CHAPTER 6

PHASE DIAGRAMS

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1. Introduction

The study of phase equilibria and phase transformations is central to nearly all branches of metallurgy and materials science. Although departures from equilibrium will occur in any real system, a knowledge of the equilibrium state under a given set of conditions is the starting point for the understanding of most processes.

A phase diagram is a graphical representation of the loci of thermodynamic variables when equilibrium among the phases of a system is established under a given set of conditions. The phase diagrams most familiar to the metallurgist are those for which temperature and composition are the axes. These are discussed in §§2 and 3 for binary (two-component) and ternary (three-component) systems, and in §4 for multicomponent systems. However, the effect of other variables such as total pressure and chemical potential of the components (e.g., the partial pressure of oxygen) may often be of interest. In §6, different types of phase diagrams are discussed along with the general rules governing their construction.

Throughout the chapter, the thermodynamic origin of phase diagrams is stressed. With the advent of modern computer techniques, the relationship between phase diagrams and the thermodynamic properties of the system has become of increasing practical importance. As discussed in §2.10, a quantitative coupling of the two is now possible. Furthermore, as discussed in §5, the computer-assisted thermodynamic approach often permits good estimates of unknown multicomponent phase diagrams to be made, and can often significantly reduce the experimental effort required to measure the phase diagram of a system.

2. Binary phase diagrams

The temperature composition (T-X) phase diagram of the Bi-Sb system is shown in fig. 1 (Hultgren et al. [1963]). The abscissa is the composition, expressed as mole fraction of Sb, $X_{\text{Sb}}$. Note that $X_{\text{Sb}} = 1 - X_{\text{Bi}}$. Phase diagrams are also often drawn with the composition axis expressed as weight percent.

At all compositions and temperatures in the area above the line labelled liquidus, single-phase liquid alloys will be observed, while at all compositions and temperatures below the line labelled solidus, alloys exist as single-phase solid solutions. An alloy sample at equilibrium at a temperature and overall composition between these two curves will consist of a mixture of solid and liquid phases, the compositions of which are given by the liquidus and solidus compositions at that temperature. For example, a Bi-Sb sample of overall composition $X_{\text{Bi}} = 0.60$ at $T = 700$ K (at point R in fig. 1) will consist, at equilibrium, of a mixture of liquid alloy of composition $X_{\text{Bi}} = 0.37$ (point P) and solid alloy of composition $X_{\text{Bi}} = 0.82$ (point Q). The line PQ is called a tie-line or conode. As the overall composition is varied at 700 K between points P and Q, the compositions of the liquid and solid phases remain fixed at P and Q, and only the relative proportions of the two phases change. From a simple mass balance, one can derive the lever rule for binary systems: (moles of liquid)/(moles of solid) = RQ/PQ. Hence, at 700 K a sample of Bi-Sb alloy with overall composition $X_{\text{Bi}} = 0.60$ consists of liquid and solid phases in the molar ratio $(0.82 - 0.60)/(0.60 - 0.37) = 0.96$. Were the composition axis expressed as weight percent, then the lever rule would give the weight ratio of the two phases.

Suppose that a liquid Bi-Sb alloy with composition $X_{\text{Bi}} = 0.60$ is cooled very slowly from an initial temperature of 900 K. When the temperature has decreased to the liquidus temperature of 780 K (point A) the first solid appears, with a composition at point B (60% Bi, 40% Sb). As the temperature is decreased further, solid continues to precipitate with the compositions of the two phases at any temperature being given by the liquidus and solidus compositions at that temperature and with their relative proportions being given by the lever rule. Solidification is complete at 630 K, the last liquid to solidify having composition $X_{\text{Bi}} = 0.18$ (point C).

The process just described is known as equilibrium cooling. At any temperature during equilibrium cooling the solid phase has a uniform (homogeneous) composition. In the preceding example, the composition of the solid phase during cooling varies along the line BQD. Hence, in order for the solid particles to have a uniform composition at any temperature, diffusion of Sb from the center to the surface of the growing particles must occur. Since solid state diffusion is a relatively slow process, equilibrium cooling conditions are only approached if the temperature is decreased very slowly. If a Bi-Sb alloy of composition $X_{\text{Bi}} = 0.60$ is cooled very rapidly from the liquid, concentration gradients will be observed in the solid grains, with the concentration of Sb decreasing towards the surface from a maximum of $X_{\text{Bi}} = 0.93$ (point B) at the center. Furthermore, in this case solidification will not be complete at 630 K since at 630 K the average concentration of Sb in the solid particles will now be greater than $X_{\text{Bi}} = 0.60$. These considerations are discussed more fully in ch. 9.

At $X_{\text{Bi}} = 0$ and $X_{\text{Bi}} = 1$ in fig. 1 the liquidus and solidus curves meet at the equilibrium melting points, or temperatures of fusion, of Bi and Sb, which are: $T_{\text{Bi}} = 1544.5$ K, $T_{\text{Sb}} = 903$ K.

The phase diagram is influenced by the total pressure, $P$. Unless otherwise stated, $T$-$X$ diagrams for alloy systems are usually presented for $P = \text{const.} = 1$ atm. However, for equilibria involving only solid and liquid phases, the phase boundaries are typically shifted only by the order of a few hundreds of a degree per bar change in $P$ (see ch. 5, §3). Hence, the effect of pressure upon the phase diagram is generally negligible.

Fig. 1. Phase diagram of the Bi-Sb system (after Hultgren et al. [1963]).
2.1. The thermodynamic origin of phase diagrams

In this section we shall consider first of all the thermodynamic origin of simple “lens-shaped” phase diagrams in binary systems with complete liquid and solid miscibility.

An example of such a diagram was given in fig. 1. Another example is the Ge-Si phase diagram in the lowest panel of fig. 2 (Hansen [1958]). In the upper three panels of fig. 2 are shown, to scale, the molar Gibbs energies of the solid and liquid phases, $g_s^0$ and $g_l^0$, at three temperatures. As illustrated in the top panel, $g_s^0$ varies with composition between the standard molar Gibbs energies of pure solid Ge and of pure solid Si, $g_{S_{Si}}^{0}$ and $g_{S_{Ge}}^{0}$, while $g_l^0$ varies between the standard molar Gibbs energies of the pure liquid components $g_{L_{Si}}^{0}$ and $g_{L_{Ge}}^{0}$. The molar Gibbs energies of mixing of the solid and liquid phases, $\Delta g_s^0$ and $\Delta g_l^0$, are negative and are equal to the difference between the Gibbs energies of the solution and a simple weighted average of the Gibbs energies of the pure unmixed components in each phase.

The difference between $g_{S_{Si}}^{0}$ and $g_{S_{Ge}}^{0}$ is equal to the standard molar Gibbs energy of fusion (melting) of pure Si, $\Delta g_{Si}^{fus} = (g_{S_{Si}}^{0} - g_{S_{Ge}}^{0})$. Similarly for Ge, $\Delta g_{Ge}^{fus} = (g_{S_{Ge}}^{0} - g_{S_{Si}}^{0})$.

The Gibbs energy of fusion of a pure component may be written as:

$$\Delta g_{fus}^{0} = \Delta h_{fus}^{0} - T\Delta s_{fus}^{0},$$

where $\Delta h_{fus}^{0}$ and $\Delta s_{fus}^{0}$ are the standard molar enthalpy and entropy of fusion. Since, to a first approximation, $\Delta h_{fus}^{0}$ and $\Delta s_{fus}^{0}$ are independent of $T$, $\Delta g_{fus}^{0}$ is approximately a linear function of $T$. If $T > T_f$, then $\Delta g_{fus}^{0}$ is negative. If $T < T_f$, then $\Delta g_{fus}^{0}$ is positive. Hence, as seen in fig. 2, as $T$ decreases, the $g_l^0$ curve descends relative to $g_s^0$. At 1500°C, $g_l^0 < g_s^0$ at all compositions. Therefore, by the principle that a system always seeks the state of minimum Gibbs energy at constant $T$ and $P$, the liquid phase is stable at all compositions at 1500°C. At 1300°C, the curves of $g_l^0$ and $g_s^0$ cross. The line $PQ$, which is the common tangent to the two curves, divides the composition range into three sections. For compositions between pure Ge and $P_1$, a single-phase liquid is the state of minimum Gibbs energy. For compositions between $Q_1$ and pure Si, a single-phase solid solution is the stable state. Between $P_1$ and $Q_1$, total Gibbs energies lying on the tangent line $P_1Q$, may be realized if the system adopts a state consisting of two phases with compositions at $P_1$ and $Q_1$, and with relative proportions given by the lever rule. Since the tangent line $P_1Q$ lies below both $g_l^0$ and $g_s^0$, this two-phase state is more stable than either phase alone. Furthermore, no other line joining any point on $g_l^0$ to any point on $g_s^0$ lies below the line $P_1Q$. Hence, this line represents the true equilibrium state of the system, and the compositions $P_1$ and $Q_1$ are the liquidus and solidus compositions at 1300°C.

It may be shown that the common tangency condition also results in equal activities of each component in the two phases at equilibrium. That is, equality of activities and minimization of total Gibbs energy are equivalent criteria for equilibrium between phases.

As $T$ is decreased to 1100°C, the points of common tangency are displaced to higher concentrations of Ge. For $T < 937°C$, $g_l^0 < g_s^0$ at all compositions.

It should be noted that absolute values of Gibbs energies cannot be defined. Hence, the relative positions of $g_{S_{Si}}^{0}$ and $g_{S_{Ge}}^{0}$ in fig. 2 are completely arbitrary. However, this is immaterial for the preceding discussion, since displacing both $g_{S_{Si}}^{0}$ and $g_{S_{Ge}}^{0}$ by the same arbitrary amount relative to $g_{L_{Si}}^{0}$ and $g_{L_{Ge}}^{0}$ will not alter the compositions of the points of common tangency.

It should also be noted that in the present discussion of equilibrium phase diagrams, we are assuming that the physical dimensions of the single-phase regions in the system are sufficiently large that surface (interfacial) energy contributions to the Gibbs energy can be neglected. For very fine grain sizes in the sub-micron range however, surface energy effects can noticeably influence the phase boundaries.
The shape of the two-phase (solid + liquid) "lens" on the phase diagram is determined by the Gibbs energies of formation, \( \Delta g^0 \), of the components and by the mixing terms, \( \Delta g^1 \) and \( \Delta g^2 \). In order to observe how the shape is influenced by varying \( \Delta g^2 \), let us consider a hypothetical system A-B in which \( \Delta g^0 \) and \( \Delta g^1 \) are ideal Raoultian (§2.2). Let \( T_{\text{Al}} = 800 \) K and \( T_{\text{Bi}} = 1200 \) K. Furthermore, assume that the entropies of fusion of A and B are equal and temperature-independent. The enthalpies of fusion are then given from eq. (1) by the expression \( \Delta h^0 = T^0 \Delta s_i^0 \) since \( \Delta s_i^0 = 0 \) when \( T = T_i^0 \). Calculated phase diagrams for \( \Delta s^0_i = 3 \), 10 and 30 l/mol K are shown in fig. 3. A value of \( \Delta s^0_i = 0 \) is typical of metal alloys (Richard's rule). Hence, when the components are ionic compounds such as oxides, halides, etc., then \( \Delta s^0_i \) can be significantly larger since there are several atoms per formula unit. Hence, two-phase "lenses" in binary ionic salt or oxide phase diagrams tend to be "fatter" than those encountered in alloy systems. If we are considering vapour-liquid equilibria rather than solid-liquid equilibria, then the shape is determined by the entropy of vaporization, \( \Delta s^v \) (§2.12). Since \( \Delta s^v = 10 \Delta s^0 \), two-phase (liquid + vapour) lenses tend to be very wide.

Fig. 3. Phase diagrams for a system A-B with ideal solid and liquid solutions with \( T_{\text{Al}} = 800 \) K and \( T_{\text{Bi}} = 1200 \) K, calculated for entropies of fusion \( \Delta s^0_A = \Delta s^0_B = 3 \), 10 and 30 l/mol K.

2.2. Minima and maxima in two-phase regions

As discussed in ch. 6, §6, the Gibbs energies of mixing, \( \Delta g^1 \) and \( \Delta g^2 \), may each be expressed as the sum of an ideal (Raoultian) term which is purely entropic and which is given by the Boltzmann equation for a random substitutional solution of A and B particles, and an excess term, \( g^E \).

\[
\Delta g = RT \left( X_A \ln X_A + X_B \ln X_B \right) + g^E.
\]

where \( X_A \) and \( X_B \) are the mole fractions of the components. An ideal or Raoultian solution is defined as in which \( g^E = 0 \). Both the solid and liquid phases in the Ge-Si system (fig. 2) are approximately ideal. With two ideal solutions, a "lens-shaped" two-phase region always results. However, in most alloy systems, even approximately ideal behaviour is the exception rather than the rule.

If \( g^E > 0 \) then the system is said to exhibit positive deviations from ideality. If \( g^E < 0 \), then we speak of negative deviations.

Curves of \( g^E \) and \( g^f \) for a hypothetical system A-B are shown schematically in fig. 4 at a constant temperature below the melting points of pure A and B such that the solid state is the stable state for both pure components. However, in this system \( g^E > g^f \) so that \( g^f \) presents a flatter curve than does \( g^E \) and there exists a central composition region in which \( g^f < g^E \). Hence, there are two common tangent lines, P1O1 and P2O2. Such a situation gives rise to a phase diagram with a minimum in the two-phase region as observed in the Au-Cu system shown in fig. 5 (Hultgren et al. [1963]). At a composition and temperature corresponding to the minimum point, liquid and solid of the same composition exist in equilibrium.

A two-phase region with a minimum point as in fig. 5 may be thought of as a two-phase "lens" which has been "pushed down" by virtue of the fact that the liquid is relatively more stable than the solid. Thermodynamically, this relative stability is expressed as \( g^E < g^f \).

Conversely, if \( g^E > g^f \), to a sufficient extent, then a two-phase region with a maximum will result. In alloy systems, such maxima are nearly always associated with the existence of an intermetallic phase, as will be discussed in §2.8.

Fig. 4. Isothermal Gibbs-energy-composition curves for solid and liquid phases in a system A-B in which \( g^E > g^f \). A phase diagram of the type in fig. 5 results.

References: p. 531.
2.3. Miscibility gaps

If \( g^\theta > 0 \) for a solution, then the solution is thermodynamically less stable than an ideal solution. In an alloy system this can result from a large difference in atomic diameter of the components, which will lead to a (positive) lattice strain energy, or from differences in valence, or from other factors.

In the Au-Ni system, \( g^\theta \) is positive in the solid phase. In the top panel of fig. 6 is plotted \( g^\text{mix} \) at 1200 K (HULTGREEN et al. [1963]) as well as the ideal Gibbs energy of mixing, \( \Delta g^\text{ideal} \), also at 1200 K. The sum of these two terms is the Gibbs energy of mixing \( \Delta g = \Delta g^\text{ideal} + g^\text{mix} \), which is plotted at 1200 K as well as at other temperatures in the central panel of fig. 6. Now,

\[
\Delta g^\text{ideal} = RT \left( X_{Au} \ln X_{Au} + X_{Ni} \ln X_{Ni} \right)
\]

is always negative and varies directly with \( T \), whereas \( g^\theta \) varies less rapidly with temperature. As a result, the sum, \( \Delta g = \Delta g^\text{ideal} + g^\theta \), becomes less negative as \( T \) decreases. However, the limiting slopes to the \( \Delta g^\text{ideal} \) curve at \( X_{Au} = 1 \) and \( X_{Ni} = 1 \) are both infinite

\[
\left( \lim_{X_{Au} \to 1} \frac{d(\Delta g^\text{ideal})}{dX_{Au}} \right) = \lim_{X_{Ni} \to 1} \frac{d(\Delta g^\text{ideal})}{dX_{Ni}} = \infty,
\]

whereas the limiting slopes of \( g^\theta \) are always finite (Henry's Law). Hence, \( g^\theta \) will always be negative as \( X_{Au} \to 1 \) and \( X_{Ni} \to 1 \) no matter how low the temperature. As a result, below a certain temperature the curves of \( \Delta g \) will exhibit two negative "humps". Common tangent lines \( P_1Q_1, P_2Q_2, P_3Q_3 \) to the two humps define the ends of tie-lines of a two-phase solid-solid miscibility gap in the Au-Ni phase diagram which is shown in the lower panel in fig. 6 (HULTGREEN et al. [1963]). The peak of the gap occurs at the critical or consolute temperature and composition, \( T_c \) and \( X_c \).

When \( g^\text{mix} \) is positive for the solid phase in a system it is usually also the case that \( g^\text{sol} < g^\text{mix} \), since the unfavourable factors (such as a difference in atomic dimensions) which are causing \( g^\text{sol} \) to be positive will have less of an influence upon \( g^\text{mix} \) in the liquid phase owing to the greater flexibility of the liquid structure to accommodate different atomic sizes, valencies, etc. Hence, a solid-solid miscibility gap is often associated with a minimum in the two-phase (solid + liquid) region as in the Au-Ni system.

Below the critical temperature the curve of \( \Delta g \) exhibits two inflection points indicated by the letter "s" in fig. 6. These are known as the spinodal points. On the phase diagram their locus traces out the spinodal curve as illustrated in fig. 6. The spinodal

Fig. 6. Phase diagram and Gibbs energy curves of solid solutions for the Au-Ni system (after HULTGREEN et al. [1963]). Letters "s" indicate spinodal points.
2.4. Simple eutectic systems

The more positive \( g^e \) in a system is, the higher is \( T_e \) and the wider is the miscibility gap at any temperature. Suppose that \( g^{\text{mix}} \) is sufficiently positive that \( T_e \) is higher than the minimum in the (solid + liquid) region. The result will be a phase diagram such as that of the Ag–Cu system shown in fig. 7 (Holtgreven et al. [1963]).

In the upper panel of fig. 7 are shown the Gibbs energy curves at 1100 K. The two common tangents define two two-phase regions. As the temperature is decreased below 1100 K, the \( g^e \) curve descends relative to \( g^l \), and the two points of tangency, \( P_1 \) and \( P_2 \), approach each other until, at \( T = 1052\) K, \( P_1 \) and \( P_2 \) become coincident at the composition \( E \). That is, at \( T = 1052 \) K there is just one common tangent line contacting the two portions of the \( g^e \) curve at compositions \( A \) and \( B \) and contacting the \( g^e \) curve at \( E \). This temperature is known as the eutectic temperature, \( T_e \), and the composition \( E \) is the eutectic composition. For temperatures below \( T_e \), \( g^e \) lies completely above the common tangent to the two portions of the \( g^l \) curve and so, for \( T < T_e \) a solid–solid miscibility gap is observed. The phase boundaries of this two-phase region are called the solvs lines. The word eutectic is from the Greek for "to melt well," since an alloy has the lowest melting point at the eutectic composition \( E \).

This description of the thermodynamic origin of simple eutectic phase diagrams is strictly correct only if the pure solid components \( A \) and \( B \) have the same crystal structure (see § 2.6).

Suppose a Ag–Cu alloy of composition \( x_{Ag} = 0.28 \) (composition \( P_1 \)) is cooled from the liquid state very slowly under equilibrium conditions. At 1100 K the first solid appears with composition \( Q_1 \). As \( T \) decreases further, solidification continues with the liquid composition following the liquidus curve from \( P_1 \) to \( E \) and the composition of the solid phase following the solidus curve from \( Q_1 \) to \( A \). The relative proportions of the two phases at any \( T \) are given by the lever rule. At a temperature \( T = (T_e + \delta) \) just above \( T_e \), two phases are observed: a solid of composition \( A \) and a liquid of composition \( E \). At a temperature \( T = (T_e - \delta) \) just below \( T_e \), two solids with compositions \( A \) and \( B \) are observed. Therefore, at \( T_e \), during cooling, the following binary eutectic reaction occurs:

\[
\text{liquid} \rightarrow \text{solid}_1 + \text{solid}_2.
\]

(3)

Under equilibrium conditions the temperature will remain constant at \( T = T_e \) until all the liquid has solidified, and during the reaction the compositions of the three phases will remain fixed at \( A \), \( B \), and \( E \). For this reason the eutectic reaction is called an invariant reaction.

The morphologies of two-phase grains resulting from the co-precipitation of two solids during eutectic reactions are discussed in detail in ch. 8.

2.5. Binary phase diagrams with no intermediate phases

2.5.1. Thermodynamic origin illustrated by simple regular solution theory

Many years ago Vanlaar [1908] showed that the thermodynamic origin of a great many of the observed features of binary phase diagrams can be illustrated at least qualitatively by simple regular solution theory. As discussed in ch. 5, § 6.2, a regular solution is one in which:

\[
g^e = \Omega X_f X_h,
\]

(4)

where \( \Omega \) is a parameter independent of temperature and composition.

In fig. 8 are shown several phase diagrams calculated for a hypothetical system \( A–B \) containing a solid and a liquid phase with melting points of \( T_{\text{m}A}^\text{sa} = 800 \) K and \( T_{\text{m}A}^\text{sa} = 1200 \) K and with entropies of fusion of both \( A \) and \( B \) set to 10 J/mole K, which is a typical value for metals. The solid and liquid phases are both regular with \( g^{\text{mix}} = \Omega X_f X_h \) and \( g^{\text{mix}} = \Omega X_f X_h \). The parameters \( \Omega \) and \( \Omega \) have been varied systematically to generate the various panels of fig. 8.

In panel (a) both phases are ideal. Panels (1–3) exhibit minima or maxima depending upon the sign and magnitude of \( (g^{\text{mix}} - g^{\text{mix}}) \), as has been discussed in § 2.2. In panel (b) the liquid is ideal but positive deviations in the solid give rise to a solid–solid miscibility gap as
2.5.2. Liquid-liquid immiscibility - monotectics

In fig. 8c, positive deviations in the liquid have given rise to a liquid-liquid miscibility gap. An example of a real system with such a phase diagram is the Cu-Pb system shown in fig. 9 (Hultgren et al. [1963]). If a Cu-Pb alloy with \(X_{\text{Cu}}=0.10\) is cooled slowly from the liquid state, solid Cu begins to appear at \(1260\) K. Upon further cooling the liquid composition follows the liquidus curve to point A at \(T=1227\) K. The following invariant monotectic reaction then occurs:

\[
\text{liquid}_A \rightarrow \text{liquid}_A + \text{Cu}_{\text{solid}}
\]  

(5)

where \(\text{liquid}_A\) and \(\text{liquid}_B\) are liquids with compositions at points A and B. The temperature remains constant at the monotectic temperature and the compositions of all phases remain fixed until \(\text{liquid}_A\) is completely consumed. Cooling then continues with precipitation of copper with the liquid composition following the liquidus line from B to the eutectic E.

Returning to fig. 8, we see that in panel (d) the positive deviations in the liquid are not large enough to produce immiscibility but they do result in a flattening of the liquidus which is often described as a "tendency to immiscibility". An example of such a flattened (or "S-shaped") liquidus resulting from a positive g\text{II} is shown later for the Cd-Pb system in fig. 12.

2.5.3. Peritectics

The invariant which appears in fig. 8i is known as a peritectic. The Au-Fe system shown in fig. 10 (Hultgren et al. [1963]) exhibits a peritectic PQR at \(1441\) K as well as another at about \(1710\) K. The Gibbs energy curves, \(g^s\) and \(g^l\), of the liquid and solid face-centred cubic phases are shown schematically at the peritectic temperature of \(T_e=1441\) K in the upper panel of fig. 10. One common tangent line PQR to \(g^l\) and to the two portions of \(g^s\) can be drawn.

![Phase diagram](image)

Fig. 9. The Cu-Pb phase diagram (after Hultgren et al. [1963]).

Fig. 8. Topological changes in the phase diagram of a system A-B with regular solid and liquid phases. Superscripted changes in the regular solution parameters \(\Gamma^A\) and \(\Gamma^B\). Melting points of pure A and B are 800 K and 1200 K. Entropies of fusion of both A and B are \(10.0\) J/mol K. (Pilat and Thompson [1975])

discussed above in § 2.4. On passing from panel (b) to panel (c), an increase in \(g^s\) results in a widening of the miscibility gap so that the solubilities of A in solid B and of B in solid A decrease. Panels (a-c) illustrate that negative deviations in the liquid cause a relative stabilization of the liquid with resultant lowering of the eutectic temperature.

Eutectic phase diagrams are often drawn with the maximum solid solubility occurring at the eutectic temperature (as in fig. 7). However fig. 8d, in which the maximum solubility of A in the B-rich solid solution occurs at approximately \(T=950\) K, illustrates that this need not be the case even for simple regular solutions.
of solid, which can rapidly become coated with solid. By preventing contact between liquid and solid, this coating may greatly retard further reaction to such an extent that equilibrium conditions can only be achieved by extremely slow cooling.

2.5.4. Syntectics

The invariant in fig. 8k in which a solid decomposes upon heating into two liquids is known as a syntectic. It is rarely observed in alloy systems. Examples are found in the K-Pb and K-Zn systems (Hanssen [1958]). A phase diagram similar to fig. 8j, although without the tiny miscibility gap, is exhibited by the Au-Pt system (Hanssen [1958]).

2.6. Limited mutual solid solubility

In § 2.4 the region of two solids in the Ag-Cu phase diagram of fig. 7 was described as a miscibility gap in the solid phase. That is, only one g curve was drawn. If, somehow, the appearance of the liquid phase could be suppressed, then the two solvs lines in fig. 7, when projected upwards, would meet at a critical point (as in the Au-Ni system in fig. 6) above which one continuous solid solution would exist at all compositions.

Such a description is justifiable only if the pure solid components have the same crystal structure. This is the case for Ag-Cu since solid Ag and Cu are both fcc. The same assumption was made in our treatment of the peritectic Au-Fe system (fig. 10) in which the region of two solids was treated as a miscibility gap. Again in this case this description is permissible since Au and Fe are both fcc in this temperature range.

However, consider the simple eutectic system A-B in fig. 11 in which pure solid A and B are hcp (hexagonal close-packed) and fcc respectively. In this case, if the formation of the liquid phase could be suppressed the two solvs lines could not project upward to meet at a critical point, since this would imply that above this critical temperature a continuous series of solid solutions varying smoothly from hcp in fcc could exist. Such a situation is prohibited by symmetry conditions. That is, one continuous curve for g cannot be drawn. Each solid phase must have its own separate Gibbs energy curve, as shown schematically in the upper panels of fig. 11. In this figure $g_{A}^{\text{solid}}$ is the standard molar Gibbs energy of pure fcc A and $g_{B}^{\text{hcp}}$ is the standard molar Gibbs energy of pure hcp B. Such quantities may be defined in a number of different and non-equivalent ways as will be discussed below.

A real system with a phase diagram similar to fig. 11 is the Cd-Pb system shown in fig. 12 (Asitakala et al. [1981]). Gibbs energy curves at a temperature below the eutectic are shown schematically in the upper panel. Let us derive an expression for $g$ under the assumption that the Pb-rich fcc solid solution is a Henrian solution. As discussed in ch. 5, § 6.2, when a solution is sufficiently dilute in one component, Henrian behaviour may be assumed. That is, the activity of the solvent is ideal ($a_{\text{solvent}}=X_{\text{solvent}}$), $\gamma_{\text{solvent}}=1$, while for the solute, $a_{\text{solute}}=\gamma_{\text{solute}}X_{\text{solute}}$, where the Henrian activity coefficient $\gamma_{\text{solute}}$ is independent of composition. At $T_{B}=247.8^\circ C$ in fig. 12, Cd in the Pb-rich fcc solution at $X_{\text{Cd}}=0.940$ exists in equilibrium with virtually pure solid hcp Cd. Thus, in the fcc solution, $a_{\text{Cd}}=1.0$ with respect to pure solid hcp Cd as standard state. Hence, $\gamma_{\text{Cd}}=a_{\text{Cd}}/X_{\text{Cd}}=1.0/0.940=1.067$ at 247.8$^\circ C$. We can now express $g$ as:

References. p 531.
Fig. 11. Phase diagram and Gibbs energy curves at two temperatures for a simple eutectic system A-B in which pure solid A and B have different crystal structures.

\[
g_{\text{fcc}} = \left( X_{\text{Cd}} \gamma_{\text{Cd}}^{(\text{hep})} + X_{\text{Pb}} \gamma_{\text{Pb}}^{(\text{hep})} \right) + RT \left[ X_{\text{Cd}} \ln \gamma_{\text{Cd}}^{(\text{hep})} + X_{\text{Pb}} \ln \gamma_{\text{Pb}}^{(\text{hep})} \right] \]

\[
= \left( X_{\text{Cd}} \gamma_{\text{Cd}}^{(\text{hep})} \right) + RT \left[ X_{\text{Cd}} \ln \gamma_{\text{Cd}}^{(\text{hep})} + X_{\text{Pb}} \ln \gamma_{\text{Pb}}^{(\text{hep})} \right] + \frac{RT \ln \gamma_{\text{Cd}}^{(\text{hep})}}{X_{\text{Cd}}}
\]

(7)

However, since \( \gamma_{\text{Cd}}^{(\text{hep})} \) is independent of composition we can combine terms as follows:

\[
g_{\text{fcc}} = \left[ X_{\text{Cd}} \left( \frac{\gamma_{\text{Cd}}^{(\text{hep})}}{X_{\text{Cd}}} + RT \ln \gamma_{\text{Cd}}^{(\text{hep})} \right) \right] + \frac{RT \ln \gamma_{\text{Cd}}^{(\text{hep})}}{X_{\text{Cd}}}
\]

\[
(8)
\]

Let us now define:

\[
g_{\text{Cd}}^{(\text{hep})} = \left( \gamma_{\text{Cd}}^{(\text{hep})} + RT \ln \gamma_{\text{Cd}}^{(\text{hep})} \right)
\]

From eq. (8) it can be seen that relative to \( g_{\text{Cd}}^{(\text{hep})} \) defined in this way and to \( g_{\text{Pb}}^{(\text{hep})} \) the fcc solution is ideal. This is illustrated in fig. 12.

At 247.8°C in Cd-Pb, \( g_{\text{Cd}}^{(\text{hep})} - g_{\text{Pb}}^{(\text{hep})} = RT \ln \gamma_{\text{Cd}} = R(247.8 + 273.15) \ln 16.67 = 12.19 \) kJ/mol. As a first approximation we could take this value to be independent of \( T \), or as a second approximation we could evaluate \( \gamma_{\text{Cd}}^{(\text{hep})} \) at other temperatures along the solidus and express \( \left( g_{\text{Cd}}^{(\text{hep})} - g_{\text{Pb}}^{(\text{hep})} \right) \) as, say, a linear function of \( T \).

Although the above treatment has the advantage of numerical simplicity, it suffers from the difficulty that the numerical value of \( g_{\text{Cd}}^{(\text{hep})} - g_{\text{Pb}}^{(\text{hep})} \) is solvent–dependent and will be different for, say, solutions of Cd in fcc Cu and Cd in fcc Pb. For purposes of predicting binary phase diagrams from first principles or for estimating ternary phase diagrams from binary phase diagrams (§5.5) it would be desirable if \( g_{\text{Cd}}^{(\text{hep})} \) could be defined to be system-independent so as to be truly the "standard molar Gibbs energy of metastable fcc Cd". A great deal of effort has been expended by the international CALPHAD group under the impetus of Kaufman (Kaufman and Bernstein [1970]) and

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co-workers to compile tables of lattice stabilities for metals in the fcc, hcp, bcc, and liquid states (that is, to obtain a set of relative values of $g^{(0)}$, $g^{(1)}$, $g^{(2)}$, and $g^{(3)}$ for every metal). In some cases, these can be calculated by extrapolating thermodynamic data from regions of $T$ and $P$ where the phases are stable. In other cases, lattice stabilities can be estimated partly from theoretical calculations and partly from the analysis of a large number of binary phase diagrams followed by a judicious choice of the "best" values which must closely fit the greatest number of systems. Tabulations of lattice stabilities are now available for many metals (Dinsdale [1991]).

### 2.7. Calculation of limiting slopes of phase boundaries

In fig. 12 we see that the solubility of Pb in solid Cd is very small. The actual solubility at $T_0^*$ is about 0.14 mol% (Hansen [1958]). In thermodynamic terms this means that $g^{(0)}$ increases very rapidly as Pb is added to solid Cd (see fig. 12), or that the Henrian activity coefficient $\gamma_{\text{mol}}^*$ is very large. The fact that the solubility of Cd in solid Pb is much greater than that of Pb in solid Cd can be understood in terms of the Hume-Rothery rule (ch. 4) that solubilities are greater when the solute atoms are smaller than the solvent atoms, since the lattice strain energy will be less and hence $g$ will rise less rapidly upon addition of solute.

As discussed later in §7, it is usually more difficult experimentally to determine a solubility than it is to measure liquidus temperatures. However, if the liquidus has been measured in the limit as $X_{\text{solid}} \rightarrow 1$, then the limiting slope of the solidus can be calculated. Let component B be the solvent in a system A–B. The partial Gibbs energies of B along the liquidus and solidus are equal ($g_B^* = g_B^{(0)} = 0$). Hence:

$$g_A^* - g_A^{(0)} = (g_B^* - g_B^{(0)}) = \frac{RT}{a_B} \ln \frac{a_A}{a_B}$$

But:

$$g_A^* - g_A^{(0)} = RT \ln \frac{a_A}{a_B}$$

where $a_A^*$ and $a_B^*$ are activities of B on the liquidus and solidus with respect to the pure liquid and pure solid standard states respectively. Hence, eq. (9) may be written as:

$$RT \ln \frac{a_B^*}{a_B} \rightarrow RT \ln \frac{a_B^*}{a_B} = -\Delta g_B^{(0)}.$$  

In the limit $X_B \rightarrow 1$, Raoult's Law holds for both phases. That is, $a_B^* \rightarrow X_B^*$ and $a_B^\infty \rightarrow X_B^\infty$. Hence, in the limit, eq. (10) may be written as:

$$RT \ln \frac{X_B^\infty}{X_B} = -\Delta g_B^{(0)}.$$  

Furthermore, in the limit, $T \rightarrow T_\text{lim}$ and from eq. (1) $\Delta g_B^{(0)} \rightarrow \Delta h_B^{(0)} (1 - T/T_\text{lim})$. Finally, $\lim_{X_{\text{solid}} \rightarrow 1} (\ln X_B^*) = (X_B - 1)$. Substituting these limiting values into eq. (11) we obtain:

$$\lim_{X_{\text{solid}} \rightarrow 1} (\frac{dX_B^\infty}{dT} - \frac{dX_B^\infty}{dT}) = \frac{\Delta h_B^{(0)}}{R(T_\text{lim})^2}.$$  

If the limiting slope of the liquidus, $\lim_{X_{\text{solid}} \rightarrow 1} (dX_B^\infty/dT)$, is known, then the limiting slope of the solidus can be calculated via eq. (12) if the enthalpy of fusion is known.

For the Cd–Pb system, limiting liquidus slopes were calculated for both components from eq. (12) under the assumption that there is no solid solubility (that is, $dX_B^\infty/dT = 0$). These are shown as the dashed lines on fig. 12. In Cd-rich solutions, agreement with the measured limiting liquidus slope is very good, but in Pb-rich solutions the poor agreement indicates the existence of appreciable solid solubility as has been confirmed by direct measurement.

### 2.8. Intermediate phases

The phase diagram of the Ag–Mg system (Hultgren et al. [1963]) is shown in fig. 13. An intermetallic phase, $\beta^*$, is seen centered approximately at the composition

![Fig. 13. Ag–Mg phase diagram](image-url)
The Gibbs energy curve for such an intermetallic phase has the form shown schematically in the upper panel of fig. 13. \( g' \) rises quite rapidly on either side of its minimum which occurs near \( X_{\text{Na}} = 0.5 \). As a result, the \( \beta' \) phase appears on the phase diagram only over a limited composition range. This form of the curve \( g' \) results from the fact that when \( X_{\text{Na}} = X_{\text{Mg}} \), a particularly stable crystal structure exists in which Ag and Mg atoms preferentially occupy different sites. The two common tangents \( P_1Q_1 \) and \( P_2Q_2 \) give rise to a maximum in the two-phase (\( \beta' + \text{liquid} \)) region in the phase diagram. (Although the maximum is observed very near \( X_{\text{Na}} = 0.5 \), there is no thermodynamic reason for the maximum to occur exactly at this composition.)

The Na–Bi phase diagram is shown in fig. 14 (Hansen [1958]). Gibbs energy curves at 700°C are shown schematically in the upper panel. \( g(Na_{x}Bi_{1-x}) \) rises extremely rapidly on either side of its minimum which occurs at \( x = 0.7 \), \( x = 1 \). (We write \( g(Na_{x}Bi_{1-x}) \) rather than \( g(Na_{x}Bi) \) in order to normalize the basis of one mole of metal atoms.) As a result, the points of tangency \( Q_1 \) and \( Q_2 \) of the common tangents \( P_1Q_1 \) and \( P_2Q_2 \) are nearly (but not exactly) coincident. Hence, the composition range over which single-phase NaBi exists (sometimes called the range of stoichiometry or homogeneity)

![Fig. 14. Na–Bi phase diagram (after Hansen [1958]) and schematic Gibbs energy curves at 700°C.](image)

range of NaBi is very narrow (but never zero). The two regions labelled (NaBi + liquid) in fig. 14 are the two sides of a two-phase region which passes through a maximum just like the (\( \beta' + \text{liquid} \)) regions in fig. 13. Because the NaBi single-phase region is so narrow we refer to NaBi as an intermetallic compound. In the case of NaBi, any slight deviation from the stoichiometric composition causes a very large increase in Gibbs energy. Owing to the large difference in electronegativities of Na and Bi, NaBi could be considered to be a semi-ionic compound. Deviations from stoichiometry would require the substitution of Na on Bi sites or vice versa which would be energetically very unfavourable.

If stoichiometric NaBi is heated, it will melt isothermally at 775°C to form a liquid of the same composition. That is, the melting behaviour of NaBi is similar to that of a pure element. Such intermetallic compounds are called congruently melting or simply congruent compounds. The \( \beta' \) phase in fig. 13 might also be called a congruent intermetallic compound AgMg (or AgMg_{1-x}). It is debatable, however, whether a phase with such a wide range of composition should really be called a "compound".

It should be noted with regard to the congruent melting of NaBi in fig. 14 that the limiting slopes d\( T/\text{d}X \) of the two liquidus curves at the congruent melting point (775°C) are both zero, since we are really dealing with a maximum in a two-phase region and not with the melting of an element.

Another intermetallic phase, the e phase, is also observed in the Ag–Mg system, fig 13. This phase has a narrow range of stoichiometry around the composition AgMg_{1-x}. This phase is associated with a peritectic invariant ABC at 744 K. The Gibbs energy curves are shown schematically at the peritectic temperature in the central panel of fig. 13. One common tangent line can be drawn to \( g' \), \( g'' \), and \( g''' \).

Suppose that a liquid alloy of composition \( X_{\text{Na}} = 0.7 \) is cooled very slowly from the liquid state. At a temperature just above 744 K a liquid phase of composition C and a \( \beta' \) phase of composition A are observed at equilibrium. At a temperature just below 744 K, the two phases at equilibrium are \( \beta' \) of composition A and e of composition B. The following invariant peritectic reaction thus occurs upon cooling (cf. § 2.5.3):

\[
\text{liquid} + \beta'(\text{solid}) \rightarrow e(\text{solid})
\]

This reaction occurs isothermally at 744 K with all three phases at fixed compositions (at points A, B and C). For an alloy with overall composition between points A and B the reaction proceeds until all the liquid has been consumed. In the case of an alloy with overall composition between B and C, the \( \beta' \) phase will be the first to be completely consumed.

The AgMg_{1-x} compound is said to melt incongruently. If solid AgMg is heated, it will melt isothermally at 744 K, by the reverse of the above peritectic reaction (14), to form a liquid of composition C and another solid phase, \( \beta' \), of composition A.

Another example of an incongruent compound is the compound NaBi in fig. 14. This compound has a very narrow range of stoichiometry. When heated, it melts incongruently (or peritectically) at the peritectic temperature of 446°C to form another solid, NaBi, and a liquid of composition \( X_{\text{Na}} = 0.53 \).

An incongruent compound is always associated with a peritectic. (The word peritectic comes from the Greek for (loosely) "to melt in an indirect way"). However, the converse...
is not necessarily true. A peritectic is not always associated with an intermediate phase. See, for example, fig. 10.

For purposes of phase diagram computations involving very stoichiometric compounds such as Na$_2$Bi we may, to a good approximation, consider the Gibbs energy curve, $g$($Na_2Bi$,T), to have zero width. Then all we need is the numerical value of $g$($Na_2Bi$,T$_{min}$) at the minimum. This value is usually expressed in terms of the Gibbs energy of formation of the compound, $\Delta G^{\text{formation}}_{Na_2Bi}$, or in terms of the "Gibbs energy of fusion of the compound", $\Delta G^{\text{fusion}}_{Na_2Bi}$, of the compound from solid Na and Bi according to the reaction $\frac{1}{2}$Na$_2$ + $\frac{1}{2}$Bi$_2$ = Na$_2$Bi$_{\text{solid}}$. Both these quantities are interpreted graphically in fig. 14.

2.9. Topology of binary phase diagrams

In ch. 5, §8.2 the Gibbs phase rule was derived:

$$F = C - P + 2,$$

(14)

where $C$ is the number of components, $P$ the number of phases in equilibrium, and $F$ the number of degrees of freedom or variance. That is, $F$ is the number of parameters which can and must be specified in order to completely specify the state of the system. In the present context, the thermodynamic parameters are temperature, total pressure, and the compositions of the phases at equilibrium. Since binary temperature-composition phase diagrams are plotted at constant pressure, usually 1 bar, one degree of freedom is already used up. In a binary system, $C = 2$. Hence, for binary isoobaric $T-X$ diagrams the phase rule reduces to:

$$F = 3 - P.$$

(15)

Binary $T-X$ diagrams contain single-phase areas and two-phase areas. In the single-phase areas, $F = 3 - 1 = 2$. That is, temperature and composition can be varied independently. These regions are thus called bivariant. In two-phase regions, $F = 3 - 2 = 1$. If, say, $T$ is chosen, then the compositions of both phases are fixed by the ends of the tie-lines. Two-phase regions are thus termed univariant. Note that the overall composition can be varied within a two-phase region at constant $T$, but the overall composition is not a variable in the sense of the phase rule. Rather, it is the compositions of the individual phases at equilibrium that are the variables to be considered in counting the number of degrees of freedom.

When three phases are at equilibrium in a binary system at constant pressure, $F = 3 - 3 = 0$. Hence, the compositions of all three phases as well as $T$ are fixed. There are two general types of three-phase invariants in binary phase diagrams. These are the eutectic-type and peritectic-type invariants as illustrated in fig. 15. Let the three phases concerned be called $\alpha$, $\beta$, and $\gamma$, with $\beta$ as the central phase as shown in fig. 15. $\alpha$, $\beta$ and $\gamma$ can be solid, liquid or gaseous phases. At the eutectic-type invariant, the following invariant reaction occurs isothermally as the system is cooled:

$$\beta \rightarrow \alpha + \gamma,$$

(16)

whereas, at the peritectic-type invariant the invariant reaction upon cooling is:

$$\alpha + \gamma \rightarrow \beta.$$

(17)

Some examples of eutectic-type invariants are: (i) eutectics (fig. 7) in which $\alpha = \text{solid}_1$, $\beta = \text{liquid}$, $\gamma = \text{solid}_2$. The eutectic reaction is $l \rightarrow s_1 + s_2$; (ii) monotectics (fig. 9) in which $\alpha = \text{liquid}$, $\beta = \text{solid}_1$, $\gamma = \text{solid}_2$. The monotectic reaction is $l \rightarrow l_1 + s_1 + s_2$; (iii) eutectoids (fig. 10) in which $\alpha = \text{solid}_1$, $\beta = \text{solid}_2$, $\gamma = \text{solid}_3$. The eutectoid reaction is $s_2 \rightarrow s_1 + s_3$; (iv) cutaeitics in which $\alpha = \text{liquid}$, $\beta = \text{solid}_2$, $\gamma = \text{solid}_3$. The cutaeitic reaction is $s_2 \rightarrow l + s_3$.

Some examples of peritectic type invariants are: (i) peritectics (fig. 10) in which $\alpha = \text{liquid}$, $\beta = \text{solid}_1$, $\gamma = \text{solid}_2$. The peritectic reaction is $l + s_1 \rightarrow s_2$; (ii) syntectics (fig. 8k) in which $\alpha = \text{liquid}$, $\beta = \text{solid}_1$, $\gamma = \text{liquid}$. The syntectic reaction is $l + l_1 \rightarrow s_2$; (iii) peritectoids in which $\alpha = \text{solid}_1$, $\beta = \text{solid}_2$, $\gamma = \text{solid}_3$. The peritectoid reaction is $s_1 + s_3 \rightarrow s_2$.

An important rule of construction which applies to invariants in binary phase diagrams is illustrated in fig. 15. This extension rule states that at an invariant the extension of a boundary of a two-phase region must pass into the adjacent two-phase region and not into the single-phase region. Examples of both correct and incorrect constructions are given in fig. 15. To understand why the "incorrect extension" shown is not correct, consider that the $(\alpha + \gamma)$ phase boundary line indicates the composition of the $\gamma$-phase in equilibrium with the $\alpha$-phase as determined by the common tangent to the

![Fig. 15. Some topological units of construction of binary phase diagrams illustrating rules of construction.](image-url)

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Gibbs energy curves. Since there is no reason for the Gibbs energy curves or their
derivatives to change discontinuously at the invariant temperature, the extension of the
(α + γ) phase boundary also represents the composition of the γ-phase in equilibrium
with the α-phase. Hence, for this line to extend into a region labelled as single-phase γ
is incorrect.

Two-phase regions in binary phase diagrams can terminate: (i) on the pure com-
ponent axes (at \(X_A = 1\) or \(X_B = 1\)) at a transformation point of pure A or B; (ii) at a
critical point of a miscibility gap; (iii) at an invariant. Two-phase regions can also exhibit
maxima or minima. In this case, both phase boundaries must pass through their max-
um or minimum at the same point as shown in fig. 15.

All the topological units of construction of binary phase diagrams have now been
discussed. The phase diagram of a binary alloy system will usually exhibit several of
these units. As an example, the Fe-Mo phase diagram (KUBASCHIESKI [1982]) is shown
in fig. 16. The invariants in this example are: peritectics at 1540, 1488, and 1450°C;
quenotypes at 1235 and 1206°C; peritectoids at 1370 and 950°C. The two-phase (liquid
+ γ) region passes through a minimum at \(X_{Mo} = 0.2\).

Between 910°C and 1390°C is a two-phase (α + γ) γ-loop. Pure Fe adopts the fcc γ
structure between these two temperatures but exists as the bcc α phase at higher and
lower temperatures. Mo however, is more soluble in the bcc than in the fcc structure.
That is, \(g_{bcc(Fe)} < g_{bcc(Mo)}\) as discussed in §2.6. Therefore, small additions of Mo
stabilize the bcc structure.

2.9.1. Order–disorder transformations

In fig. 13 for the Ag–Mg system, a transformation from an α' to an α phase is shown
occurring at approximately 390 K at the composition Ag_6Mg. This is an order–disorder
transformation. Below the transformation temperature, long-range ordering (superlattice
formation) is observed. An order parameter may be defined which decreases to zero at
the transformation temperature. This type of phase transformation is not necessarily a
first-order transformation like those considered so far in this chapter. Unlike transforma-
tions which involve atomic displacements over distances large compared with atomic
dimensions, order–disorder transformations, at least at the stoichiometric composition
(Ag,Mg is this example), occur by atomic rearrangement over distances of the order of
atomic dimensions. The slope of the curve of Gibbs energy versus \(T\) is not necessarily
discontinuous at the transformation temperature. For a detailed discussion see ch. 4,
§4.1.1, INDEN [1982], and PITSCH and INDEN [1991].

A type of order–disorder transformation of importance in ferrous metallurgy is the
magnetic transformation. Below its Curie temperature of 769°C, Fe is ferromagnetic.
Above this temperature it is not. The transformation involves a change in ordering of
the magnetic domains and is not first-order. Additions of alloying elements will change
the temperature of transformation. Magnetic transformations are treated in ch. 29. See also
MODROWNIK [1982], INDEN [1982] and HILBERT and JARL [1978].

2.10. Application of thermodynamics to phase diagram analysis

In recent years, the development of solution models, numerical methods and computer
software has permitted a quantitative application of thermodynamics to phase diagram
analysis. Computer programs are available which permit phase diagrams to be generated
from equations for the Gibbs energies of the phases. Other programs have been written
to perform simultaneous critical evaluations of available phase diagram measurements
and of available thermodynamic data (calorimetric data, measurements of activities, etc.)
with a view to obtaining optimized equations for the Gibbs energies of each phase which
best represent all the data. These equations are consistent with thermodynamic principles
and with theories of solution behaviour.

The phase diagram can be calculated from these optimized thermodynamic equations,
and so one set of self-consistent equations describes all the thermodynamic properties
and the phase diagram. This technique of analysis greatly reduces the amount of
experimental data needed to characterize a system fully. All data can be tested for
internal consistency. The data can be interpolated and extrapolated more accurately, and
metastable phase boundaries can be calculated. All the thermodynamic properties and the
phase diagram can be represented and stored by means of a small set of coefficients.

Finally and most importantly, it is often possible to estimate the thermodynamic
properties and phase diagrams of ternary and higher-order systems from the assessed
parameters for their binary sub-systems as will be discussed in §5. The analysis of
binary systems is thus the first and most important step in the development of databases
for multicomponent systems.

The computer coupling of thermodynamics and phase diagrams is a growing field of
much current research interest. The international Calphad Journal, published by Per-
gamon Press, and an annual international meeting, the Calphad Conference, are now
devoted to this subject.

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2.10.1. Polynomial representation of excess properties

Empirical equations are required to express the excess thermodynamic properties of the solution phases as functions of composition and temperature. For many simple binary solution systems, a good representation is obtained by expanding the molar excess enthalpy and entropy as polynomials in the mole fractions $X_A$ and $X_B$ of the components:

\[ h^e = X_A X_B (h_0 + h_1 (X_B - X_A) + h_2 (X_B - X_A)^2 + h_3 (X_B - X_A)^3 + \ldots) \]  
\[ s^e = X_A X_B (s_0 + s_1 (X_B - X_A) + s_2 (X_B - X_A)^2 + s_3 (X_B - X_A)^3 + \ldots) \]  

(18)  
(19)

where the $h_i$ and $s_i$ are empirical coefficients. As many coefficients are used as are required to represent the data in a given system. For most systems it is a good approximation to assume that the coefficients $h_i$ and $s_i$ are independent of temperature.

If the series are truncated after the first term, then:

\[ g^e = h^e - T s^e = X_A X_B (h_0 - T s_0) \]  

(20)

This is the same as eq. (4) for a regular solution. Hence, the polynomial representation can be considered to be an extension of regular solution theory. When the expansions are written in terms of the composition variable $(X_B - X_A)$ as in eqs. (18) and (19) they are said to be in Redlich-Kister form. Other equivalent polynomial expansions such as orthogonal Legendre series have been discussed by Pelton and Bale [1986].

Differentiation of eqs. (18) and (19) yields the following expansions for the partial excess properties:

\[ h_A^e = X_B \sum_{i=0}^\infty h_i (X_B - X_A)^i - 2iX_A (X_B - X_A)^i \]  
\[ h_B^e = X_A \sum_{i=0}^\infty h_i (X_B - X_A)^i + 2iX_B (X_B - X_A)^i \]  
\[ s_A^e = X_B \sum_{i=0}^\infty s_i (X_B - X_A)^i - 2iX_A (X_B - X_A)^i \]  
\[ s_B^e = X_A \sum_{i=0}^\infty s_i (X_B - X_A)^i + 2iX_B (X_B - X_A)^i \]  

(21)  
(22)  
(23)  
(24)

2.10.2. Least-squares optimization

Eqs. (18), (19) and (21) to (24) are linear in terms of the coefficients. Through the use of these equations, all integral and partial excess properties $(g^e, h^e, s^e, g_A^e, h_A^e, s_A^e)$ can be expressed by linear equations in terms of the one set of coefficients $[h_i, s_i]$. It is thus possible to include all available experimental data for a binary phase in one simultaneous linear least-squares optimization as discussed by Bale and Pelton [1983].

Lukas et al. [1977] and Dörner et al. [1980], and specialized software for such optimizations is available.

The technique of coupled thermodynamic/phase diagram analysis is best illustrated by an example. The phase diagram of the Cd–Na system with points measured by several authors is shown in fig. 17. From electromotive force measurements on alloy concentration cells, several authors have measured the activity coefficient of Na in liquid alloys. These data are shown in fig. 18 at 400°C. From the temperature dependence of $\gamma_{Na} = \exp(\frac{\Delta F}{RT})$ in $\gamma_{Na}$, the partial enthalpy of Na in the liquid was obtained via the Gibbs-Helmholtz equation. The results are shown in fig. 19. Also, $h^e$ of the liquid has been measured (Kleinsteuber [1961]) by direct calorimetry.

Along the Cd-liquidus in fig. 17 the partial Gibbs energy of Cd in the liquid is equal to that of essentially pure solid Cd with which it is in equilibrium:

\[ \Delta g_{Cd} = \Delta g_{Cd}^{(0)} \]  

(25)

Hence,

\[ \Delta g_{Cd} - \Delta g_{Cd}^{(0)} = \Delta g_{Cd}^{(0)} - \Delta g_{Cd} \]  

(26)

Fig. 17. Cd–Na phase diagram calculated from optimized thermodynamic parameters (Reprinted from Pelton [1988]).

- Kurnakov and Rosenzweig [1907]
- Mathiew [1966]
- Wykes and Davies [1964]

References: p. 531.
Fig. 18. Sodium activity coefficient in liquid Cd-Na alloys at 400°C. Line is calculated from optimized thermodynamic parameters (Reprinted from Pelton [1988]).

\[ RT \ln X^\text{liq}_{\text{Cd}} + 8600 = -\Delta G^\text{liq}_{\text{Cd}} \]

(27)

Therefore, from the experimental liquidus composition \( X^\text{liq}_{\text{Cd}} \), and from a knowledge of the Gibbs energy of fusion, \( \Delta G^\text{liq}_{\text{Cd}} \), at the measured liquidus points can be calculated from eq. (27).

Similar equations relating the liquidus compositions along the \( \text{Cd}_{85}\text{Na}_{15} \) and \( \text{Cd}_{75}\text{Na}_{25} \) liquidus lines to the partial excess Gibbs energies of the liquid and to the Gibbs energies of fusion of \( \text{Cd}_{85}\text{Na}_{15} \) and \( \text{Cd}_{75}\text{Na}_{25} \) can be written based upon the graphical construction shown in fig. 14.

The thermodynamic data for \( \Delta G^\text{liq}_{\text{Cd}}, \Delta H^\text{liq}_{\text{Cd}} \), and \( \Delta H^\text{liq}_{\text{Na}} \) as well as the measured liquidus points and the Gibbs energies of fusion of the compounds were optimized simultaneously by a least-squares technique to obtain the following optimized expressions (Pelton [1988]):

\[ h^\text{liq}_{\text{Cd}} = X_{\text{Cd}} X_{\text{Na}}(-12508 + 20316(X_{\text{Na}} - X_{\text{Cd}})) \]

\[ -8714(X_{\text{Na}} - X_{\text{Cd}})^2 \text{J/mol} \]

\[ \Delta G^\text{liq}_{\text{Cd}} = 8368 - 12.737T \text{ J/g-atom} \]

\[ \Delta H^\text{liq}_{\text{Cd}} = 5620 - 10.4344T \text{ J/g-atom} \]

\[ \Delta G^\text{liq}_{\text{Na}} = 2598 - 7.0035T \text{ J/g-atom} \]

The optimizations of the fusion of \( \text{Cd} \) and \( \text{Na} \) were taken from Chase [1983] and were not changed in the optimization. The optimized enthalpies of fusion of 6816 and 8368 J/g-atom for the two compounds in eqs. (28), (31) were modified from the values of 6987 and 7878 J/g-atom measured by Ross [1916]. These changes are within the experimental error limits. Eq. (28) reproduces the calorimetric data within 200 J/mol. Eqs. (22), (24) can be used to calculate \( h^\text{liq}_{\text{Cd}} \) and \( \Delta G^\text{liq}_{\text{Cd}} \). The calculated curves are compared to the measured points in figs. 18 and 19. The phase diagram shown in fig. 17 was calculated from eqs. (28) to (33). Complete details of the analysis of the Cd-Na system are given by Pelton [1988].

It can thus be seen how one simple set of equations can simultaneously and self-consistently describe all the thermodynamic properties and the phase diagram of a binary system. The exact optimization procedure will vary from system to system depending on the type and accuracy of the available data, the number of phases present, the extent of

References: p. 531. 
solid solubility, etc. A large number of optimizations have been published in the Calphad Journal since 1977.

2.10.3. Calculation of metastable phase boundaries

In the Cd–Na system just discussed, the liquid exhibits positive deviations from ideal mixing. That is, $g^\text{ex}>0$. This fact is reflected in the very flat liquidus in fig. 17 as was discussed in §2.5.2.

By simply not including any solid phases in the calculation, the metastable liquid miscibility gap as well as the spinodal curve (§2.3) can be calculated as shown in fig. 17. These curves are of importance in the formation of metallic glasses by rapid quenching (see ch. 19, §2.1).

Other metastable phase boundaries, such as the extension of a liquidus curve below a eutectic, can also be calculated thermodynamically simply by excluding one or more phases during the computations.

2.11. Solution models

Polynomial expansions, as in eqns (18, 19), give an adequate representation of the excess mixing properties for simple substitutional solutions in which deviations from regular solution behaviour are not too large. In other cases, more sophisticated models are required.

The Gibbs energy of a regular solution is given by combining eqns. (2) and (4). The ideal mixing term in eq. (2) is a consequence of the assumption that A and B atoms form a random substitutional solution. The parameter $\Omega$ in eq (4) can be interpreted as resulting from the fact that the energy of A-B bonds in the solution is different from that of A-A and B-B bonds. Suppose that A-B bonds are energetically favourable. The solution is thereby stabilized, $\Omega<0$ and $g^a<0$. However, the distribution will then no longer be random because A and B atoms will tend to favour each other as nearest neighbours, and so the ideal mixing term, $RT(X_A \ln X_A + X_B \ln X_B)$ in eq. (2) is no longer correct. For relatively small deviations from ideality, the random mixing approximation is often acceptable. However, for larger deviations, the non-randomness becomes important. In such cases, a simple polynomial expansion for $g^a$ as in eqns. (18, 19) is insufficient.

The regular solution model can be extended to account for this non-randomness through the quasichemical model for short-range ordering developed by Guggenheim [1935] and Fowler and Guggenheim [1939]. Many liquid alloy solutions exhibit short-range ordering. The ordering is strongest when one component is relatively electropositive (on the left side of the periodic table) and the other is relatively electronegative. Liquid alloys such as AlK–Au (Hensel [1979]), AlK–Pb (Saroungi et al. [1985]) and AlK–Bi (Petricek et al. [1988]), where AlK = (Na, K, Rb, Cs) exhibit strong short-range ordering, as do liquid semiconductor solutions such as GaAs and InSb. The quasichemical model has been recently adapted to permit thermodynamic/phase diagram optimizations of such systems (Pfitzner and Blander [1984, 1986, 1988]).

Short-range ordering in liquid alloys has also been modeled by treating such solutions as substitutional solutions of A atoms, B atoms and A-B, "complexes". See for example, Luck et al. [1989] For most alloy systems, however, such association models are not physically realistic.

For an interstitial solution the ideal Gibbs energy of mixing is that of a random distribution of the solute atoms over the interstitial sites. For example, in an interstitial solution of C in γ-Fe, Xc, moles of C atoms are distributed over Xr octahedral sites. The molar Gibbs energy of mixing is thus:

$$\Delta g = RT \left( \frac{Xr}{Xr + Xc} \right) Xc \ln \frac{Xc}{Xr} + Xr \ln \left( \frac{Xr - Xc}{Xr} \right) \frac{Xr - Xc}{Xr}$$

(34)

$$= RT Xc \ln \frac{Xc}{1 - 2Xc} + Xr \ln \left( 1 - \frac{Xc}{Xr} \right) \frac{Xr}{Xr}$$

The ideal activities are thus:

$$a^\text{ideal}_c = \frac{Xc}{Xr}$$

(35)

$$a^\text{ideal}_r = \left( 1 - \frac{Xc}{Xr} \right)$$

(36)

When modeling an interstitial solution, one should employ these expressions.

A multicomponent interstitial solution such as Mg–Mg–C–N, where Mg and Mg are metals, can be considered to consist of two sublattices: a metallic sublattice on which C, N and Mg sites are distributed, and an interstitial sublattice on which C, N (and vacant sites) are distributed. General sublattice models, of which such solutions are a special case, have been discussed by HILLERT et al. [1985]. An example of application to the Fe–Cr–V–C system is given in §5.

Examples of non-stoichiometric compound phases were shown in figs 13 and 16. When these exhibit a relatively narrow range of stoichiometry, as is the case for AgMg, in fig. 14, the phase is conveniently described as a dilute solution of defects in the stoichiometric compound. For example, consider a compound A$_x$B$_{1-x}$. The lattice sites normally occupied by A atoms we shall call "A sites", and those normally occupied by B atoms are "B sites". The dissolution of excess B in the compound can occur by the formation of defects. Example of such defects are (i) B atoms occupying A sites; (ii) vacant A sites; (iii) B atoms occupying interstitial sites; etc. Generally, one type of defect will predominate in any given system when B is in excess, and this is called the majority defect for solutions with excess B. When excess A is added to A$_x$B$_{1-x}$, then another majority defect predominates. It should, of course, be noted that certain compounds, such as FeO, or Ni$_x$Al near room temperature, do not even contain the stoichiometric composition within their range of single-phase stoichiometry.

Despite the large number of defect types which can occur, a quite general thermodynamic model can be proposed. Let $X_i$ be the mole fraction of the majority defects which occur when A is in excess. This is the mole fraction of these defects on the sublattice (or interstitial lattice) which they occupy. Similarly, $X_j$ is the mole fraction of

References: p. 531.
the majority defects which occur when B is in excess. Let $g_1$ and $g_2$ be the energies required to form one mole of each type of defect in the limit when $X_2$ and $X_2$ are very small. Assume that the concentrations $X_1$ and $X_2$ are small enough that interactions between defects are negligible (Henry's Law) and that the number of lattice sites does not change appreciably from that in the defect-free compound. Assume further that the defects are randomly distributed. The molar Gibbs energy of the solution relative to the hypothetical defect-free compound is then:

$$ g = \frac{RT}{\beta_1} \left( X_1 \ln X_1 + (1 - X_1) \ln(1 - X_1) \right) $$

$$ + \frac{RT}{\beta_2} \left( X_2 \ln X_2 + (1 - X_2) \ln(1 - X_2) \right) + \frac{1}{\beta_1} g_1 X_1 + \frac{1}{\beta_2} g_2 X_2 $$

(37)

where $1/\beta_1$ and $1/\beta_2$ are the numbers of moles of lattice sites available to each type of defect. For a given deviation from the stoichiometric lattice composition represented by $A_{1+y}B_{1+z}$,

$$ \delta = \frac{X_2}{\beta_2} - \frac{X_1}{\beta_1} $$

(38)

and by minimizing $g$ with respect to $X_1$ and $X_2$, it can be shown that:

$$ \left( \frac{X_1}{1 - X_1} \right)^{\beta_2} \left( \frac{X_2}{1 - X_2} \right)^{\beta_1} = \exp \left( \frac{g_1}{RT} + \frac{g_2}{RT} \right) $$

(39)

If values of the energy parameters $g_1$ and $g_2$ are given, eqs. (38, 39) can be solved for any $\delta$ to give $X_1$ and $X_2$, which can then be substituted back into eq. (37) to give $g$. When $g_1$ and $g_2$ are very large, $g$ rises very steeply on either side of its minimum, and the range of stoichiometry is very narrow as for the case of the compounds in fig. 14. In the case of the compound AgMg, in fig. 13, $g > 0$. That is, it is easier to form defects by adding excess Mg than by adding excess Ag. Hence, the Gibbs energy curve rises more steeply on the Ag side, and as a result, Mg is more soluble in Ag than is Ag.

Defects are discussed in chs. 9, 18 and 20. For an example of an application of the defect model to phase diagram calculations, see Pelton [1991]. For a treatment of defect models as examples of general sublattice models, see Hillert et al. [1985].

### 2.12. Binary phase diagrams involving a gaseous phase

The effect of total pressure, $P$, upon the Gibbs energy change for the transformation of one mole of pure component $A$ from the $\alpha$- to the $\beta$-phase is given by:

$$ \Delta g_A^{\alpha \rightarrow \beta} = \Delta g_A^{\alpha \rightarrow P} + \int_{P_{\alpha}}^{P_{\beta}} \left( v_A^{\alpha} - v_A^{\beta} \right) dP $$

(40)

where $\Delta g_A^{\alpha \rightarrow \beta}(P)$ is the standard (i.e., at $P = 1$ atm) molar Gibbs energy of transformation and where $v_A^{\alpha}$ and $v_A^{\beta}$ are the molar volumes of the phases. For solids and liquids, molar volumes are sufficiently small that the final term in eq. (40) is negligible unless $P$ is very large. If a gaseous phase is involved, however, this is no longer the case. If gaseous $A$ is ideal and monatomic, and since $v_A^{\alpha} = RT/P >> v_A^{\beta}$, the molar Gibbs energy of vaporization is given by:

$$ \Delta g_A^{\alpha \rightarrow \beta} = \Delta h_A^{\alpha \rightarrow \beta} - RT \ln P $$

(41)

where $\Delta h_A^{\alpha \rightarrow \beta}$ is the standard Gibbs energy of vaporization (when $P = 1$ atm) which is given by:

$$ \Delta h_A^{\alpha \rightarrow \beta} = \Delta h_A^{\alpha \rightarrow \beta} - T \Delta s_A^{\alpha \rightarrow \beta} $$

(42)

For example, the enthalpy of vaporization of Zn is $\Delta h_{Zn}^{\alpha \rightarrow \beta} = 115300 \text{ J/mol}$ at its normal boiling point of 1180 K (Barnes et al. [1971]). Assuming that $\Delta h_A^{\alpha \rightarrow \beta}$ is independent of $T$, we calculate that $\Delta s_{Zn}^{\alpha \rightarrow \beta} = 115300/1180 = 97.71 \text{ J/mol K}$. Hence, $\Delta g_A^{\alpha \rightarrow \beta}$ at any $T$ and $P$ is given by:

$$ \Delta g_A^{\alpha \rightarrow \beta} = \left( 115300 - 97.71 T \right) + RT \ln P $$

(43)

A similar expression can be derived for the other component, Mg.

Curves of $g$ and $g^0$ at a constant $T$ and $P$ are shown in the upper panel of fig. 20. The common tangent construction generates the equilibrium vapour and liquid compositions. A temperature-composition phase diagram, at constant pressure, can then be generated as the curve for $g^0$ descends relative to $g^0$ as the temperature is raised. Alternatively, the isothermal pressure-composition diagram shown in the lower panel of fig. 20 is generated as the curve for $g^0$ descends relative to $g^0$ as the pressure is lowered.

The diagram at 1250 K in fig. 20 was calculated under the assumption of ideal liquid and vapour mixing ($g^0 = g^0 = 0$).

### 3. Ternary phase diagrams

In this section, an introduction to ternary phase diagrams will be given. A complete discussion of the subject is beyond the scope of this chapter. For more detailed treatments see Prince [1966], West [1965] or Bergerson and Rishon [1984].

#### 3.1. The ternary composition triangle

In a ternary system with components A–B–C the sum of the mole fractions is unity. $(X_A + X_B + X_C) = 1$. Hence, there are two independent composition variables. A representation of composition, symmetrical with respect to all three components may be obtained with the equilateral "composition triangle" as shown in fig. 21. Compositions at the corners of the triangle correspond to the pure components. Along the edges of the triangle are found compositions corresponding to the three binary subsystems A–B, B–C and C–A. Lines of constant mole fraction $X_C$ are parallel to the B–C edge, while lines of
constant $X_a$ and $X_c$ are parallel to the C-A and A-B edges respectively. For example at point a in fig. 21, $X_a = 0$, $X_b = 0.7$ and $X_c = 0.3$. At point b, $X_a = 0.3$, $X_b = 0.2$ and $X_c = 0.5$.

Similar equilateral composition triangles can also be drawn with coordinates in terms of weight% of the three components.

3.2. Ternary space model

A ternary temperature-composition "phase diagram" at constant total pressure may be plotted as a three-dimensional "space model" within a right triangular prism with the equilateral composition triangle as base and temperature as vertical axis. Such a space model for a simple eutectic ternary system A-B-C is illustrated in fig. 22. On the three vertical faces of the prism we find the phase diagrams of the three binary subsystems, A-B, B-C and C-A which, in this example, are all simple eutectic binary systems. The binary eutectic points are at $e_1$, $e_2$ and $e_3$. Within the prism we see three *liquidus surfaces* descending from the melting points of pure A, B and C. Compositions on these surfaces correspond to compositions of liquid in equilibrium with A-, B- and C-rich solid phases.

In a ternary system at constant pressure, the Gibbs phase rule, eq. (14), becomes:

$$F = 4 - P.$$  \hspace{1cm} (44)

When the liquid and one solid phase are in equilibrium, $P = 2$. Hence, $F = 2$, and the system is invariant. A ternary liquidus is thus a two-dimensional surface. We may choose two variables, say $T$ and one composition coordinate of the liquid, but then the other liquid composition coordinate and the composition of the solid are fixed.

References: p. 531.
The A- and B-liquidus surfaces in fig. 22 intersect along the line e,E. Liquids with compositions along this line are therefore in equilibrium with A-rich and B-rich solid phases simultaneously. That is, \( P = 3 \) and \( F = 1 \). Such "valleys" are thus called univariant lines. The three univariant lines meet at the ternary eutectic point E at which \( P = 4 \) and \( F = 0 \). This is an invariant point since the temperature and the compositions of all four phases in equilibrium are fixed.

3.3. Polytectal projections of liquidus surfaces

A two-dimensional representation of the ternary liquidus surface may be obtained as an orthogonal projection upon the base composition triangle. Such a polytectal projection of the liquidus of the Bi-Sn-Cd system \( (\text{Bray et al. [1966-62]} \) is shown in fig. 23. This is a simple eutectic ternary system with a space model like that shown in fig. 22. The constant temperature lines on fig. 23 are called liquidus isotherms. The univariant valleys are shown as the heavier lines. By convention, the large arrows indicate the directions of decreasing temperature along these lines.

Let us consider the sequence of events which occur during the equilibrium cooling from the liquid of an alloy of overall composition a in fig. 23 \( (X_{\text{Bi}}=0.05, X_{\text{Sn}}=0.45, X_{\text{Cd}}=0.50) \). Point a lies within the field of primary crystallization of Cd. That is, it lies within the composition region in fig. 23 in which Cd-rich solid will be the first solid to precipitate upon cooling. As the liquid alloy is cooled, the Cd-liquidus surface is reached at \( T = 465 \) K (slightly below the 473 K isotherm). A solid Cd-rich phase begins to precipitate at this temperature. Now, in this particular system, Bi and Sn are nearly insoluble in solid Cd, so that the solid phase is virtually pure Cd (note that this fact cannot be deduced from fig. 23 alone). Therefore, as solidification proceeds, the liquid becomes depleted in Cd, but the ratio \( X_{\text{Cd}}/X_{\text{Bi}} \) in the liquid remains constant. Hence, the composition path followed by the liquid (its crystallization path) is a straight line passing through point a and projecting to the Cd-corner of the triangle. This crystallization path is shown on fig. 23 as the line ab.

In the general case in which a solid solution rather than a pure component or stoichiometric compound is precipitating, the crystallization path will not be a straight line. However, for equilibrium cooling, a straight line joining a point on the crystallization path at any \( T \) to the overall composition point a will extend through the composition on the solidus surface, of the solid phase in equilibrium with the liquid at that temperature.

When the composition of the liquid has reached point b in fig. 23 at \( T = 435 \) K, the relative proportions of the solid Cd and liquid phases at equilibrium are given by the lever rule applied to the tie-line dab: \( \text{mole of liquid}/\text{mole of Cd} = \text{mole of liquid}/\text{mole of Cd} \). Upon further cooling the liquid composition follows the univariant valley from b to E while Cd and Sn-rich solids co-precipitate as a binary eutectic mixture. When the liquid composition attains the ternary eutectic composition E at \( T = 380 \) K the invariant ternary eutectic reaction occurs:

\[
\text{liquid} \rightarrow s_1 + s_2 + s_3, \tag{45}
\]

where \( s_1, s_2, \) and \( s_3 \) are the three solid phases and where the compositions of all four phases as well as \( T \) remain fixed until all liquid is solidified.

In order to illustrate several of the features of polynuclear projections of liquidus surfaces, a projection of the liquidus of a hypothetical system A-B-C is shown in fig. 24. For the sake of simplicity, isotherms are not shown, but only the univariant lines with arrows to show the directions of decreasing temperature. The binary subsystems A-B and C-A are simple eutectic systems, while the binary subsystem B-C contains one congruent binary phase, e, and one incongruent binary phase, \( \delta \), as shown in the inset of fig. 24. The letters e and \( \delta \) indicate binary eutectic compounds since they have compositions within a binary subsystem. Two ternary compounds, \( \eta \) and \( \zeta \), with compositions within the ternary triangle as indicated in fig. 24, are also found in this system. All compounds as well as pure solid A, B and C (the "\( \alpha, \beta \), and \( \gamma \)" phases) are assumed to be stoichiometric (i.e. there is no solid solubility). The fields of primary crystallization of all the solids are indicated in parentheses in fig. 24. The composition of the e phase lies within its field.

References: p. 531.
Fig. 24. Projection of the liquidus surface of a system A-B-C. The binary subsystems A-B and C-A are simple eutectic systems. The binary phase diagram B-C is shown in the inset. All solid phases are assumed pure stoichiometric compounds or compounds. Small arrows show crystallization paths of alloys of compositions at points a and b.

since e is a congruent compound, while the composition of the δ phase lies outside of its field since δ is incongruent. Similarly for the congruent compounds, η is a congruent melting compound while ε is incongruent. For the congruent compound η, the highest temperature on the η-liquidus occurs at the composition of η.

The univariant lines meet at a number of ternary eutectics F1 (three arrows converging), a ternary peritectic P (one arrow entering, two arrows leaving the point), and several ternary quasi-peritectics P1 (two arrows entering, one arrow leaving). Two saddle points s are also shown. These are points of maximum T along the univariant line but of minimum T on the liquidus surface along a section joining the compositions of the two solids. For example, s is at a maximum along the univariant F1P1, but it is a minimum point on the liquidus along the straight line εs.

Let us consider the events occurring during the cooling from the liquid of an alloy of overall composition a in fig. 24. The primary crystallization product will be the e phase. Since this is a pure stoichiometric solid the crystallization path of the liquid will be along a straight line passing through a and extending to the composition of e as shown on the figure.

Solidification of e continues until the liquid attains a composition on the univariant valley. Then the liquid composition follows the valley towards the point P' in co-existence with ε and η. At point P' the invariant ternary quasi-peritectic reaction occurs isothermally:

\[ \text{liquid} + \epsilon + \eta \rightarrow \delta + \zeta. \]  

(46)

Since there are two reactants in a quasi-peritectic reaction, there are two possible outcomes: (i) The liquid is completely consumed before the e-phase; in this case, solidification will be complete at the point P'. (ii) e is completely consumed before the liquid; in this case, solidification will continue with decreasing T along the univariant line P1P, with p-co-precipitation of δ and ζ until, at E, the liquid will solidify eutectically (liquid → δ + ζ + η). To determine whether condition (i) or (ii) occurs, we use the mass balance criterion that, for three-phase equilibrium, the overall composition must always lie within the tie-triangle formed by the compositions of the three phases. Now, the triangle joining the compositions of δ, e, and ζ does not contain the point a, but the triangle joining the compositions of δ, η, and liquid at P' does contain the point a. Hence, case (ii) occurs.

An alloy of overall composition b in fig. 24 solidifies with e as primary crystallization product until the liquid composition contacts the univariant line. Thereafter, co-precipitation of e and β occurs with the liquid composition following the univariant valley until the liquid reaches the peritectic composition P. The invariant ternary peritectic reaction then occurs isothermally:

\[ \text{liquid} + \epsilon + \beta \rightarrow \zeta. \]  

(47)

Since there are three reactants, there are three possible outcomes: (i) Liquid is consumed before either ε or β and solidification terminates at P; (ii) e is consumed first; solidification then continues along the path PP', (iii) β is consumed first and solidification continues along the path PP'. Which outcome occurs depends on whether the overall composition b lies within the tie-triangle (i) eβC, (ii) βεP or (iii) eCP. In the example shown, case (i) will occur.

3.4. Ternary isothermal sections

Isothermal projections of the liquidus surface do not give information on the compositions of the solid phases at equilibrium. However, this information can be presented at any one temperature on an isothermal section such as that shown for the Bi–Sn–Cd system at 423 K in fig. 25. This phase diagram is a constant temperature slice through the space model of fig. 22.

The liquidus lines bordering the one-phase liquid region of fig. 25 are identical to the 423 K isotherms of the projection in fig. 23. Point e in fig. 25 is point e on the univariant line in fig. 23. An alloy with overall composition in the one-phase liquid region of fig. 25 at 423 K will consist of a single liquid phase. If the overall composition lies within one of the two-phase regions, then the compositions of the two phases are given

References: p. 331.
of composition $c$. To understand this better, consider an alloy of composition $a$ in fig. 25, which is the same composition as the point $a$ in fig. 23. In § 3.3 we saw that when a alloy of this composition is cooled, the liquid follows the path $ab$ on fig. 23 with primary precipitation of Cd and then follows the univariant line with co-precipitation of Cd and Sn so that at 423 K the liquid will be at the composition point $c$, and two solid phases are in equilibrium with the liquid.

3.4.1. Topology of ternary isothermal sections

At constant temperature the Gibbs energy of each phase in a ternary system is represented as a function of composition by a surface plotted in a right triangular prism with Gibbs energy as vertical axis and the composition triangle as base. Just as the compositions of phases at equilibrium in binary systems are determined by the points of contact of a common tangent line to their isothermal Gibbs energy curves, so the compositions of phases at equilibrium in a ternary system are given by the points of contact of a common tangent plane to their isothermal Gibbs energy surfaces. A common tangent plane can contact two Gibbs energy surfaces at an infinite number of pairs of points, thereby generating an infinite number of tie-lines within a two-phase area on an isothermal section. A common tangent plane to three Gibbs energy surfaces contacts each surface at a unique point, thereby generating a three-phase tie-triangle.

Hence, the principal topological units of construction of an isothermal ternary phase diagram are three-phase ($\alpha + \beta + \gamma$) tie-triangles as in fig. 26 with their accompanying two-phase and single-phase areas. Each corner of the tie-triangle contacts a single-phase region, and from each edge of the triangle there extends a two-phase region. The edge of the triangle is a limiting tie-line of the two-phase region.

For overall compositions within the tie-triangle, the compositions of the three phases at equilibrium are fixed at the corners of the triangle. The relative proportions of the three phases are given by the lever rule of tie-triangles which can be derived from mass balance considerations. At an overall composition $q$ in fig. 26, for example, the relative proportion of the $\gamma$-phase is given by projecting a straight line from the $\gamma$-corner of the triangle (point $c$) through the overall composition $q$ to the opposite side of the triangle, point $p$. Then: (moles of $\gamma$)/(total moles) = $qp/cp$ if compositions are expressed in mole fractions, or (weight of $\gamma$)/(total weight) = $qp/cp$ if compositions are in weight percent.

Isothermal ternary phase diagrams are generally composed of a number of these topological units. An example for the Al-Zn-Mg system at 25°C is shown in fig. 27 (Köster and Dulleruppe [1936]). The $\beta$, $\gamma$, $\delta$, $\eta$, and $\zeta$ phases are binary intermetallic compounds with small ($\pm 1\%$) ranges of stoichiometry which can dissolve a limited amount ($\pm 6\%$) of the third component. The $\tau$ phase is a ternary phase with a single-phase region existing over a fairly extensive oval-shaped central composition range. Examination of fig. 27 shows that it consists of the topological units of fig. 26.

An extension rule, a case of Schreinemakers's rule (Schreinemakers [1915]) for ternary tie-triangles is illustrated in fig. 26. At each corner, the extension of the boundaries of the single-phase regions, indicated by the dashed lines, must either both project into the triangle as at point $a$, or must both project outside the triangle as at point $b$, and furthermore the angle between these extensions must be less than 180°. For a proof, see Lipson and Wilson [1940].

References: p. 531.
Fig. 26. A tie-triangle in a ternary isothermal section illustrating the lever rule and the extension rule.

Many published phase diagrams violate this rule. For example, it is violated in fig. 27 at the δ-corner of the (ε + δ + γ) tie-triangle.

Another important rule of construction, whose derivation is evident, is that within any two-phase region tie-lines must never cross each other.

3.5. Ternary isopleths (constant composition sections)

A vertical isopleth, or constant composition section through the space model of the Bi–Sn–Cd system is shown in fig. 28. The section follows the line AB in fig. 23.

Fig. 27. Ternary isothermal section of the Al–Zn–Mg system at 25°C (after Köster and Drickmrodt [1936]).

Fig. 28. Isopleth (constant composition section) of the Bi–Sn–Cd system following the line AB of fig. 23.

The phase fields on fig. 28 indicate which phases are present when an alloy with an overall composition on the line AB is equilibrated at any temperature. For example, consider the cooling from the liquid state, of an alloy of composition a which is on the line AB (see fig. 23). At T = 465 K, precipitation of the solid (Cd) phase begins at point a in fig. 28. At T = 435 K (point b in figs. 23 and 28) the solid (Sn) phase begins to appear. Finally, at the eutectic temperature T_e, the ternary eutectic reaction occurs, leaving solid (Cd) + (Bi) + (Sn) at lower temperatures. The intersection of the isopleth with the univariant lines on fig. 23 occurs at points f and g which are also indicated in fig. 28. The intersection of this isopleth with the isothermal section at 423 K is shown in fig. 25. The points s, t, u and v of fig. 25 are also shown on fig. 28.

It is important to note that on an isopleth, the tie-lines do not, in general, lie in the plane of the diagram. Therefore, the diagram gives information only on which phases are present, not on their compositions. The boundary lines on an isopleth do not in general indicate the phase compositions, but only the temperature at which a phase appears or disappears for a given overall composition. The lever rule cannot be applied on an isopleth.

Certain topological rules apply to isopleths. As a phase boundary line is crossed, one and only one phase either appears or disappears. This Law of Adjoining Phase Regions (Paulson and Landau [1964]) is illustrated by fig. 28. The only apparent exception occurs for the horizontal invariant line at T_e. However, if we consider this line to be a degenerate infinitely narrow four-phase region (L + (Cd) + (Bi) + (Sn)), then the law is also obeyed here.

Three or four boundary lines meet at intersection points. At an intersection point, Schreinemakers' rule applies (Schreinemakers [1915]). This rule states that the boundaries of the phase field with the smallest number of phases, when extrapolated, must either both fall within the phase field with the greatest number of phases (as at point f in fig. 28) or else both fall outside this region (as at point g in fig. 28).

Apparent exceptions to these rules (such as, for example, five boundaries meeting at an intersection point) can occur if the section passes exactly through a node (such as a ternary eutectic point) of the space model. However, these apparent exceptions are really only limiting cases. See Prince [1963] or Prince [1966].

References: p. 531.
4. Multicomponent phase diagrams

Only a brief outline of multicomponent phase diagrams can be presented here. For more detailed treatments see Palatnik and Landau [1964], Prince [1963], Prince [1966], and Hills [1985].

For alloy systems of four or more components, two-dimensional sections are usually plotted with one or more compositional variables held constant. Hence, these sections are similar to the ternary isopleths discussed in § 3.5. In certain cases, sections at constant chemical potential of one or more components (for example, at constant oxygen partial pressure) can be useful. These are discussed in § 6.

Two sections of the Fe–Cr–V–C system (Lee and Lee [1992]) are shown in figs. 29, 30. The diagram in fig. 29 is a T-composition section at constant Cr and V content, while fig. 30 is a section at constant T = 850°C and constant C content of 0.3 wt.%. The interpretation and topological rules of construction of these sections are the same as those for ternary isopleths as discussed in § 3.5. In fact, the same rules apply to a two-dimensional constant-composition section for a system of any number of components. The phase fields on the diagram indicate the phases present at equilibrium for an overall composition lying on the section. Tie-lines do not, in general, lie in the plane of the diagram so the diagram does not give information on the compositions or amounts of the phases present. As a phase boundary is crossed, one and only one phase appears or disappears (Law of Adjoining Phase Regions). If temperature is an axis, as in fig. 29, then horizontal invariants like the line AB in fig. 29 can appear. These can be considered as degenerate infinite narrow phase fields of (C + 1) phases, where C is the number of components (for isotopic diagrams). For example, in fig. 29, on the line AB, five phases are present. Three or four phase boundaries meet at intersection points at which Schreinemakers' rule applies. This rule was given in § 3.5. It is illustrated by the extrapolations in fig. 29 at points a, b, and c and in fig. 30 at points h, e, f, l, and s. The applicability of Schreinemakers' rule to systems of any number of components was noted by Hills [1985], although no formal proof has been presented.

4.1. Zero phase fraction lines

An interesting and useful method of constructing multicomponent phase diagrams through the use of zero phase fraction (ZPF) lines has recently been proposed (Gupta et al. [1986]). A ZPF line divides a two-dimensional phase diagram into two regions. On one side of the line a phase occurs, while on the other side it does not. For example, in fig. 30 the ZPF line for the α phase is the line abcd. The ZPF line for the γ phase is ghijk. For the MC phase the ZPF line is muncp. The ZPF line for M₄C₆ is reihs. The five ZPF lines yield the entire two-dimensional phase diagram. The usefulness of this methodology for estimating phase diagrams for multicomponent systems from experimental data was discussed by Gupta et al. [1986]. The method also holds promise for the thermodynamic calculation of phase diagrams (§ 5).

4.2. Nomenclature for invariant reactions

As discussed in § 2.9, in a binary isobaric temperature–composition phase diagram there are two possible types of invariant reactions: "eutectic type" invariant reactions ($β \rightarrow α + γ$), and "peritectic type" invariant reactions ($α + γ \rightarrow β$). In a ternary system, there are "eutectic type" (α→β+γ+δ), "peritectic type" (α+β+γ→δ) and "quasi-peritectic type" (α+β→γ+δ) invariants (§ 3.3). In a system of C components, the number of types of invariant reaction is equal to C. A reaction with one reactant, such as $α+β→γ+δ$ is clearly a "eutectic type" invariant reaction but in general there is no standard terminology. These reactions are conveniently described according to the numbers of reactants and products (in the direction which occurs upon cooling). Hence, the reaction $α+β→γ+δ+e$ is a 2→3 reaction; the reaction $α+β+γ→δ$ is a 1→3 reaction; and so on. The ternary peritectic type 3→1 reaction ($α+β+γ→δ$) is an invariant reaction in a ternary system, a unvariant reaction in a quaternary system, a bivariant reaction in a quinary system, etc.

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5. Thermodynamic calculation of ternary and multicomponent phase diagrams

Among 70 metallic elements are formed $70! / 31! 67! = 54740$ ternary systems and 916895 quaternary systems. In view of the amount of work involved in measuring even one isothermal section of a relatively simple ternary phase diagram, it is very important to have means of estimating ternary and higher-order phase diagrams. The most fruitful approach to such predictions is via thermodynamic methods. In recent years, large advances have been made in this area by the international Calphad group. Many key papers have been published in the Calphad Journal.

As a first step in the thermodynamic approach to calculating a ternary phase diagram, one critically analyzes the experimental phase diagrams and thermodynamic data for the three binary subsystems of the ternary system in order to obtain a set of mathematical expressions for the Gibbs energies of the binary phases as was discussed in §2.10 and §2.11. Next, equations based on solution models are used to estimate the Gibbs energies of the ternary phases from the Gibbs energies of the binary phases. The ternary phase diagram is then calculated from these estimated ternary Gibbs energies by means of common tangent plane or total Gibbs energy minimization algorithms.

For a phase for which the excess Gibbs energies in the binary systems have been expressed by polynomial expansions (§2.10.1) a satisfactory estimation of the Gibbs energy of the ternary phase can often be obtained with the following equation proposed by Kohler [1966]:

$$g^E = (1 - X_A)^3 \delta_{BC} + (1 - X_B)^3 \delta_{CA} + (1 - X_C)^3 \delta_{AB}$$  (48)

In this equation, $g^E$ is the excess molar Gibbs energy at a composition point in the ternary phase and $\delta_{BC}$, $\delta_{CA}$ and $\delta_{AB}$ are the excess Gibbs energies in the three binary subsystems at the same molar ratios $X_A$, $X_B$, $X_C$ and $X_A$, $X_B$, $X_C$ as at the ternary point. If the ternary solution as well as the three binary solutions are all regular then eq. (48) is exact. In the general case, a physical interpretation of eq. (48) is that the contribution to $g^E$ from, say, pair interactions between A and B particles is constant at a constant ratio $X_A$, $X_B$ apart from the dilutive effect of the C particles which is accounted for by the term $(1 - X_C)^3$ taken from regular solution theory. Other very similar equations, all based upon extension of regular solution theory, are also regularly used. These all give quite similar results. For a discussion see Spencer and Barin [1979] or Hillert [1980].

For more complex solutions involving structural ordering or more than one sublattice, appropriate solution models for representing the binary properties have been discussed in §2.11. In such cases, eq. (48) or similar equations should not be used for estimating the ternary excess Gibbs energies. Rather, equations consistent with the appropriate solution model should be used. For the quasichemical model, these have been discussed by Pelton and Blander [1985]. For the sublattice model, see Hillert et al. [1985].

As an example of the calculation of a ternary phase diagram, the experimental isothermal section at 923 K of the Cr-Ni-Fe phase diagram is compared in fig. 31 with the diagram calculated solely from optimized binary thermodynamic properties (Chart et al. [1979]). Such estimated phase diagrams are often quite acceptable for many purposes. However, the agreement between the experimental and calculated diagrams can usually be greatly improved by the inclusion of one or more "ternary terms" with adjustable coefficients in the equations for $g^E$. For example, the ternary term $aX_AX_BX_C$, which is zero in all three binary subsystems could be added to eq. (48) and the value of the parameter $a$ which gives the best optimized fit to measured ternary phase diagram points could be determined. This, of course, requires that ternary measurements be made, but only a very few experimental points will usually suffice rather than the large number of measurements required for a fully experimental determination. In this way, the coupling of the thermodynamic approach with a few well chosen experimental measurements can greatly reduce the experimental effort involved in determining multicomponent phase diagrams.

An example of a coupled thermodynamic/phase diagram evaluation and calculation for a multicomponent system is the work of Lee and Lee [1992] on the Fe-Cr-V-C

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6. Phase diagrams with potentials as axes

So far we have considered mainly isobaric temperature-composition phase diagrams. However, there are many other kinds of phase diagrams of metallurgical interest with pressure, chemical potentials, volume, etc. as axes. These can be classified into geometrical types according to their topological rules of construction.

For instance, binary isothermal P-X diagrams as in fig. 20 are members of the same type as binary isobaric T-X diagrams since they are both formed from the same topological units of construction. Other useful phase diagrams of this same geometrical type are isothermal chemical potential-composition diagrams for ternary systems. An example is shown in the lowest panel of fig. 32 (Pelton and Thompson [1975]) for the Co-Ni-O system at T=1600 K (and at a constant total hydrostatic pressure of 1 atm).

Here the logarithm of the equilibrium partial pressure of O₂ is plotted versus the metal ratio \( \xi = n_{\text{Co}}/(n_{\text{Ni}} + n_{\text{O}}) \), where \( n_i \) = number of moles of i. There are two phases in this system under these conditions; a solid alloy solution stable at lower \( p_{\text{O}_2} \), and a solid solution of CoO and NiO stable at higher \( p_{\text{O}_2} \). For instance, point a gives \( p_{\text{O}_2} \) for the equilibrium between pure Co and pure CoO at 1600 K. Between the two single phase regions is a two-phase (alloy + oxide) region. At any overall composition on the tie-line cd between points c and d, two phases will be observed, an alloy of composition d and an oxide of composition c. The lever rule applies just as for binary T-X diagrams.

The usual isothermal section of the ternary Co-Ni-O system at 1600 K is shown in the top panel of fig. 32. There are two single-phase regions with a two-phase region between them. The single-phase areas are very narrow since oxygen is only very slightly soluble in the solid alloy and since CoO and NiO are very stoichiometric oxides. In the central panel of fig. 32 this diagram is shown but with the composition triangle "opened out" by putting the oxygen corner at infinity. This can be done if the vertical axis becomes \( \eta = n_{\text{O}}/(n_{\text{CO}} + n_{\text{Ni}}) \) with the horizontal axis as \( \xi = n_{\text{Co}}/(n_{\text{Ni}} + n_{\text{O}}) \). These are known as Jänecke coordinates. It can be seen in fig. 32 that each tie-line, ef, of the isothermal section corresponds to a tie-line, cd of the log \( p_{\text{O}_2} \) diagram. This underscores the fact that every tie-line of a ternary isothermal section corresponds to a constant chemical potential of each of the components.

Another example of a log \( p_{\text{O}_2} \) diagram is shown for the Fe-Cr-O system at 1573 K in the lower panel of fig. 33 (Pelton and Schmalzried [1973]). The corresponding ternary isothermal section in Jänecke coordinates is shown in the upper panel. Each of the invariant three-phase tie-triangles in the isothermal section corresponds to an invariant line in the log \( p_{\text{O}_2} \) diagram. For example, the spinel + (Fe, Cr)O + alloy triangle with corners at points a, b and c corresponds to the "eutectic-like" invariant with the same phase compositions a, b and c at log \( p_{\text{O}_2} = -10.7 \). We can see that within a three-phase tie-triangle, \( p_{\text{O}_2} \) is constant.

An example of yet another kind of phase diagram of this same geometrical type is shown in fig. 34. For the quaternary Fe-Cr-O-SO₃ system at T=1273 K and at constant \( p_{\text{O}_2} = 10^{-3} \) atm, fig. 34 is a plot of log \( p_{\text{O}_2} \) versus the molar metal ratio \( \xi \) (Pelton [1991]). Since log \( p_{\text{O}_2} \) varies as \(-1/2 \log p_{\text{O}_2} \) when \( p_{\text{O}_2} \) and T are constant, fig. 34 is also a plot of log \( p_{\text{O}_2} \) versus \( \xi \).

It can be seen that the diagrams discussed above are of the same geometrical type as binary T-X diagrams since they are all composed of the same topological units of

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construction as in fig. 15. Their interpretation is thus immediately clear to anyone familiar with binary T-X diagrams. Chemical potential–composition diagrams (figs. 32–34) are useful in the study of high temperature oxidation of alloys, metallurgical reactions, etc.

The log $p_0^\varepsilon$ diagrams in figs. 33, 34 were calculated by the same algorithm which produced the binary phase diagram of fig. 17. This algorithm operates by computing common tangent lines to the Gibbs energy–composition curves of the phases. The diagrams in figs. 33, 34 were calculated from optimized mathematical expressions for the Gibbs energy curves of all the phases. With these same optimized equations, log $p_0^\varepsilon$ diagrams at other temperatures can be calculated, as can T-ε diagrams at constant $p_0$, which are also of the same geometrical type. For details see Pelton et al. [1979].

Another important geometrical type of phase diagram is exemplified by P-T phase diagrams for one-component systems as shown for $H_2O$ in fig. 35. In such diagrams, which are discussed in ch. 5, §3, bivariant single-phase regions are indicated by areas, univariant two-phase regions by lines, and invariant three-phase regions by triple points. An important rule of construction is the extension rule which is illustrated by the dashed lines in fig. 35. At a triple point, the extension of any two-phase line must pass into the single-phase region of the third phase.

Another kind of phase diagram of the same geometrical type is shown in fig. 36. For the Fe–S–O system at $T=800$ K, the axes of the diagram are the equilibrium partial pressures of $S_2$ and $O_2$. Single-phase areas indicate which pure compounds of Fe are stable under the given conditions. Two-phase regions are lines. Three phases can co-exist only at triple points. The extension rule given above applies at all triple points. Such stability diagrams or predominance diagrams are useful in the study of oxidation, corrosion, mixing, etc. They have been treated in ch. 5, §1.2 and have been discussed by Kellogg and Basu [1960], Ingraham and Kellogg [1963], Pelton and Thompson [1975], Bale et al. [1986], and Bale [1990]. They lend themselves to rapid computer calculation by Gibbs energy minimization from thermodynamic data stored in computerized data banks (Bale et al. [1986], Bale [1990]). Their usefulness is by no means restricted to metal–sulphur–oxygen systems or to systems of three components.

As another example of this same geometrical type of diagram, a plot of $RT \ln p_0$, concentration as a function of temperature, is shown in fig. 37.
versus $T$ for the Fe–O system is shown in fig. 37b. Again, one-, two-, and three-phase regions are indicated by areas, lines and triple points respectively. In fig. 37a is the binary T-composition phase diagram for the Fe–O system. The correspondence between figs. 37a and 37b is evident. Each two-phase line of fig. 37b “opens up” to a two-phase region of fig. 37a. Each tie-line of a two-phase region in fig. 37a can thus be seen to correspond to a constant $p_{O_2}$. Triple points in fig. 37b become horizontal invariant lines in fig. 37a.

Yet another type of phase diagram is shown in fig. 38. This is an isothermal section at constant molar metal ratio $n_{Fe}/(n_{S}+n_{O}) = 0.21$ for the Fe–Cr–S–O system. This diagram was calculated thermodynamically from model parameters (Laplante [1993]). The axes are the equilibrium sulfur and oxygen partial pressures. Three or four boundary lines can meet at an intersection point. Some of the boundary lines on fig. 38 separate a two-phase region ($\alpha + \beta$)

Fig. 36. Type-I predominance diagram for Fe–S–O at 800 K.

Fig. 37. Corresponding type-1 and type-2 phase diagrams for the Fe–O system (after Miller and Osborn [1955]).

Fig. 38. Phase diagram of $\log p_{S_2}$ versus $\log p_{O_2}$ at 1273 K and constant molar metal ratio $n_{Fe}/(n_{S}+n_{O}) = 0.21$ in the Fe–Cr–S–O system (Laplante [1993]).

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from another two-phase region \((\alpha + \gamma)\). These lines thus represent the conditions for three-phase \((\alpha + \beta + \gamma)\) equilibrium. The Law of Adjoining Phase Regions (§ 3.5) applies to fig. 38 if these 3-phase lines are considered as degenerate infinitely narrow phase fields.

6.1. Classification of phase diagrams

In a system of \(C\) components we can define \((C + 2)\) thermodynamic potentials, \(\phi_i\). These are \(T, P, \mu_1, \mu_2, \ldots, \mu_C\) (where \(\mu_i\) is the chemical potential of component \(i\)). For each potential \(\phi_i\), we can define a "corresponding" extensive variable \(a_i\). For the potentials \\(T, P\) and \(\mu_i\), the corresponding extensive variables are \(S, V\) and \(n_i\) (entropy, volume and moles of component \(i\)). When two phases, \(\alpha\) and \(\beta\), are in equilibrium, \(\phi_\alpha = \phi_\beta\) for all \(i\).

If we choose any three potentials, designated \(\phi_1, \phi_2, \phi_3\), and if we hold \(\phi_1, \phi_2, \ldots, \phi_{c-2}\) constant, then a plot of \(\phi_1\) versus \(\phi_2\) will have the geometry of figs. 35, 36. Such diagrams were termed type-1 phase diagrams by Pelton and Schmalzried [1973]. A general type-1 diagram is shown in fig. 39b. On a type-1 diagram the lines give the conditions for two-phase equilibrium, and the triple points are the three-phase points.

If we now replace the \(\phi_2\) axis of the type-1 diagram by the ratio \(q_2/q_3\) (or equivalently, by \(q_2/(q_2 + q_3)\)), then we obtain a "corresponding" type-2 phase diagram as illustrated in fig. 39a. A corresponding type-2 diagram is also obtained by replacing \(\phi_1\) by \(q_2/q_3\) as in fig. 39d. Two phase lines in the type-1 diagram become two-phase regions with tie-lines in the corresponding type-2 diagrams. Tripole points become invariant lines.

Consider the binary Fe-O system in fig. 37. Let \(\phi_1 = T, \phi_2 = \mu_o, \phi_3 = \mu_n, \phi_4 = P\). Fig. 37b is a type-1 diagram of \(\phi_4\) versus \(\phi_3\) with \(\phi_1\) constant. Fig. 37a is the corresponding type-2 diagram obtained by replacing \(\phi_4\) by the ratio \(q_2/q_3\) or \(q_2/(q_2 + q_3)\) at constant \(\phi_1\) and \(\phi_3\). In the Fe-Cr-O-SO\(_2\) system in fig. 33, let \(\phi_1 = \mu_o, \phi_3 = \mu_n, \phi_4 = \mu_{SO_2}, \phi_5 = P\). The lower panel in fig. 33 is a type-2 diagram of \(\phi_5\) versus \(q_2/(q_2 + q_3)\) at constant \(\phi_1\) and \(\phi_3\). In the Fe-Cr-O-SO\(_2\) system in fig. 34 there is one more component and therefore, one more potential, \(\phi_4 = \phi_{SO_2}\). By also holding this potential constant, we obtain the type-2 diagram of fig. 34.

If, as well as replacing \(\phi_2\) in a type-1 diagram by \(q_2/q_3\), we also replace \(\phi_1\) by \(q_2/q_3\), then a corresponding type-2 phase diagram results as shown in fig. 39e. In this diagram, tie-line points have become tie-triangles. Type-3 diagrams are exemplified by isothermal isobaric sections of ternary systems as in figs. 25, 27 and 31. The upper panel of fig. 33 shows the type-3 diagram corresponding to the type-2 diagram in the lower panel. The potential \(\phi_1 = \mu_o\) has been replaced by \(q_2/(q_2 + q_3) = n_o/(n_o + n_c)\). This gives the type-3 diagram in Jänecke coordinates. This is usually transformed to the more usual Gibbs triangle representation as illustrated in fig. 32.

For a more detailed discussion of this classification scheme, see Pelton and Schmalzried [1973] and Pelton and Thompson [1975].

Type-1, -2, and -3 phase diagrams are all sections at constant potentials \((\phi_1, \phi_2, \ldots, \phi_C)\). Hence, all tie-lines lie in the plane of the diagram. When sections are taken at constant composition, then different geometries result. Fig. 38 is an example of a constant composition section in which both axes are potentials. Figs. 28 and 29 are constant composition sections in which one axis is a potential, \(T\), while the other axis is a composition variable. In fig. 30, both axes are composition variables. The geometrical rules of construction of these diagrams have already been discussed (§ 3.5, § 4). The difference among them is that fig. 30 contains no degenerate phase fields, while in fig. 38 lines can be degenerate phase fields, and in figs. 28 and 29 only horizontal lines can be degenerate phase fields.

For more detailed discussions of the classification of phase diagrams, including projections and diagrams with more than two dimensions, see Palamid and Landau [1964], Prince [1963] and Hillert [1985].

As a final note on the topology of phase diagrams, the construction of multicomponent constant-composition sections by means of zero phase fraction (ZPF) lines was discussed in § 4.1 and illustrated by fig. 30. It should be noted that this method applies to any two-dimensional phase diagram section and can be used to construct any phase diagram in the present article (with the exception of the projections in figs. 23, 24 and 27). When one or both axes are potentials, then parts of the ZPF lines for two phases may be coincident.

7. Experimental techniques of measuring phase diagrams

It is beyond the scope of the present article to give a complete discussion of experimental techniques. Only a brief survey of the major techniques will be presented.
with a view to providing the reader with some insight into the difficulties involved. More
detailed discussions are given by Raynor (1970), Macchesney and Rosenberg (1970),
Buckley (1970), and Home-Rothery et al. (1952).

As has been discussed in § 5, modern techniques of computer coupling of thermodynamics and phase diagrams can significantly reduce the amount of experimental effort required to characterize a phase diagram completely, particularly in the case of multi-component systems.

7.1. Thermal analysis

Liquidus temperatures are commonly determined by the measurement of cooling curves. Consider the binary alloy A-B of composition 1 in fig. 40. A sample of liquid alloy, of the order of 50 g, is held in a crucible in a furnace. The furnace temperature is then decreased slowly at a uniform rate, usually not exceeding 1°C per minute, while the temperature of the alloy is measured by a calibrated recording thermocouple. A graph of sample temperature versus time (the cooling curve) is shown in fig. 41a. At the liquidus temperature (point a in fig. 40), solidification commences with the evolution of heat. This causes a decrease in the cooling rate of the specimen, with, ideally, a resultant abrupt change of slope of the curve as shown in fig. 41a. When solidification is complete at the solidus composition (point b in fig. 40), heat evolution ceases and, ideally, another change of slope of the cooling curve is observed. From the “idealized” cooling curve of fig. 41a, one can then read the liquidus and solidus temperatures. For an alloy of composition 2, the idealized cooling curve is shown in fig. 41b. There is a change of

Fig. 40. Binary phase diagram to illustrate some experimental techniques; solid circles: single phase alloy; open circles: two-phase alloy.

Fig. 41. Cooling curves for alloys of compositions 1 and 2 of fig. 40.

slope at the liquidus, and a plateau at the eutectic temperature since, ideally, the sample temperature remains constant until the invariant eutectic solidification reaction is complete.

In a real experiment, however, cooling curves of the type labelled “realized” in fig. 41 are usually obtained. Some degree of undercooling (or supercooling) is almost always observed. The sample must be cooled below the transformation temperature before nucleation of the new phase occurs. The temperature then rises again. However, at a liquidus the temperature will never rise all the way back up to the liquidus, so that some extrapolation technique must be used to estimate the liquidus temperature. At a eutectic, the equilibrium eutectic temperature may be regained by the sample after supercooling, provided that the quantity of material solidifying eutectically is large enough to yield a sufficient evolution of heat. Supercooling may be minimized by stirring or by constantly jolting the sample to induce nucleation.

It is important that temperature gradients within the sample be eliminated by stirring and by the use of a furnace with a good constant temperature zone. Otherwise, part of the sample will start to solidify before the rest and the cooling curve will show a rounded rather than an abrupt change of slope.

At compositions where the liquidus is steep, such as the composition 3 in fig. 40, the rate of heat evolution is small. That is, on descending from the liquidus at point f to a point g an appreciable distance below the liquidus, only a small amount of heat is evolved since, as can be seen from the lever rule, only a small amount of solid is precipitated. Hence, it is more difficult to determine the exact temperature of the change in slope of the cooling curve, and the technique of thermal analysis is less precise. For very steep liquidus lines, a method of segregation and sampling or quenching may be preferable, as will be discussed below.

For liquidus temperatures below about 1000°C, absolute accuracies of the order of ±1°C can be obtained by cooling curve methods under optimal conditions. For temperat-
ures of the order of 100°C or lower, accuracies of ±0.25°C may be obtained.

In principle, solidus temperatures can be determined by the method of cooling curves as shown for the idealized curve in fig. 41a. In certain very favourable cases, with very slow cooling rates, this may be possible. However, in most cases a curve such as the “realized” curve of fig. 41a will be observed, in which determination of the solidus temperature is extremely imprecise. The reasons for this are, firstly, that the solid phase will contain concentration gradients so that solidification will not be complete at the equilibrium solidus temperature; secondly, that the precipitated solid phase will insulate the thermocouple from the sample thereby reducing sensitivity; and thirdly, that by the time the solidus temperature is approached the sample temperature will have lagged well behind the furnace temperature so that the cooling rate will start to accelerate rapidly. For these reasons, solidus temperatures are better measured by heating curves which are, in most respects, analogous to cooling curves. An important precaution here is to ensure, by means of a long anneal, that the solid sample is homogeneous before commencing the experiment. In general, it is more difficult to measure solidus temperatures with accuracy than it is to measure liquidus temperatures.

In principle, a peritectic invariant can also be evidenced by a plateau on a cooling curve. However, as discussed in §2.5.3, peritectic reactions are frequently greatly retarded kinetically so that only a weak short thermal arrest may actually be observed.

In general, the precision of thermal analysis experiments may be increased by the use of Differential Thermal Analysis (DTA) in which two thermocouples, connected in opposition, are placed, respectively, in the sample and in a standard specimen which undergoes no phase transformation in the temperature range of study. The danger in DTA experiments is that, because of the large surface to volume ratio of the small samples used, specimen temperatures often do not increase sufficiently after supercooling.

### 7.2. Sampling techniques and quenching techniques

As discussed above, thermal analysis may be inaccurate for determining the position of a steep liquidus. In such a case, a segregation and sampling technique may prove best. Suppose an alloy of overall composition and temperature in the (liquid + solid) region at point g in fig. 40 is held at temperature until equilibrium is established. A specimen of the liquid phase is then obtained, perhaps by suction in a ceramic tube. Chemical analysis will then give the composition of the liquidus at this temperature. A similar technique might be used to measure the compositions of the boundaries of a liquid–solid miscibility gap. Clearly these methods depend for accuracy on a clean separation of the phases and on the prevention of oxidation and of volatilization losses while the sampling device is inserted into the container.

The principle of quenching techniques for solidus determinations is illustrated at temperature T_1 in fig. 40. Samples at each of the four overall compositions shown at T_1 are held at temperature long enough for equilibrium to be attained. They are then quenched rapidly. When examined microscopically, samples from the two-phase zone will exhibit regions of rapidly quenched liquid which can be distinguished from the solid grains. In this way the solidus composition can be bracketed. Alternatively, one could quench samples of the same composition annealed at different temperatures, thereby bracketing the solidus temperature as is also illustrated in fig. 40.

Because of the slowness of solid state reactions, thermal analysis is rarely a useful technique for locating phase boundaries involving two solid phases. However, in some cases annealing and quenching followed by microscopic observation to determine whether one or two phases are present can often be used to bracket the phase boundary as illustrated for the solvus line in fig. 40 at T_1.

Another method of determining phase boundaries in the solid state involves the annealing of a sample in a two-phase (solid + solid) region followed by quenching and subsequent quantitative analysis by any of several techniques to determine the compositions of the two phases present. The relevant techniques of quantitative metallography are discussed in ch. 10, §7, where several examples are quoted of the use of such techniques to determine solid solubility limits.

In all techniques involving quenching, it is essential that the quench be as rapid as possible so as to avoid any diffusion, segregation or reaction during cooling.

### 7.3. Other techniques

Suppose that one wishes to determine the compositions (points h and l) of the phase boundaries at T_2 in fig. 40. Samples at a number of compositions at T_2 between points j and k are annealed and quenched. The lattice spacings of the α and β phases are then measured by X-ray techniques. The lattice spacings, when plotted versus composition, vary continuously in the single-phase regions, but remain constant in the two-phase region. Extrapolation of the single-phase and two-phase portions of the lattice spacing versus composition curve to their point of intersection then gives the composition of the phase boundary. If too much decomposition occurs upon quenching, then high-temperature X-ray techniques may be required to perform the measurements at temperature.

A technique which is similar in principle consists in measuring the electrical conductivity of specimens at various compositions at T_2 along the line between points j and k. Again, sharp breaks in the plot of conductivity versus composition are noted at the phase boundaries. This technique is often quite rapid, and can be carried out at elevated temperatures without the necessity of quenching.

In the interdiffusion technique, polished pellets of compositions j and k are clamped together and annealed at T_2. Following quenching, a composition versus distance scan is performed across the specimen by, say, microprobe analysis. A sharp discontinuity in the curve is observed at the interface, the compositions at either side being the phase boundary compositions h and l. This technique can also often be used to indicate the presence and compositions of one or more intermediate phases in one single experiment (see for example, Schmalzried [1974]).

A great many other techniques of phase diagram measurement exist, such as dilatometric (Hume-Rothery et al. [1952], Sinha et al. [1967]), hardness (Barreau and Cizeron [1979]), and magnetic measurements (ch. 29, §6, also Sucksmith [1939]). The complete determination of an alloy phase diagram usually requires a combination of several techniques (e.g., a combination of dilatometry and magnetic measurements [Servant et al. [1973]]).
8. Bibliography

8.1. Compilations of phase diagrams

The classic compilation in the field of binary alloy phase diagrams is that of Hansen [1958]. This work was continued by Elliott [1965] and Shunk [1969]. These compilations contain critical commentaries. A non-critical compilation of binary alloy phase diagrams was prepared by Moffat [1978-1992]. Hultgren et al. [1973] have critically evaluated the phase diagrams and thermodynamic properties of several binary alloy systems. An extensive non-critical compilation of binary and ternary phase diagrams of metallic systems has been edited by Ageev [1959-1978]. An index to all compilations of binary alloy phase diagrams up to 1979 was prepared by Moffat [1979]. A critical compilation of binary phase diagrams involving Fe has been published by Ortud Kubiczkowski [1982].

Ternary alloy phase diagrams were compiled by Ageev [1959-1978] and by Guertler et al. [1969]. A bibliography of ternary and multicomponent metallic phase diagrams for the period 1955-1973 was published by Prince [1978]. VCH Publishers (NY) are producing a series of volumes of compilations of ternary alloy phase diagrams known as "Ternary Alloys." Eight volumes, in alphabetical order, have already appeared.

Since 1979, the American Society for Metals in collaboration with the National Institute of Science and Technology and with national organizations in several countries, has undertaken a project whose goal is a complete critical evaluation of all binary and ternary alloy phase diagrams. All available literature on phase equilibria, crystal structures, and often on thermodynamic properties is cited and critically evaluated in detail by "category editors" who are each responsible for a group of systems.

Evaluations of important systems usually run to several pages. The evaluations are peer reviewed and the majority are published in the Journal of Phase Equilibria, formerly the Bulletin of Alloy Phase Diagrams (ASM International, Materials Park, Ohio). More than 2500 binary evaluations have been completed. Condensed versions of approximately 2800 evaluations have been published in three volumes (Massalski et al. [1990]). When a "category" of evaluations (e.g. all binary phase diagrams with Cu) is completed, a monograph is published as part of the ASM Monograph Series.

An extensive bibliography of binary and multicomponent phase diagrams of all types of systems (metallic, ceramic, aqueous, organic, etc.) has been compiled by Wisniak [1981]. A bibliographical database known as THERMOCAL on thermodynamic properties and phase diagrams of systems of interest to materials scientists, with monthly updates, is available through Thermodata (Domaine Universitaire, Saint-Martin d'Hères, France).

8.2. Texts and review articles

A large number of texts and review articles covering all aspects of the theory, measurement and applications of phase diagrams are available. Only a selected few are listed here. A classical discussion of phase diagrams in metalurgy was given by Rhines [1956]. A definitive text on the theory of phase diagrams is that of Palatin and Laudau [1964]. Treatments of the geometry of multicomponent phase diagrams are given by Prince [1963], Prince [1966] and Hultgren [1985]. Good discussions of the interpretation of binary and ternary diagrams are given by West [1965] and Bergeron and Risbud [1984]. A series of five volumes edited by Alper [1970-1978] discusses many aspects of the theory, interpretation, measurement and applications of phase diagrams in materials science.

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References


Bergeron, C. J. and S. H. Risbud, 1984, Introduction to Phase Equilibria in Ceramics (American Ceramic Society, Columbus, Ohio).


Morrison, K., 1940, Z. Elektrochem. 46, 348.


