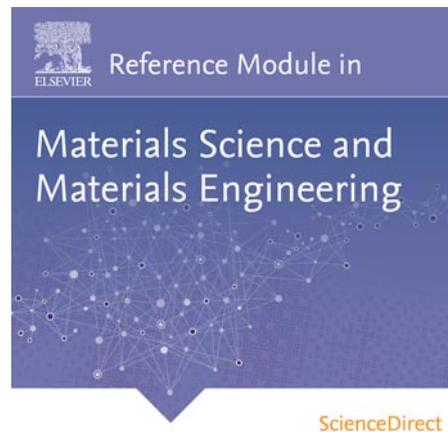


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Phase Diagrams [☆]

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1 Introduction

The extrinsic properties of materials are related to their *microstructure*. In turn, for a given material, the expected microstructure is related to the material's *constitution* which, under conditions of achieved equilibrium, is defined as the expected number of phases to be present, their proportion, and their composition. The information that allows us to predict the constitution from a graphical plot of the phases that may be present in any given system is known as a phase diagram. Attempts to determine phase diagrams are being made both experimentally and theoretically.

Typically, in a solid, microstructure consists of grains of the phases present. These grains may consist of only one phase (a single-phase microstructure), or they may be grains of many different phases (a poly-phase microstructure).

An assessment of some of the expected properties resulting from a given microstructure may proceed by considering first the constitution, then combine this with the knowledge of the specific properties of the phases involved (i.e., crystal structures, physical properties, degree of order, etc.) and, finally and very importantly, incorporating the knowledge of the *distribution* of the phases in the microstructure, (i.e., the shapes and sizes of the grains, how they touch and fit together, how they interact, etc.).

In a microstructure consisting of numerous 'grains' of the same phase, the grains abut against one another and the surface between them is called a grain boundary, or an *interface*. If the interface is between grains of different phases it is referred to as an interphase interface. Understanding the nature of interfaces and their role in determining properties constitutes a wide area of materials science research.

The independent state variables that control the phases depicted in a given phase diagram are the number of components (i.e., elements) involved, the chemical composition (i.e., the proportion of the components in the material), the temperature, the external pressure, magnetic field, electrostatic field, etc. Phase diagrams of simple systems generally involve only two state variables, for example, the temperature and composition. If one is plotted vertically and the other horizontally, a graphical

[☆]*Change History:* July 2015. T.B. Massalski and D.E. Laughlin made updates to the text and the references section.

representation is obtained, showing the distribution of the various possible phase fields allowed by the two variables, as will be discussed below.

2 Phases

Materials exist in gaseous, liquid, or solid form, usually referred to as a phase, which, depend on the conditions of state (i.e., the magnitude of state variables involved).

A phase "... is a physically distinct homogeneous portion of a thermodynamic system delineated in space by a bounding surface, called an interphase interface, and distinguished by its state of aggregation (solid, liquid, or gas), crystal structure, composition and/or degree of order. Each phase in a material system generally exhibits a characteristic set of physical, mechanical and chemical properties and is, in principle, mechanically separable from the whole" (Soffa and Laughlin, 2014).

Typically, on a phase diagram, each single-phase field is indicated by a single label. Engineers often find it convenient to use this label as referring to all compositions having a constitution related to this field, regardless of how much the physical properties of the alloys may be continuously changing from one part of the phase field to another. This means that in engineering practice the distinction between the terms 'phase' and 'phase field' is often neglected, and all materials labeled by the same symbol are referred to as the same phase.

In the *thermodynamic description of phase stability*, a phase is considered to be controlled by the independent state variables as mentioned above, and the laws of thermodynamics can be used to examine the competition for stability between the different possible phases in a given system, as the independent state variables are changed. In this approach, the various possible forms of the resulting phase diagram can be calculated without the need for experimental work. The role of interfaces in determining the ultimate properties is often not considered (see, e.g., Porter and Easterling, 1992).

3 Equilibrium

There are three states of equilibrium: stable, metastable, and unstable. This means that whether or not the constitution that is predicted by the phase diagram is actually achieved will depend on the kinetics, and hence on diffusion. These three conditions can be illustrated schematically as in Figure 1. Stable equilibrium exists when the system is in its lowest energy condition; metastable equilibrium exists when additional energy (ΔG) must be introduced before the system can reach true stability; unstable equilibrium exists when no additional energy is needed before the system moves to its metastable or stable configuration. Although true stable equilibrium conditions seldom exist in real materials, the study of equilibrium systems is extremely valuable, because it constitutes a limiting condition from which actual conditions can be estimated.

4 Thermodynamic Considerations

The state variables that are selected to control a given system determine the free energy values of all the possible phases that can exist in that system for all possible combinations of the variables (all the state points in a state diagram plot). The phases that are actually recorded in a phase diagram represent those with the lowest value of the free energy at each state point.

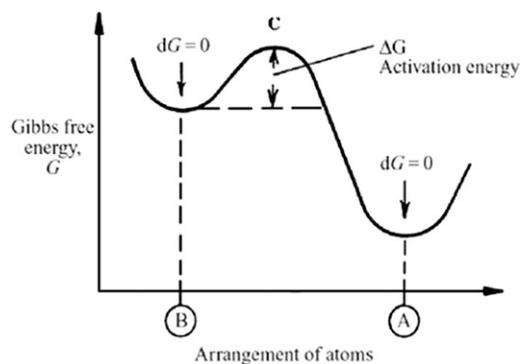


Figure 1 Free energy schematic of various arrangements or configurations of atoms in phases. A, stable configuration. B, metastable configuration. C, unstable configuration.

5 The Gibbs Free Energy

The Gibbs free energy of a system may be defined as:

$$G \equiv H - TS \quad [1]$$

where H is the enthalpy, T is the absolute temperature, and S is the entropy. Enthalpy is sometimes called the 'heat content,' and is defined as:

$$H \equiv U + PV \quad [2]$$

where U is the internal energy of the system, P is the pressure, and V the volume. A system in equilibrium shows no tendency to change, or

$$dG = 0 \quad [3]$$

The states for which $dG \neq 0$ are not stable and are only realized for limited periods of time, unless the temperature is very low and atoms cannot move. If, as the result of thermal fluctuations, the atoms become arranged in an intermediate state, they will rearrange again into a free energy minimum. If by a change of temperature or pressure, for example, a system is moved from a stable to a metastable state, it will, given time, transform to the new equilibrium state.

Graphite and diamond at room temperature and pressure are examples of stable and metastable equilibrium states. Given enough time therefore, diamond under these conditions will transform into graphite. Similarly, the cementite constituent in steels (Fe_3C) is metastable and should transform to graphite and iron. Any transformation that results in a decrease in Gibbs free energy is possible if the kinetics are favorable. Therefore a necessary criterion for any phase transformation is

$$\Delta G = G_2 - G_1 < 0 \quad [4]$$

where G_1 and G_2 are the free energies of the initial and final states respectively. The transformation need not go directly to the stable equilibrium state, but can pass through a series of intermediate metastable states. With extremely rapid freezing of liquids, even structures that are not thermodynamically stable (such as amorphous metallic 'glasses') can be produced.

6 Systems

A physical system consists of a set of components that is isolated from its surroundings, a concept used to facilitate study of the effects of conditions of state. 'Isolated' means that there is no interchange of mass or energy between the substance and its surroundings. The components in alloy systems, for example, may 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, titanium, and vanadium. These components comprise the system and should not be confused with the various phases found within the system.

7 Phase Diagrams

Phase diagrams are graphical plots that are devised 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 changes in the given component (e.g., in iron) as temperature and/or pressure changes. Most diagrams, however, are two-dimensional plots describing the phase relationships in systems made up of two or more components. These usually contain fields (areas) consisting of multiple phase fields, as well as single-phase fields. Some typical examples are shown below.

8 The Gibbs Equilibrium Phase Rule

The equilibrium phase rule, which was first announced by J. Willard Gibbs, relates the number of components of a system in equilibrium (c), the number of phases in the system at equilibrium (p), and the number of thermodynamic variables that can be changed without changing the phases that are in equilibrium. The latter is known as the variance or degree of freedom of the system, f . When the state of a phase in the system is determined by its pressure, temperature, and composition, the relationship is written as:

$$f = c - p + 2 \quad [5]$$

The Gibbs equilibrium phase rule applies to all states of matter (solid, liquid, and gaseous) and can be modified if additional external fields, such as magnetic or electric, are present and determine the states of the phases present.

When the pressure is held constant, the rule reduces to:

$$f = c - p + 1 \quad [6]$$

9 Unary Systems and Phase Diagrams

In single-component systems, $c = 1$ and the phase rule denoted in eqn [5] reduces to:

$$f = 3 - p \quad [7]$$

Since the degree of freedom must be a positive integer, the number of phases present in such a system may only be 1, 2, or 3.

9.1 Three-Phase Equilibrium: Invariant Equilibrium

According to the phase rule for one-component systems (see eqn [7]), three phases can exist in a stable equilibrium only at a single point of a pressure/temperature (PT) diagram. This limitation is illustrated as point 0 (designated as the triple point) in the hypothetical one-component PT diagram shown in [Figure 2](#). At this single pressure and temperature all three states of matter coexist in equilibrium. If the pressure is increased slightly, the equilibrium is disrupted and the system becomes a single-phase solid. If the temperature is slightly increased, the system becomes a single-phase vapor. The triple point is also called an invariant point, since $f = 0$.

9.2 Two-Phase Equilibrium: Univariant Equilibrium

The phase rule for a single-component system shows that stable equilibrium between two phases allows for one thermodynamic degree of freedom.

This condition, called univariant equilibrium, or monovariant equilibrium, is indicated by the curves 1, 2, and 3 separating the single-phase fields in [Figure 2](#). If the pressure and temperature of the system are such that they fall on one of those curves, the two phases whose fields abut the lines coexist in thermodynamic equilibrium. The pressure or temperature may be freely selected along the line, but not both. Once a pressure is selected, there is only one temperature that will satisfy equilibrium conditions. Curve 1 represents the equilibrium between the solid and the gas phases, and is called the sublimation curve. Curve 2 represents the equilibrium between the solid and the liquid phases and is the melting curve. Curve 3 represents the equilibrium between the liquid and the gas phases and is the vaporization curve. The vaporization curve ends at point 4, called a critical point, where the physical distinction between the liquid and gas phases disappears.

9.3 Single-Phase Equilibrium: Bivariant Equilibrium

All states within the single-phase fields allow for the phase to remain the equilibrium phase with (small) changes in both the temperature and pressure. This situation corresponds to having two thermodynamic degrees of freedom. This situation is called bivariant equilibrium.

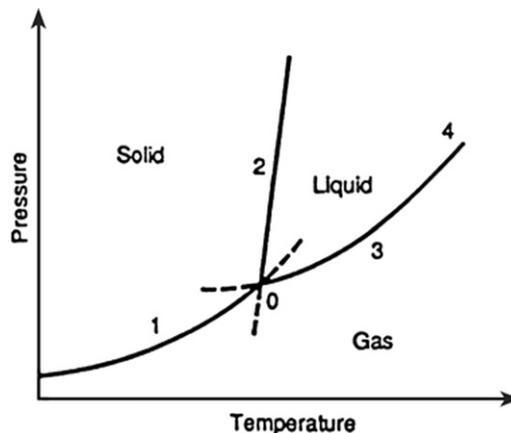


Figure 2 Schematic pressure–temperature phase diagram (after [Baker, 1992](#)).

9.4 The Geometry of the PT Curves

It is interesting to see what other information can be determined from the PT diagram. The slope of the curves ($\frac{dP}{dT}$) can be shown to be equal to:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \quad [8]$$

where ΔS , ΔV , and ΔH are the changes in the molar entropy, volume, and enthalpy when the phase changes from one state to the other, and T is the absolute temperature. This equation is known as the Claperyon Equation. For most solid material systems the phase with the larger molar volume has the larger entropy, so the slopes are all positive. This is because the lattice (vibrational) entropy term usually dominates.

9.5 The PT Diagram for Iron

A schematic of the PT boundaries for iron is shown in **Figure 3**. Note that the slope of the α/γ equilibrium curve is negative. This is unusual for a solid to solid transformation because it implies that the phase with the lower molar volume (FCC, γ) has the higher molar entropy. To understand this we must look more carefully at the contributions to the entropy of the α and γ phases.

At intermediate temperatures and pressures there are two main contributions to the entropy of a solid that has magnetic spins associated with its atoms, namely: (1) the lattice or vibrational entropy and (2) the spin entropy, which arises from the random orientation of spins in the paramagnetic phases. Since γ has the higher molar entropy we write:

$$\begin{aligned} S^\gamma &> S^\alpha \\ S_{lattice}^\gamma + S_{spin}^\gamma &> S_{lattice}^\alpha + S_{spin}^\alpha \\ S_{spin}^\gamma &> (S_{lattice}^\alpha - S_{lattice}^\gamma) + S_{spin}^\alpha \end{aligned}$$

The lattice entropy for BCC γ is larger than that for FCC γ so it can be further concluded since both terms on the right hand side are positive that:

$$S_{spin}^\gamma > S_{spin}^\alpha \quad [9]$$

FCC γ -iron thus has a larger spin entropy than BCC α -iron does. The origin of this high spin entropy in γ iron is from the low temperature Neel transition of γ from its low temperature antiferromagnetic state to its paramagnetic state.

10 Magnetic Phase Transitions and the Phase Diagram

Phase diagrams should include information on the magnetic or ferroelectric transformations which may occur between equilibrium phases. For example, when the low temperature ferromagnetic phase of iron (known as α iron) transforms into a paramagnetic form of iron, a phase transformation has occurred. This transformation temperature is denoted as the Curie temperature of iron. Below the

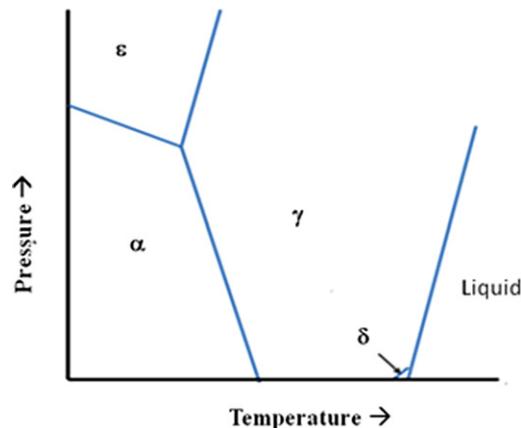


Figure 3 Schematic of the pressure–temperature phase diagram for iron.

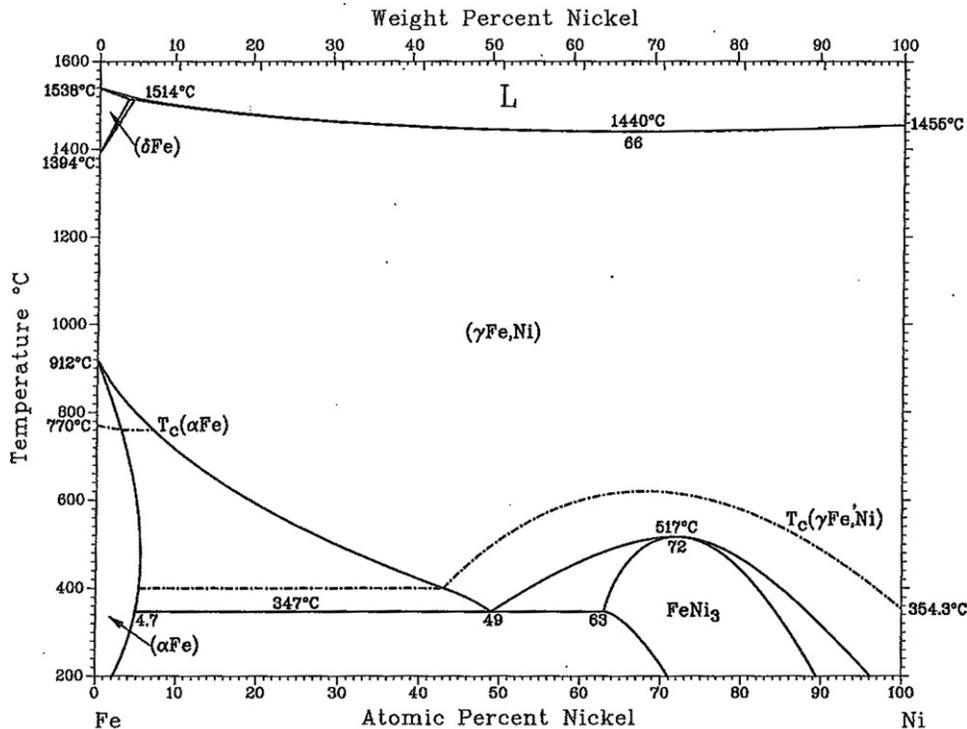


Figure 4 Phase diagram of the Fe–Ni System, illustrating the inclusion of Curie temperature information. Note how Ni decreases the Curie temperature when first added to Fe and Fe increases the Curie temperature when first added to Ni. Also note that in two-phase fields the Curie temperature is constant (Massalski, T. B. Binary Alloy Phase Diagrams, second edition, ASM).

Curie temperature, α iron is ferromagnetic and the crystals in each of its magnetic domains have tetragonal symmetry. When α iron transforms into the paramagnetic phase at the Curie temperature, its symmetry and magnetic properties change to cubic and paramagnetic: therefore a new phase forms. This phase has been called the β phase of iron and it used to be so designated on Fe based phase diagrams. It is not usually so indicated today but we urge that it be returned to its rightful place!

When iron is alloyed with various solutes, the Curie temperature changes and is usually a linear function of composition. This information should be recorded on a phase diagram. See, for example, [Figure 4](#).

11 Phase Stability

The extent of solid solubility of phases, the stability of phases, the temperature dependence of stability, and the choice of structures that are actually observed in phase diagrams are the result of competition among numerous possible structures that could be stable in a given system. This competition is based on the respective values of the Gibbs free energy of each competing phase and the variation of this energy with temperature, pressure, composition, and other intensive parameters, such as magnetic field or electric field.

In its simplest form, the free energy can be written as in eqn [1]. As is well known, numerous factors contribute to the thermodynamic functions enthalpy (H) and entropy (S). A major contribution to the entropy is from statistical mixing of atoms (ΔS_{mix}), but there can be additional contributions from lattice vibrational effects ($\Delta S_{\text{lattice}}$), distribution of magnetic moments, and other possible various long-range configurational effects. The main contributions to the enthalpy result from atomic mixing (ΔH_{mix}), which are in turn related to the interaction energies (electronic) between neighboring and further distant atoms in a given structure and other terms that are based upon elastic, magnetic, and vibrational effects. Much progress has been made in measuring, calculating, and predicting many such effects, and hence progress continues to be made in the evaluation of the related thermodynamic quantities and ultimately the phase diagrams.

In a binary system, the free energy, G , of a given phase typically has a parabolic like form with positive curvature between the values for the two components (say A and B) as its composition changes. This is illustrated schematically in [Figure 5\(a\)](#). The change in the free energy when the pure components A and B are mixed at this temperature is given as ΔG_{mix} . This is negative because of the large negative $T\Delta S_{\text{mix}}$ term. If the structures are different, two free energy curves may have to be considered at every temperature to determine the lowest free energy configuration, as in [Figure 5\(b\)](#). Such curves will become displaced as temperature changes (for increasing temperatures, the curves move downward by an amount proportional to the entropy of the phase) and at each temperature the lowest free energy configuration across the diagram will determine the form of the phase diagram at each

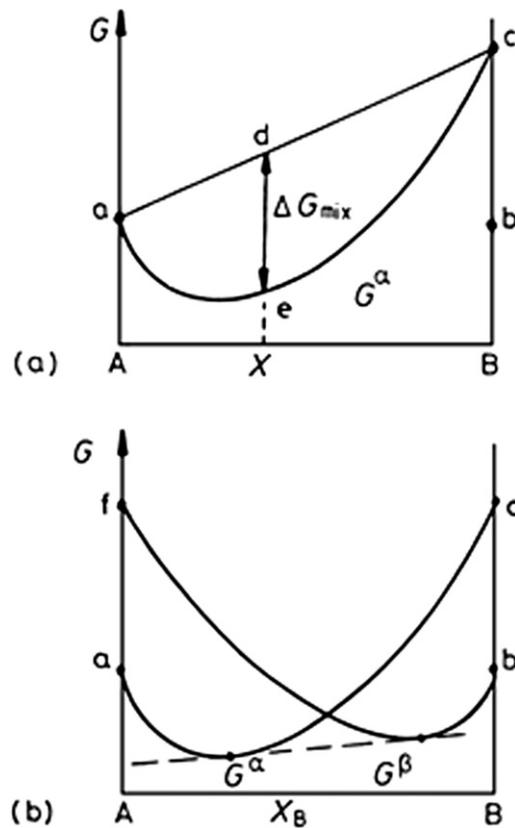


Figure 5 (a) Schematic molar free energy curve for an α phase at a fixed temperature, T . (b) Schematic molar free energy curves for α and β phases at a fixed temperature, T , showing a region of two-phase equilibrium between G^α and G^β (after Porter and Easterling, 1992).

composition. The well-known ‘common tangent construction’ is used for that purpose to determine the free energies when mixtures of phases result in lowest G . At the temperature T , [Figure 5\(b\)](#) shows that there are single-phase regions and a two-phase region.

12 Phase Field Rule

The areas (fields) in phase diagrams, and the positions and shapes of the points, curves, surfaces, and intersections in them, are controlled by thermodynamic principles and the thermodynamic properties of all of the phases that constitute the system. 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. That is, a two phase region of the phase diagram will have a one phase region on either side of it.

13 Binary Diagrams

The study of systems of more than one component involves the study of solutions. The simplest type of a multicomponent system is a binary, and the least complex structure in such a system is a single solution. Some of the aspects of single-phase binary systems will now be considered.

13.1 Solid Solutions

We shall consider here only two state variables: temperature and composition, holding pressure constant. The replacement of nickel atoms by copper atoms on the lattice of nickel is an example of a substitutional solid solution. At high enough temperatures, nickel can dissolve copper at all proportions, providing an example of complete solid solubility. This is possible only if the sizes of the atoms differ by no more than about 15%. There are many examples of restricted mutual solid solubilities, even

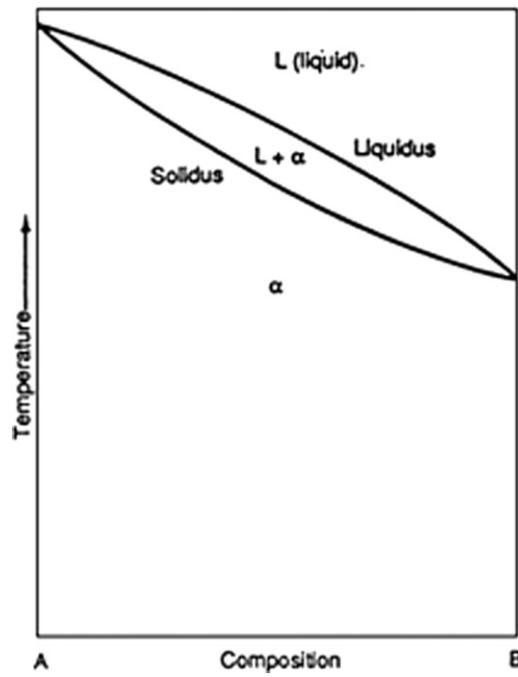


Figure 6 Schematic binary phase diagram showing miscibility in both the liquid and the solid states.

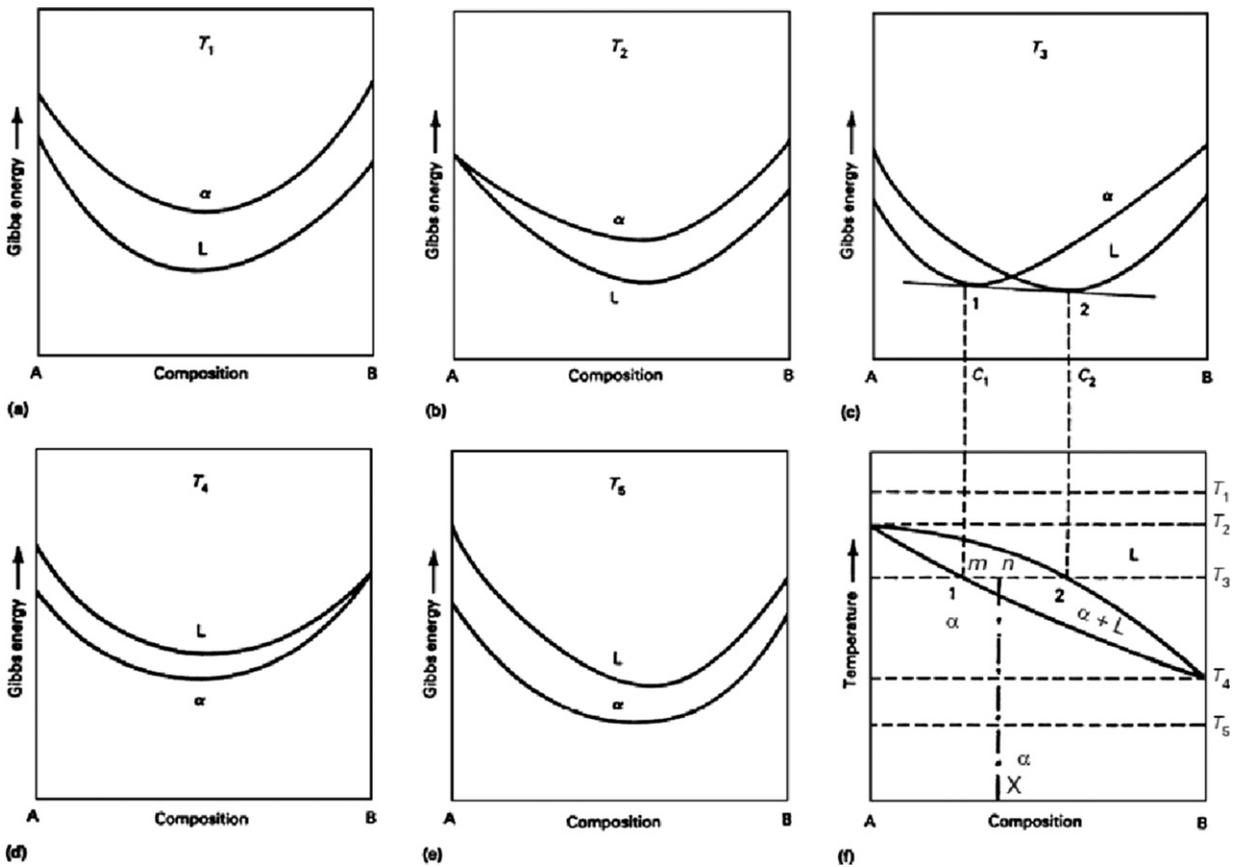


Figure 7 Derivation of a phase diagram with complete liquid and solid miscibility from free energy curves (after Prince, 1966).

between elements with similar crystal structures and atom sizes. When a continuous solid solution occurs in a binary system, the phase diagram in the immediate region of the melting points of the elements has the general appearance of that shown in **Figure 6**. The diagram consists of two single-phase fields (the α field and the liquid, L, field) separated by a two-phase field, consisting of both α and L phases. The boundary between the liquid field and the two-phase field is called the *liquidus*; that between the two-phase field and the solid field is called the *solidus*.

In general, the *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 from the liquid state, 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 **Figure 6** (the liquid and the solid solutions) are called conjugate phases.

13.2 Free Energies and Binary Phase Diagrams

We can now illustrate a few examples of how binary phase diagrams such as that shown in **Figure 6** can be derived from free energy curves. This system is completely, if not ideally, miscible in both the liquid and solid states. The free energies $G_{(L)}$ and $G_{(s)}$ are both parabola like with positive curvature. The relative positions of the $G_{(L)}$ and $G_{(s)}$ free energy curves change with temperature are shown in **Figure 7**. If the melting points of the pure metals are different, the solid curve (α) becomes somewhat tilted. Intersections and tangent constructions then become possible, yielding the well-known phase diagram with a liquid and solid showing complete miscibility, as in **Figure 6**. The Ti-Zr phase diagram (**Figure 9(a)**) displays this type of behavior, though it is slightly more complicated in that it also displays two solid phases, α , the low temperature HCP phase and β , the higher temperature BCC phase. This system is an example of the stabilization of the solid phase with the higher lattice entropy (β), at high temperatures.

13.3 Constitution and Lever Rule

Figure 7 also provides the basis for understanding how the constitution (which is the identity and composition of the phases and the amount of the phases) can be derived for any given alloy at equilibrium.

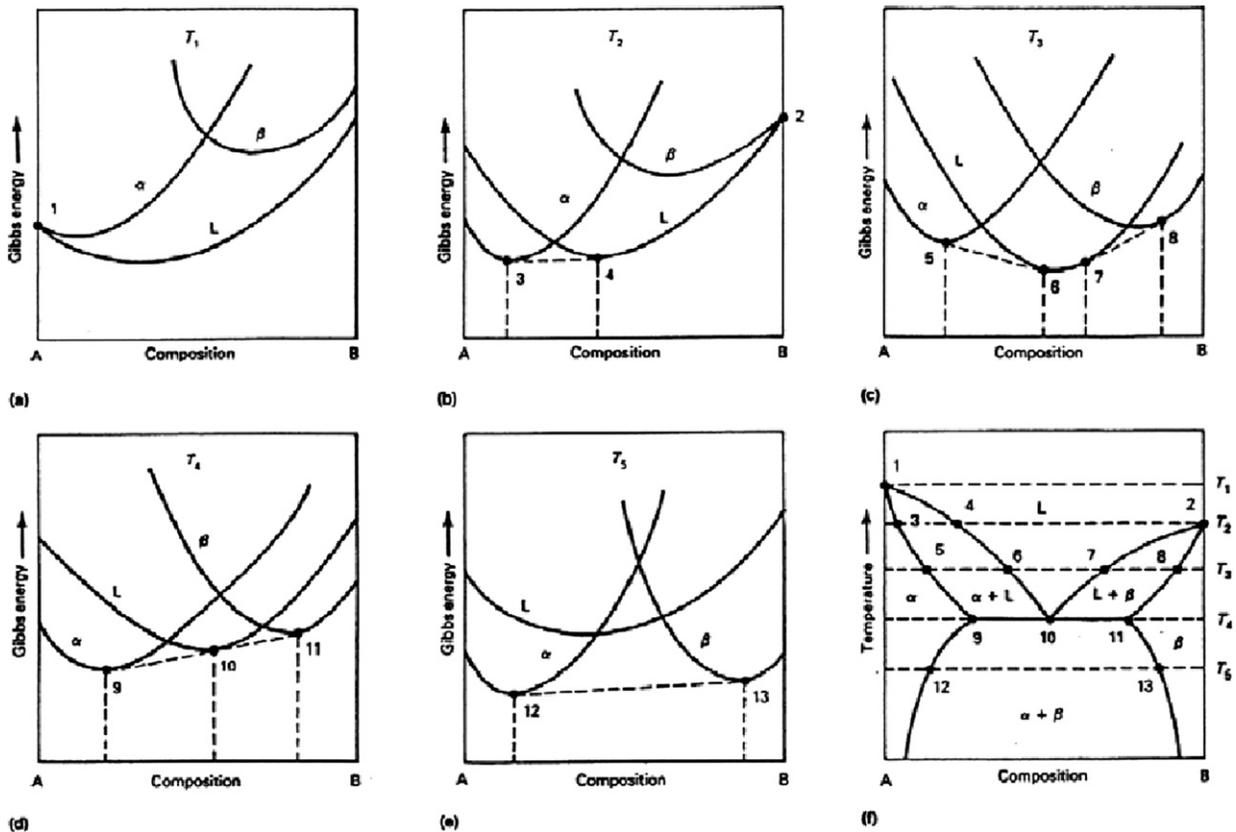


Figure 8 Derivation of a eutectic phase diagram involving free energies of α , β , and liquid phases (after [Gordon, 1968](#)).

Figure 7(c) illustrates that at temperature T_3 , the lowest free energy path between A and B will be along the G curve for the α phase (from A to C_1), then along the tangent between C_1 and C_2 , and finally, along the G curve for the liquid between C_2 and B. The tangent between 1 and 2 represent the situation when the alloy is two-phase (α of composition C_2 and L of composition C_2), and this is the basis of the phase diagram shown in Figure 7(f), at temperature T_3 . The knowledge of constitution stipulates that we also determine proportions of the two phases present in equilibrium for any alloy within the two-phase field, and this is done by employing the lever rule. Thus, for an alloy of composition X at T_3 , the proportion is given by the ratio of the two segments m and n as follows:

$$\begin{aligned} \text{fraction of solid} &= \frac{n}{m+n} \\ \text{fraction of liquid} &= \frac{m}{m+n} \end{aligned} \quad [10]$$

and hence the proportion of solid to liquid is $\frac{\alpha}{L} = \frac{n}{m}$

Other forms of phase diagrams may be derived in the same way. For example, a eutectic form of the phase diagram is obtained if two free energy curves are involved for the solid phases, or if a solid phase free energy curve displays a double minimum with a region of negative curvature in the middle.

A eutectic deriving from two separate solid phases is illustrated schematically in Figure 8, which the Cu–Ag phase diagram (Figure 9(b)) is an actual example. The constitution of any alloy in this system, for any state point, could be derived by the same procedure as mentioned above for alloy X in Figure 7(f). It can be seen for a eutectic phase diagram to occur the liquid free energy curve must lie between the two solid free energy curves. It can also be seen that at the eutectic temperature, T_4 , three phases are in equilibrium, namely the α , L, and β phases. This invariant temperature follows from the Gibbs equilibrium phase rule which for a binary system with three phases in equilibrium displays no degrees of freedom.

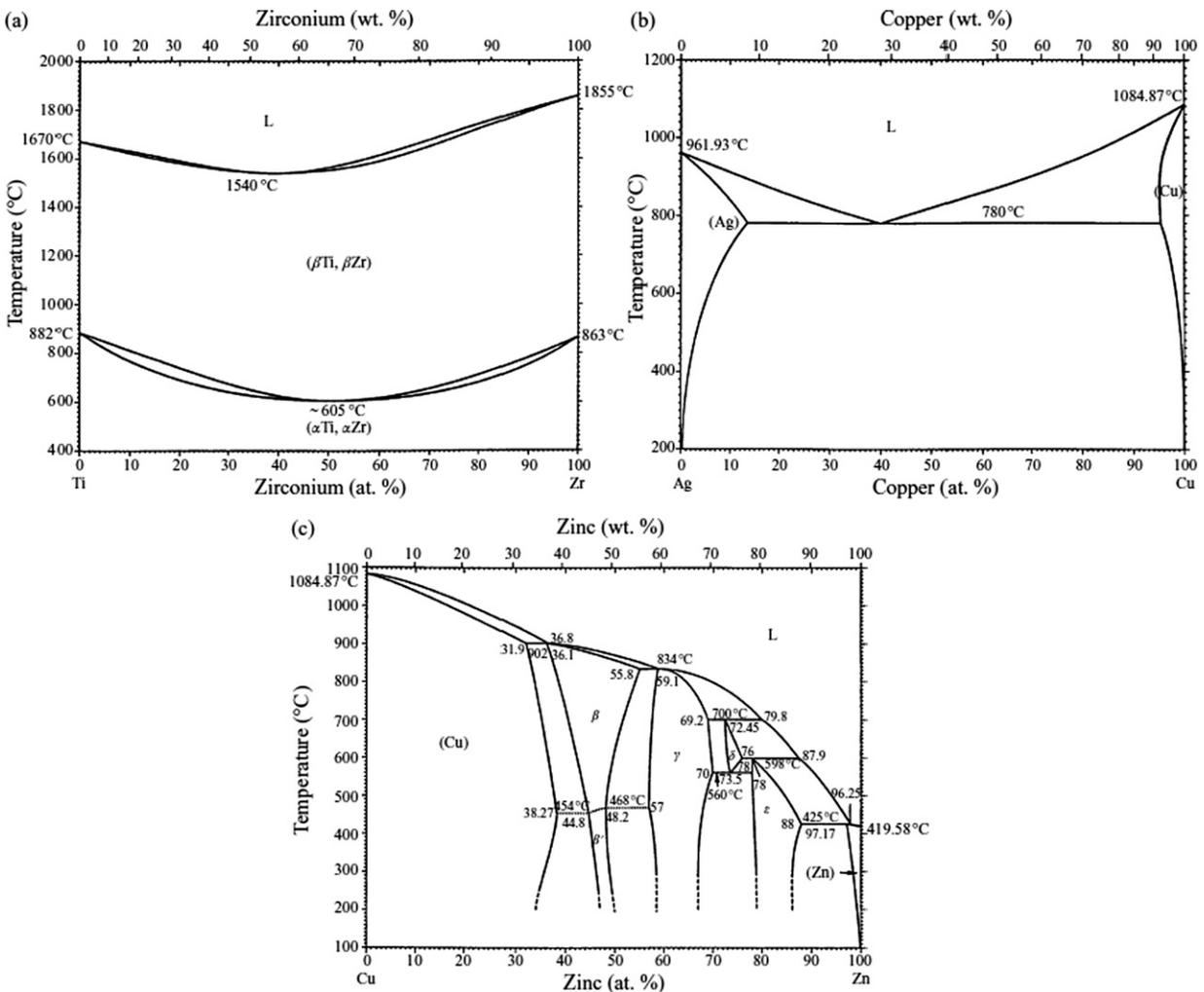


Figure 9 Assessed phase diagrams: (a) Ti–Zr, (b) Cu–Ag, (c) Cu–Zn (after Massalski, 1990, ASM/NIST Phase Evaluation Program).

13.4 More Complex Diagrams

More complex phase diagrams may involve the presence of one or more 'intermediate phases,' which have the lowest free energies in the system at some temperatures and compositions. A good example is the Cu–Zn binary phase diagram, shown in [Figure 9\(c\)](#), which involves two terminal phases, Cu (α) and Zn (η), and five intermediate phases: β , β' , γ , δ , and ϵ . With a little practice, a set of hypothetical free energy curves could be constructed for all the phases, as well as their respective displacements with temperature, such that the overall free energy trends would yield the observed diagram. Many selected sets of free energy curves can be postulated that would reproduce an actual phase diagram. Only experimental measurements of some of the thermodynamic quantities representing the actual phases can confirm which free energy curves are really valid and represent the actual free energy situations.

14 Ternary (and Higher)-Component Phase Diagrams

When a third component is added to a binary system, the graphic representation of the equilibrium conditions in two dimensions becomes complex, as there are three independent variables, so a series of graphs is necessary. One option is to add a third composition dimension, by using a triangular base. Free energy curves now become free energy surfaces (with positive curvature). This is illustrated in [Figure 10](#). A corresponding phase diagram may be as that illustrated schematically in [Figure 11](#). Even more complex graphics have been proposed for higher systems, but generally only selected portions of the actual diagrams can be represented. Further details will be found in the cited literature.

15 Phase Diagram Errors

Because phase diagrams are an expression of thermodynamic conditions, it is necessary to ensure that the constructed graphics are thermodynamically correct and compatible. Unfortunately, this is frequently not the case, and hence many efforts have been made in the past, and continue to be made, to evaluate critically the existing literature on phase diagrams.

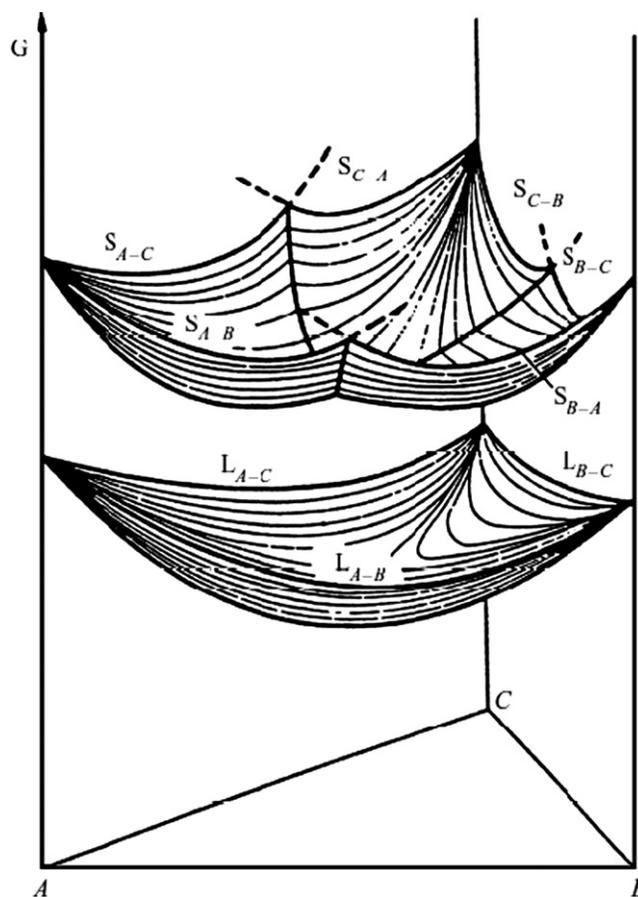


Figure 10 Schematic free energies of a liquid and three solid phases of a ternary system (after [Haasen, 1996](#)).

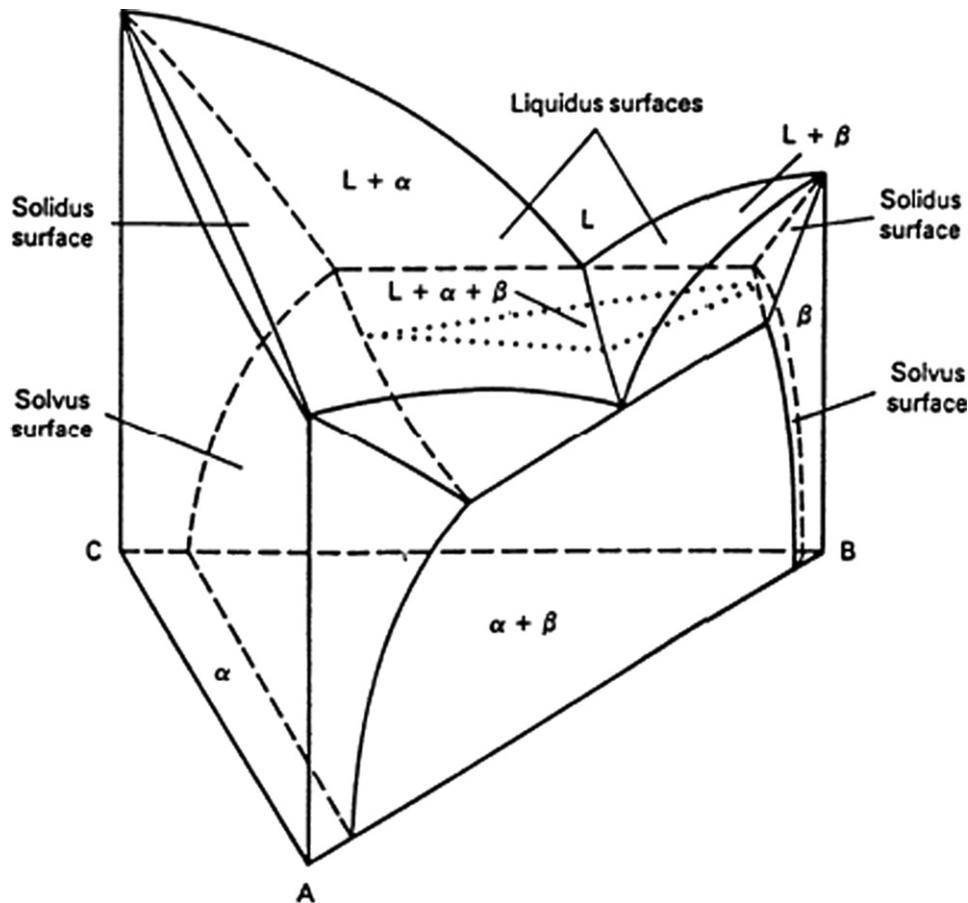


Figure 11 Ternary phase diagram (after Rhines, 1956).

An example of a hypothetical complex phase diagram involving 23 errors is shown in [Figure 12\(a\)](#), and an error-free version of the same diagram is shown in [Figure 12\(b\)](#). Some errors are quite obvious, but the reader will need to consult the cited literature ([Okamoto and Massalski, 1991](#)) for a detailed discussion of all the depicted errors and their correction.

There are at least three possible kinds of errors in phase diagram construction. The first is one in which the construction violates the Gibbs phase rule or corollary rules derived from it. For example, a pure component must have an invariant melting temperature at a fixed pressure (error 1, [Figure 12\(a\)](#)). Another is that three-phase equilibrium in a binary alloy with pressure held constant must be an invariant from the phase rule. See [Figure 12\(a\)](#), error 16.

Another kind of error also may exist which have been termed by Okamoto and Massalski as improbable constructions. These are construction of the phase diagram which would entail highly improbable variations in the free energy curves with respect to temperature or composition to produce the phase diagram as depicted.

A third kind of error also exists and can be called Third Law violations. The Third Law of thermodynamics posits that the various aspects of entropy of a system in equilibrium approach zero as the temperature approaches zero. This entails that at the zero in temperature, phases should be either of pure composition (no solid solutions that have configurational entropy) or the phases should be stoichiometric compounds. (see [Abriata and Laughlin, 2004](#); [Fedorov, 2010](#)). This rather rigid rule is often not followed in published diagrams, since it is not easy to keep a real system in thermodynamic equilibrium at very low temperatures. Nevertheless it should be kept in mind when presenting a phase diagram and perhaps could also be incorporated in extrapolations of solution models to low temperature. [Figure 13](#) shows a schematic phase diagram that conforms to the Third Law restrictions.

16 Determination of Phase Diagrams

A very large literature exists on the various methods for determining phase diagrams. Historically, many of the well-known diagrams were determined experimentally, long before the obvious connection between solution thermodynamics and phase diagrams was fully realized. Experimental techniques involve metallography, cooling and heating, thermal arrest studies (DSC

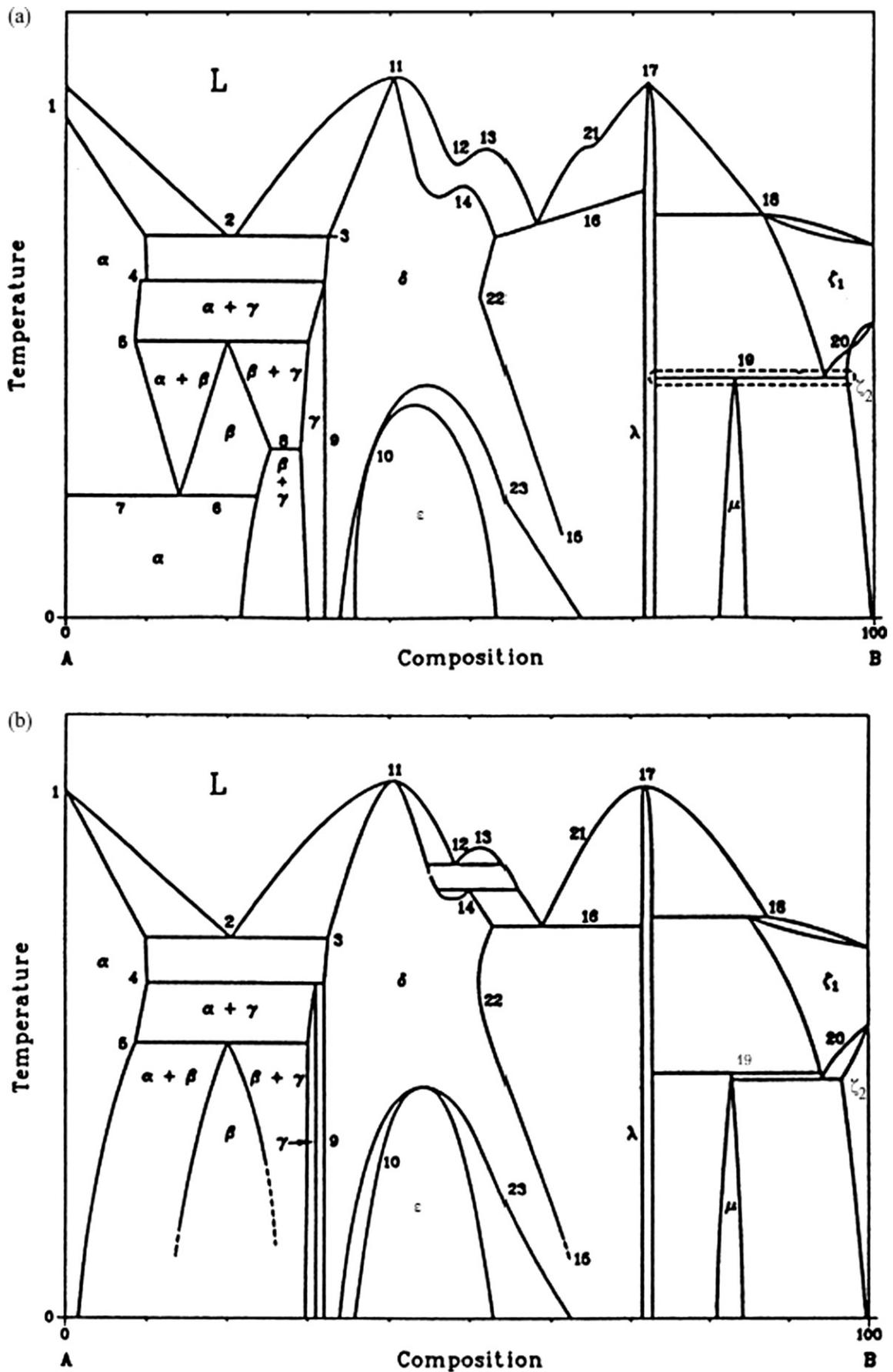


Figure 12 (a) Hypothetical binary phase diagram showing many typical errors of construction. (b) Error-free version of the phase diagram shown in (a) (after Okamoto and Massalski, 1991).

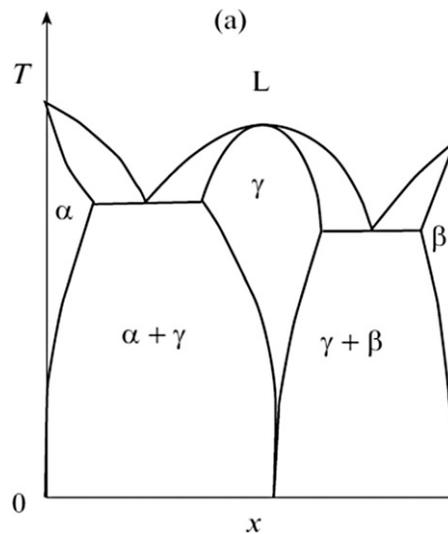


Figure 13 Schematic of a phase diagram showing the phases in equilibrium at 0 K to be either elements or compounds (after Fedorov, 2010).

techniques), X-ray measurements, magnetic measurements, dilatometry, electron probes, etc., to mention only a few. Parallel with this activity, an extensive literature has grown on the measurements of the thermodynamic properties of elements, compounds, and phases, which can then be used to derive the respective free energies and their changes with different state variables. Once free energies are known, phase diagrams can be derived via computer calculation and modeling.

It is also possible to perform no experimental work at all (either metallurgical or thermodynamic), and to use computer programs that will simulate and optimize free energies from assumed models of different structures, and their bonding energies, and then to derive phase diagrams entirely by calculation. It is obvious that many opportunities and pitfalls exist in all of these approaches. Care should always be made to incorporate into the calculations the most reliable of the thermodynamic solution models and not to rely on merely phenomenological power law expansions.

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