac{x}{L} = \frac{\alpha}{\alpha_2}$. Similarly, the mass fraction of solid in the two-phase mixture at this temperature is $\frac{xL}{xL + \alpha_2}$. Clearly, the phase compositions are of greater structural significance than the average composition of the alloy. If the volumetric relations of two phases are required, these being what we naturally assess in microscopy, then the above values must be corrected for phase density.

**WORKED EXAMPLE**

With reference to Figure 2.8, prove the Lever Rule.

**Solution**

Consider a tie-line $\alpha-x-L$ between the solidus and liquidus lines in the two-phase region $\alpha+\text{liquid}$ in Figure 2.8. The overall composition of the two-phase mixture is marked by $x$.

which is the mass% of component A (say Cu in Figure 2.8). In 1 unit mass of the mixture, let $M_s = $ mass of solid and $M_l = $ mass of liquid. Mass% of A in solid = $\alpha$ and mass% of A in liquid = $L$, which are the two end points of the tie-line.

Total amount of A in mixture is distributed between the solid and liquid, and so $x = M_s\alpha + M_l L$.

Furthermore, mass of solid and liquid must add up to the mass of the mixture, so $M_s + M_l = 1$.

Solving these two equations gives

$$M_s = \frac{L-x}{L-\alpha} \quad \frac{xL}{\alpha L}$$

Ratio of the two phases is

$$M_s = \frac{x}{\alpha}$$

In most systems, solid solubility is far more restricted and is often confined to the phase field adjacent to the end component. A portion of a binary phase diagram for the copper–beryllium system, which contains a primary, or terminal, solid solution, is shown in Figure 2.9. Typically, the curve line known as the solvs shows an increase in the ability of the solvent copper to dissolve beryllium solute as the temperature is raised. If a typical “beryllium–copper” containing 2% beryllium is first held at a temperature just below the solidus (solution-treated), water-quenched to preserve the $\alpha$-phase and then aged at a temperature of 425°C, particles of a second phase ($\gamma$) will form within the $\alpha$-phase matrix because the alloy is equilibrating in the ($\alpha+\gamma$) field of the diagram. This type of treatment, closely controlled, is known as precipitation hardening; the mechanism of this important strengthening process will be discussed in detail in Chapter 13. Precipitation hardening of a typical beryllium–copper, which also contains up to 0.5% cobalt or nickel, can raise the 0.1% proof stress to 1200 MN m$^{-2}$ and the tensile strength to 1400 MN m$^{-2}$. Apart from being suitable for non-sparking tools, it is a valuable spring material, being principally used for electrically conductive brush springs and contact fingers in electrical switches. A curved solvs is an essential feature of phase diagrams for precipitation-hardenable alloys (e.g. aluminium–copper alloys (Duramumin)).

When solid-state precipitation takes place, say of $\beta$ within a matrix of supersaturated $\alpha$ grains, this precipitation occurs in one or more of the following preferred locations: (i) at grain boundaries, (ii) around dislocations and inclusions and (iii) on specific crystallographic planes. The choice of site for precipitation depends on several factors, of which grain size and rate of nucleation are particularly important. If the grain size is large, the amount of grain boundary surface is relatively small, and deposition of $\beta$-phase within the grains is favoured. When this precipitation occurs preferentially on certain sets of crystallographic planes within the grains, the etched structure has a mesh-like appearance which is known as a Widmanstätten-type structure.° Widmanstätten structures have been observed in many alloys (e.g. overheated steels).

°Named after Count Alois von Widmanstätten who discovered this morphology within an iron–nickel meteorite sample in 1808.
2.7 Three-phase equilibria and reactions

2.7.1 The eutectic reaction

In many metallic and ceramic binary systems it is possible for two crystalline phases and a liquid to coexist. The modified Phase Rule reveals that this unique condition is invariant; that is, the temperature and all phase compositions have fixed values. Figure 2.10 shows the phase diagram for the lead–tin system. It will be seen that solid solubility is limited for each of the two component metals, with α and β representing primary solid solutions of different crystal structure. A straight line, the eutectic horizontal, passes through three-phase compositions (α, Lα, and β) at the temperature Tα. As it will become clear when ternary systems are discussed (Section 2.11), this line is a collapsed three-phase triangle: at any point on this line, three phases are in equilibrium. During slow cooling or heating, when the average composition of an alloy lies between its limits, αα and ββ, a eutectic reaction takes place in accordance with the equation Lα → α + β. The sharply defined minimum in the liquidus, the eutectic (easy melting) point, is a typical feature of the reaction.

Consider the freezing of a melt, average composition 37Pb–63Sn. At the temperature Tα of approximately 180°C, it freezes abruptly to form a mechanical mixture of two solid phases, i.e. liquid Lα → α + β. From the Lever Rule, the α/β mass ratio is approximately 9:11. As the temperature falls further, slow cooling will allow the compositions of the two phases to follow their respective solvus lines. Tie-lines across this (α + β) field will provide the mass ratio for any temperature. In contrast, a hypo-eutectic alloy melt, say of composition 70Pb–30Sn, will form primary crystals of α over a range of temperature until Tα is reached. Successive tie-lines across the (α + liquid) field show that the crystals and the liquid become enriched in tin as the temperature falls. When the liquid composition reaches the eutectic value Lα, all of the remaining liquid transforms into a two-phase mixture, as before. However, for this alloy, the final structure will comprise primary grains of α in a eutectic matrix of α and β. Similarly, one may deduce that the structure of a solidified hyper-eutectic alloy containing 30Pb–70Sn will consist of a few primary β grains in a eutectic matrix of α and β.

Low-lead or low-tin alloys, with average compositions beyond the two ends of the eutectic horizontal,6 freeze by transforming completely over a small range of temperature into a primary phase. (Changes in composition are similar to those described for Figure 2.8.) When the

6Theoretically, the eutectic horizontal cannot cut the vertical line representing a pure component: some degree of solid solubility, however small, always occurs.
temperature 'crosses' the relevant solvus, this primary phase becomes unstable and a small amount of second phase precipitates. Final proportions of the two phases can be obtained by superimposing a tie-line on the central two-phase field: there will be no signs of a eutectic mixture in the microstructure.

The eutectic (75Pt–25Sn) and hypoeutectic (70Pt–30Sn) alloys chosen for the description of freezing represent two of the numerous types of solders used for joining metals. Eutectic solders containing 60–65% tin are widely used in the electronics industry for making precise, high-integrity joints on a mass-production scale without the risk of damaging heat-sensitive components. These solders have excellent 'wetting' properties (contact angle <10°), a low liquidus and a negligible freezing range. The long freezing range of the 70Pt–30Sn alloy (plumbers' solder) enables the solder to act as a jointing 'wet' while 'plastic'.

The shear strength of the most widely used solders is relatively low, say 25–55 MN m⁻², and mechanically interlocking joints are often used. Phases (corrosive zinc chloride, non-corrosive organic resins) facilitate essential 'wetting' of the metal to be joined by dissolving thin oxide films and preventing re-oxidation. In electronic applications, minute solder preforms have been used to solve the problems of excess solder and flux.

Figure 2.10 shows the sequence of structures obtained across the breadth of the Pt–Sn system. Cooling curves for typical hypoeutectic and eutectic alloys are shown schematically in Figure 2.11(a). Separation of primary crystals produces a change in slope while heat is being evolved. Much more heat is evolved when the eutectic reaction takes place. The lengths (duration) of the plateaux are proportional to the amounts of eutectic structure formed, as summarized in Figure 2.11(b). Although it follows that cooling curves can be used to determine the form of such a simple system, it is usual to confirm details by means of microscopical examination (optical, scanning electron) and X-ray diffraction analysis.

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**WORKED EXAMPLE**

The Pb–Sn system has a eutectic at 183°C (see Figure 2.11). How does this manifest itself in the modified Phase Rule \( F + E = C + 1 \)?

**Solution**

Using the metallurgist's form of the Phase Rule \( F + E = C + 1 \), with \( C = 2, P = 3 \), then \( F = 0 \). This indicates that there is only one temperature at which the three phases \( \alpha, \beta \) and liquid coexist.

---

### 2.7.2 The peritectic reaction

Whereas eutectic systems often occur when the melting points of the two components are fairly similar, the second important type of invariant three-phase condition, the peritectic reaction, is often found when the components have a large difference in melting points. Usually they occur in the more complicated systems; for instance, there is a cascade of five peritectic reactions in the Cu–Zn system (Figure 2.14).

A simple form of peritectic system is shown in Figure 2.12(a); although relatively rare in practice (e.g. Ag–Pb), it can serve to illustrate the basic principles. A horizontal line, the key to

---

5Soft solders for engineering purposes range in composition from 30% to 65% tin; the first standard specifications for solders were produced in 1918 by the ASTM. The United States is currently contemplating the banning of lead-bearing products; lead-free solders are being sought.
the reaction, links three critical phase compositions, i.e. \( \alpha \), \( \beta \), and liquid \( L_2 \). A peritectic reaction occurs if the average composition of the alloy crosses this line during either slow heating or cooling. It can be represented by the equation \( \alpha + L_2 \rightarrow \beta \). Binary alloys containing less of component B than the point \( \alpha \), will behave in the manner previously described for solid solutions. A melt of alloy 1, which is of peritectic composition, will freeze over a range of temperature, depositing crystals of primary \( \alpha \)-phase. The melt composition will move down the liquidus, becoming richer in component B. At the peritectic temperature \( T_p \), liquid of composition \( L_2 \) will react with these primary crystals, transforming them completely into a new phase, \( \beta \), of different crystal structure in accordance with the equation \( \alpha + L_2 \rightarrow \beta \). In the system shown, \( \beta \) remains stable during further cooling. Alloy 1 will also deposit primary \( \alpha \), but the reaction at temperature \( T_p \) will not consume all these crystals and the final solid will consist of \( \beta \) formed by peritectic reaction and residual \( \alpha \). Initially, the \( \alpha/\beta \) mass ratio will be approximately 2.5 to 1 but both phases will adjust their compositions during subsequent cooling. In the case of alloy 3, fewer primary crystals of \( \alpha \) form; later, they are completely destroyed by the peritectic reaction. The amount of \( \beta \) in the resultant mixture of \( \beta \) and liquid increases until the liquid disappears and an entire structure of \( \beta \) is produced.

The above descriptions assume that equilibrium is attained at each stage of cooling. Although very slow cooling is unlikely in practice, the nature of the peritectic reaction introduces a further complication. The reaction product \( \beta \) tends to form a shell around the particles of primary \( \alpha \); its presence obviously inhibits the exchange of atoms by diffusion which equilibrium demands (Figure 2.12(b)).

**WORKED EXAMPLE**

The alloy system Ag–Pt has a peritectic form similar to that of Figure 2.12. Draw the free energy curves for the phases which exist at a temperature (a) just above and (b) just below the peritectic temperature.

**Solution**

![Energy curves for peritectic reaction](image)

**Table 2.1 Classification of Three-Phase Equilibria**

<table>
<thead>
<tr>
<th>Eutectic-type reactions</th>
<th>Eutectic $L_2 = \alpha + \beta$</th>
<th>$\alpha \rightarrow \beta$</th>
<th>$\gamma \rightarrow \alpha + \beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eutectoid $\gamma = \alpha + \beta$</td>
<td>$L_2$</td>
<td>$\alpha + \beta$</td>
<td>Fe–C, Cu–Zn</td>
</tr>
<tr>
<td>Monotectic $L_1 = \alpha + L_1$</td>
<td>$L_2$</td>
<td>$\alpha + \beta$</td>
<td>Cu–Pt, Ag–Ni</td>
</tr>
<tr>
<td>Peritectic $\alpha + L_2 = \beta$</td>
<td>$\alpha + \beta$</td>
<td>$\gamma$</td>
<td>Cu–Zn, Ag–Pt</td>
</tr>
<tr>
<td>Peritectic $\alpha + \beta = \gamma$</td>
<td>$\alpha + \beta$</td>
<td>$\gamma$</td>
<td>Ag–Al</td>
</tr>
<tr>
<td>Synthetict $L_1 = \alpha + L_2 = \gamma$</td>
<td>$\alpha + \beta$</td>
<td>$\gamma$</td>
<td>Na–Zn</td>
</tr>
</tbody>
</table>

**2.7.3 Classification of three-phase equilibria**

The principal invariant equilibria involving three condensed (solid, liquid) phases can be conveniently divided into eutectic- and peritectic-types and classified in the manner shown in Table 1. Interpretation of these reactions follows the methodology already set out for the more common eutectic and peritectic reactions.

The inverse relation between eutectic- and peritectic-type reactions is apparent from the line diagrams. Eutectoid and peritectoid reactions occur wholly in the solid state. (The eutectoid reaction \( \gamma \rightarrow \alpha + Fe\gamma \) is the basis of the heat treatment of steels.) In all the systems so far described, the components have been completely miscible in the liquid state. In monotectic and syntectic systems, the liquid phase field contains a region in which two different liquids (\( L_1 \) and \( L_3 \)) are immiscible.

**2.8 Intermediate phases**

An intermediate phase differs in crystal structure from the primary phases and lies between them in a phase diagram. In Figure 2.13, which shows the diagram for the Mg–Si system, Mg₃Si is the intermediate phase. Sometimes intermediate phases have definite stoichiometric ratios of constituent atoms and appear as a single vertical line in the diagram. However, they frequently exist over a range of composition, and it is therefore generally advisable to avoid the term 'compound'.
In some diagrams, such as Figure 2.13, they extend from room temperature to the liquidus and melt or freeze without any change in composition. Such a melting point is said to be congruent; the melting point of a eutectic alloy is incongruent. A congruently melting phase provides a convenient means to divide a complex phase diagram (binary or ternary) into more readily understandable parts. For instance, an ordinate through the vertex of the intermediate phase in Figure 2.13 produces two simple eutectic sub-systems. Similarly, an ordinate can be erected to pass through the minimum (or maximum) of the liquidus of a solid solution (Figure 2.7(b)).

In general, intermediate phases are hard and brittle, having a complex crystal structure (e.g. Fe₃C, CuAl₂(θ)). For instance, it is advisable to restrict time and temperature when soldering copper alloys; otherwise it is possible for undesirable brittle layers of Cu₃Sn and Cu₅Sn₃ to form at the interface.

2.9 Limitations of phase diagrams

Phase diagrams are extremely useful in the interpretation of metallic and ceramic structures but they are subject to several restrictions. Primarily, they identify which phases are likely to be present and provide compositional data. The most serious limitation is that they give no information on the structural form and distribution of phases (e.g. lamellae, spheroids, intergranular films). This is unfortunate, since these two features, which depend upon the surface energy effects between different phases and strain energy effects due to volume and shape changes during transformations, play an important role in the mechanical behaviour of materials. This is understood if we consider a two-phase (α + β) material containing only a small amount of β-phase. The β-phase may be dispersed evenly as particles throughout the α-grains, in which case the mechanical properties of the material would be largely governed by those of the α-phase. However, if the β-phase is concentrated at grain boundary surfaces of the α-phase, then the mechanical behaviour of the material will be largely dictated by the properties of the β-phase. For instance, small amounts of sulphide particles, such as grey manganese sulphide (MnS), are usually tolerable in steels but sulphide films at the grain boundaries cause unacceptable embrittlement.

A second limitation is that phase diagrams portray only equilibrium states. As indicated in previous sections, alloys are rarely cooled or heated at very slow rates. For instance, quenching, as practised in the heat treatment of steels, can produce metastable phases known as martensite and bainite that will then remain unchanged at room temperature. Neither appears in phase diagrams. In such cases it is necessary to devise methods for expressing the rate at which equilibrium is approached and its temperature dependency.

Whilst it is often convenient to express the composition of an alloy in terms of the percentage by weight (wt.%) of the constituent elements, it is sometimes necessary to describe the composition in terms of the percentage of atoms x and y. It is therefore convenient to be able to convert from wt.% to at.% for which it is necessary to know the atomic weight of the constituent atoms. Thus the conversion from wt.% to at.% is given by

\[
\text{(at.\%)}_A = \left(\frac{\text{(wt.\%)}_A}{\text{(wt.\%)}_A + \text{(wt.\%)}_B}\right) \times 100
\]

where A and B are the atomic weights of atoms x and y, respectively. Correspondingly the conversion from at.% to wt.% is

\[
\text{(wt.\%)}_A = \left(\frac{\text{(at.\%)}_A}{\text{(at.\%)}_A + \text{(at.\%)}_B}\right) \times 100
\]

2.10 Some key phase diagrams

2.10.1 Copper–zinc system

Phase diagrams for most systems, metallic and ceramic, are usually much more complex than the examples discussed so far. Figure 2.14 for the Cu–Zn system illustrates this point. The structural characteristics and mechanical behaviour of the industrial alloys known as brasses can be understood in terms of the copper-rich end of this diagram. Copper can dissolve up to 40% w/w of zinc, and cooling of any alloy within this range will produce an extensive primary solid solution (fcc-α). By contrast the other primary solid solution (γ) is extremely limited. A special feature of the diagram is the presence of four intermediate phases (β, γ, δ, ε). Each is formed during freezing by peritectic
reaction and each exists over a range of composition. Another notable feature is the order—disorder transformation which occurs in alloys containing about 50% zinc over the temperature range 450–470°C. Above this temperature range, bcc β-phase exists as a disordered solid solution. At lower temperatures, the zinc atoms are distributed regularly on the bcc lattice; this ordered phase is denoted by β.

Suppose that two thin plates of copper and zinc are held in very close contact and heated at a temperature of 400°C for several days. Transverse sectioning of the diffusion couple will reveal five phases in the sequence α/β/αFeZn6/βFeZn6/αFe, separated from each other by a planar interface. The l-phase will be absent because it is unstable at temperatures below its eutectoid horizontal (560°C). Continuation of diffusion will eventually produce one or two phases, depending on the original proportions of copper and zinc.

2.10.2 Iron–carbon system

Another interesting diagram, shown in Figure 2.15, is that for the iron–carbon system, which gives rise to the group of alloys known as steels. The polymorphic changes which take place in pure iron result in the formation of three different single-phase fields in iron-rich alloys, namely, α-iron, or ferrite (bcc), γ-iron, or austenite (fcc) and δ-iron (bcc). The temperatures at which these phase changes take place are known as A-points as a result of the arrests noted on a cooling curve. In addition to the solution formed with carbon in bcc and fcc iron, a compound known as cementite, Fe₃C, is also formed, and the diagram in the range 0–2.0% carbon, where the austenite transforms

![Phase diagram for copper–zinc.](image1)

**FIGURE 2.14**
Phase diagram for copper–zinc.


![Phase diagram for iron–carbon systems.](image2)

**FIGURE 2.15**
Phase diagram for iron–carbon systems.
by a eutectoid reaction to ferrite and cementite, is similar to that of the eutectic diagrams already discussed. The alternate formation of ferrite and cementite in eutectoid steel, 0.8% carbon, gives rise to a finely divided eutectoid structure known as pearlite.

2.10.3 Copper—lead system

The phase diagram for the Cu—Pb system (Figure 2.16) provides an interesting example of extremely limited solubility in the solid state and partial immiscibility in the liquid state. The two components differ greatly in density and melting point. Solid solutions, α and β, exist at the ends of the diagram. The 'miscibility gap' in the liquid phase takes the form of a dome-shaped two-phase (L1 + L2) field. At temperatures above the top of the dome, the critical point, liquid miscibility is complete. The upper isothermal represents a monotectic reaction, i.e., L1 → α + L2.

On cooling, a hyper-monotectic 50Cu—50Pb melt will separate into two liquids of different composition. The degree of separation depends on cooling conditions. Like oil and water, the two liquids may form an emulsion of droplets or separate into layers according to density. At a temperature of 954°C, the copper-rich liquid L1 disappears, forming α crystals and more of the lead-rich liquid L2. This liquid phase gets richer in lead and eventually decomposes by eutectic reaction, i.e., L2 → α + β. (Tie lines can be used for all two-phase fields; of course, however, because of density differences, mass ratios may differ greatly from observed volume ratios.)

The hypo-monotectic 70Cu—30Pb alloy, rapidly cast, has been used for steel-backed bearings; dispersed friction-reducing particles of lead-rich β are supported in a supporting matrix of copper-rich α. Binary combinations of conductive metal (Cu, Ag) and refractory arc-resistant metal (W, Mo, Ni) have been used for electrical contacts (e.g., 60Ag–40Ni). These particular monotectic systems, with their liquid immiscibility, are difficult to cast and are therefore made by powder metallurgy techniques.

2.11 Ternary phase diagrams

In considering equilibrium diagrams for ternary systems three independent variables have to be specified, i.e., two to define the composition and the third to define temperature. Consequently a 3-D space is required, and an equilateral triangle ABC with a temperature axis perpendicular to it is used. The corners of the triangle represent the pure metals; the sides, the three appropriate binaries and a point inside the triangle represent a ternary alloy composition. For the ternary alloy O in Figure 2.17, the concentration of the components is given by C_A = PC, C_B = RA and C_C = RP and since C_A + C_B + C_C = 1, then PB = RA + RP = 1. From the triangular representation ABC all alloys lying on a line (i) parallel to a side must have the same composition of the component opposite to the base, e.g., C_A is constant along PQ and (ii) through one corner must have a constant proportion of the other two components.

2.11.1 Ternary diagrams for complete solid miscibility

This is shown in Figure 2.18(a). The binaries along each side are similar to that of Figure 2.8. The liquids and solidus lines of the binaries become liquidus and solidus surfaces in the ternary system.
the (solid + liquid) region forming a convex lens shape and the solid phase becoming a volume in the ternary bounded by a surface. An example of this system is Ag–Au–Pd.

A series of isothermal or horizontal sections can be examined over the complete temperature range to give a full representation of the equilibrium diagram. For the simple diagram of Figure 2.18 (a) horizontal sections from room temperature up to the solidus surface show no variation, merely solid phase. At temperature $T$, the horizontal section cuts through the (solid + liquid) phase field and looks like Figure 2.18(b); alloys can be liquid, solid or (solid + liquid) depending on the composition. The liquidus surface varies in extent with temperature increasing or decreasing and can be shown as a 'contour' line on the diagram.

Vertical sections may also be useful, particularly if they are taken either (i) parallel to one side of the base triangle, i.e. at constant proportion of one of the components (Figure 2.18(c)) or (ii) along a line through a corner of the triangle.

2.11.2 Ternary eutectic

For the case when there is complete immiscibility in the solid state, e.g. Pb–Bi–Sn, the three binary eutectics are constructed on the sides of the diagrams (Figure 2.19(a)). The liquidus of the ternary forms three separate smooth liquidus surfaces, extending inwards from the melting point of each pure metal and sloping downwards to form three valleys which meet at $E$, the ternary eutectic point. A projection of this liquidus surface on to the base is shown in Figure 2.19(b).

Let us consider the solidification of an alloy $X$ which starts at the temperature $T_f$ when solid of pure $A$ separates out and the liquid becomes richer in $B$ and $C$. The ratio of $B$ to $C$ in the liquid remains constant as the temperature falls to $T_e$, when the liquid composition is given by the point $X_e$ in the valley between the two liquidus surfaces. This liquid is in equilibrium with both solid $A$ (when solid/liquid $= XX_e/AX_e$) and pure $B$. On further cooling the composition of the liquid follows the valley $X_eE$, and in the secondary stage of freezing pure $B$ separates out as well as $A$. The freezing behaviour for $B$-rich or $C$-rich alloys is similar, and the liquid phase eventually reaches either the valley $E_1E$ or $E_2E$, depositing either $A$ and $C$ or $B$ and $C$ before finally reaching the ternary eutectic point $E$. Here the liquid is in equilibrium with $A$, $B$ and $C$, and at $T_e$ the three-phase mixture freezes into the ternary eutectic structure. Every ternary alloy will completely solidify at the same temperature $T_e$ and so the solidus or tertiary surface is a horizontal plane across the diagram; this can be seen in the vertical section shown in Figure 2.19(c). The compositions and proportions of the phases present in an alloy at a given temperature can be found from horizontal sections. Four such sections at temperatures above $T_e$ are shown in Figure 2.20. From these sections it can be seen that boundaries between single- and two-phase regions are curved, between two- and three-phase regions, straight lines, and three-phase regions are bounded by straight lines. In a three-phase field, the compositions of the three phases are given by the corners of the triangle, e.g. $U$ in Figure 2.21. For any alloy in this field only the proportions of $U$, $V$ and $W$ change and an alloy $X$ has the proportions $U:V:W$ given by $HK:WH:VK$.

2.11.3 Ternary diagrams with solid solutions

If primary solid solubility exists, then instead of pure $A$, $B$ or $C$ separating out, the solid solutions $\alpha$, $\beta$ or $\gamma$ form. In Figure 2.22 the liquidus surface has the same form as before, but beneath it there is a new phase boundary near each corner of the diagram, representing the limit of solid solubility in each of the pure metals $A$, $B$ and $C$.

Horizontal sections above $T_e$ are shown in Figure 2.23, and below $T_e$ the horizontal section is contained in the base triangle $ABC$ of Figure 2.22. It is readily seen that alloys with compositions
2.11 Ternary phase diagrams

**Figure 2.19**
(a) Schematic ternary system for complete incongruency in solids state. (b) Schematic ternary system for projection of liquidus surface on to base. (c) Schematic ternary system for a vertical section.

**Figure 2.20**
Horizontal sections at four temperatures above $T_c$ through the ternary diagram in Figure 2.19.

**Figure 2.21**
Constitution in a three-phase field UHW.
2.11 Ternary phase diagrams

A ternary phase diagram with solid solutions. After Rhines, *Phase Diagrams in Metallurgy*.

near the corners solidify in one stage to primary solid solutions α, β or γ while alloys near the sides of the diagram do not under a tertiary stage of solidification, since no ternary eutectic (which is now a phase mixture of α, β and γ) is formed.

2.11.4 Ternary diagrams with a peritectic

There are no new principles involved if other reactions are introduced, but a peritectic system AB is included in Figure 2.24 to illustrate the way in which new features may be considered. The curve EL running into the body of the ternary system represents the path of the liquid composition taking

Horizontal sections of five temperatures above $T_d$ through the ternary in Figure 2.22.
part in the $L + a \rightarrow \beta$ peritectic reaction. The curve DL represents the liquid composition for the eutectic reaction, $L \rightarrow a + \gamma$. The intersection point L is the peritectic point where $L + a \rightarrow \beta + \gamma$. From L the eutectic valley LF runs to the lower eutectic where $L \rightarrow \beta + \gamma$. At the peritectic temperature four phases $L$, $a$, $\beta$ and $\gamma$, with compositions lying at the corners of the shaded trapezium, coexist; the trapezium is termed the peritectic plane.

Horizontal sections for five temperatures $T_1$ to $T_5$ are given in Figure 2.25, and it is instructive to follow the solidification of four alloys lying in the four different sections of the trapezium (see isotherm $T_2$). Alloy 1 starts to solidify with a primary separation of $a$ followed by a secondary deposition of $\alpha + \beta$. On cooling through the four-phase reaction temperature $L + a + \beta + a + \beta + \gamma$, for alloy 2, primary $\alpha$ also separates initially but the secondary deposition is $a + \gamma$ and in the four-phase reaction $L + a + \gamma + a + \beta + \gamma$. For alloys 3 and 4, the primary $\alpha$ is quite small and the secondary deposition is $a + \beta$ and $a + \gamma$, respectively. Both alloys will decrease the $\alpha$ and liquid content to form $\beta + \gamma$ in the four-phase reaction and $\beta + \gamma$ will continue to form at lower temperatures until the liquid is consumed. It must be remembered however that peritectic alloys do not often solidify under equilibrium conditions because of the envelopment of the $\alpha$-phase by reaction products which hinder diffusion. An excess amount of $\alpha$ is generally present and also liquid after the four-phase reaction.

### 2.11.5 Ternary diagrams containing intermetallic phases

More complex ternary systems can often be broken down into simpler, basic forms in certain regions of the diagram. A common example of this is of a system containing an intermetallic phase.
2.12 Principles of alloy theory

2.12.1 Primary substitutional solid solutions

2.12.1.1 The Hume-Rothery rules

The key phase diagrams outlined in Section 2.10 exhibit many common features (e.g. primary solid solutions, intermediate phases), and for systems based on simple metals some general rules governing the formation of alloys have been formulated. These rules can form a useful basis for predicting alloying behaviour in other more complex systems. In brief the rules for primary solid solubility are as follows:

1. Atomic size factor: If the atomic diameter of the solute atom differs by more than 15% from that of the solvent atom, the extent of the primary solid solution is small. In such cases it is said that the size factor is unfavourable for extensive solid solution.

2. Electrochemical effect: The more electropositive the one component and the more electronegative the other, the greater is the tendency for the two elements to form compounds rather than extensive solid solutions.

3. Relative valency effect: A metal of higher valency is more likely to dissolve to a large extent in one of lower valency than vice versa.

2.12.1.2 Size-factor effect

Two metals are able to form a continuous range of solid solutions only if they have the same crystal structure (e.g. copper and nickel). However, even when the crystal structure of the two elements is the same, the extent of the primary solubility is limited if the atomic size of the two metals, usually taken as the closest distance of approach of atoms in the crystal of the pure metal, is unfavourable. This is demonstrated in Figure 2.27 for alloy systems where rules 2 and 3 have been observed, i.e. the electrochemical properties of the two elements are similar and the solute is dissolved in a metal of lower valency. As the size difference between the atoms of the two component metals A and B approaches 15%, the equilibrium diagram changes from that of the copper—nickel type to one of a eutectic system with limited primary solid solubility.

The size-factor effect is due to the distortion produced in the parent lattice around the dissolved misfitting solute atom. In these localized regions the interatomic distance will differ from that given by the minimum in the E—r curve of Figure 1.3 so that the internal energy and hence the free energy, G, of the system is raised. In the limit when the lattice distortion is greater than some critical value the primary solid solution becomes thermodynamically unstable relative to some other phase.

2.12.1.3 Electrochemical effect

This effect is best demonstrated by reference to the alloying behaviour of an electropositive solvent with solutes of increasing electronegativity. The electronegativity of elements in the periodic table increases from left to right in any period and from bottom to top in any group. Thus, if magnesium is alloyed with elements of group IV the compounds formed, Mg3Si, Sn or Pb, become more stable in the order lead, tin, silicon, as shown by their melting points, 550°C, 778°C...
and 1085°C, respectively. In accordance with rule 2 the extent of the primary solid solution is small (≈ 7.75 at%, 3.35 at% and negligible, respectively, at the eutectic temperature) and also decreases in the order lead, tin, silicon. Similar effects are also observed with elements of group V, which includes the elements bismuth, antimony and arsenic, when the compounds MgSb, Sb or AsSb are formed.

The importance of compound formation in controlling the extent of the primary solid solution can be appreciated by referring to Figure 2.28, where the curves represent the free energy versus composition relationship between the α-phase and compound at a temperature T. It is clear from Figure 2.28(a) that at this temperature the α-phase is stable up to a composition c₁, above which the phase mixture (α + compound) has the lower free energy. When the compound becomes more stable, as shown in Figure 2.28(b), the solid solubility decreases, and correspondingly the phase mixture is now stable over a greater composition range which extends from c₁ to c₁.

![Figure 2.27](Figure showing phase diagrams for different alloys)

The above example is an illustration of a more general principle that the solubility of a phase decreases with increasing stability and may also be used to show that the concentration of solute in solution increases as the radius of curvature of the precipitate particle decreases. Small precipitate particles are less stable than large particles, and the variation of solubility with particle size is recognized in classical thermodynamics by the Thomson–Freundlich equation

\[
\ln(c_r/c) = 2\gamma \Omega/kT
\]

where \(c_r\) is the concentration of solute in equilibrium with small particles of radius \(r\), \(c\) the equilibrium concentration, \(\gamma\) the precipitate/matrix interfacial energy and \(\Omega\) the atomic volume.

### 2.12.1.4 Relative valency effect

This is a general rule for alloys of the univalent metals, copper, silver and gold, with those of higher valency. Thus, for example, copper will dissolve approximately 40% zinc in solid solution but the solution of copper in zinc is limited. For solvent elements of higher valencies the application is not so general, and in fact exceptions, such as that exhibited by the magnesium–indium system, occur.

### 2.12.1.5 The primary solid solubility boundary

It is not yet possible to predict the exact form of the α-solid solubility boundary, but in general terms the boundary may be such that the range of primary solid solution either increases or decreases with rise in temperature. Both forms arise as a result of the increase in entropy which occurs when solute atoms are added to a solvent. It will be remembered that this entropy of mixing is a measure of the extra disorder of the solution compared with the pure metal.

The most common form of phase boundary is that indicating that the solution of one metal in another increases with rise in temperature. This follows from thermodynamic reasoning since
increasing the temperature favours the structure of highest entropy (because of the $-TS$ term in the relation $G = H - TS$) and in alloy systems of the simple eutectic type an $\alpha$-solid solution has a higher entropy than a phase mixture ($\alpha + \beta$). Thus, if the alloy exists as a phase mixture ($\alpha + \beta$) at the lower temperatures, it does so because the value of $H$ happens to be less for the mixture than for the homogeneous solution at that composition. However, because of its greater entropy term, the solution gradually becomes preferred at high temperatures. In more complex alloy systems, particularly those containing intermediate phases of the secondary solid solution type (e.g. copper–zinc, copper–galium, copper–aluminium), the range of primary solid solution decreases with rise in temperature. This is because the $\beta$-phase, like the $\alpha$-phase, is a disordered solid solution. However, since it occurs at a higher composition, it has a higher entropy of mixing, and consequently its free energy will fall more rapidly with rise in temperature. This is shown schematically in Figure 2.29. The point of contact on the free energy curve of the $\alpha$-phase, determined by drawing the common tangent to the $\alpha$ and $\beta$ curves, governs the solubility $c$ at a given temperature $T$. The steep fall with temperature of this common tangent automatically gives rise to a decreasing solubility limit.

Many alloys of copper or silver reach the limit of solubility at an electron-to-atom ratio of about 1.4. The divalent elements zinc, cadmium and mercury have solubilities of approximately 40 at. % (e.g. copper–zinc, silver–cadmium, silver–mercury), the trivalent elements approximately 20 at. % (e.g. copper–aluminium, copper–galium, silver–aluminium, silver–indium) and the tetravalent elements about 13 at. % (e.g. copper–germanium, copper–silicon, silver–tin), respectively.

The limit of solubility has been explained by Jones in terms of the Brillouin zone structure (see Chapter 8). It is assumed that the density of states–energy curve for the two phases, $\alpha$ (the close-packed phase) and $\beta$ (the more open phase), is of the form shown in Figure 2.30, where the $N(E)$ curve deviates from the parabolic relationship as the Fermi surface approaches the zone boundary. As the solute is added to the solvent lattice and more electrons are added the top of the Fermi level moves towards $A$, i.e. where the density of states is high and the total energy $E$ for a given electron concentration is low. Above this point the number of available energy levels decreases so markedly that the introduction of a few more electrons per atom causes a sharp increase in energy. Thus, just above this critical point the $\alpha$ structure becomes unstable relative to the alternative $\beta$ structure which can accommodate the electrons within a smaller energy range, i.e. the energy of the Fermi level is lower if the $\beta$-phase curve is followed rather than the $\alpha$-phase curve. The composition for which $E_{\text{max}}$ reaches the point $E_A$ is therefore a critical one, since the alloy will adopt that phase which has the lowest energy. It can be shown that this point corresponds to an electron-to-atom ratio of approximately 1.4.

2.12.2 Interstitial solid solutions

Interstitial solid solutions are formed when the solute atoms can fit into the interstices of the lattice of the solvent. However, an examination of the common crystal lattices shows that the size of the available interstices is restricted, and consequently only the small atoms, such as hydrogen, boron, carbon or nitrogen, with atomic radii very much less than one nanometre form such solutions. The most common examples occur in the transition elements and in particular the solution of carbon or nitrogen in iron is of great practical importance. In fcc iron (austenite) the largest interstice or ‘hole’ is at the centre of the unit cell (coordinates $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) where there is space for an atom of radius $52$ pm, i.e. $0.41r$ if $r$ is the radius of the solvent atom. A carbon atom (80 pm (0.8 Å) diameter) or

$^\text{10}$The shape of the Fermi surface may be determined from measurements of physical properties as a function of orientation in a single crystal. The surface resistance to a high-frequency current at low temperatures (the anomalous skin effect) shows that in copper the Fermi surface is distorted from the spherical shape but becomes more nearly spherical in copper alloys.
We have already seen that a strong tendency for compound formation exists when one element is electropositive and the other is electronegative. The magnesium-based compounds are probably the most common examples having the formula MgX(Pb, Sn, Ge or Si). These have many features in common with salt-like compounds since their compositions satisfy the chemical valency laws, their range of solubility is small and usually they have high melting points. Moreover, many of these types of compounds have crystal structures identical to definite chemical compounds such as sodium chloride, NaCl, or calcium fluoride, CaF₂. In this respect the MgX series are anti-isomorphous with the CaF₂ fluorospar structure, i.e. the magnesium metal atoms are in the position of the non-metallic fluoride atoms and the metalloid atoms such as tin or silicon take up the position of the metal atoms in calcium fluoride.

Even though these compounds obey all the chemical principles they may often be considered as special electron compounds. For example, the first Brillouin zone of the CaF₂ structure is completely filled at \( \frac{1}{2} \) electrons per atom, which significantly is exactly that supplied by the compound Mg₁₋ₓPbₓSn and so on. Justification for calling these full-zone compounds is also provided by electrical conductivity measurements. In contrast to the behaviour of salt-like compounds which exhibit low conductivity even in the liquid state, the compound Mg₁₋ₓPbₓ shows the normal conduction (which indicates the possibility of zone overlapping) while Mg₃Sn behaves like a semiconductor (indicating that a small energy gap exists between the first and second Brillouin zones).

In general, it is probable that both concepts are necessary to describe the complete situation. As we shall see in Section 2.12.3.3, with increasing electrochemical factor even true electron compounds begin to show some of the properties associated with chemical compounds, and the atoms in the structure take up ordered arrangements.

2.12.3.2 Size-factor compounds

When the atomic diameters of the two elements differ only slightly, electron compounds are formed, as discussed in the next section. However, when the difference in atomic diameter is appreciable, definite size-factor compounds are formed which may be of the (i) interstitial or (ii) substitutional type.

A consideration of several interstitial solid solutions has shown that if the interstitial atom has an atomic radius 0.41 times that of the metal atom then it can fit into the largest available structural interstice without distortion. When the ratio of the radius of the interstitial atom to that of the metal atom is greater than 0.41 but less than 0.59, interstitial compounds are formed; hydrides, borides, carbides and nitrides of the transition metals are common examples. These compounds usually take up a simple structure of either the cubic or hexagonal type, with the metal atoms occupying the normal lattice sites and the non-metal atoms the interstices. In general, the phases occur over a range of composition which is often centred about a simple formula such as Mg₅X and MX. Common examples are carbides and nitrides of titanium, zirconium, hafnium, vanadium, niobium and tantalum, all of which crystallize in the NaCl structure. It is clear, therefore, that these phases do not form merely as a result of the small atom fitting into the interstices of the solvent structure, since vanadium, niobium and tantalum are bcc, while titanium, zirconium and hafnium are cph. By changing their structure to ccc the transition metals allow the interstitial atom not only a larger "hole" but also six metallic neighbours. The formation of bonds in three directions at right angles,

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![Diagram](image)

**Figure 2.31**

(a) Lattice of bcc showing the relative positions of the main lattice sites, the octahedral interstices marked *, and the tetrahedral interstices marked 0. (b) Structure cell of iron showing the distortions produced by the two different interstitial sites. Only three of the iron atoms surrounding the octahedral sites are shown; the fourth, centered at A, has been omitted for clarity.

After Williamson and Smallman (1953).

A nitrogen atom (70 pm diameter) therefore expands the lattice on solution, but nevertheless dissolves in quantities up to 1.7 wt% and 2.8 wt%, respectively. Although the bcc lattice is the more open structure the largest interstice is smaller than that in the fcc. In bcc iron (ferrite) the largest hole is at the position \( (\frac{1}{2}, \frac{1}{2}, 0) \) and is a tetrahedral site where four iron atoms are situated symmetrically around it; this can accommodate an atom of radius 36 pm, i.e. 0.29\( \phi \), as shown in Figure 2.31(a). However, internal friction and X-ray diffraction experiments show that the carbon or nitrogen atoms do not use this site, but instead occupy a smaller site which can accommodate an atom only 0.15\( \phi \), or 19 pm. This position \( (0, 0, \frac{1}{2}) \) at the mid-points of the cell edges is known as the octahedral site since, as can be seen from Figure 2.31(b), it has a distorted octahedral symmetry for which two of the iron atoms are nearer to the centre of the site than the other four nearest neighbours. The reason for the interstitial atoms preferring this small site is thought to be due to the elastic properties of the bcc lattice. The two iron atoms which lie above and below the interface, and which are responsible for the smallness of the hole, can be pushed away more easily than atoms around the larger interstice. As a result, the solution of carbon in \( \alpha \)-iron is extremely limited (0.02 wt%) and the structure becomes distorted into a body-centred tetragonal lattice. The c-axis for each interstitial site is, however, disordered, so that this gives rise to a structure which is statistically cubic. The body-centred tetragonal structure forms the basis of martensite (an extremely hard martensitic constituent of steel), since the quenching treatment given to steel retains the carbon in supersaturated solution (see Chapter 12).

2.12.3 Types of intermediate phases

2.12.3.1 Electrochemical compounds

The phases which form in the intermediate composition regions of the equilibrium diagram may be (i) electrochemical or full-zone compounds, (ii) size-factor compounds or (iii) electron compounds. The term 'compound' still persists even though many of these phases do not obey the valency laws of chemistry and often exist over a wide composition range.
such as that occurring in the sodium chloride arrangement, imparts a condition of great stability to these MX carbidcs.

When the ratio $r_{\text{cation}}/r_{\text{anion}}$ exceeds 0.59 the distortion becomes appreciable, and consequently more complicated crystal structures are formed. Thus, iron nitride, where $r_{Fe}/r_{N} = 0.56$, takes up a structure in which nitrogen lies at the centre of six atoms as suggested above, while iron carbide, i.e., cementite, Fe$_3$C, for which the ratio is 0.63, takes up a more complex structure.

For intermediate atomic size difference, i.e., about 20–30%, an efficient packing of the atoms can be achieved if the crystal structure common to the Laves phases is adopted (Table 2.2). These phases, classified by Laves and his co-workers, have the formula AB$_2$ and each A atom has 12 B neighbours and 4 A neighbours, while each B atom is surrounded by six like and six unlike atoms. The average coordination number of the structure (13.33) is higher, therefore, than that achieved by the packing of atoms of equal size. These phases crystallize in one of three closely related structures which are isomorphous with the compounds MgCu$_2$ (cubic), MgNi$_2$ (hexagonal) or MgZn$_2$ (hexagonal). The secret of the close relationship between these structures is that the small atoms are arranged on a space lattice of tetrahedra.

The different ways of joining such tetrahedra account for the diversity of these structures. This may be demonstrated by an examination of the MgCu$_2$ structure. The small B atoms lie at the corners of tetrahedra which are joined point-to-point throughout space, as shown in Figure 2.32(a). Such an arrangement provides large holes of the type shown in Figure 2.32(b), and these are best filled when the atomic ratio $r_{\text{cation}}/r_{\text{anion}} = 1.225$. The complete cubic structure of MgCu$_2$ is shown in Figure 2.32(c). The MgZn$_2$ structure is hexagonal, and in this case the tetrahedra are joined alternately point-to-point and base-to-base to form a wurtzite type of structure. The MgNi$_2$ structure is also hexagonal, and although very complex it is essentially a mixture of both the MgCu$_2$ and MgNi$_2$ types.

The range of homogeneity of these phases is narrow. This limited range of homogeneity is not due to any ionic nature of the compound, since ionic compounds usually have low coordination numbers, whereas Laves phases have high coordination numbers, but because of the stringent geometrical conditions governing the structure. However, even though the chief reason for their existence is that the ratio of the radius of the large atom to that of the small is about 1.2, there are indications that electronic factors may play some small part. For example, provided the initial size-factor condition is satisfied then if the $e/a$ ratio is high (e.g., 2), there is a tendency for compounds to crystallize in the

| Table 2.2 Compounds Which Exist in a Laves Phase Structure |
|-----------------|-----------------|-----------------|
| MgCu$_2$       | MgNi$_2$       | MgZn$_2$       |
| AgB$_2$        | BaMg$_2$       | NbCu$_2$       |
| Bi$_2$         | Bi$_2$         | TaCu$_2$       |
| NbNi$_2$       | TiMn$_2$       | TaNi$_2$       |
| TiNi$_2$, Co, or Cu$_2$ | TiMn$_2$ or FeNi$_2$ | TCo$_2$ |
| U$_3$Ni$_4$, Co or Fe$_3$Ni$_4$ | ZrNi$_2$ | ZrNi$_2$, Ir, Mn, Re, Ru, Os or V$_2$ |

FIGURE 2.32
(a) Framework of the MgCu$_2$ structure. (b) Shape of hole in which large Mg atom is accommodated.
(c) Complete MgCu$_2$ structure.

After Hume-Rothery et al. (1969); by courtesy of the Institute of Metals, Minerals and Mining.

MgCu$_2$ structure, while if the $e/a$ ratio is low (e.g., $\frac{1}{2}$), then there is a tendency for the MgCu$_2$ type of structure to be formed. This electronic feature is demonstrated in the magnesium–nickel–zinc ternary system. Thus, even though the binary systems contain both the MgZn$_2$ and MgNi$_2$ phases the ternary compound MgNiZn has the MgCu$_2$ structure, presumably because its $e/a$ ratio is $\frac{1}{2}$.

Table 2.2 shows a few common examples of each type of Laves structure, from which it is evident that there is also a general tendency for transition metals to be involved.

2.12.3.3 Electron compounds

Alloys of copper, silver and gold with the B subgroup all possess the structure $\omega$, $\beta$, $\gamma$, $\epsilon$ of structurally similar phases, and while each phase does not occur at the same composition when this is measured in weight per cent or atomic per cent, they do so if composition is expressed in terms of electron concentration. Hume-Rothery and his co-workers have pointed out that the $e/a$ ratio is important not only in governing the limit of the $\alpha$-solid solution but also in controlling the formation of certain intermediate phases; for this reason they have been termed 'electron compounds'.

In terms of those phases observed in the copper–zinc system (Figure 2.14), $\beta$-phases are found at an $e/a$ ratio of $\frac{1}{3}$ and these phases are often either disordered bcc in structure or ordered CsCl-type, $\gamma$. In the copper–aluminium system for example, the $\beta$-structure is found at Cu$_3$Al, where the three valence electrons from the aluminium and the one from each copper atom make up a ratio of 6 electrons to 4 atoms, i.e. $e/a = \frac{3}{2}$. Similarly, in the copper–tin system the $\beta$-phase occurs at Cu$_3$Sn with 9 electrons to 6 atoms giving the governing $e/a$ ratio. The $\gamma$-brass phase, Cu$_3$Zn$_8$, has a complex cubic (32 atoms per unit cell) structure, and is characterized by an $e/a$ ratio of $\frac{1}{2}$, while
Table 2.3 Some Selected Structurally Analogous Phases

<table>
<thead>
<tr>
<th>Electron-Atom Ratio</th>
<th>Electron-Atom Ratio</th>
<th>Electron-Atom Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(β-Brass (bcc))</td>
<td>(β-Manganese</td>
<td>(β-Brass)</td>
</tr>
<tr>
<td>Cu, Ag or Au(1)</td>
<td>Complex Cubic)</td>
<td>Cu, Ag or Au(1)</td>
</tr>
<tr>
<td>(Complex Cubic)</td>
<td>Ag or Au(1)</td>
<td>Zn or Cd(1)</td>
</tr>
<tr>
<td>Cu, Ag or Au(1)</td>
<td>Ag or Au(1)</td>
<td>Zn or Cd(1)</td>
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<tr>
<td>Ag or Au(1)</td>
<td>Ag or Au(1)</td>
<td>Zn or Cd(1)</td>
</tr>
<tr>
<td>Cu or Ag(1)</td>
<td>Ag or Au(1)</td>
<td>Zn or Cd(1)</td>
</tr>
<tr>
<td>Cu2Zn or (β)</td>
<td>Cu2Sn or (β)</td>
<td>Fe, Co, Ni, Pd or</td>
</tr>
<tr>
<td>Cu or Ag(1)</td>
<td>Cu2Sn or (β)</td>
<td>Pbd, Zn, (β)</td>
</tr>
</tbody>
</table>

The β-brass phase, Cu2Zn, has a cph structure and is governed by an e/a ratio of 2. A list of some of these structurally analogous phases is given in Table 2.3.

A close examination of this table shows that some of these phases, e.g., Cu2Si and Ag2Al, exist in different structural forms for the same e/a ratio. Thus, Ag2Al is basically a 2/3 bcc phase, but it only exists as such at high temperatures; at intermediate temperatures it is cph and at low temperatures β-Mn. It is also noticeable that to conform with the appropriate electron-to-atom ratio the transition metals are credited with zero valency. The basis for this may be found in their electronic structure which is characterized by an incomplete d-band below an occupied outermost s-band. The nickel atom, for example, has an electronic structure denoted by (2) (8) (16) (2), i.e., two electrons in the first quantum shell, eight in the second, sixteen in the third and two in the fourth shells, and while this indicates that the free atom has two valence electrons, it also shows two electrons missing from the third quantum shell. Thus, if nickel contributes valence electrons, it also absorbs an equal number from other atoms to fill up the third quantum shell so that the net effect is zero.

Without doubt the electron concentration is the most important single factor which governs these compounds. However, for the other intermediate phases, a closer examination shows an interplay of all factors. Thus, in general, the bcc 2/3 compounds are only formed if the size factor is less than 2.18%, an increase in the valency of the solute tends to favour cph and β-Mn structures at the expense of the bcc structure, a high electrochemical factor leads to ordering up to the melting point and an increase in temperature favours the bcc structure in preference to the cph or β-Mn structure.

2.12.4 Order-disorder phenomena

A substitutional solid solution can be one of two types, either ordered in which the A and B atoms are arranged in a regular pattern, or disordered in which the distribution of the A and B atoms is random. From the previous section it is clear that the necessary condition for the formation of a superlattice, i.e., an ordered solid solution, is that dissimilar atoms must attract each other more than similar atoms. In addition, the alloy must exist at or near a composition which can be expressed by a simple formula such as AB, A3B or AB3. The following are common structures:

1. CuZn: While the disordered solution is bcc with equal probabilities of having copper or zinc atoms at each lattice point, the ordered lattice has copper atoms and zinc atoms segregated to cube corners (0, 0, 0) and centres (1/2, 1/2, 1/2), respectively. The superlattice in the β-phase therefore takes the CuCl structure (also described as I2 or L23 structure) as illustrated in Figure 2.33(a). Other examples of the same type, which may be considered as being made up of two interpenetrating simple cubic lattices, are Ag(Mg, Zn or Cd), AuNi, NiAl, FeAl and FeCo.

2. Cu2Zn: This structure, which occurs less frequently than the β-brass type, is based on the fcc structure with copper atoms at the centres of the faces (0, 1/2, 1/2) and gold atoms at the corners (0, 0, 0), as shown in Figure 2.33(b). Other examples of the L12 structure include Ni3Al, Ni3Ti, Ni3Si, Pt3Al, Fe3Ga and Zr3Al.

3. AuCu: The AuCu structure shown in Figure 2.33(c) is also based on the fcc lattice, but in this case alternate (0 0 1) layers are made up of copper and gold atoms, respectively. Hence, because the atomic sizes of copper and gold differ, the lattice is distorted into a tetragonal structure having an axial ratio e/a = 0.93. Other examples of the L10 include CuPt, FePt and TiAl.

4. Fe3Al: Like FeAl, the Fe3Al structure is based on the bcc lattice but, as shown in Figure 2.33(d), eight simple cells are necessary to describe the complete ordered arrangement. In this structure
any individual atom is surrounded by the maximum number of unlike atoms and the aluminium atoms are arranged tetrahedrally in the cell. Other examples of the D0$_{19}$ include Fe$_3$Si and Co$_3$Al.

5. Mg$_2$Cd: This ordered structure is based on the cph lattice. Other examples of the D0$_{19}$ structure are Ti$_3$Al, MgCu$_2$, and Ni$_3$Sn.

Another important structure which occurs in certain intermetallics is the defect lattice. In the compound Ni$_3$Al, as the composition deviates from stoichiometry towards pure aluminium, the electron-to-atom ratio becomes greater than $\frac{2}{3}$, but to prevent the compound becoming unstable the lattice takes up a certain proportion of vacancies to maintain the number of electrons per unit cell at a constant value of 3. Such defects obviously increase the entropy of the alloy, but the fact that these phases are stable at low temperatures, where the entropy factor is unimportant, demonstrates that their stability is due to a lowering of internal energy. Such defects produce an anomalous decrease in both the lattice parameter and the density above 50 at.% Al.

PROBLEMS

2.1 How many ways are there of arranging two A atoms and two B atoms in a square array? Draw the corresponding diagrams to illustrate the value.

2.2 The specific heat of copper is given by $C_p = 22.64 + 6.28 \times 10^{-3}T$ J$^{-1}$ mol$^{-1}$ K$^{-1}$. Calculate the change in entropy from room temperature to the melting point.

2.3 A pressure–temperature diagram for a typical metal is shown in Figure 2.1. How is this diagram modified for the metals Bi and Ga, and why?

2.4 A 100-g sample of gold–silver alloy contains 40 wt% of gold. Calculate the mole fractions of gold and silver, and the total entropy of mixing. (Atomic weight of Au = 197, atomic weight of Ag = 108.)

2.5 Change the following alloy compositions (a) Cu–40 wt% Zn, (b) Cu–10 wt% Al, and (c) Cu–20 wt% In into (i) atomic percent and (ii) electron–atom ratio, etc. What is the significance of the e/a ratio? Why is Cu–In different from Cu–Zn and Cu–Al?

2.6 A hypothetical alloy transforms from simple cubic structure to close-packed hexagonal structure. Assuming a hard sphere model, calculate the volume change during the transformation.

2.7 From the Cu–Ni phase diagram (Figure 2.3) determine for a Cu–40% Ni alloy the composition and amount of each phase at 1250°C.

2.8 From the Pb–Sn phase diagram (Figure 2.10) determine for the eutectic alloy the amount and composition of each phase, just below the eutectic temperature at 182°C.

2.9 The Cu–Ni alloy system is an ideal solid solution system in which entire solubility is observed while the Cu–Ag system is a typical eutectic system in which limited solubility of Cu into Ag and vice versa is observed. Which one of the Hume-Rothery alloying rules best accounts for this difference?

Further reading