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Home Explore Search Tools Help
Element 1: Element 2: Element 3: Go

Introduction to Phase Diagrams

Return to Contents

Alloy phase diagrams are useful to metallurgists, materials engineers, and materials scientists in four major areas:

- Development of new alloys for specific applications,
- Fabrication of these alloys into useful configurations,
- Design and control of heat treatment procedures for specific alloys that will produce the required mechanical, physical, and chemical properties
- Solving problems that arise with specific alloys in their performance in commercial applications, thus improving product predictability.

In all these areas, the use of phase diagrams allows research, development, and production to be done more efficiently and cost effectively.

Common Terms

Several commonly used terms are described below.

Phases. All materials exist in gaseous, liquid, or solid form (usually referred to as a *phase*), depending on the conditions of state. State variables include compositions, temperature, pressure, magnetic field, electrostatic field, gravitational field, and so on. The term "phase" refers to that region of space occupied by a physically homogeneous material. However, there are two uses of the term: the strict sense normally used by scientists and the somewhat looser sense normally used by materials engineers.

In the strictest sense, homogeneous means that the physical properties throughout the region of space occupied by the phase are absolutely identical, and any change in condition of state, no matter how small, will result in a different phase. For example, a sample of solid metal with an apparently homogeneous appearance is not truly a single-phase material, because the pressure condition varies in the sample due to its own weight in the gravitational field.

In a phase diagram, however, each single-phase field (phase fields are discussed in a following section) is usually given a single label, and engineers often find it convenient to use this label to refer to all the materials lying within the field, regardless of how much the physical properties of the materials continuously change from one part of the field to another. This means that in engineering practice, the distinction between the terms "phase" and "phase field" is seldom made, and all materials having the same name are referred to as the same phase.

Equilibrium. There are three types of equilibria: stable, metastable, and unstable. These three conditions are illustrated in a mechanical sense in Fig. 1.

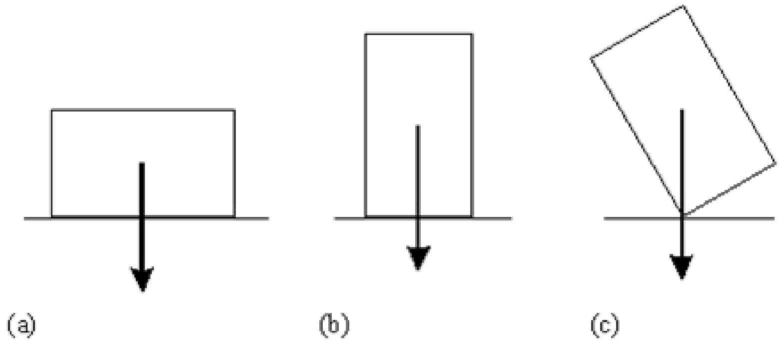


Fig. 1 Mechanical equilibria: (a) Stable. (b) Metastable. (c) Unstable.

Stable equilibrium exists when the object is in its lowest energy condition; metastable equilibrium exists when additional energy must be introduced before the object can reach true stability; unstable equilibrium exists when no additional energy is needed before reaching metastability or stability. Although true stable equilibrium conditions seldom exist, the study of equilibrium system is extremely valuable, because it constitutes a limiting condition from which actual conditions can be estimated.

Polymorphism. The structure of solid elements and compounds under stable equilibrium conditions is crystalline, and the crystal structure of each is unique. Some elements and compounds, however, are polymorphic (multishaped); that is, their structure transforms from one crystal structure to another with changes in temperature. The term allotropy (existing in another form) is usually used to describe polymorphic changes in chemical elements.

Metastable Phases. Under some conditions, metastable crystal structures can form instead of stable structure. Rapid freezing is a common method of producing metastable structures, but some (such as Fe_3C, or cementite) are produced at moderately slow cooling rates. With extremely rapid freezing, even thermodynamically unstable structures (such as amorphous metal glasses) can be produced.

Systems. A physical *system* consists of a substance (or group of substances) that is isolated from its surroundings, this concept is used to facilitate study of the effects of conditions of state. "Isolated" means that there is no interchange of mass between the substance and its surroundings. The substances in alloy systems, for example, might be two metals, such as copper and zinc; a metal and a nonmetal, such as iron and carbon, a metal and an intermetallic compound, such as iron and cementite; or several metals such as aluminum, magnesium, and manganese. These substances constitute the components bordering the system and should not be confused with the various phases found with in the system. A system, however, can also consist of a single component such as an element or compound.

Phase Diagram. In order to record and visualize the result of studying the effect of stage variable on a system, diagrams were introduced to show the relationships between the various phases that appear within the system under equilibrium conditions, As such, the diagrams are variously called *constitutional diagrams*, *equilibrium diagrams*, or *phase diagrams*. A single-component phase diagram can be simply a one- or two-dimensional plot showing the phase change in the substance as temperature and/or pressure change. Most diagrams, however, are two-or three-dimensional plots describing the phase relationships in systems made up of two or more components, and these usually contain fields (areas) consisting of mixed-phase fields, as well as single-phase fields.

Phase Rule. The *phase rule*, first announced by J. Willard Gibbs in 1876, relates the physical state of a mixture to the number of constituents in the system and to its conditions. It was also Gibbs who first called each homogeneous region in a system by the term "phase." When pressure and temperature are the state variables, the rule can be written as:

$f = c - p + 2$ where f is the number of independent variables (called degrees of freedom), c is the number of components, and p is the number of stable phases in the system.

Binary Diagrams

If a system being considered is bordered by two components, the system is called a binary system. Most metallurgical problems are concerned only with a fixed pressure of 1 atm, and the phase diagram is expressed by a two-dimensional plot of temperature and composition.

The Gibbs phase rule applies to all states of matter (solid, liquid, and gaseous), but when the effect of pressure is constant, the rule reduces to:

$f = c - p + 1$

The stable equilibria for binary systems are summarized as:

Number of components	Number of phases	Degree of freedom	Equilibrium
2	3	0	Invariant
2	2	1	Univariant
2	1	2	Bivariant

Miscible Solids. Many systems are bordered by components having the same crystal structure, and the components of some of these systems are completely miscible (completely soluble in each other) in the solid form, thus forming a continuous solid solution. When this occurs in a binary system, the phase diagram usually has the general appearance of that shown in Fig. 2.

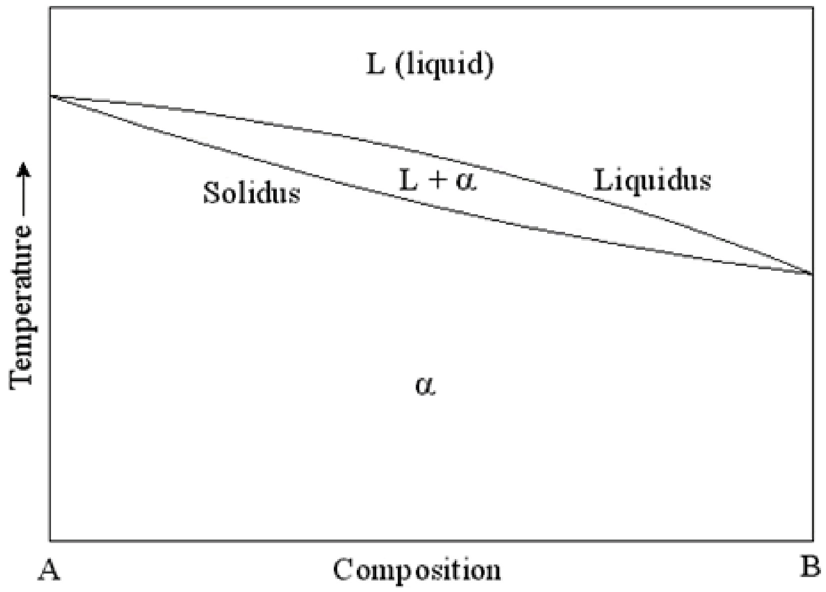


Fig. 2 Schematic binary phase diagram showing miscibility in both the liquid and solid states.

The diagram consists of two single-phase fields separated by a two-phase field. The boundary between the liquid field and the two-phase field in Fig. 2 is called the liquidus; that between the two-phase field and the solid field is the solidus. In general, a liquidus is the locus of points in a phase diagram representing the temperatures at which alloys of the various compositions of the system begin to freeze on cooling or finish melting on heating; a solidus is the locus of points representing the temperatures at which the various alloys finish freezing on cooling or begin melting on heating. The phases in equilibrium across the two-phase field in Fig. 2 (the liquid and solid solutions) are called conjugate phases. If the solidus and liquidus meet tangentially at some point, a maximum or minimum is produced in the two-phase field, splitting it into two portions, as shown in Fig. 3.

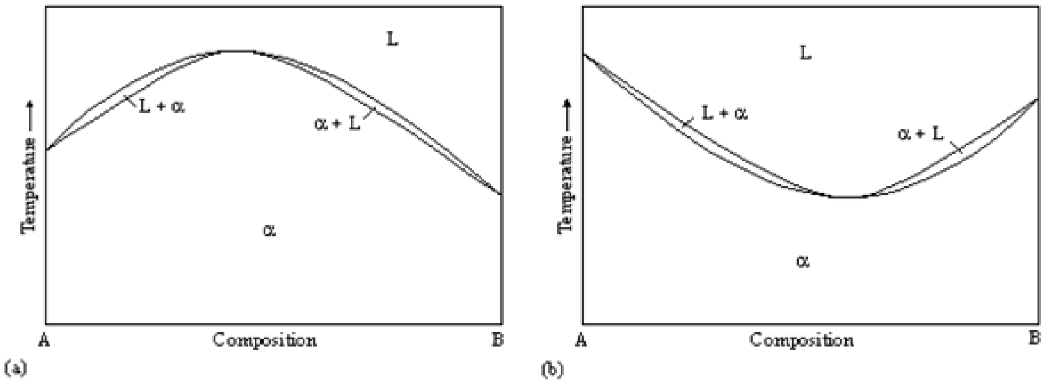


Fig. 3 Schematic binary phase diagrams with solid state miscibility where the liquidus shows a maximum (a) and a minimum (b).

It also is possible to have a gap in miscibility in a single-phase field; this is shown in Fig. 4. Point T_c, above which phase α1 and α2 become indistinguishable, is a critical point. Lines a-T_c and b-T_c, called solvus lines, indicate the limits of solubility of component B in A and A in B, respectively. The configuration of these and all other phase diagrams depends on the thermodynamics of the system, as discussed later.

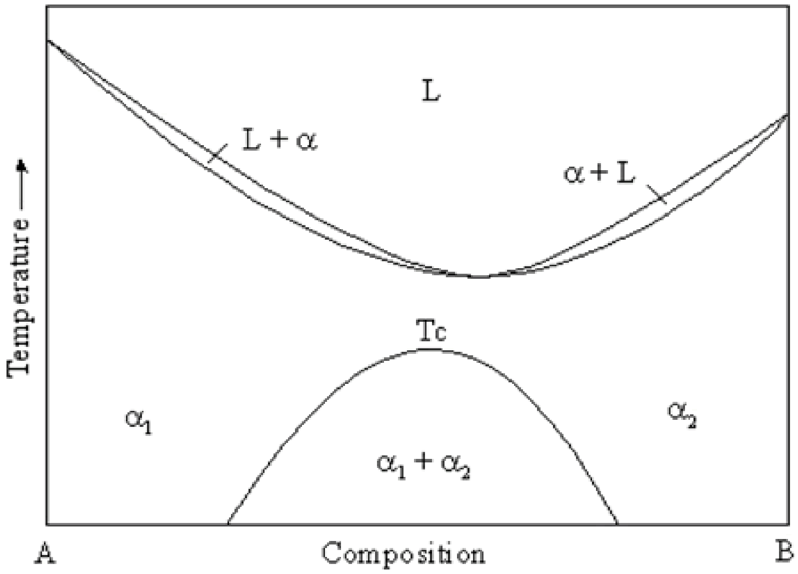
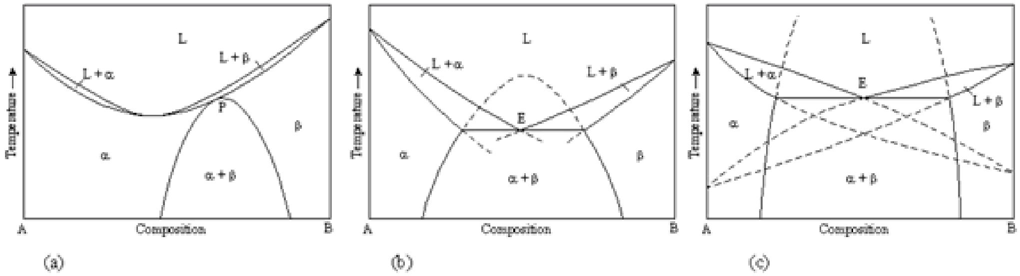


Fig. 4 Schematic binary phase diagrams with a gap in miscibility in a single-phase field.

Eutectic Reactions. If the two-phase field in the solid region of Fig. 4 is expanded so that it touches the solidus at some point, as shown in Fig. 5(a), complete miscibility of the components is lost. Instead of a single solid phase, the diagram now shows two separate solid terminal phases, which are in three-phase equilibrium with the liquid at point P, an invariant point that occurred by coincidence (Three-phase equilibrium is discussed in the next section.)



(a) (b) (c)

Fig. 5 Schematic binary phase diagrams with invariant points. (a) Hypothetical diagram of the type shown in Fig. 4 except that the miscibility gap in the solid touches the solidus curve at invariant point P;an actual diagram of this type probably does not exist. (b) and (c) Typical eutectic diagrams for components having the same crystal structure (b) and components having different crystal structures (c). The eutectic (invariant) points are labeled E. The dashed lines in (b) and (c) are metastable extensions of the stable equilibria lines.

Then, if this two-phase field in the solid region is even further widened so that the solvus lines no longer touch at the invariant point, the diagram passes through a series of configurations, finally taking on the more familiar shape shown in Fig. 5(b). The three-phase reaction that takes place at the invariant point E, where the liquid phase freezes into a mixture of two solid phases, is called a eutectic reaction (from the Greek word for "easily melted"). The alloy that corresponds to the eutectic composition is called a eutectic alloy. An alloy having a composition to the left of the eutectic point is called a hypoeutectic alloy (from the Greek word for "less than"); an alloy to the right is a hypereutectic alloy (meaning "greater than"). In the eutectic system described previously, the two components of the system have the same crystal structure. This, and other factors, allows complete miscibility between them. Eutectic systems, however, also can be formed by two components having different crystal structures. When this occurs, the liquidus and solidus curves (and their extensions into the two-phase field) for each of the terminal phases (see Fig. 5c) resemble those for the situation of complete miscibility between system components shown in Fig. 2.

Three-Phase Equilibrium. Reactions involving three conjugate phases are not limited to the eutectic reaction. For example, upon cooling, a single solid phase can change into a mixture of two new solid phases or, conversely, two solid phases can react to form a single new phase. These and the other various types of invariant reactions observed in binary systems are illustrated in Fig. 6.

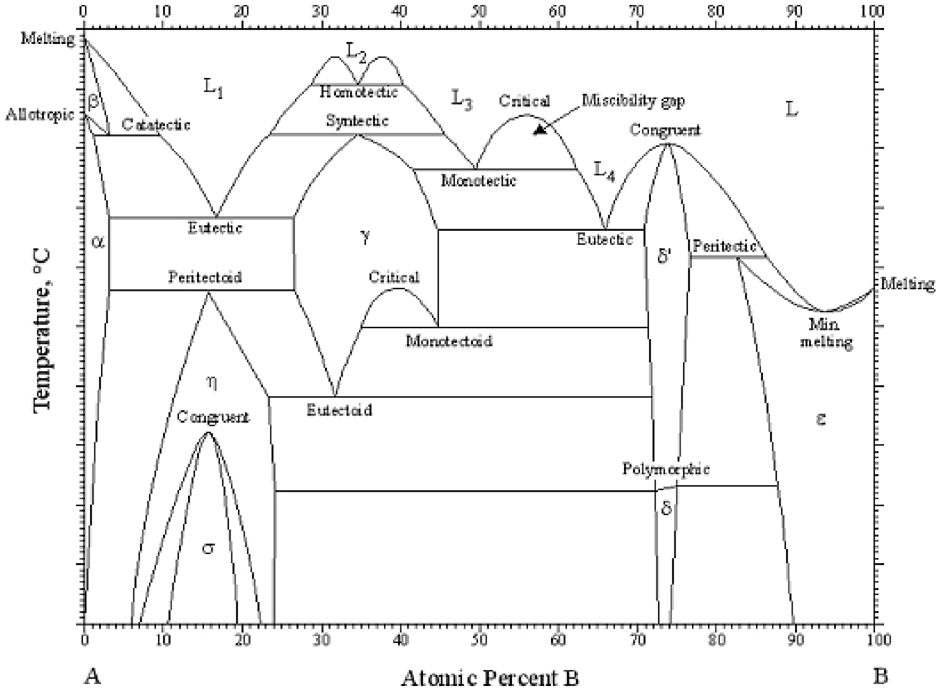


Fig. 6 This Schematic phase diagram showing various types of invariant reactions observed in binary systems.

Intermediate Phases. In addition to the three solid terminal phases α, β, and ε, the diagram in Fig. 6 displays five other solid phase fields, γ, δ, δ', η, and σ, at intermediate compositions. Such phases are called intermediate phases. Many intermediate phases, such as those illustrated in Fig. 6, have a fairly wide range of homogeneity. However, many others have a very limited or no significant homogeneity range.

When an intermediate phase of limited (or no) homogeneity range is located at or near a specific ratio of component elements that reflects the normal positioning of the component atoms in the crystal structure of the phase, it is often called a compound (or line compound). When the components of the system are metallic, such an intermediate phase is often called an intermetallic compound. Three intermetallic compounds (with four types of melting reactions) are shown in Fig. 7.

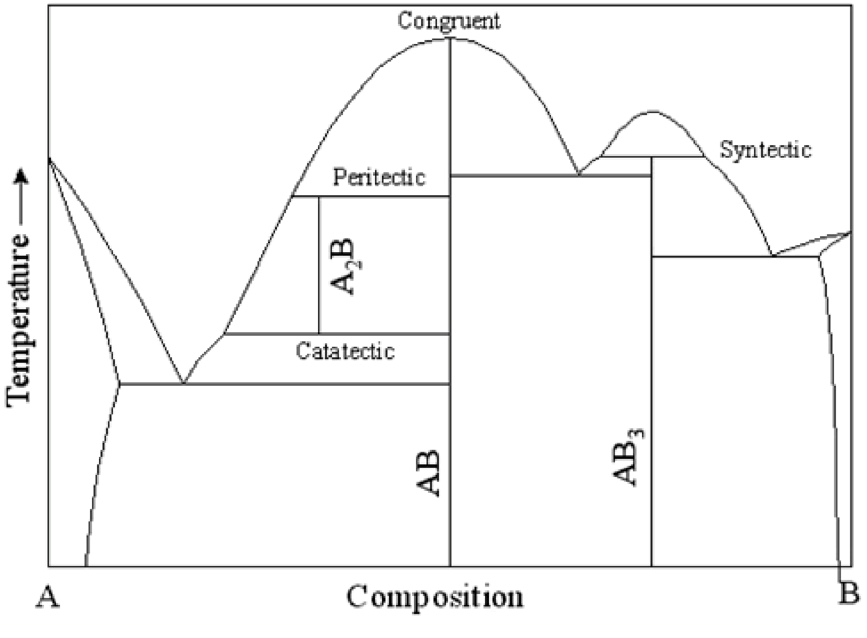


Fig. 7 Schematic phase diagram showing three intermetallic line compounds and four melting reactions.

In the hypothetical diagram shown in Fig. 7, an alloy of composition AB will freeze and melt isothermally, without the liquid or solid phases undergoing changes in composition; such a phase change is called congruent. All other reactions are incongruent; that is two phases are formed from one phase on melting. Congruent and incongruent phase changes, however, are not limited to line compounds: the terminal component B (pure phase ε) and the highest-melting composition of intermediate phase δ' in Fig. 6, for example, freeze and melt congruently, while δ' and ε freeze and melt incongruently at other compositions.

Metastable Equilibrium. In Fig. 5(c), dashed lines indicate the portion of the liquidus and solidus lines that disappear into the two-phase solid region. These dashed lines represent valuable information, as they indicate a condition that would exist under metastable equilibrium, such as might theoretically occur during extremely rapid cooling.

Ternary Diagrams

When a third component is added to a binary system, illustrating equilibrium conditions in two dimensions becomes more complicated. One option is to add a third composition dimension to the base, forming a solid diagram having binary diagrams as its vertical sides. This can be represented as a modified isometric projection, such as shown in Fig. 8. Here, boundaries of single-phase fields (liquidus, solidus, and solvus lines in the binary diagrams) become surfaces; single- and two-phase areas become volumes; three-phase lines become volumes; and four-phase points, while not shown in Fig. 8, can exist as an invariant plane. The composition of a binary eutectic liquid, which is a point in a two-component system, becomes a line in a ternary diagram, as shown in Fig. 8.

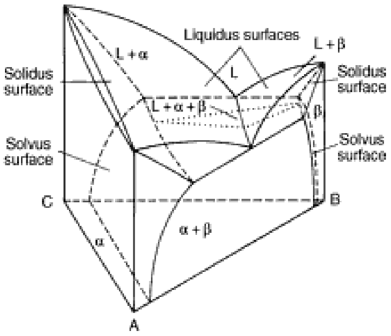


Fig. 8 Ternary phase diagram showing three-phase equilibrium.[1]

While three-dimensional projections can be helpful in understanding the relationships in the diagram, reading values from them is difficult. Ternary systems, therefore, are often represented by views of the binary diagrams that comprise the faces and two-dimensional projections of the liquidus and solidus surfaces, along with a series of two-dimensional horizontal sections (isotherms) and vertical sections (isopleths) through the solid diagram.

Vertical sections are often taken through one corner (one component) and a congruently melting binary compound that appears on the opposite face; when such a plot can be read like any other true binary diagram, it is called a quasi-binary section. One possibility of such a section is illustrated by line 1-2 in the isothermal section shown in Fig. 9. A vertical section between a congruently melting binary compound on one face and one on a different face might also form a quasi-binary section (see line 2-3).

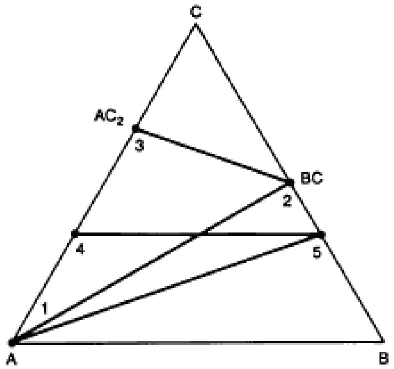


Fig. 9 Isothermal section of a ternary diagram with phase boundaries deleted for simplification

All other vertical sections are not true binary diagrams, and the term *pseudobinary* is applied to them. A common pseudobinary section is one where the percentage of one of the components is held constant (the section is parallel to one of the faces), as shown by line 4-5 in Fig. 9. Another is one where the ratio of two constituents is held constant, and the amount of the third is varied from 0 to 100% (line 1-5).

Isothermal Sections. Composition values in the triangular isothermal sections are read from a triangular grid consisting of three sets of lines parallel to the faces and placed at regular composition intervals (see Fig. 10). Normally, the point of the triangle is placed at the top of the illustration, component A is placed at the bottom left, B at the bottom right, and C at the top. The amount of constituent A is normally indicated from point C to point A, the amount of constituent B from point A to point B, and the amount of constituent C from point B to point C. This scale arrangement is often modified when only a corner area of the diagram is shown.

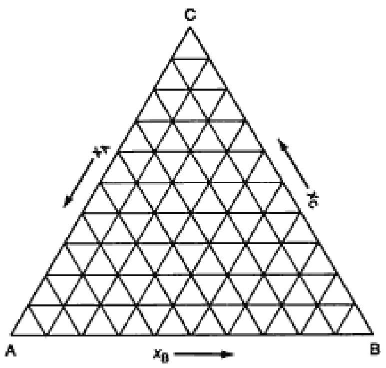


Fig. 10 Triangular composition grid for isothermal sections; X is the composition of each constituent in mole fraction or percent

Projected Views. Liquidus, solidus, and solvus surfaces by their nature are not isothermal. Therefore, equal-temperature (isothermal) contour lines are often added to the projected views of these surfaces to indicate the shape of the surfaces (see Fig. 11). In addition to (or instead of) contour lines, views often show lines indicating the temperature troughs (also called "valleys" or "grooves") formed at the intersections of two surfaces. Arrowheads are often added to these lines to indicate the direction of decreasing temperature in the trough.

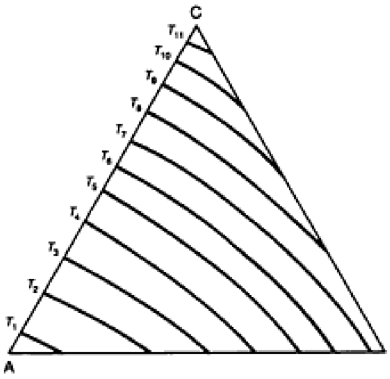


Fig. 11 Liquidus projection of a ternary phase diagram showing isothermal contour lines.[1]

Thermodynamic Principles

The reactions between components, the phases formed in a system, and the shape of the resulting phase diagram can be explained and understood through knowledge of the principles, laws, and terms of thermodynamics, and how they apply to the system.

Internal Energy. The sum of the kinetic energy (energy of motion) and potential energy (stored energy) of a system is called its internal energy, U. Internal energy is characterized solely by the state of the system.

Closed System. A thermodynamic system that undergoes no interchange of mass (material) with its surroundings is called a closed system. A closed system, however, can interchange energy with its surroundings.

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

$$dU = dQ - dW$$

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

$$dU = dQ - pdV$$

Enthalpy. Thermal energy changes under constant pressure (again neglecting any field effects) are most conveniently expressed in terms of the enthalpy, H, of a system. Enthalpy, also called heat content, is defined by:

$$H = U + pV$$

Enthalpy, like internal energy, is a function of the state of the system, as is the product pV.

Heat Capacity The heat capacity, C, of a substance is the amount of heat required to raise its temperature one degree; that is:

$$C = dQ/dT$$

However, if the substance is kept at constant volume ($dV = 0$):

$$C_V = (\partial Q/\partial T)_V = (\partial U/\partial T)_V$$

If, instead, the substance is kept at constant pressure (as in many metallurgical systems),

$$C_p = (\partial H/\partial T)_p$$

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

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

$$\Delta S = \Delta Q/T = \Delta U + p\Delta V/T$$

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

Gibbs Energy. Because both S and V are difficult to control experimentally, an additional term, Gibbs energy, G, is introduced, whereby:

$$G = U + pV - TS = H - TS$$

and

$$dG = dU + pdV + Vdp - TdS - SdT$$

However,

$$dU = TdS + pdV$$

Therefore,

$$dG = Vdp - SdT$$

Here, the change in Gibbs energy of a system undergoing a process is expressed in terms of two independent variables, pressure and absolute temperature, which are easily controlled experimentally. If the process is carried out under conditions of constant pressure and temperature, the change in Gibbs energy of a system at equilibrium with its surroundings (a reversible process) is zero. For a spontaneous (irreversible) process, the change in Gibbs energy is less than zero (negative); that is, the Gibbs energy decreases during the process, and it reaches a minimum at equilibrium.

Features of Phase Diagrams

The areas (fields) in a phase diagram, and the position and shapes of the points, lines, surfaces, and intersections in it, are controlled by thermodynamic principles and the thermodynamic properties of all of the phases that constitute the system.

Phase-Field Rule. The phase-field rule specifies that at constant temperature and pressure, the number of phases in adjacent fields in a multi-component diagram must differ by one.

Theorem of Le Chatelier. The theorem of Henri Le Chatelier, which is based on thermodynamic principles, states that if a system in equilibrium is subjected to a constraint by which the equilibrium is altered, a reaction occurs that opposes the constraint, that is, a reaction that partially nullifies the alteration.

Clausius-Clapeyron Equation. The theorem of Le Chatelier was quantified by Benoit Clapeyron and Rudolf Clausius to give:

$$dp/dT = \Delta H/T\Delta V$$

where dp/dT is the slope of the univariant line in a p-T diagram, ΔV is the difference in molar volume of the two phases in the reaction, and ΔH is the difference in molar enthalpy of the two phases (the heat of reaction).

Solutions. The shape of liquidus, solidus, and solvus curves (or surfaces) in a phase diagram are determined by the Gibbs energies of the relevant phases. In this instance, the Gibbs energy must include not only the energy of the constituent components, but also the energy of mixing of these components in the phase. Consider, for example, the situation of complete miscibility shown in Fig. 2. The two phases, liquid and solid, are in stable equilibrium in the two-phase field between the liquidus and solidus lines. The Gibbs energies at various temperatures are calculated as a function of composition for ideal liquid solutions and for ideal solid solutions of the two components, A and B. The result is a series of plots similar to those shown in Fig. 12(a) to (e).

At temperature T_1, the liquid solution has the lower Gibbs energy and, therefore, is the more stable phase. At T_2, the melting temperature for component A, the liquid and solid are equally stable only at a composition of pure A. At temperature T_3, between the melting temperatures of components A and B, the Gibbs energy curves cross. Temperature T_4 is the melting temperature of component B, while T_5 is below it.

Construction of the two-phase liquid-plus-solid field of the phase diagram in Fig. 12(f) is as follows. According to thermodynamic principles, the compositions of the two phases in equilibrium with each other at temperature T_3 can be determined by constructing a straight line that is tangential to both curves in Fig. 12(c). The points of tangency, 1 and 2, are then transferred to the phase diagram as points on the solidus and liquidus, respectively. This is repeated at sufficient temperatures to determine the curves accurately. If, at some temperature, the Gibbs energy curves for the liquid and the solid tangentially touch at some point, the resulting phase diagram will be similar to those shown in Fig. 3(a) and (b), where a maximum or minimum appears in the liquidus and solidus curves.

Mixture. The two-phase field in Fig. 12(f) consists of a mixture of liquid and solid phases. As stated above, the compositions of the two phases in equilibrium at temperature T_3 are C_1 and C_2. The horizontal isothermal line connecting points 1 and 2, where these compositions intersect temperature T_3, is called a tie line. Similar tie lines connect the coexisting phases throughout all two-phase fields in binary systems.

Eutectic phase diagrams, a feature of which is a field where there is a mixture of two solid phases, also can be constructed from Gibbs energy curves. Consider the temperatures indicated on the phase diagram in Fig. 13(f) and the Gibbs energy curves for these temperatures (Fig. 13a-e).

When the points of tangency on the energy curves are transferred to the diagram, the typical shape of a eutectic system results. Binary diagrams that have three-phase reactions other than the eutectic reaction, as well as diagrams with multiple three-phase reactions, also can be constructed from appropriate Gibbs energy curves.

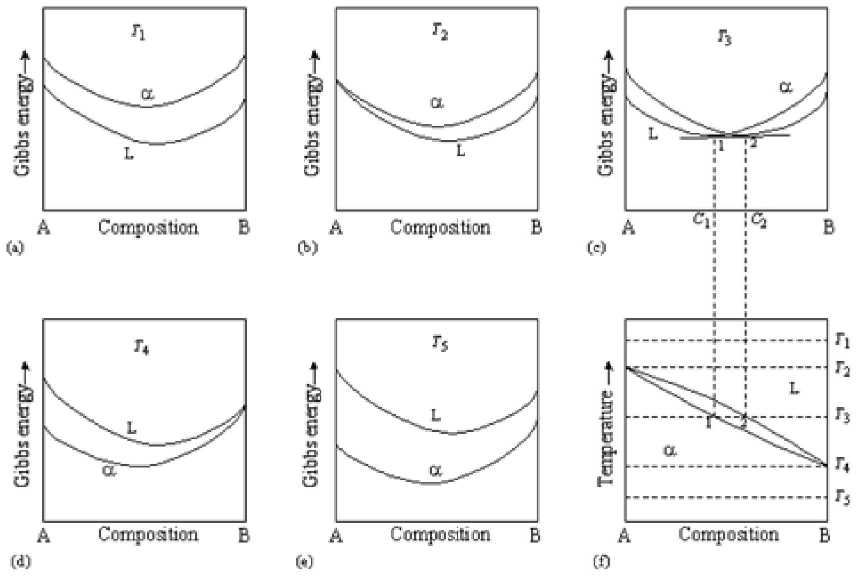


Fig. 12 Use of Gibbs energy curves to construct a binary phase diagram that shows miscibility in both the liquid and the solid.

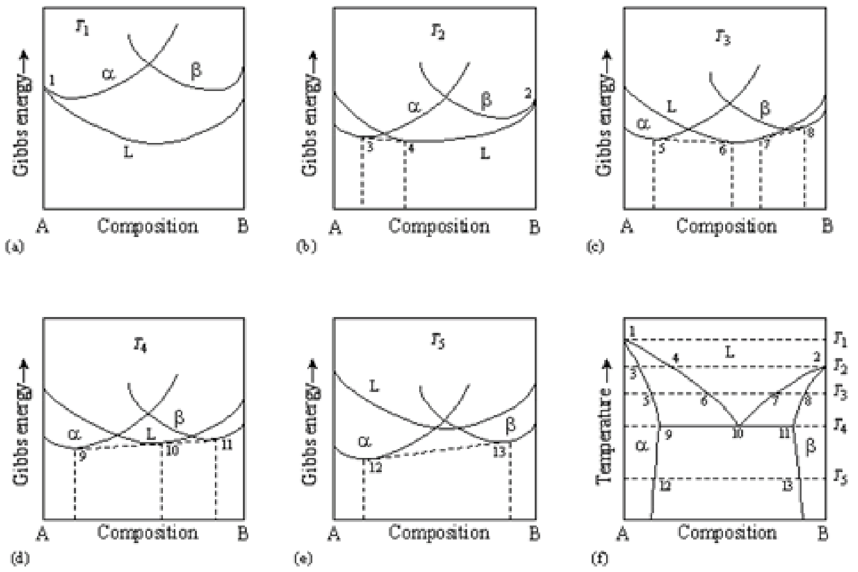


Fig. 13 Use of Gibbs energy curves to construct a binary phase diagram of the eutectic type.

Curves and Intersections. Thermodynamic principles also limit the shape of the various boundary curves (or surfaces) and their intersections. For example, see the *PT* diagram shown in Fig. 14. The Clausius-Clapeyron equation requires that at the intersection of the triple curves in such a diagram, the angle between adjacent curves should never exceed 180°, or alternatively, the extension of each triple curve between two phases must lie within the field of third phase.

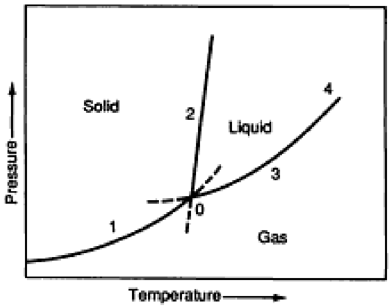


Fig. 14 Pressure-temperature phase diagram.

The angle at which the boundaries of two-phase fields meet also is limited by thermodynamics. That is, the angle must be such that the extension of each beyond the point of intersection projects into a two-phase field, rather than a one-phase field. An example of correct intersections can be seen in Fig. 15(b), where both the solidus and solvus lines are concave. However, the curvature of both boundaries need not be concave.

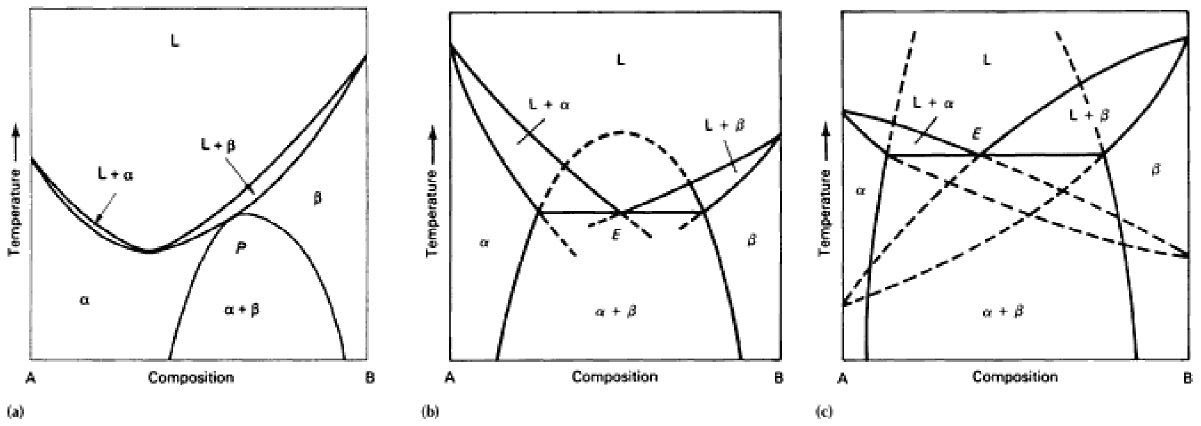


Fig. 15 Binary phase diagrams with invariant points. (a) Hypothetical diagram in which the miscibility gap in the solid touches the solidus curve at invariant point P; an actual diagram of this type probably does not exist. (b) and (c) Typical eutectic diagrams for (b) components having the same crystal structure, and (c) components having different crystal structures; the eutectic (invariant) points are labeled E. The dashed lines in (b) and (c) are metastable extensions of the stable-equilibria lines.

Congruent Transformations. The *congruent point* on a phase diagram is where different phases of same composition are in equilibrium. The *Gibbs-Konovalov Rule* for congruent points, which was developed by Dmitry Konovalov from a thermodynamic expression given by J. Willard Gibbs, states that the slope of phase boundaries at congruent transformations must be zero (horizontal). Examples of correct slope at the maximum and minimum points on liquidus and solidus curves can be seen in Fig. 16.

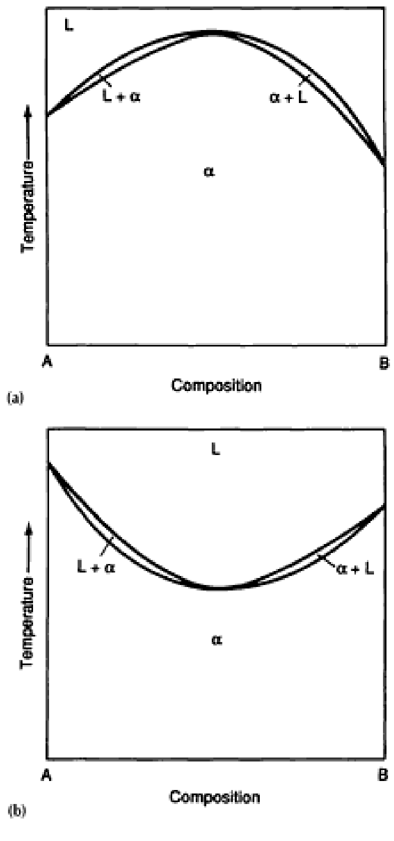


Fig. 16 Binary phase diagrams with solid-state miscibility where the liquidus shows (a) a maximum and (b) a minimum.

Higher-Order Transitions. *First-order transitions* are those involving distinct phases having different lattice parameters, enthalpies, entropies, densities, and so forth. Transitions not involving discontinuities in composition, enthalpy, entropy, or molar volume are called *higher-order transitions* and occur less frequently. The change in the magnetic quality of iron from ferromagnetic to paramagnetic as the temperature is raised above 771 °C (1420 °F) is an example of a second-order transition: no phase change is involved and the Gibbs phase rule does not come into play in the transition.

Another example of a higher-order transition is the continuous change from a random arrangement of the various kinds of atoms in a multicomponent crystal structure (a *disordered structure*) to an arrangement where there is some degree of *crystal ordering* of the atoms (an *ordered structure*, or *superlattice*), or the reverse reaction.

Reading Phase Diagrams

Composition Scales. Phase diagrams to be used by scientists are usually plotted in atomic percentage (or mole fraction), while those to be used by engineers are usually plotted in weight percentage.

Lines and Labels. Magnetic transitions (Curie temperature and Néel temperature) and uncertain or speculative boundaries are usually shown in phase diagrams as nonsolid lines of various types.

The components of metallic systems, which usually are pure elements, are identified in phase diagrams by their symbols. Allotropes of polymorphic elements are distinguished by small (lower-case) Greek letter prefixes.

Terminal solid phases are normally designated by the symbol (in parentheses) for the allotrope of the component element, such as (Cr) or (αTi). Continuous solid solutions are designated by the names of both elements, such as (Cu,Pd) or (βTi, βY).

Intermediate phases in phase diagrams are normally labeled with small (lower-case) Greek letters. However, certain Greek letters are conventionally used for certain phases, particularly disordered solutions: for example, β for disordered body-centered cubic (bcc), ζ or ε for disordered close-packed hexagonal (cph), γ for the γ-brass-type structure, and δ for the δ CrFe-type structure.

For line compounds, a stoichiometric phase name is used in preference to a Greek letter (for example, A_2B_3 rather than δ). Greek letter prefixes are used to indicate high- and low-temperature forms of the compound (for example, αA_2B_3 for the low-temperature form and βA_2B_3 for the high-temperature form).

Lever Rule. A tie line is an imaginary horizontal line drawn in a two-phase field connecting two points that represent two coexisting phases in equilibrium at the temperature indicated by the line. Tie lines can be used to determine the fractional amounts of the phases in equilibrium by employing the lever rule. The *lever rule* is a mathematical expression derived by the principle of conservation of matter in which the phase amounts can be calculated from the bulk composition of the alloy and compositions of the conjugate phases, as shown in Fig. 17(a).

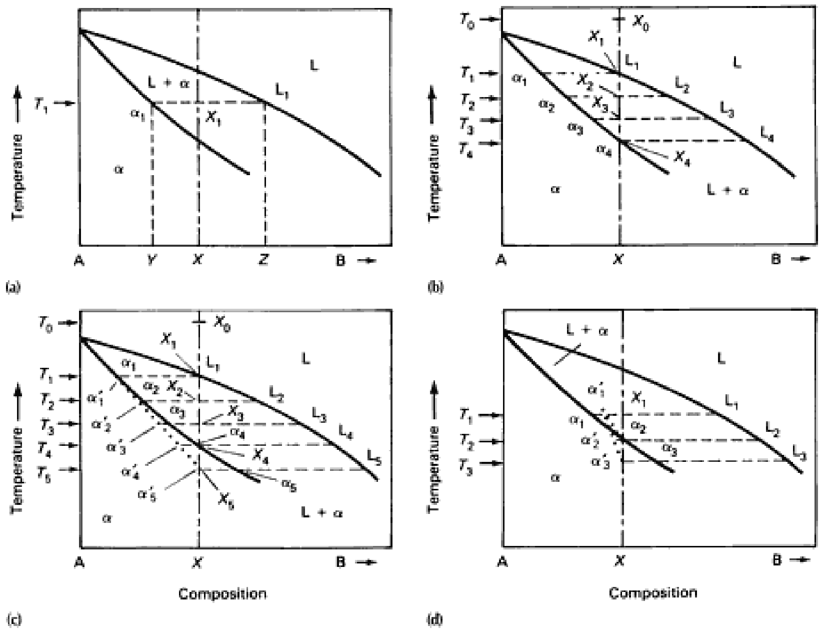


Fig. 17 Portion of a binary phase diagram containing a two-phase liquid-plus-solid field illustrating (a) application of the lever rule to (b) equilibrium freezing, (c) nonequilibrium freezing, and (d) heating of a homogenized sample.1

At the left end of the line between α_1 and L_1, the bulk composition is *Y*% component B and 100 - *Y*% component A, and consists of 100% a solid solution. As the percentage of component B in the bulk composition moves to the right, some liquid appears along with the solid. With further increases in the amount of B in the alloy, more of the mixture consists of liquid, until the material becomes entirely liquid at the right end of the tie line. At bulk composition *X*, which is less than halfway to point L_1, there is more solid present than liquid. The lever rule says that the percentages of the two phases present can be calculated as follows:

$$\%\,\text{liquid} = \frac{\text{Length of line } \alpha_1 X_1}{\text{Length of line } \alpha_1 L_1} \times 100$$

$$\%\,\text{solid}\,\alpha = \frac{\text{Length of line } X_1 L_1}{\text{Length of line } \alpha_1 L_1} \times 100$$

It should be remembered that the calculated amounts of the phases present are either in weight or atomic percentages, and, as shown in Table 1, do not directly indicate the area or volume percentages of the phases observed in microstructures.

Table 1 Volume fraction

In order to relate the weight fraction of a phase present in an alloy specimen as determined from a phase diagram to its two-dimensional appearance as observed in a micrograph, it is necessary to be able to convert between weight-fraction values and area-fraction values, both in decimal fractions. This conversion can be developed:
The weight fraction of the phase is determined from the phase diagram, using the lever rule.
Volume portion of the phase = (Weight fraction of the phase)/(Phase density)
Total volume of all phases present = Sum of the volume portions of each phase.
Volume fraction of the phase = (Weight fraction of the phase)/(Phase density × total volume)
It has been shown by stereology and quantitative metallography that areal fraction is equal to volume fraction.2 (Areal fraction of a phase is the sum of areas of the phase intercepted by a microscopic traverse of the observed region of the specimen divided by the total area of the observed region.) Therefore:
Areal fraction of the phase = (Weight fraction of the phase)/(Phase density × total volume)
The phase density value for the preceding equation can be obtained by measurements or calculation. The densities of chemical elements, and some line compounds, can be found in the literature. Alternatively, the density of a unit cell of a phase comprising one or more elements can be calculated from information about its crystal structure and the atomic weights of the elements comprising it as follows:
Weight of each element = number of atoms × [(Atomic weight)/(Avogadro's number)]

Total cell weight = Sum of weights of each element
Density = Total cell weight/cell volume
For example, the calculated density of pure copper, which has a face-centered cubic (fcc) structure and a lattice parameter of 0.36146 nm, is:
$\rho = \frac{4\ \text{atoms/cell} \times 63.546\ \text{g/mol}}{6.0227 \times 10^{23}\ \text{atoms/mol} \times (0.36146 \times 10^{-9}\ \text{m})^3}$ $= 8.937\ \text{Mg/m}^3$
This compares favorably with the published value of 8.93.

Phase-Fraction Lines. Reading phase relationships in many ternary diagram sections (and other types of sections) can often be difficult due to the great many lines and areas present. *Phase-fraction lines* are used by some to simplify this task. In this approach, the sets of often nonparallel tie lines in the two-phase fields of isothermal sections (see Fig. 18a) are replaced with sets of curving lines of equal phase fraction (Fig. 18b). Note that the phase-fraction lines extend through the three-phase region where they appear as a triangular network. As with tie lines, the number of phase-fraction lines used is up to the individual using the diagram. While this approach to reading diagrams may not seem helpful for such a simple diagram, it can be a useful aid in more complicated systems.[3,4]

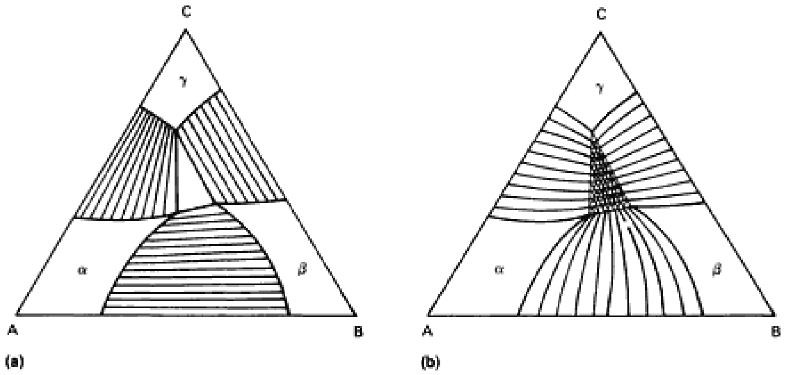


Fig. 18 Alternative systems for showing phase relationships in multiphase regions of ternary-diagram isothermal sections. (a) Tie lines. (b) Phase-fraction lines.[3]

Solidification. Tie lines and the lever rule can be used to understand the freezing of a solid-solution alloy. Consider the series of tie lines at different temperature shown in Fig. 17(b), all of which intersect the bulk composition X. The first crystals to freeze have the composition α1. As the temperature is reduced to T_2 and the solid crystals grow, more A atoms are removed from the liquid than B atoms, thus shifting the composition of the remaining liquid to composition L_2. Therefore, during freezing, the compositions of both the layer of solid freezing out on the crystals and the remaining liquid continuously shift to higher B contents and become leaner in A. Therefore, for equilibrium to be maintained, the solid crystals must absorb B atoms from the liquid and B atoms must migrate (diffuse) from the previously frozen material into subsequently deposited layers. When this happens, the average composition of the solid material follows the solidus line to temperature T_4 where it equals the bulk composition of the alloy.

Coring. If cooling takes place too rapidly for maintenance of equilibrium, the successive layers deposited on the crystals will have a range of local compositions from their centers to their edges (a condition known as coring). Development of this condition is illustrated in Fig. 17(c). Without diffusion of B atoms from the material that solidified at temperature T_1 into the material freezing at T_2, the average composition of the solid formed up to that point will not follow the solidus line. Instead it will remain to the left of the solidus, following compositions α'1 through α'3. Note that final freezing does not occur until temperature T_5, which means that nonequilibrium solidification takes place over a greater temperature range than equilibrium freezing. Because most metals freeze by the formation and growth of "treelike" crystals, called *dendrites*, coring is sometimes called *dendritic segregation*. An example of cored dendrites is shown in Fig. 19.

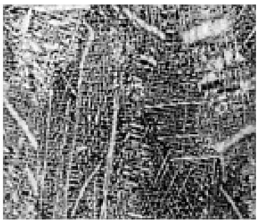


Fig. 19 Copper alloy 71500 (Cu-30Ni) ingot. Dendritic structure shows coring: light areas are nickel-rich; dark areas are low in nickel. 20×.[2]

Liquation. Because the lowest freezing material in a cored microstructure is segregated to the edges of the solidifying crystals (the grain boundaries), this material can remelt when the alloy sample is heated to temperatures below the equilibrium solidus line. If grain-boundary melting (called *liquation* or "burning") occurs while the sample is also under stress, such as during hot forming, the liquefied grain boundaries will rupture and the sample will lose its ductility and be characterized as *hot short*.

Liquation also can have a deleterious effect on the mechanical properties (and microstructure) of the sample after it returns to room temperature. This is illustrated in Fig. 17(d) for a homogenized sample. If homogenized alloy X is heated into the liquid-plus-solid region for some reason (inadvertently or during welding, etc.), it will begin to melt when it reaches temperature T_2; the first liquid to appear will have the composition L_2. When the sample is heated at normal rates to temperature T_1, the liquid formed so far will have a composition L_1, but the solid will not have time to reach the equilibrium composition α_1. The average composition will instead lie at some intermediate value such as α'_1. According to the lever rule, this means that less than the equilibrium amount of liquid will form at this temperature. If the sample is then rapidly cooled from temperature T_1, solidification will occur in the normal manner, with a layer of material having composition a1 deposited on existing solid grains. This is followed by layers of increasing B content up to composition α_3 at temperature T_3, where all of the liquid is converted to solid. This produces coring in the previously melted regions along the grain boundaries and sometimes even voids that decrease the strength of the sample. Homogenization heat treatment will eliminate the coring, but not the voids.

Eutectic Microstructures. When an alloy of eutectic composition is cooled from the liquid state, the eutectic reaction occurs at the eutectic temperature, where the two distinct liquidus curves meet. At this temperature, both α and β solid phases must deposit on the grain nuclei until all of the liquid is converted to solid. This simultaneous deposition results in microstructures made up of distinctively shaped particles of one phase in a matrix of the other phase, or alternate layers of the two phases. Examples of characteristic eutectic microstructures include spheroidal, nodular, or globular; acicular (needles) or rod; and lamellar (platelets, Chinese script or dendritic, or filigreed). Each eutectic alloy has its own characteristic microstructure, when slowly cooled (see Fig. 20). Cooling more rapidly, however, can affect the microstructure obtained (see Fig. 21). Care must be taken in characterizing eutectic structures because elongated particles can appear nodular and flat platelets can appear elongated or needlelike when viewed in cross section.

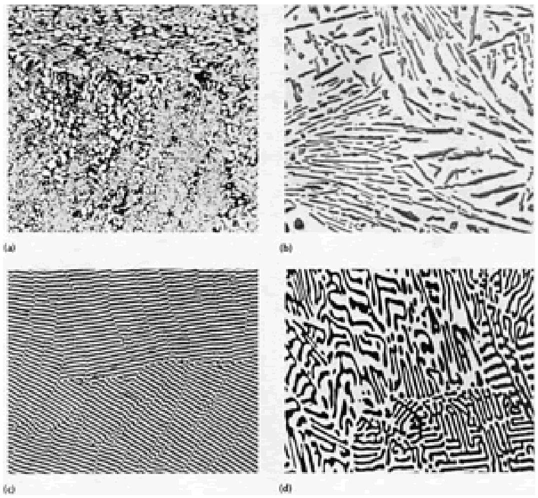


Fig. 20 Examples of characteristic eutectic microstructures in slowly cooled alloys. (a) 40Sn-50In alloy showing globules of tin-rich intermetallic phase (light) in a matrix of dark indium-rich intermetallic phase. 150×. (b) Al-13Si alloy showing an acicular structure consisting of short, angular particles of silicon (dark) in a matrix of aluminum. 200×. (c) Al-33Cu alloy showing a lamellar structure consisting of dark platelets of CuAl2 and light platelets of aluminum solid solution. 180×. (d) Mg-37Sn alloy showing a lamellar structure consisting of Mg2Sn "Chinese-script" (dark) in a matrix of magnesium solid solution. 250×.[2]

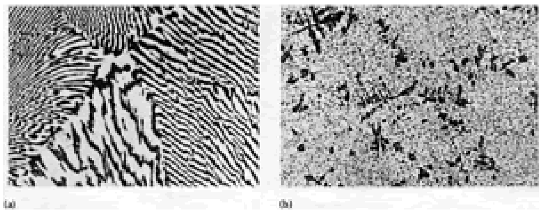


Fig. 21 Effect of cooling rate on the microstructure of Sn-37Pb alloy (eutectic soft solder). (a) Slowly cooled sample shows a lamellar structure consisting of dark platelets of lead-rich solid solution and light platelets of tin. 375×. (b) More rapidly cooled sample shows globules of lead-rich solid solution, some of which exhibit a slightly dendritic structure, in a matrix of tin. 375×.[2]

If the alloy has a composition different than the eutectic composition, the alloy will begin to solidify before the eutectic temperature is reached. If the alloy is hypoeutectic, some dendrites of α will form in the liquid before the remaining liquid solidifies at the eutectic temperature. If the alloy is hypereutectic, the first (primary) material to solidify will be dendrites of β. The microstructure produced by slow cooling of a hypoeutectic and hypereutectic alloy will consist of relatively large particles of *primary constituent*, consisting of the phase that begins to freeze first surrounded by relatively fine eutectic structure. In many instances, the shape of the particles will show a relationship to their dendritic origin (see Fig. 22a). In other instances, the initial dendrites will have filled out somewhat into *idiomorphic particles* (particles having their own characteristic shape) that reflect the crystal structure of the phase (see Fig. 22b).

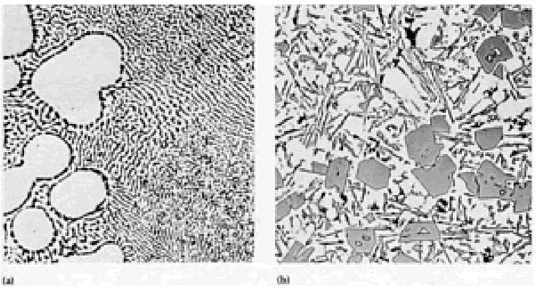


Fig. 22 Examples of primary-particle shape. (a) Sn-30Pb hypoeutectic alloy showing dendritic particles of tin-rich solid solution in a matrix of tin-lead eutectic. 500×. (b) Al-19Si hypereutectic alloy, phosphorus-modified, showing idiomorphic particles of silicon in a matrix of aluminum-silicon eutectic. 100×[2]

As stated earlier, cooling at a rate that does not allow sufficient time to reach equilibrium conditions will affect the resulting microstructure. For example, it is possible for an alloy in a eutectic system to obtain some eutectic structure in an alloy outside the normal composition range for such a structure. This is illustrated in Fig. 23. With relatively rapid cooling of alloy X, the composition of the solid material that forms will follow line α_1-α'_4 rather than solidus line to α_4. As a result, the last liquid to solidify will have the eutectic composition L_4 rather than L_3 and will form some eutectic structure in the microstructure. The question of what takes place when the temperature reaches T_5 is discussed later.

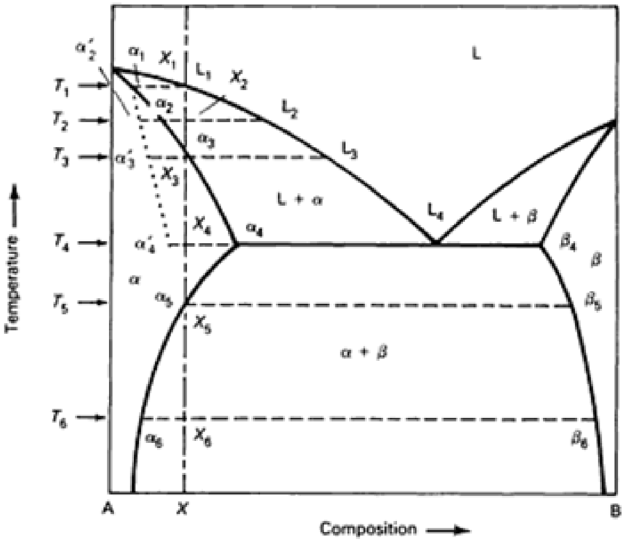


Fig. 23 Binary phase diagram, illustrating the effect of cooling rate on an alloy lying outside the equilibrium eutectic-transformation line. Rapid solidification into a terminal phase field can result in some eutectic structure being formed; homogenization at temperatures in the single-phase field will eliminate the eutectic structure; β phase will precipitate out of solution upon slow cooling into the a + β field. Adapted from Ref 1.

Eutectoid Microstructures. Because the diffusion rates of atoms are so much lower in solids than liquids, nonequilibrium transformation is even more important in solid/solid reactions (such as the eutectoid reaction) than in liquid/solid reactions (such as the eutectic reaction). With slow cooling through the eutectoid temperature, most alloys of eutectoid composition such as alloy 2 in Fig. 24 transform from a single-phase microstructure to a lamellar structure consisting of alternate platelets of α and β arranged in groups (or "colonies"). The appearance of this structure is very similar to lamellar eutectic structure (see Fig. 25). When found in cast irons and steels, this structure is called "pearlite" because of its shiny mother-of-pearl-like appearance under the microscope (especially under oblique illumination); when similar eutectoid structure is found in nonferrous alloys, it often is called "pearlite-like" or "pearlitic."

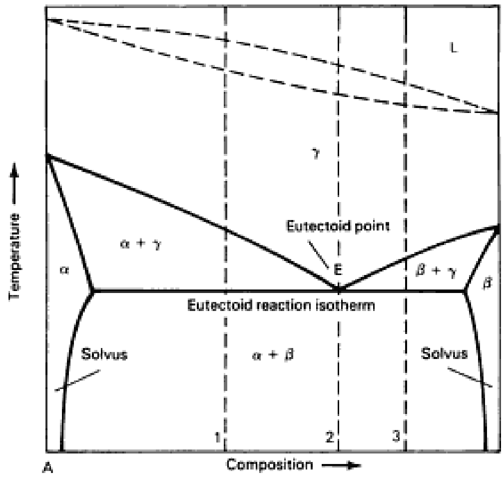


Fig. 24 Binary phase diagram of a eutectoid system. Adapted from Ref 1.

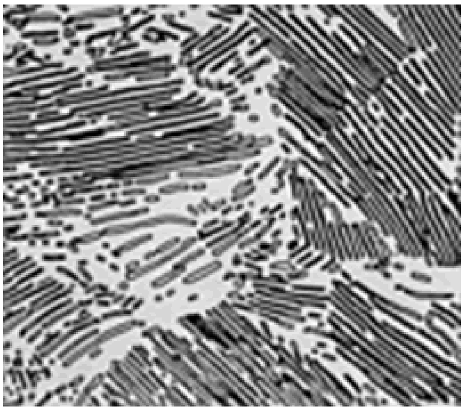
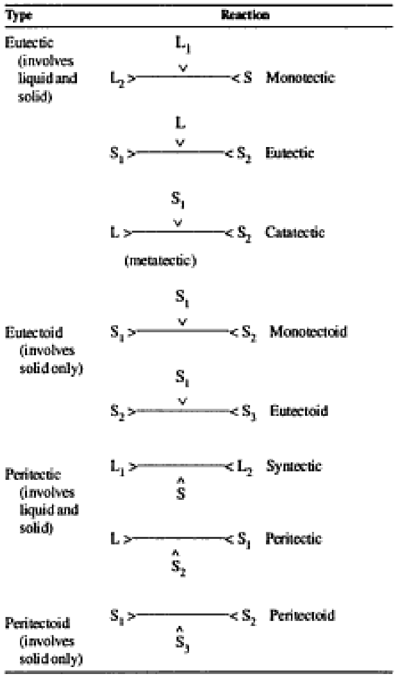


Fig. 25 Fe-0.8C alloy showing a typical pearlite eutectoid structure of alternate layers of light ferrite and dark cementite. 500×.[2]

The terms, hypoeutectoid and *hypereutectoid* have the same relationship to the eutectoid composition as hypoeutectic and hypereutectic do in a eutectic system; alloy 1 in Fig. 24 is a hypoeutectoid alloy, while alloy 3 is hypereutectoid. The solid-state transformation of such alloys takes place in two steps, much like freezing of hypoeutectic and hypereutectic alloys except that the microconstituents that form before the eutectoid temperature is reached are referred to as proeutectoid constituents rather than "primary."

Microstructures of Other Invariant Reactions. Phase diagrams can be used in a manner similar to that used in the discussion of eutectic and eutectoid reactions to determine the microstructures expected to result from cooling an alloy through any of the other six types of reactions listed in Table 2.

Table 2 Invariant reactions



Type	Reaction	
Eutectic (involves liquid and solid)	L_1 ∨ $L_2 >$———$< S$	Monotectic
	L ∨ $S_1 >$———$< S_2$	Eutectic
	S_1 ∨ $L >$———$< S_2$ (metatectic)	Catatectic
Eutectoid (involves solid only)	S_1 ∨ $S_1 >$———$< S_2$	Monotectoid
	S_1 ∨ $S_2 >$———$< S_3$	Eutectoid
Peritectic (involves liquid and solid)	$L_1 >$———$< L_2$ ^ S	Syntectic
	$L >$———$< S_1$ ^ S_2	Peritectic
Peritectoid (involves solid only)	$S_1 >$———$< S_2$ ^ S_3	Peritectoid

Solid-State Precipitation. If alloy *X* in Fig. 23 is homogenized at a temperature between T_3 and T_5, it will reach equilibrium condition; that is, the β portion of the eutectic constituent will dissolve and the microstructure will consist solely of α grains. Upon cooling below temperature T_5, this microstructure will no longer represent equilibrium conditions, but instead will be supersaturated with B atoms. In order for the sample to return to equilibrium, some of the B atoms will tend to congregate in various regions of the sample to form colonies of new β material. The B atoms in some of these colonies, called *Guinier-Preston zones*, will drift apart, while other colonies will grow large enough to form incipient, but not distinct, particles. The difference in crystal structures and lattice parameters between the α and β phases causes lattice strain at the boundary between the two materials, thereby raising the total energy level of the sample and hardening and strengthening it. At this stage, the incipient particles are difficult to distinguish in the microstructure. Instead, there usually is only a general darkening of the structure. If sufficient time is allowed, the β regions will break away from their host grains of α and precipitate as distinct particles, thereby relieving the lattice strain and returning the hardness and strength to the former levels. While this process is illustrated for a simple eutectic system, it can occur wherever similar conditions exist in a phase diagram; that is, there is a range of alloy compositions in the system for which there is a transition on cooling from a single-solid region to a region that also contains a second solid phase, and where the boundary between the regions slopes away from the composition line as cooling continues. Several examples of such systems are shown schematically in Fig. 26.

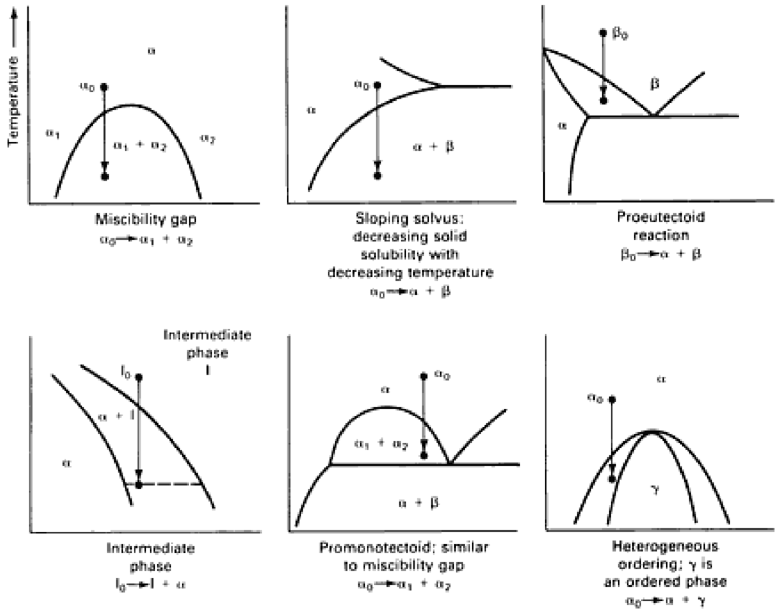


Fig. 26 Examples of binary phase diagrams that give rise to precipitation reactions.[2]

Although this entire process is called *precipitation hardening*, the term normally refers only to the portion before much actual precipitation takes place. Because the process takes a while to be accomplished, the term *age hardening* is often used instead. The rate at which aging occurs depends on the level of supersaturation (how far from equilibrium), the amount of lattice strain originally developed (amount of lattice mismatch), the fraction left to be relieved (how far along the process has progressed), and the aging temperature (the mobility of the atoms to migrate). The β precipitate usually takes the form of small idiomorphic particles situated along the grain boundaries and within the grains of α phase. In most instances, the particles are more or less uniform in size and oriented in a systematic fashion.

Problems in Published Phase Diagrams

Impossible Diagrams. Thermodynamic principles also limit the shape of the various boundary curves and their intersections. If a phase boundary of a phase diagram violates such thermodynamic requirements, the diagram is thermodynamically impossible at least in the related segment. Various impossible phase relationships often found in published phase diagrams are summarized in Fig. 27.

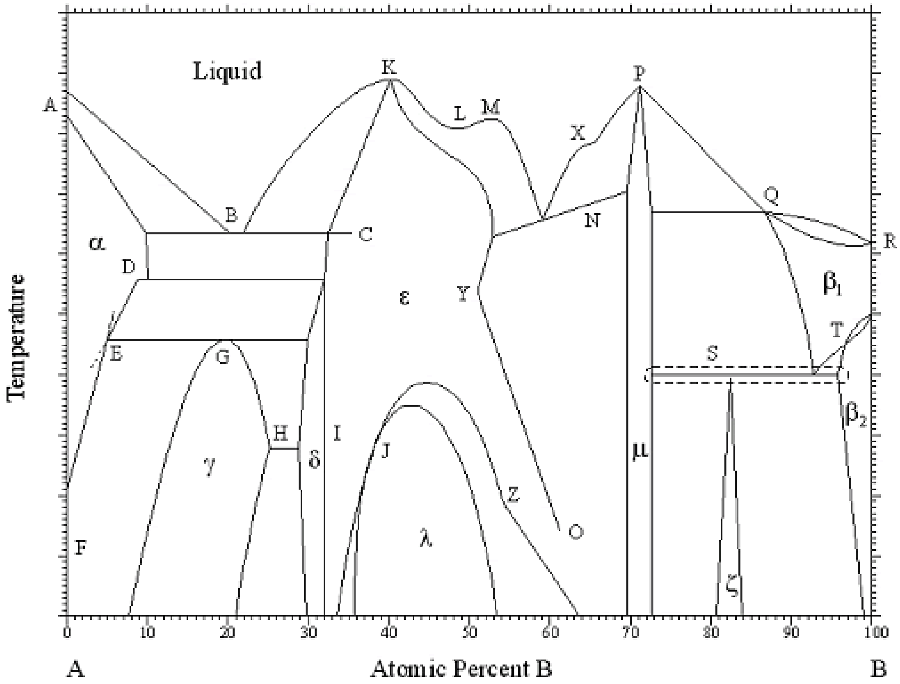


Fig. 27 Summary of impossible phase relationships in published phase diagrams

These problems are:

A: The liquidus and solidus must meet at the melting point of the pure element.
B: Two liquidus curves must meet at one composition at a eutectic temperature.
C: A tie line must terminate at a phase boundary.
D: Two solvus boundaries (or two liquidus, or two solidus, or a solidus and a solvus) of the same phase must intersect at one composition at an invariant temperature.
E: A phase boundary must extrapolate into a two-phase field after crossing an invariant point.
F: A two-phase field cannot be extended to a pure element end.
G: Two boundaries of g must not be continuous at the invariant temperature. They must cross one another.
H: An invariant temperature line should involve equilibrium among three phases.
I: There should be a two-phase field between two single phase fields.
J: When two phase boundaries touch at a point, they should touch at an extremity of temperature.
K: A touching liquidus and solidus (or any two touching boundaries) must have a horizontal common tangent at the congruent point. In this case, the slope of the solidus appears to be discontinuous at the melting point.
L: A local minimum point in the lower part of a single-phase field cannot be drawn without an additional boundary in contact with it (minimum congruent point or monotectic reaction in this case).
M: A local maximum point in the lower part of a single-phase field cannot be drawn without a monotectic, monotectoid, syntactic, and syntectoid reaction occurring at a lower temperature. Alternatively, a solidus curve must be drawn to touch the liquidus at point M. (If the maximum is not local, as in a miscibility gap, this is not a phase rule violation.)
N: The temperature of an invariant reaction must be constant. (The reaction line must be horizontal.)
O: A phase boundary cannot terminate within a phase field (except the case when the boundary is unknown beyond this point).
P: The liquidus should not have a discontinuous sharp peak at the melting point of a compound. (See exceptions below.)
Q: The compositions of all three phases at an invariant reaction must be different.
R: Temperatures of liquidus and solidus (or any two boundaries) must either increase or decrease together from one point on the pure element line as the content of a second element increases.
S: A four-phase equilibrium is not allowed in a binary system. (See exceptions below.)
T: Two separate phase boundaries that create a two-phase field between two phases in equilibrium should not cross one another.

Although phase rules are not violated, three additional unusual situations (X, Y, and Z) are also included in Fig. 27. These unlikely situations are discussed in the next section.

An additional problem, not shown in Fig. 27:

- would be a continuous solid solution phase between two phases with different crystal structures.

For example, a fcc phase and a bcc phase cannot form a continuous phase. There must be a two-phase field between them.

Exceptions

- A four-phase reaction in appearance, as S in Fig. 27, may occur if temperatures of two invariant reactions with an overlapping composition range are very close to one another.
- A sharp peak as P may occur if this phase exists in the same molecular state in the liquid phase as it does in the solid state. The apparent sharpness of the peak varies depending on the degree of association of the liquid molecules.

Improbable Diagrams. Some diagrams involve errors that are generally acceptable from the viewpoint of phase rule, but the proposed phase boundaries have atypical or abnormal forms, or have been forced to have abnormal forms in order to satisfy the phase rule, or uncertain experimental data. First, it must be noted that an abrupt change of slope of a phase boundary, as shown X, Y, and Z in Fig. 27, is thermodynamically unlikely. An abrupt change of slope can occur only if the thermodynamic property of either one of the two phases in equilibrium suddenly changes at the corresponding temperature or composition. Because the thermodynamic properties are expected to change gradually in one phase field, the phase boundary slope is also expected to change gradually. If an abrupt change of slope is real, it must be related to a unique situation affecting a phase associated with this phase field, such as the onset of an order-disorder transformation, or a magnetic transition. Figure 28 shows various types of improbable phase boundaries.

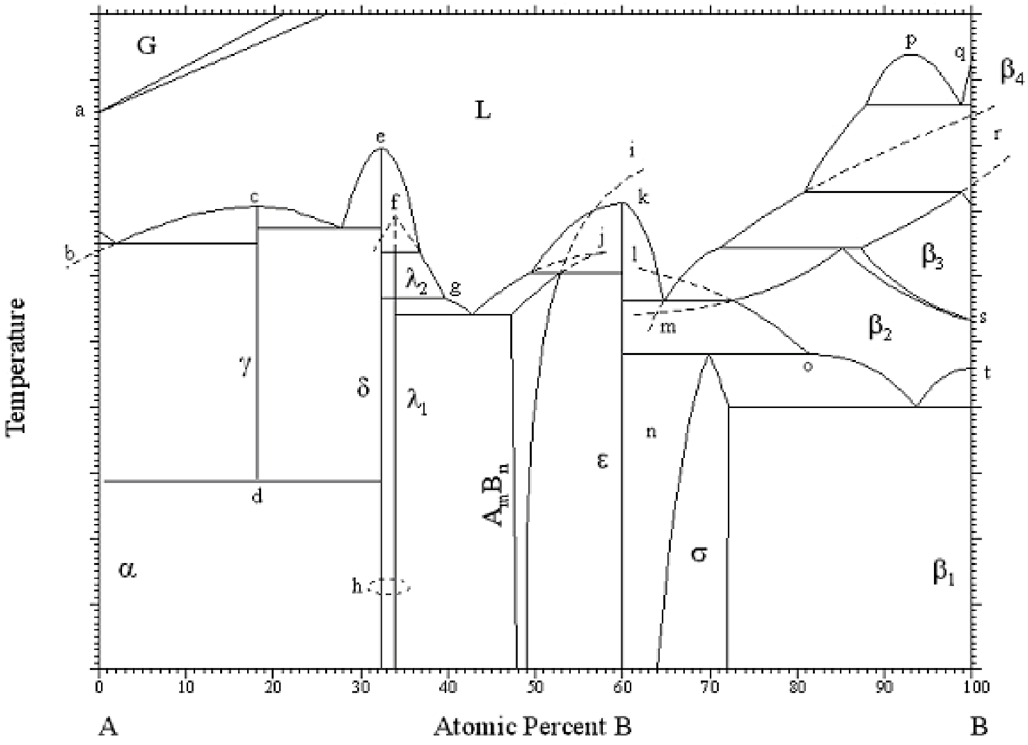


Fig. 28 Various types of improbable phase boundaries

a: G + L two-phase field is too narrow. The opening angle of G + L at 0 at.% must be much larger because the heat of vaporization of an element is usually much greater than the heat of fusion.
b: Extrapolation of the liquidus should not cross the 0 at.% line. Otherwise, problem F of Fig. 27 occurs.
c: The liquidus of δat point c is too flat in comparison with the liquidus of δat point e. Problems c, d, and e are related. Because entropy of fusion of elements and compounds cannot differ much, curvatures of liquidus curves for compounds in a binary system must be similar. A phase with a sharper liquidus tends to decompose into two neighboring phases at low temperatures.
d: A compound with a flat liquidus is stable and will not decompose at low temperatures.
e: Liquidus at point e is too sharp in comparison with the liquidus at point c.
f: Extrapolation of the liquidus of λ_2 must have a peak at the composition of λ_2. Otherwise, problem P of Fig. 27 occurs.
g: Change of liquidus slope associated with an allotropic transformation must be small.
h: Two compounds having similar compositions cannot be stable over a wide temperature range.
i: A phase field of a compound cannot extend over a neighboring phase. Problem T of Fig. 27 occurs.
j: The congruent melting point of AmBn compound is too far away from its stoichiometric composition.

k: The liquidus is too asymmetric. According to the author's criterion, a liquidus is already too asymmetric if the liquidus width ratio to the left and right of a compound exceeds 2 to 3.
l: The transformation temperature of ε to β_2 should be higher than the melting point of ε. Otherwise, the β_2 phase is stable above point j.
m: Extrapolation of two boundaries of L + β_2 should not cross. Problem T of Fig. 27 occurs.
n: A two-phase field must be narrower at higher temperatures.
o: The slope is too flat to have a maximum point at the composition of φ.
p: The liquid miscibility gap is too close to the edge of a phase diagram.
q: The liquidus slope is too steep. The initial slope of a liquidus must conform to the van't Hoff relationship. If no solubility can be assumed for the solid phase, extrapolation of the initial liquidus should go through the horizontal axis at 0 K near approximately 110 at.%.
r: Extrapolation of two boundaries of L + β_3 should cross at the 100 at.% line, not at some composition exceeding 100 at.%. Problem A of Fig. 27.
s: Two phase boundaries should have different initial slopes.
t: The slopes of two phase boundaries are too far apart.

There are many other improbable phase relationships that cannot be generalized in Fig. 28. Please refer to the related articles: H. Okamoto and T.B. Massalski, *J. Phase Equilibria*, Vol 12, 1991, p 148–168; H. Okamoto, *J. Phase Equilibria*, Vol 12, 1991, p 623–643; H. Okamoto and T.B. Massalski, *J. Phase Equilibria*, Vol 14, 1993, p 316–335; and H. Okamoto and T.B. Massalski, *J. Phase Equilibria*, Vol 15, 1994, p 500–521.

Acknowledgments

The information in this article was largely taken from:

- Alloy Phase Diagrams and Microstructure, *Metals Handbook, Desk Edition, Second Edition*, J.R. Davis, Ed., ASM International, 1998, p 95–112
- H. Baker, Introduction to Alloy Phase Diagrams, *Alloy Phase Diagrams*, Vol 3, *ASM Handbook*, ASM International, 1992, p 1-1 to 1-29
- T.B. Massalski, forewords to various monographs of Phase Diagrams of Binary Alloys, ASM International, 1987 to present
- H. Okamoto and T.B. Massalski, Impossible and Improbable Forms of Binary Phase Diagrams, *Desk Handbook: Phase Diagrams for Binary Alloys*, H. Okamoto, Ed., ASM International, 2000, p xxxix–xliii

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References

1. F.N. Rhines, *Phase Diagrams in Metallurgy: Their Development and Application*, McGraw-Hill, 1956
2. *Metallography and Microstructures*, Vol 9, 9th ed., ASM Handbook, ASM International, 1985
3. J.E. Morral, Two-Dimensional Phase Fraction Charts, *Scr. Metall.*, Vol 18 (No. 4), 1984, p 407-410
4. J.E. Morral and H. Gupta, Phase Boundary, ZPF, and Topological Lines on Phase Diagrams, *Scr. Metall.*, Vol 25 (No. 6), 1991, p 1393-1396

Return to Contents

ASM Alloy Phase Diagrams Center, P. Villars, editor-in-chief; H. Okamoto and K. Cenzual, section editors;
http://www1.asminternational.org/AsmEnterprise/APD, ASM International, Materials Park, OH, USA, 2006-2015