

ASM HANDBOOK

VOLUME 3

Alloy Phase Diagrams



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Alloy Phase Diagrams was published in 1992 as Volume 3 of the *ASM Handbook*. The Volume was prepared under the direction of the ASM International Alloy Phase Diagram and the Handbook Committees.

Foreword

Phase diagrams, thermodynamic data in graphical form, are one of the basic tools of the metallurgist, materials scientist, and materials engineer. They can be used for alloy design, selection of hot-working and fabricating parameters, prediction of performance, guidance in selection of hot-working and fabricating parameters, prediction of performance, guidance in selection of heat-treating process parameters, solving performance problems, including failure analysis, and for many other purposes.

The formation of The American Society of Steel Treating, the forerunner of ASM International, was based on better understanding of heat-treating technology; this understanding was, of course, rooted in part in the proper utilization of phase diagrams. Experimental tools such as metallography were used in those early days, both to determine phase diagrams and to link the heat-treating process with the desired microstructure.

In 1978 ASM International joined with the National Bureau of Standards (now the National Institute of Standards of Technology, or NIST) in an effort to improve the reliability of phase diagrams by evaluating the existing data on a system-by-system basis. ASM raised \$4 million from industry and government sources and NIST provided a similar amount of financial and in-kind support for this historic undertaking. An international effort was mounted simultaneously with similar objectives. As a result, all of the important binary systems have been evaluated, and international partners have evaluated more than 2000 ternary systems.

ASM actively participates in the Alloy Phase Diagram International Commission (APDIC), which comprises cooperative national or regional committees in 13 countries. APDIC was formed "to set overall objectives, determine priorities for alloy systems to be assessed, coordinate the assessment programs of APDIC members and associate members, establish scope and quality standards for assessment programs in other countries, and assist in the timely dissemination of the resultant phase diagram data."

The complete results of the international effort are recorded in various periodical and reference publications. However, we have continued to hear from ASM members that a summary version consisting primarily of phase diagrams should be published as an ASM Handbook for the practicing engineer. While such a Handbook could not contain all the diagrams and data, careful selection would ensure the inclusion of the most important systems, with references to other more complete sources. The present Handbook is the result of our attempts to meet these criteria and the stated need.

No reference book of this nature could be published without the contributions of literally hundreds of technical and staff workers. On behalf of ASM International, we extend our sincere thanks and appreciation to the category editors, contributors, reviewers, and staff who worked in this international effort. Thanks are also due to the ASM Alloy Phase Diagram and Handbook Committees for their guidance and support of the project.

- Edward H. Kottcamp, Jr.
President
ASM International
- Edward L. Langer
Managing Director
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Preface

Alloy phase diagrams have long been used successfully by the scientific, engineering, and industrial communities as "road maps" to solve a variety of practical problems. It is, thus, not surprising that such diagrams have always been an important part of ASM Handbooks. The previous ASM compilation of commercially important diagrams appeared in Volume 8 of the 8th Edition of *Metals Handbook*.

Shortly after publication of the earlier volume in 1973, recognition of the universal importance of alloy phase diagrams led to the formation of several national phase diagram programs, as well as the International Programme for Alloy Phase Diagrams to act as the coordinating body for these activities. In the U. S., the national program has been spearheaded jointly by ASM International and the National Institute of Standards and Technology.

To meet the pressing need for diagrams, the national programs and the entire International Programme had two main goals: to increase the availability of phase diagrams and to ensure that the diagrams made available were of the highest possible quality. The specific tasks that were undertaken to accomplish these goals included assembling *all* existing data related to alloy phase diagrams, critically evaluating these data, using the data to construct the most up-to-date and accurate diagrams possible, and making the resulting diagrams readily available for use.

With the publication of the three-volume set of *Binary Alloy Phase Diagrams*, Second Edition, by ASM in 1991, the binary alloy portion of this monumental task is virtually complete. In addition, the first-ever truly comprehensive collection of ternary diagrams, the multivolume *Handbook of Ternary Alloy Phase Diagrams*, is scheduled for publication by ASM in 1994. Information from these two extensive and current diagram sources have been used as the basis of this updated engineering reference book, which reproduces the diagrams of the most commercially important systems (1046 binaries plus 80 ternaries) in a single, convenient volume. These alloy systems are represented by more than 1100 binary diagrams and 313 ternary diagrams, all plotted in weight percent as the primary scale.

The binary diagrams reproduced in this Handbook were selected from the 2965 systems covered in *Binary Alloy Phase Diagrams*, with updated diagrams from literature published since January 1991. Included with the binary diagrams is a complete index of all known alloy phase diagrams from *all* sources, listing where each can be found should a problem arise concerning a binary system not covered in this Handbook. Although many of the diagrams listed in this index (and a few of those reproduced in this volume) have not been evaluated under the Programme, they were selected to represent the best available. Updated binary diagrams from the phase diagram update section of the *Journal of Phase Equilibria* and abstracts of new full-length evaluation from the *Journal of Phase Equilibria* and the Monograph Series on Alloy Phase Diagrams are available from ASM International on a continuing basis through the Binary Alloy Phase Diagrams Updating Service.

The ternary diagrams reproduced here were selected from more than 12,000 diagrams being assembled for the ternary handbook. Where available, diagrams from recently published evaluated compilations were selected. The remainder were selected to represent the best available.

To aid in the full and effective use of these diagrams to solve practical problems, we have included an Introduction to Alloy Phase Diagrams, which contains sections on the theory and use of phase diagrams, and an Appendix listing the relevant properties of the elements and their crystal structures.

While the work of developing additional data, expanding alloy system coverage, and refining existing diagrams must and will continue, the quality checks built into the programme ensure that the diagrams reproduced here are as accurate and reliable as possible. Credit for this belongs to the conscientious work of all the experts involved in the worldwide Programme, especially Prof. Thaddeus B. Massalski and Dr. Alan A. Prince, who coordinated the evaluation efforts during the period of greatest activity.

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Introduction to Alloy Phase Diagrams

Hugh Baker, Editor

Introduction

ALLOY PHASE DIAGRAMS are useful to metallurgists, materials engineers, and materials scientists in four major areas: (1) development of new alloys for specific applications, (2) fabrication of these alloys into useful configurations, (3) design and control of heat treatment procedures for specific alloys that will produce the required mechanical, physical, and chemical properties, and (4) 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.

In the area of alloy development, phase diagrams have proved invaluable for tailoring existing alloys to avoid overdesign in current applications, designing improved alloys for existing and new applications, designing special alloys for special applications, and developing alternative alloys or alloys with substitute alloying elements to replace those containing scarce, expensive, hazardous, or "critical" alloying elements. Application of alloy phase diagrams in processing includes their use to select proper parameters for working ingots, blooms, and billets, finding causes and cures for microporosity and cracks in castings and welds, controlling solution heat treating to prevent damage caused by incipient melting, and developing new processing technology.

In the area of performance, phase diagrams give an indication of which phases are thermodynamically stable in an alloy and can be expected to be present over a long time when the part is subjected to a particular temperature (e.g., in an automotive exhaust system). Phase diagrams also are consulted when attacking service problems such as pitting and intergranular corrosion, hydrogen damage, and hot corrosion.

In a majority of the more widely used commercial alloys, the allowable composition range encompasses only a small portion of the relevant phase diagram. The nonequilibrium conditions that are usually encountered in practice, however, necessitate the knowledge of a much greater portion of the diagram. Therefore, a thorough understanding of alloy phase diagrams in general and their practical use will prove to be of great help to a metallurgist expected to solve problems in any of the areas mentioned above.

Common Terms

Before the subject of alloy phase diagrams is discussed in detail, several of the commonly used terms will be discussed.

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 composition, 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 physical 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 phase 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. 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 in metal objects, the study of equilibrium systems is extremely valuable, because it constitutes a limiting condition from which actual conditions can be estimated.

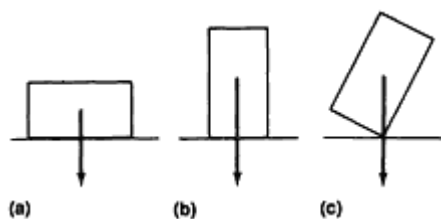


Fig. 1 Mechanical equilibria: (a) Stable. (b) Metastable. (c) Unstable

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 and pressure, each unique structure constituting a distinctively separate phase. The term *allotropy* (existing in another form) is usually used to describe polymorphic changes in chemical elements. Crystal structure of metals and alloys is discussed in a later section of this Introduction; the allotropic transformations of the elements are listed in the Appendix to this Volume.

Metastable Phases. Under some conditions, metastable crystal structures can form instead of stable structures. 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 a group of substances) 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 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* comprising the system and should not be confused with the various phases found within the system. A system, however, also can consist of a single component, such as an element or compound.

Phase Diagrams. In order to record and visualize the results of studying the effects of state variables on a system, diagrams were 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 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. The plotting schemes in common use are described in greater detail in subsequent sections of this Introduction.

System Components. Phase diagrams and the systems they describe are often classified and named for the number (in Latin) of components in the system:

Number of components	Name of system or diagram
One	Unary
Two	Binary
Three	Temary
Four	Quaternary
Five	Quinary
Six	Sexinary
Seven	Septenary
Eight	Octanary
Nine	Nonary
Ten	Decinary

Phase Rule. The *phase rule*, first announced by J. William Gibbs in 1876, related 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 follows:

$$f = c - p + 2$$

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.

Unary Diagrams

Invariant Equilibrium. According to the phase rule, three phases can exist in stable equilibrium only at a single point on a unary diagram ($f = 1 - 3 + 2 = 0$). This limitation is illustrated as point O in the hypothetical unary pressure-temperature (PT) diagram shown in Fig. 2. In this diagram, the three states (or phases)--solid, liquid, and gas--are represented by the three correspondingly labeled fields. Stable equilibrium between any two phases occurs along their mutual boundary, and *invariant equilibrium* among all three phases occurs at the so-called *triple point*, O , where the three boundaries intersect. This point also is called an *invariant point* because, at that location on the diagram, all externally controllable factors are fixed (no degrees of freedom). At this point, all three states (phases) are in equilibrium, but any changes in pressure and/or temperature will cause one or two of the states (phases) to disappear.

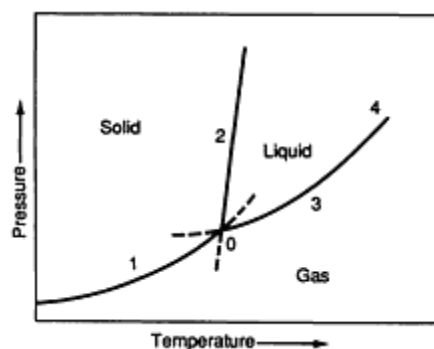


Fig. 2 Schematic pressure-temperature phase diagram

Univariant Equilibrium The phase rule says that stable equilibrium between two phases in a unary system allows one degree of freedom ($f = 1 - 2 + 2$). This condition, called *univariant equilibrium* or *monovariant equilibrium*, is illustrated as line 1, 2, and 3 separating the single-phase fields in Fig. 2. Either pressure or temperature may be freely selected, but not both. Once a pressure is selected, there is only one temperature that will satisfy equilibrium conditions, and conversely. The three curves that issue from the triple point are called *triple curves*: line 1, representing the reaction between the solid and the gas phases, is the *sublimation curve*; line 2 is the *melting curve*; and line 3 is the *vaporization curve*. The vaporization curve ends at point 4, called a *critical point*, where the physical distinction between the liquid and gas phase disappears.

Bivariant Equilibrium. If both the pressure and temperature in a unary system are freely and arbitrarily selected, the situation corresponds to having two degrees of freedom, and the phase rule says that only one phase can exist in stable equilibrium ($p = 1 - 2 + 2$). This situation is called *bivariant equilibrium*.

Binary Diagrams

If the system being considered comprises two components, a composition axis must be added to the PT plot, requiring construction of a three-dimensional graph. Most metallurgical problems, however, are concerned only with a fixed pressure of one atmosphere, and the graph reduces to a two-dimensional plot of temperature and composition (TX diagram).

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 follows:

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

Miscible Solids. Many systems are comprised of 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. 3. 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. 3 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 compositing 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. 3 (the liquid and solid solutions) are called *conjugate phases*.

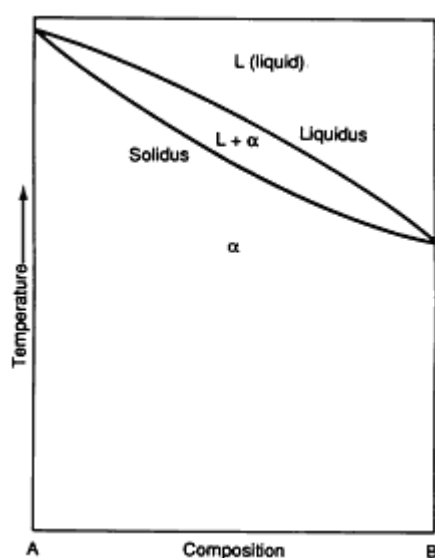


Fig. 3 Schematic binary phase diagram showing miscibility in both the liquid and solid states

If the solidus and liquids 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. 4. It also is possible to have a gap in miscibility in a single-phase field; this is shown in Fig. 5. Point T_c , above which phases α_1 and α_2 become indistinguishable, is a critical point similar to point 4 in Fig. 2. 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 configurations of these and all other phase diagrams depend on the thermodynamics of the system, as discussed later in this Introduction.

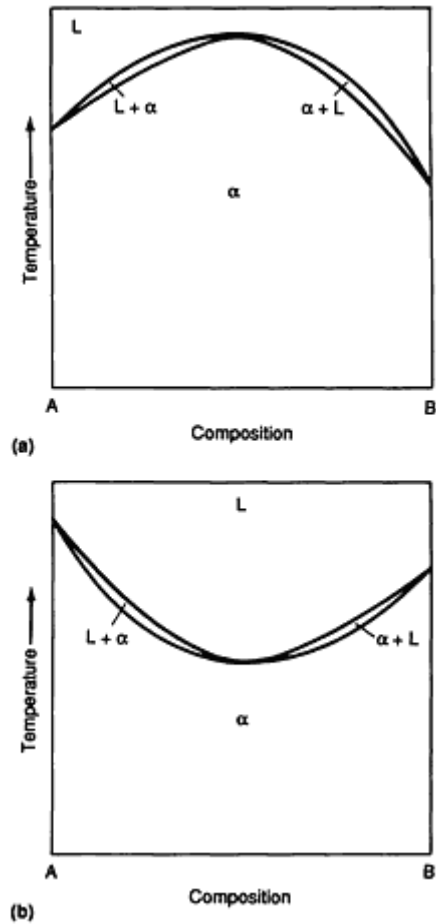


Fig. 4 Schematic binary phase diagrams with solid-state miscibility where the liquidus shows a maximum (a) and a minimum (b)

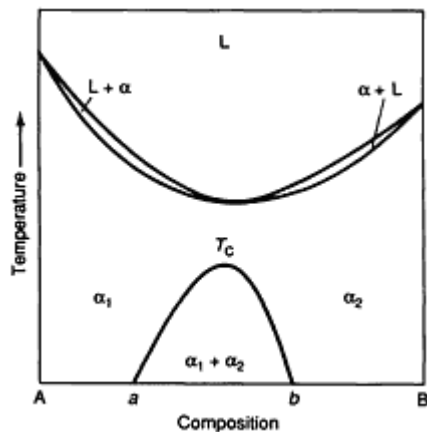


Fig. 5 Schematic binary phase diagram with a minimum in the liquidus and a miscibility gap in the solid state

Eutectic Reactions. If the two-phase field in the solid region of Fig. 5 is expanded so that it touches the solidus at some point, as shown in Fig. 6(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 following section.) 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. 6(b). The three-phase reaction that takes place at the invariant point *E*, where a liquid phases, 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").

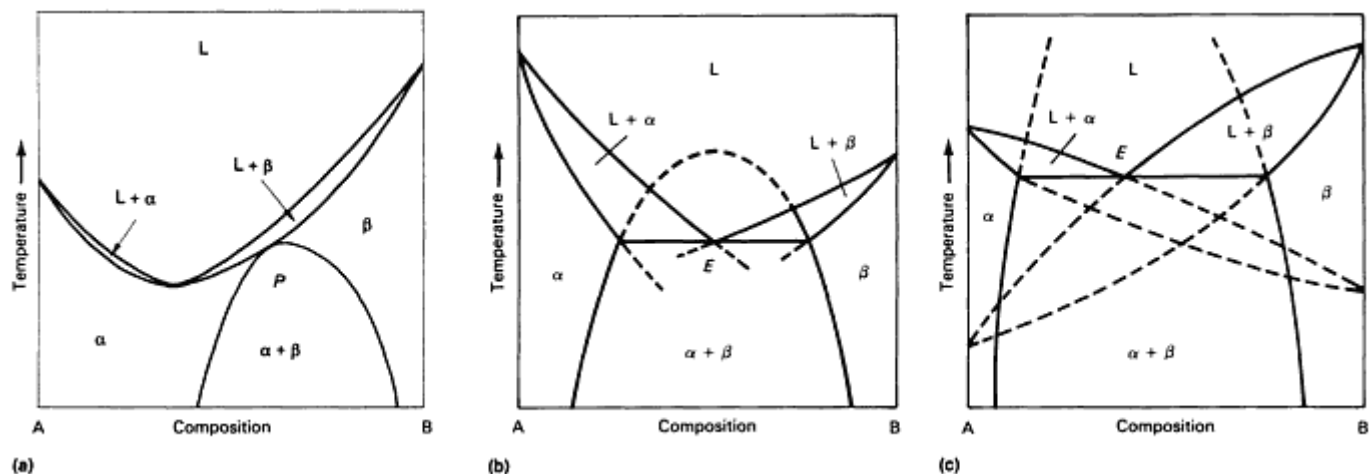


Fig. 6 Schematic binary phase diagrams with invariant points. (a) Hypothetical diagram of the type shown in Fig. 5, except that the miscibility gap in the solid touches the solidus curve at invariant point *P*; an actual diagram of this type probably does not exist. (b) and (c) Typical eutectic diagrams 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.

In the eutectic system described above, 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. 6c) resemble those for the situation of complete miscibility between system components shown in Fig. 3.

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 listed in Table 1 and illustrated in Fig. 7 and 8.

Table 1 Invariant reactions

Type	Reaction
Eutectic (involves liquid and solid)	$L_1 \xrightarrow{\quad} L \xleftarrow{\quad} S$ Monotectic
	$S_1 \xrightarrow{\quad} L \xleftarrow{\quad} S_2$ Eutectic
	$L \xrightarrow{\quad} S_1 \xleftarrow{\quad} S_2$ Catatctic (Metatectic)
Eutectoid (involves solid only)	$S_1 \xrightarrow{\quad} S_2 \xleftarrow{\quad} S_3$ Monotectoid
	$S_2 \xrightarrow{\quad} S_1 \xleftarrow{\quad} S_3$ Eutectoid
Peritectic (involves liquid and solid)	$L_1 \xrightarrow{\quad} L_2 \xleftarrow{\quad} S$ Syntectic
	$L \xrightarrow{\quad} S_1 \xleftarrow{\quad} S_2$ Peritectic
Peritectoid (involves solid only)	$S_1 \xrightarrow{\quad} S_2 \xleftarrow{\quad} S_3$ Peritectoid

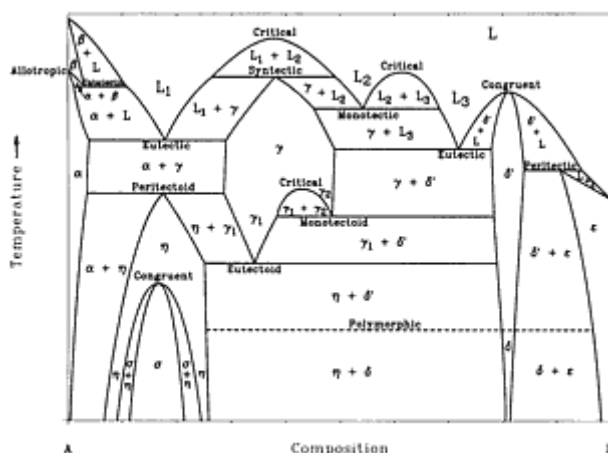


Fig. 7 Hypothetical binary phase diagram showing intermediate phases formed by various invariant reactions and a polymorphic transformation

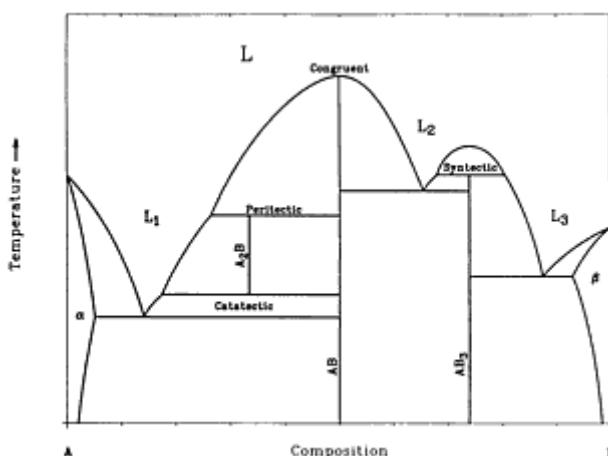


Fig. 8 Hypothetical binary phase diagram showing three intermetallic line compounds and four melting reactions

Intermediate Phases. In addition to the three solid terminal-phase fields, α , β , and ϵ , the diagram in Fig. 7 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. 7, have fairly wide ranges of homogeneity. However, many others have 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*. (Intermetallic compounds should not be confused with chemical compounds, where the type of bonding is different from that in crystals and where the ratio has chemical significance.) Three intermetallic compounds (with four types of melting reactions) are shown in Fig. 8.

In the hypothetical diagram shown in Fig. 8, 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. 7, for example, freeze and melt congruently, while δ' and ϵ freeze and melt incongruently at other compositions.

Metastable Equilibrium. In Fig. 6(c), dashed lines indicate the portions of the liquidus and solidus lines that disappear into the two-phase solid region. These dashed lines represent valuable information, as they indicate conditions that would exist under metastable equilibrium, such as might theoretically occur during extremely rapid cooling. Metastable extensions of some stable-equilibria lines also appear in Fig. 2 and 6(b).

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. 9. 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. 9, 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. 9.

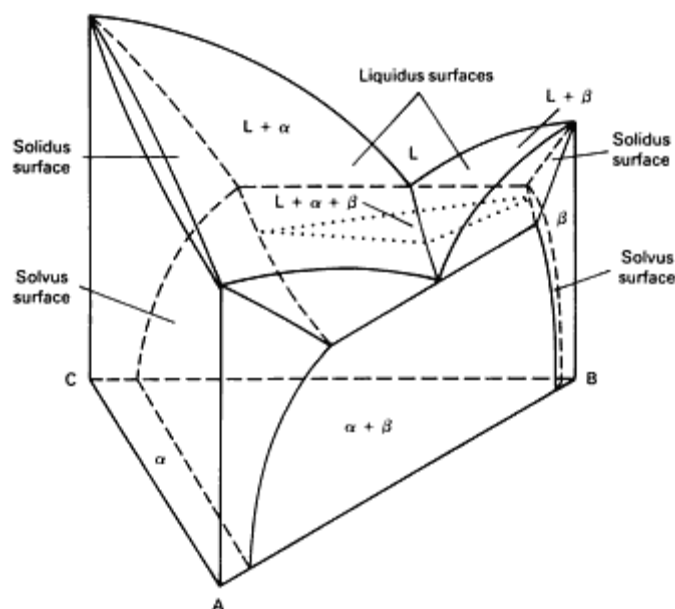


Fig. 9 Ternary phase diagram showing three-phase equilibrium. Source: 56Rhi 3

Although three-dimensional projections can be helpful in understanding the relationship in a diagram, reading values from them is difficult. Therefore, ternary systems 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 *quasibinary* section. One possibility is illustrated by line 1-2 in the isothermal section shown in Fig. 10. A vertical section between a congruently melting binary compound on one face and one on a different face might also form a quasibinary section (see line 2-3).

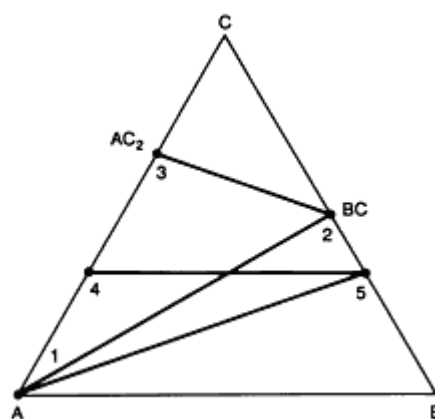


Fig. 10 Isothermal section of a ternary diagram with phase boundaries deleted for simplification.

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. 10. 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. 11). 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 component A is normally indicated from point C to point A, the amount of component B from point A to point B, and the amount of component C from point B to point C. This scale arrangement is often modified when only a corner area of the diagram is shown.

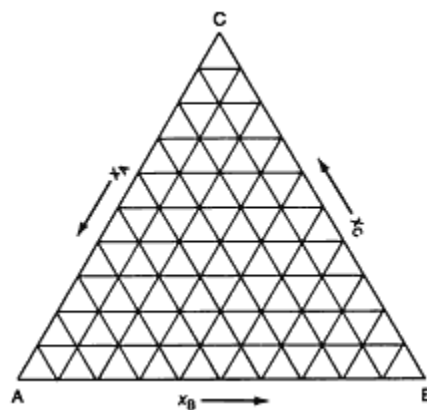


Fig. 11 Triangular composition grid for isothermal section; x is the composition of each constituent in mole fraction or percent.

Projected Views. Liquidus, solids, 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 their shape (see Fig. 12). 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.

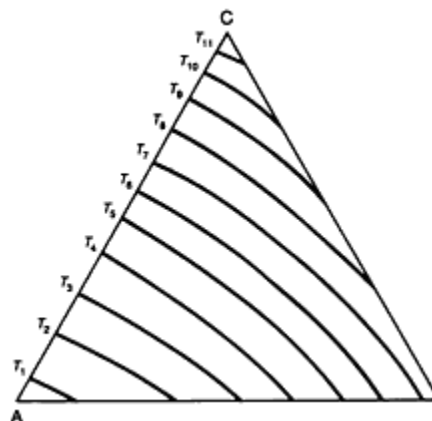


Fig. 12 Liquidus projection of a ternary phase diagram showing isothermal contour lines. Source: Adapted from 56Rhi 3

Reference cited in this section

3. **56Rhi:** F.N. Rhines, *Phase Diagrams in Metallurgy: Their Development and Application*, McGraw-Hill, 1956. This out-of-print book is a basic text designed for undergraduate students in metallurgy.

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 thermodynamic, 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*, E . 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 δQ , is added and a quantity of work, δW , is extracted. The First Law describes the change in internal energy, dE , of the system as follows:

$$dE = \delta Q - \delta W$$

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 earths. 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:

$$dE = \delta Q - PdV$$

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:

$$H = E + PV$$

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:

$$C = \frac{\delta Q}{\delta T}$$

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

$$\delta Q = dE$$

and

$$C_v = \left(\frac{\delta Q}{\delta T} \right)_v = \left(\frac{dE}{dT} \right)_v$$

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

$$C_p = \left(\frac{dE}{dT} + \frac{PdV}{dT} \right)_p$$

$$C_p = \left[\frac{d(E + PV)}{dT} \right]_p$$

and

$$C_p = \left(\frac{dH}{dT} \right)_p$$

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 not 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 always is such as to lead to an increase in entropy*. For processes taking place in a system in equilibrium with its surroundings, the change in entropy is defined as follows:

$$dS \equiv \frac{\delta Q}{T} \equiv \frac{dE + PdV}{T}$$

Third Law. A principle advanced by Theodore Richards, Walter Nernst, Max Planck, and others, often called *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:

$$G \equiv E + PV - TS \equiv H - TS$$

and

$$dG = dE + PdV + VdP - TdS - SdT$$

However,

$$dE = TdS - PdV$$

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 readily 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 Châtelier. The *theorem of Henri Le Châtelier*, 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, i.e., a reaction that partially nullifies the alteration*. The effect of this theorem on lines in a phase diagram can be seen in Fig. 2. The slopes of the sublimation line (1) and the vaporization line (3) show that the system reacts to increasing pressure by making the denser phases (solid and liquid) more stable at higher pressure. The slope of the melting line (2) indicates that this hypothetical substance contracts on freezing. (Note that the boundary between liquid water and ordinary ice, which expands on freezing, slopes toward the pressure axis.)

Clausius-Clapeyron Equation. The theorem of Le Châtelier was quantified by Benoit Clapeyron and Rudolf Clausius to give the following equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

where dP/dT is the slope of the univariant lines in a PT diagram such as those shown in Fig. 2, 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 the reaction).

Solutions. The shapes 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. 3. The two phases, liquid and solid α , 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. 13(a) to (e).

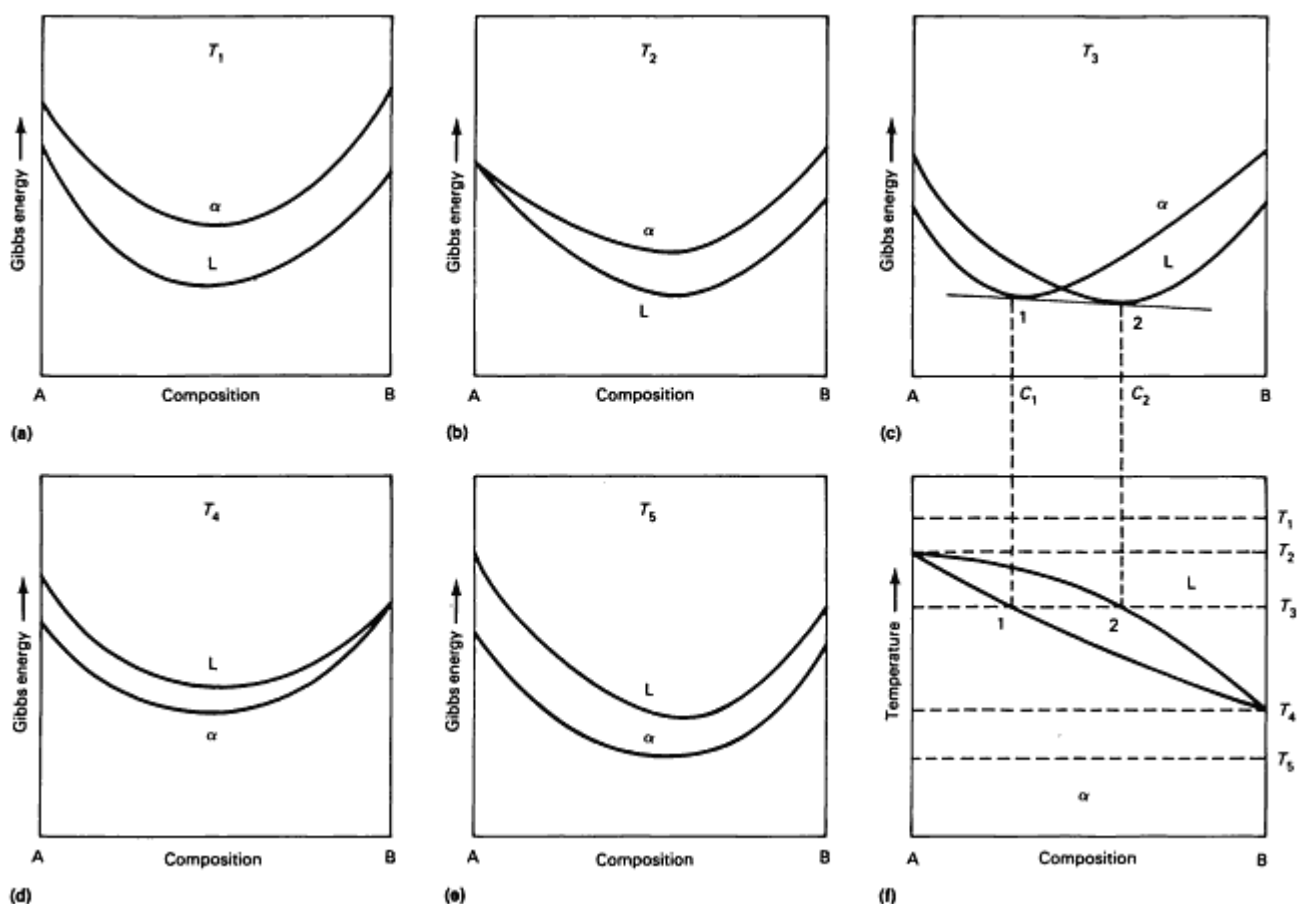


Fig. 13 Use of Gibbs energy curves to construct a binary phase diagram that shows miscibility in both the liquid and solid states. Source: Adapted from 66Pri 4

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 of A, the liquid and solid are equally stable only at a composition of pure A. At temperature T_3 , between the melting temperatures of A and B, the Gibbs energy curves cross. Temperature T_4 is the melting temperature of B, while T_5 is below it.

Construction of the two-phase liquid-plus-solid field of the phase diagram in Fig. 13(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. 13(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. 4(a) and (b), where a maximum or minimum appears in the liquidus and solidus curves.

Mixtures. The two-phase field in Fig. 13(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 (areas) in binary and (volumes) in ternary systems, while *tie triangles* connect the coexisting phases throughout all three-phases regions (volumes) in ternary 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. 14(f) and the Gibbs energy curves for these temperatures (Fig. 14a-e). When the points of tangency on the energy curves are transferred to the

diagram, the typical shape of a eutectic system results. The mixture of solid α and β that forms upon cooling through the eutectic point k has a special microstructure, as discussed later.

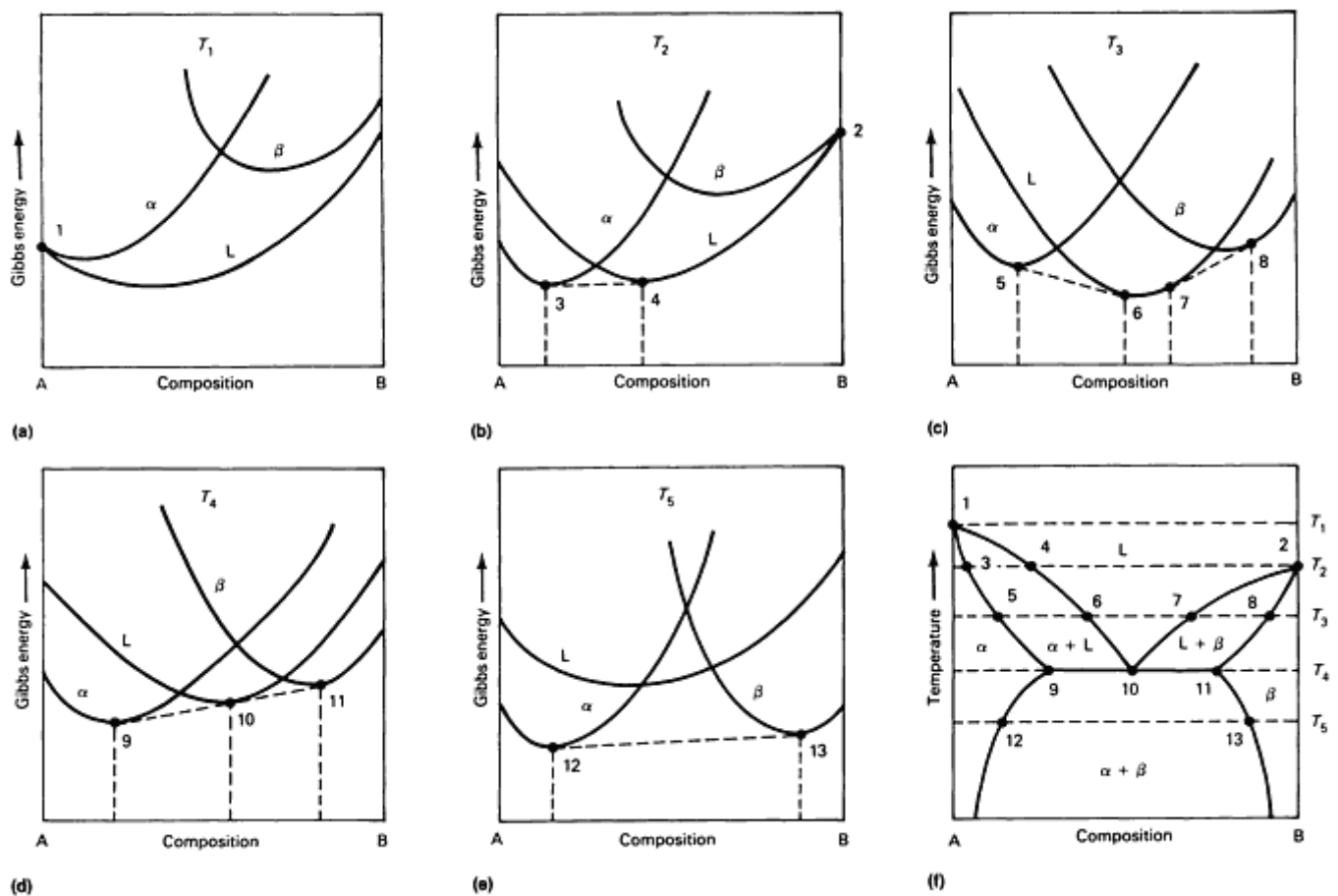


Fig. 14 Use of Gibbs energy curves to construct a binary phase diagram of the eutectic type. Source: Adapted from 68Gor 5

Binary phase 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. Likewise, Gibbs energy surfaces and tangential planes can be used to construct ternary phase diagrams.

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. 2. 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.

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. 6(b), where both the solidus and solvus lines are concave. However, the curvature of both boundaries need not be concave; Fig. 15 shows two equally acceptable (but unlikely) intersections where convex and concave lines are mixed.

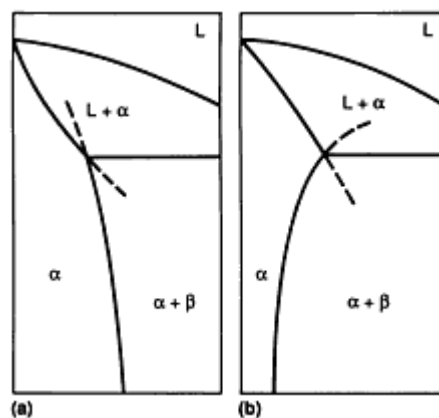


Fig. 15 Examples of acceptable intersection angles for boundaries of two-phase fields. Source: 56Rhi 3

Congruent Transformations. The *congruent point* on a phase diagram is where different phases of the same composition are 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. 4. Often, the inner curve on a diagram such as that shown in Fig. 4 is erroneously drawn with a sharp inflection (see Fig. 16).

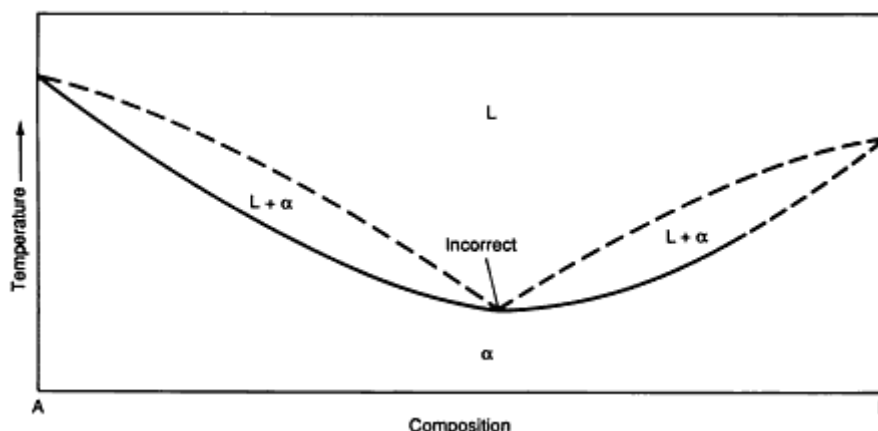


Fig. 16 An Example of a binary phase diagram with a minimum in the liquidus that violates the Gibbs-Konovalov Rule. Source: 81Goo 9

A similar common construction error is found in the diagrams of systems containing congruently melting compounds (such as the line compounds shown in Fig. 17) but having little or no association of the component atoms in the melt (as with most metallic systems). This type of error is especially common in partial diagrams, where one or more system components is a compound instead of an element. (The slope of liquids and solidus curves, however, must *not* be zero when they terminate at an, element, or at a compound having complete association in the melt.)

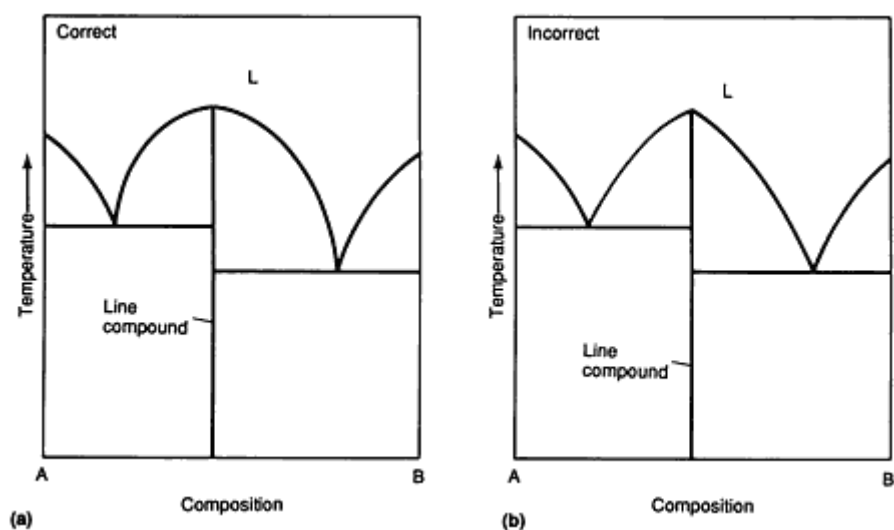


Fig. 17 Schematic diagrams of binary systems containing congruent-melting compounds but having no association of the component atoms in the melt common. The diagram in (a) is consistent with the Gibbs-Konovalov Rule, whereas that in (b) violates the rule. Source: 81Goo 9

Common Construction Errors. Hiroaki Okamoto and Thaddeus Massalski have prepared the hypothetical binary shown in Fig. 18, which exhibits many typical errors of construction (marked as points 1 to 23). The explanation for each error is given in the accompanying text; one possible error-free version of the same diagram is shown in Fig. 19.

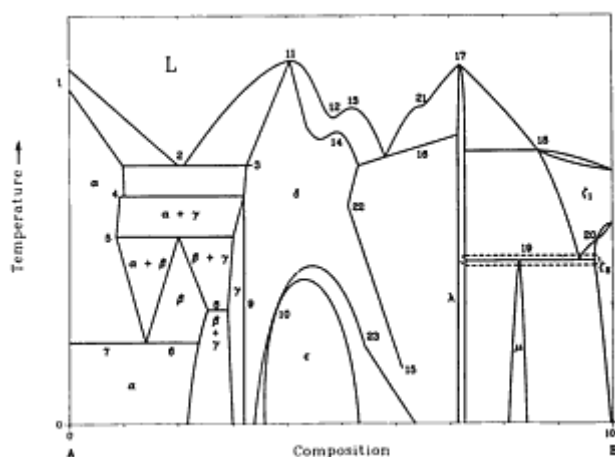


Fig. 18 Hypothetical binary phase diagram showing many typical errors of construction. See the accompanying text for discussion of the errors at points 1 to 23. Source: 91OKa1 18

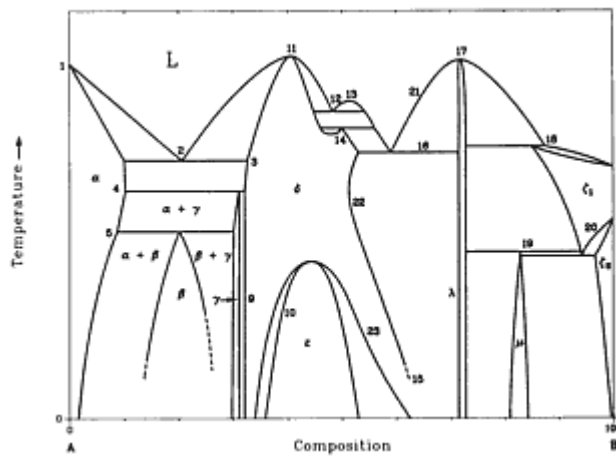


Fig. 19 Error-free version of the phase diagram shown in Fig. 18. Source: 910Ka1 18

Typical phase-rule violations in Fig. 18 include:

1. A two-phase field cannot be extended to become part of a pure-element side of a phase diagram at zero solute. In example 1, the liquidus and the solidus must meet at the melting point of the pure element.
2. Two liquidus curves must meet at one composition at a eutectic temperature.
3. A tie line must terminate at a phase boundary.
4. Two solvus boundaries (or two liquidus, or two solidus, or a solidus and a solvus) of the same phase must meet (i.e., intersect) at one composition at an invariant temperature. (There should not be two solubility values for a phase boundary at one temperature.)
5. A phase boundary must extrapolate into a two-phase field after crossing an invariant point. The validity of this feature, and similar features related to invariant temperatures, is easily demonstrated by constructing hypothetical free-energy diagrams slightly below and slightly above the invariant temperature and by observing the relative positions of the relevant tangent points to the free energy curves. After intersection, such boundaries can also be extrapolated into metastable regions of the phase diagram. Such extrapolations are sometimes indicated by dashed or dotted lines.
6. Two single-phase fields (α and β) should not be in contact along a horizontal line. (An invariant-temperature line separates two-phase fields in contacts.)
7. A single-phase field (α in this instance) should not be apportioned into subdivisions by a single line. Having created a horizontal (invariant) line at 6 (which is an error), there may be a temptation to extend this line into a single-phase field, α , creating an additional error.
8. In a binary system, an invariant-temperature line should involve equilibrium among three phases.
9. There should be a two-phase field between two single-phase fields (Two single phases cannot touch except at a point. However, second-order and higher-order transformations may be exceptions to this rule.)
10. When two phase boundaries touch at a point, they should touch at an extremity of temperature.
11. A touching liquidus and solidus (or any two touching boundaries) must have a horizontal common tangent at the congruent point. In this instance, the solidus at the melting point is too "sharp" and appears to be discontinuous.
12. A local minimum point in the lower part of a single-phase field (in this instance, the liquid) cannot be drawn without additional boundary in contact with it. (In this instance, a horizontal monotectic line is most likely missing.)
13. A local maximum point in the lower part of a single-phase field cannot be drawn without a monotectic, monotectoid, systectic, and syntectoid reaction occurring below it at a lower temperature. Alternatively, a solidus curve must be drawn to touch the liquidus at point 13.
14. A local maximum point in the upper part of a single-phase field cannot be drawn without the phase boundary touching a reversed monotectic, or a monotectoid, horizontal reaction line occurring with the

temperature of the maximum. When a 14 type of error is introduced, a minimum may be created on either side (or on one side) of 14. This introduces an additional error, which is the opposite of 13, but equivalent to 13 in kind.

15. A phase boundary cannot terminate within a phase field. (Termination due to lack of data is, of course, often shown in phase diagrams, but this is recognized to be artificial.
16. The temperature of an invariant reaction in a binary system must be constant. (The reaction line must be horizontal.)
17. The liquidus should not have a discontinuous sharp peak at the melting point of a compound. (This rule is not applicable if the liquid retains the molecular state of the compound, i.e., in the situation of an ideal association.)
18. The compositions of all three phases at an invariant reaction must be different.
19. A four-phase equilibrium is not allowed in a binary system.
20. Two separate phase boundaries that create a two-phase field between two phases in equilibrium should not cross each other.
21. Two inflection points are located too closely to each other.
22. An abrupt reversal of the boundary direction (more abrupt than a typical smooth "retro-grade"). This particular change can occur only if there is an accompanying abrupt change in the temperature dependence of the thermodynamic properties of either of the two phases involved (in this instance, δ or λ in relation to the boundary). The boundary turn at 22 is very unlikely to be explained by an realistic change in the composition dependence of the Gibbs energy functions.
23. An abrupt change in the slope of a single-phase boundary. This particular change can occur only by an abrupt change in the composition dependence of the thermodynamic properties of the single phase involved (in this instance, the δ phase). It cannot be explained by any possible abrupt change in the temperature dependence of the Gibbs energy function of the phase. (If the temperature dependence were involved, there would also be a change in the boundary of the ϵ phase.)

Problems Connected With Phase-Boundary Curvatures Although phase rules are not violated, there additional unusual situations (21, 22, and 23) have also been included in Fig. 18. In each instance, a more subtle thermodynamic problem may exist related to these situations. Examples are discussed where several thermodynamically unlikely diagrams are considered. The problems with each of these situations involve an indicated rapid change of slope of a phase boundary. If such situations are to be associated with realistic thermodynamics, the temperature (or the composition) dependence of the thermodynamic functions of the phase (or phases) involved would be expected to show corresponding abrupt and unrealistic variations in the phase diagram regions where such abrupt phase boundary changes are proposed, without any clear reason for them. Even the onset of ferromagnetism in a phase does not normally cause an abrupt change of slope of the related phase boundaries. The unusual changes of slope considered here are shown in points 21-23.

Higher-Order Transitions. The transitions considered in this Introduction up to this point have been limited to the common thermodynamic types called *first-order transitions*--that is, changes involving distinct phases having different lattice parameters, enthalpies, entropies, densities, and so on. 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.

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Crystal Structure

A *crystal* is a solid consisting of atoms or molecules arranged in a pattern that is repetitive in three dimensions. The arrangement of the atoms or molecules in the interior of a crystal is called its *crystal structure*. The *unit cell* of a crystal is the smallest pattern of arrangement that can be contained in a parallelepiped, the edges of which form the *a*, *b*, and *c* axes of the crystal. The three-dimensional aggregation of unit cells in the crystal forms a *space lattice*, or *Bravais lattice* (see Fig. 20).

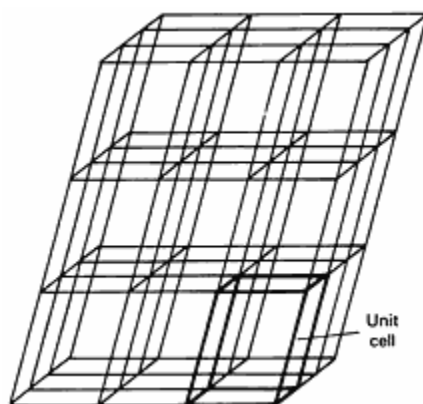


Fig. 20 A space lattice

Crystal Systems. Seven different *crystal systems* are recognized in crystallography, each having a different set of axes, unit-cell edge lengths, and interaxial angles (see Table 2). Unit-cell *edge lengths* *a*, *b*, and *c* are measured along the corresponding *a*, *b*, and *c* axes (see Fig. 21). Unit-cell faces are identified by capital letters: face *A* contains axes *b* and *c*, face *B* contains *c* and *a*, and face *C* contains *a* and *b*. (Faces are not labeled in Fig. 21.) *Interaxial angle* α occurs in face *A*, angle β in face *B*, and angle γ in face *C* (see Fig. 21).

Table 2 Relationships of edge lengths and of interaxial angles for the seven crystal systems.

Crystal system	Edge lengths	Interaxial angles	Examples
Triclinic (anorthic)	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	HgK
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	β -S; CoSb ₂
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	α -S; Ga; Fe ₃ C (cementite)

Tetragonal	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	β -Sn (white); TiO ₂
Hexagonal	$a \neq b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Zn; Cd; NiAs
Rhombohedral ^(a)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	As; Sb; Bi; calcite
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Cu; Ag; Au; Fe; NaCl

(a) Rhombohedral crystals (sometimes called trigonal) also can be describe by using hexagonal axes (rhombohedral-hexagonal).

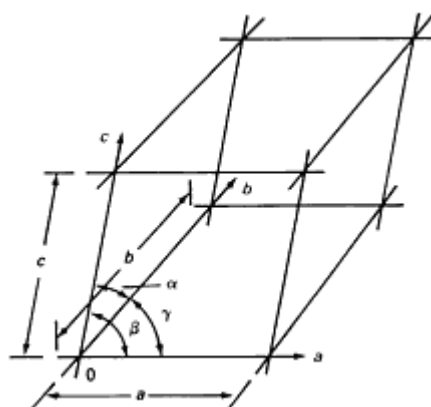


Fig. 21 Crystal axes and unit-cell edge lengths. Unit-cell faces are shown, but to avoid confusion they are not labeled.

Lattice Dimensions. It should be noted that the unit-cell edge lengths and interaxial angles are unique for each crystalline substance. The unique edge lengths are called *lattice parameters*. The term *lattice constant* also has been used for the length of an edge, but the values of edge length are not constant, varying with composition within a phase field and also with temperature due to thermal expansion and contraction. (Reported lattice parameter values are assumed to be room-temperature values unless otherwise specified.) Interaxial angles other than 90° or 120° also can change slightly with changes in composition. When the edges of the unit cell are not equal in all three directions, all unequal lengths must be stated to completely define the crystal. The same is true if all interaxial angles are not equal. When defining the unit-cell size of an alloy phase, the possibility of crystal ordering occurring over several unit cells should be considered. For example, in the copper-gold system, a superlattice forms that is made up of 10 cells of the disordered lattice, creating what is called *long-period ordering*.

Lattice Points. As shown in Fig. 20, a space lattice can be viewed as a three-dimensional network of straight lines. The intersections of the lines (called *lattice points*) represent locations in space for the same kind of atom or group of atoms of identical composition, arrangement, and orientation. There are five basic arrangements for lattice points within a unit cell. The first four are: primitive (simple), having lattice points solely at cell corners; base-face centered (end-centered), having lattice points centered on the *C* faces, or ends of the cell; all-face centered, having lattice points centered all faces; and innercentered (body-centered), having lattice points at the center of the volume of the unit cell. The fifth arrangement, the primitive rhombohedral unit cell, is considered a separate basic arrangement, as shown in the following section on crystal structure nomenclature. These five basic arrangements are identified by capital letters as follows: *P* for the primitive cubic, *C* for the cubic cell with lattice points on the two *C* faces, *F* for all-face-centered cubic, *I* for innercentered (body-centered) cubic, and *R* for primitive rhombohedral.

Crystal Structure Nomenclature. When the seven crystal systems are considered together with the five space lattices, the combinations listed in Table 3 are obtained. These 14 combinations form the basis of the system of *Pearson symbols* developed by William B. Pearson, which are widely used to identify crystal types. As can be seen in Table 3, the Pearson symbol uses a small letter to identify the crystal system and a capital letter to identify the space lattice. To these is added a number equal to the number of atoms in the unit cell conventionally selected for the particular crystal type. When determining the number of atoms in the unit cell, it should be remembered that each atom that is shared with an adjacent cell (or cells) must be counted as only a fraction of an atom. The Pearson symbols for some simple metal crystals are shown in Fig. 22(a), 22(b), 22(c), and 22(d), along with schematic drawings illustrating the atom arrangements in the unit cell. It should be noted that in these schematic representations, the different kinds of atoms in the prototype crystal illustrated are drawn to represent their relative sizes, but in order to show the arrangements more clearly, all the atoms are shown much smaller than their true effective size in real crystals.

Table 3 The 14 space (Bravais) lattices and their Pearson symbols

Crystal system	Space lattice	Pearson symbol
Triclinic (anorthic)	Primitive	<i>aP</i>
Monoclinic	Primitive	<i>mP</i>
	Base-centered ^(a)	<i>mC</i>
Orthorhombic	Primitive	<i>oP</i>
	Base-centered ^(a)	<i>oC</i>
	Face-centered	<i>oF</i>
	Body-centered	<i>oI</i>
Tetragonal	Primitive	<i>tP</i>
	Body-centered	<i>tI</i>
Hexagonal	Primitive	<i>hP</i>
Rhombohedral	Primitive	<i>hR</i>
Cubic	Primitive	<i>cP</i>
	Face-centered	<i>cF</i>

- (a) The face that has a lattice point at its center may be chosen as the c face (the xy plan), denoted by the symbol C , or as the a or b face, denoted by A or B , because the choice of axes is arbitrary and does not alter the actual translations of the lattice.

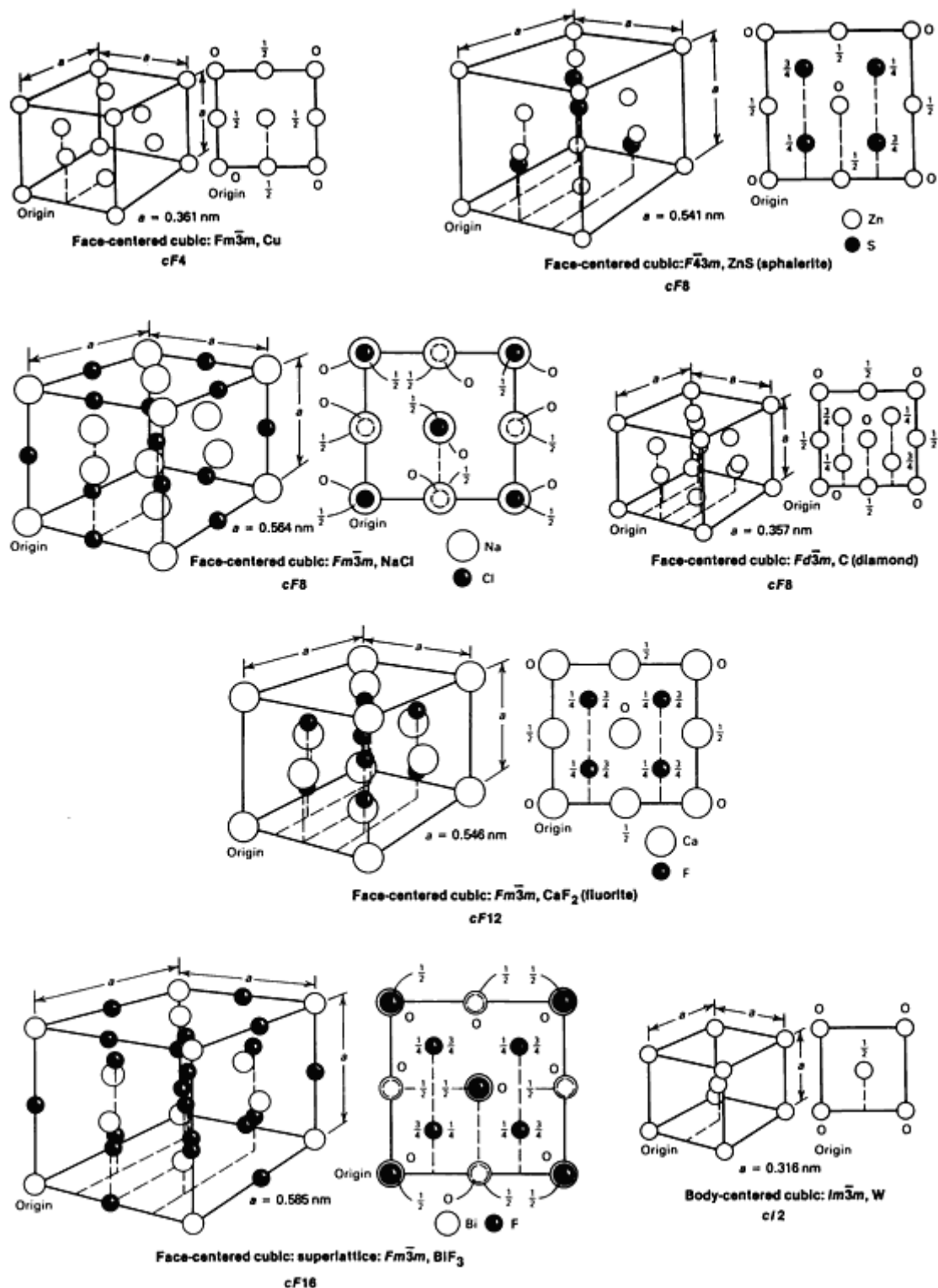


Fig. 22(a) Schematic drawings of the unit cells and ion positions for some simple metal crystals, arranged alphabetically according to Pearson symbol. Also listed are the space lattice and crystal system, space-group notation, and prototype for each crystal. Reported lattice parameters are for the prototype crystal.

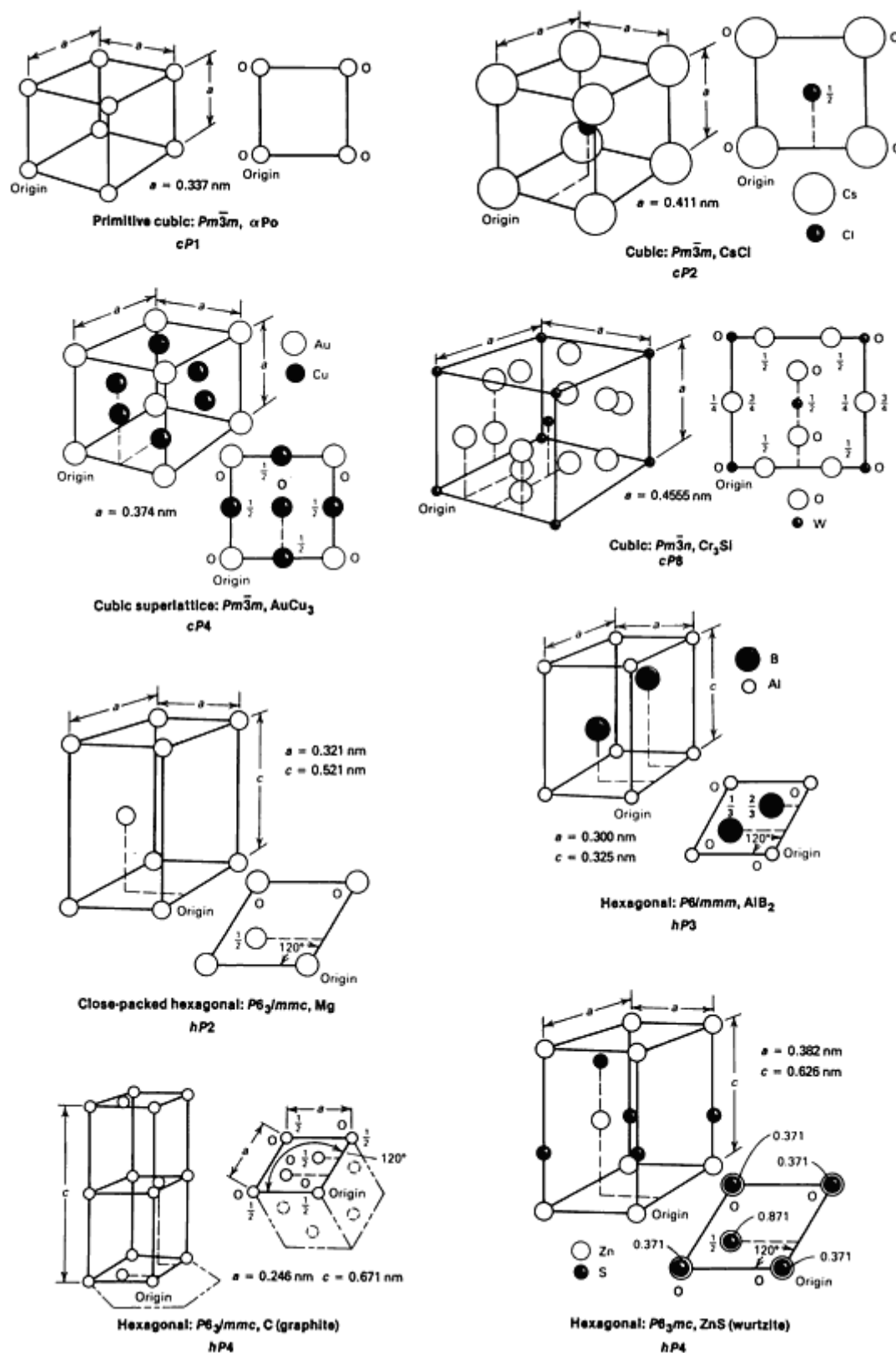


Fig. 22(b) Schematic drawings of the unit cells and ion positions for some simple metal crystals, arranged alphabetically according to Pearson symbol. Also listed are the space lattice and crystal system, space-group notation, and prototype for each crystal. Reported lattice parameters are for the prototype crystal.

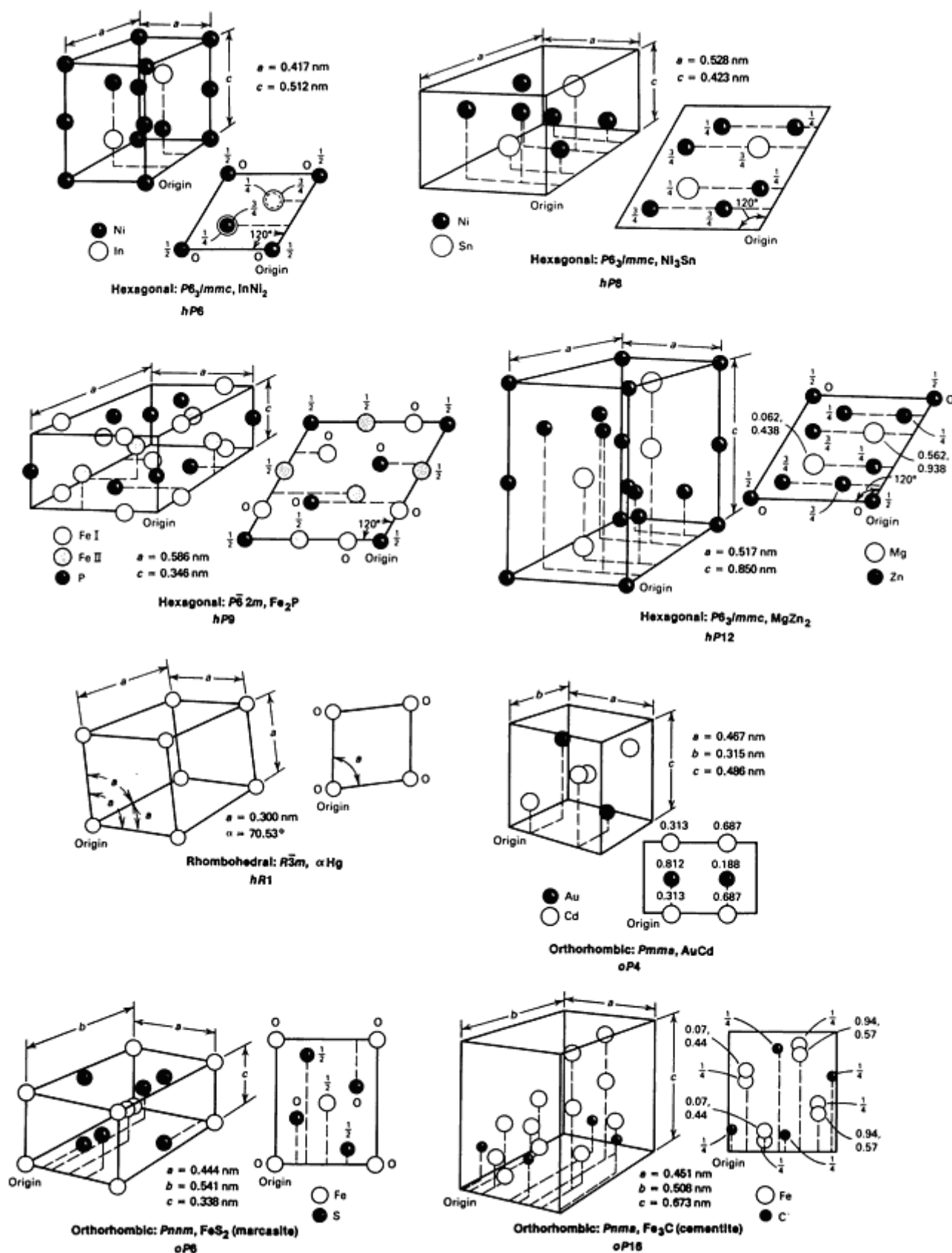


Fig. 22(c) Schematic drawings of the unit cells and ion positions for some simple metal crystals, arranged alphabetically according to Pearson symbol. Also listed are the space lattice and crystal system, space-group notation, and prototype for each crystal. Reported lattice parameters are for the prototype crystal.

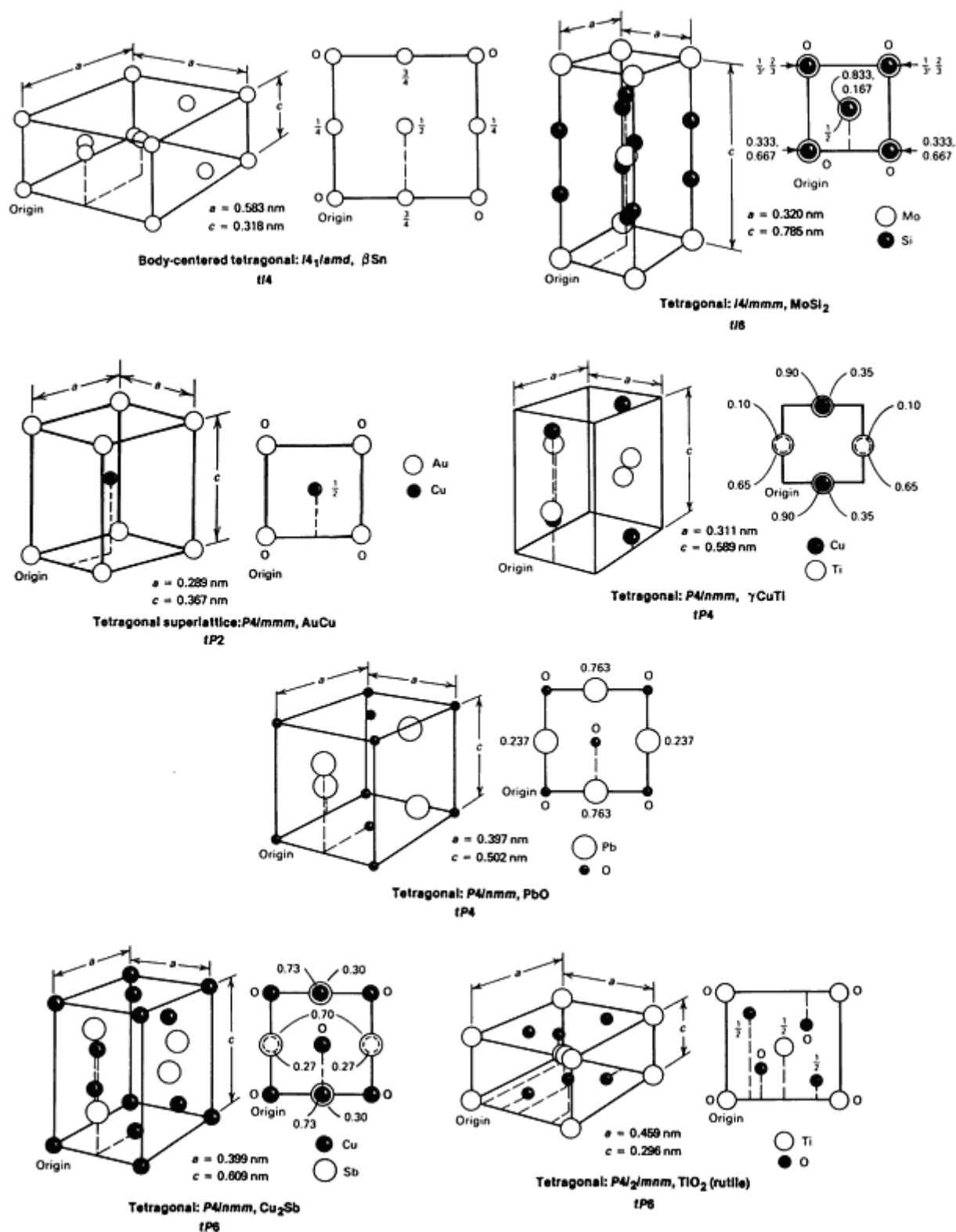


Fig. 22(d) Schematic drawings of the unit cells and ion positions for some simple metal crystals, arranged alphabetically according to Pearson symbol. Also listed are the space lattice and crystal system, space-group notation, and prototype for each crystal. Reported lattice parameters are for the prototype crystal.

Several of the many possible crystal structures are so commonly found in metallic systems that they are often identified by three-letter abbreviations that combine the space lattice with the crystal system. For example, bcc is used for body-centered cubic (two atoms per unit cell), fcc for face-centered cubic (four atoms per unit cell), and hcp for close-packed hexagonal (two atoms per unit cell).

Space-group notation is a symbolic description of the space lattice and symmetry of a crystal. It consists of the symbol for the space lattice followed by letters and numbers that designate the symmetry of the crystal. The space-group notation for each unit cell illustrated in Figs. 22(a), 22(b), 22(c), and 22(d) is identified next to it. For a more complete list of Pearson symbols and space-group notations, consult the Appendix.

To assist in classification and identification, each crystal structure type is assigned a representative substance (element or phase) having that structure. The substance selected is called the *structure prototype*. Generally accepted prototypes for some metal crystals are listed in Figs. 22(a), 22(b), 22(c), and 22(d).

An important source of information on crystal structures for many years was *Structure Reports* (*Strukturbericht* in German). In this publication, crystal structures were classified by a designation consisting of a capital letter (*A* elements, *B* for AB-type phase, *C* for AB₂-type phases, *D* for other binary phases, *E* for ternary phases, and *L* for superlattices), followed by a number consecutively assigned (within each group) at the time the type was reported. To further distinguish among crystal types, inferior letters and numbers, as well as prime marks, were added to some designations. Because the Strukturbericht designation cannot be conveniently and systematically expanded to cover the large variety of crystal structures currently being encountered, the system is falling into disuse.

The relations among common Pearson symbols, space groups, structure prototypes, and Strukturbericht designations for crystal systems are given in various tables in the Appendix. Crystallographic information for the metallic elements can be found in the table of allotropes in the Appendix; data for intermetallic phases of the systems included in this Volume are listed with the phase diagrams. Crystallographic data for an exhaustive list of intermediate phases are presented in 91Vil 20 (see the Bibliography at the end of this Introduction).

Solid-Solution Mechanisms. There are only two mechanisms by which a crystal can dissolve atoms of a different element. If the atoms of the solute element are sufficiently smaller than the atoms comprising the solvent crystal, the solute atoms can fit into the spaces between the larger atoms to form an *interstitial solid solution* (see Fig. 23a). The only solute atoms small enough to fit into the interstices of metal crystals, however, are hydrogen, nitrogen, carbon, and boron. (The other small-diameter atoms, such as oxygen, tend to form compounds with metals rather than dissolve in them.) The rest of the elements dissolve in solid metals by replacing a solvent atom at a lattice point to form a *substitutional solid solution* (see Fig. 23b). When both small and large solute atoms are present, the solid solution can be both interstitial and substitutional. The addition of foreign atoms by either mechanism results in distortion of the crystal lattice and an increase in its internal energy. This distortion energy causes some hardening and strengthening of the alloy, called *solution hardening*. The solvent phase becomes saturated with the solute atoms and reaches its limit of homogeneity when the distortion energy reaches a critical value determined by the thermodynamics of the system.

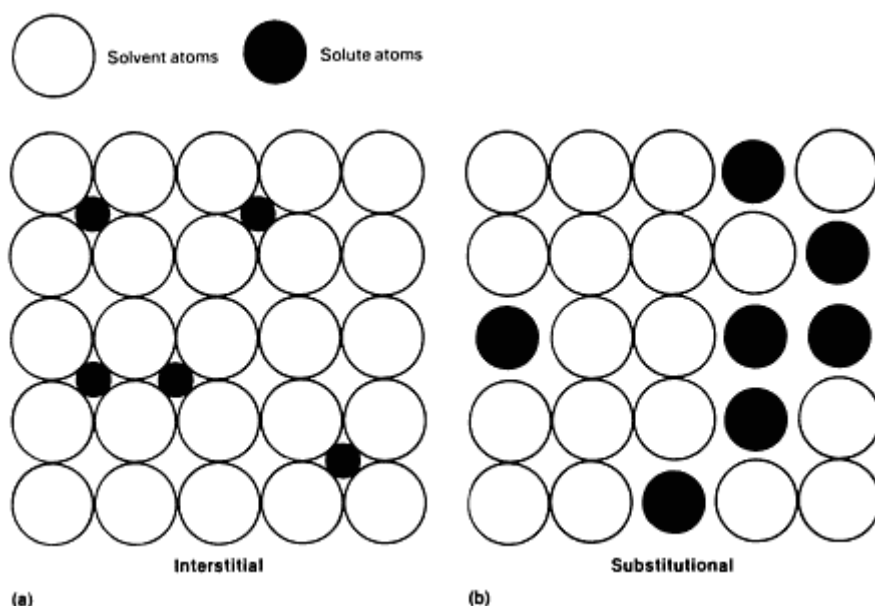


Fig. 23 Solid-solution mechanisms. (a) Interstitial. (b) Substitutional

Reference cited in this section

20. **91Vil:** P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermediate Phases*, ASM International, 1991. *This third edition of Pearson's comprehensive compilation includes data from all the international literature from 1913 to 1989.*

Determination of Phase Diagrams

The data used to construct phase diagrams are obtained from a wide variety of measurements, many of which are conducted for reasons other than the determination of phase diagrams. No one research method will yield all of the information needed to construct an accurate diagram, and no diagram can be considered fully reliable without corroborating results obtained from the use of at least one other method.

Knowledge of the chemical composition of the sample and the individual phases is important in the construction of accurate phase diagrams. For example, the samples used should be prepared from high-purity constituents and accurately analyzed.

Chemical analysis is used in the determination of phase-field boundaries by measuring compositions of phases in a sample equilibrated at a fixed temperature by means of such methods as the diffusion-couple technique. The composition of individual phases can be measured by wet chemical methods, electron probe microanalysis, and so on.

Cooling Curves. One of the most widely used methods for the determination of phase boundaries is thermal analysis. The temperature of a sample is monitored while allowed to cool naturally from an elevated temperature (usually in the liquid field). The shape of the resulting curves of temperature versus time are then analyzed for deviations from the smooth curve found for materials undergoing no phase changes (see Fig. 24).

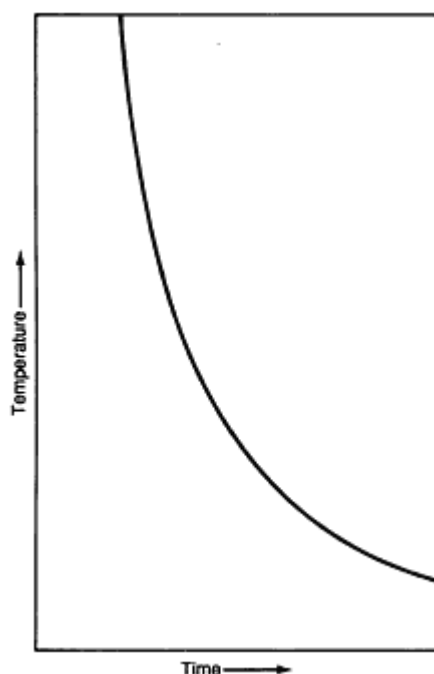


Fig. 24 Ideal cooling curve with no phase change

When a pure element is cooled through its freezing temperature, its temperature is maintained near that temperature until freezing is complete (see Fig. 25). The true freezing/melting temperature, however, is difficult to determine from a cooling curve because of the nonequilibrium conditions inherent in such a dynamic test. This is illustrated in the cooling and heating curves shown in Fig. 26, where the effects of both supercooling and superheating can be seen. The dip in the cooling curve often found at the start of freezing is caused by a delay in the start of crystallization.

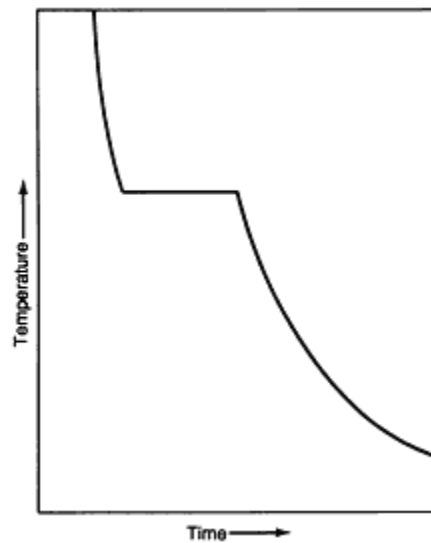


Fig. 25 Ideal freezing curve of a pure metal.

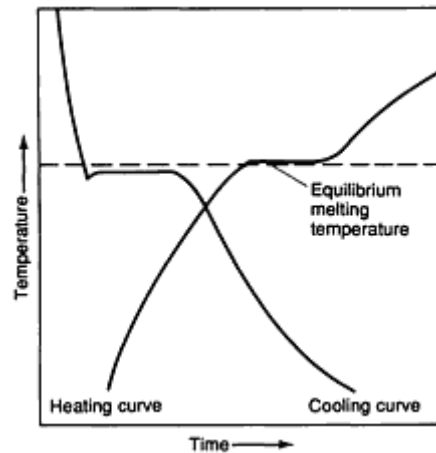


Fig. 26 Natural freezing and melting curves of a pure metal. Source: 56Rhi 3

The continual freezing that occurs during cooling through a two-phase liquid-plus-solid field results in a reduced slope to the curve between the liquidus and solidus temperatures (see Fig. 27). By preparing several samples having compositions across the diagram, the shape of the liquidus curves and the eutectic temperature of eutectic system can be determined (see Fig. 28). Cooling curves can be similarly used to investigate all other types of phase boundaries.

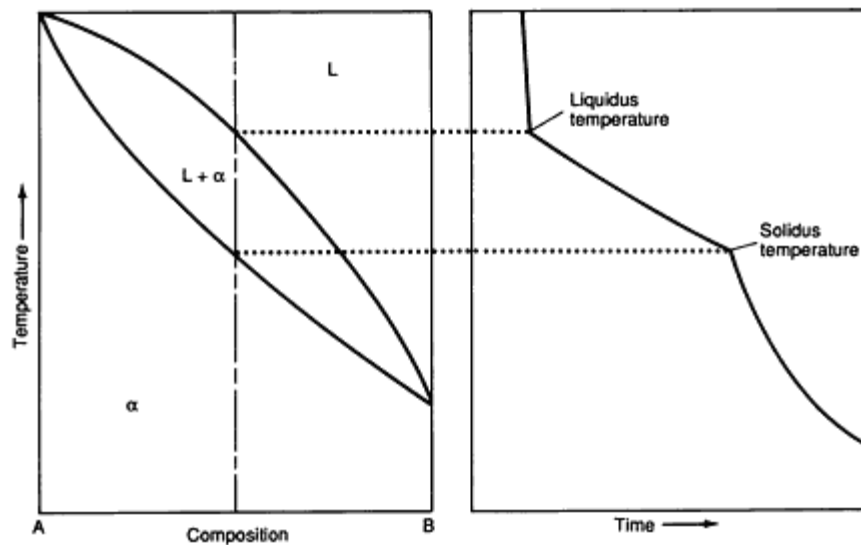


Fig. 27 Ideal freezing curve of a solid-solution alloy

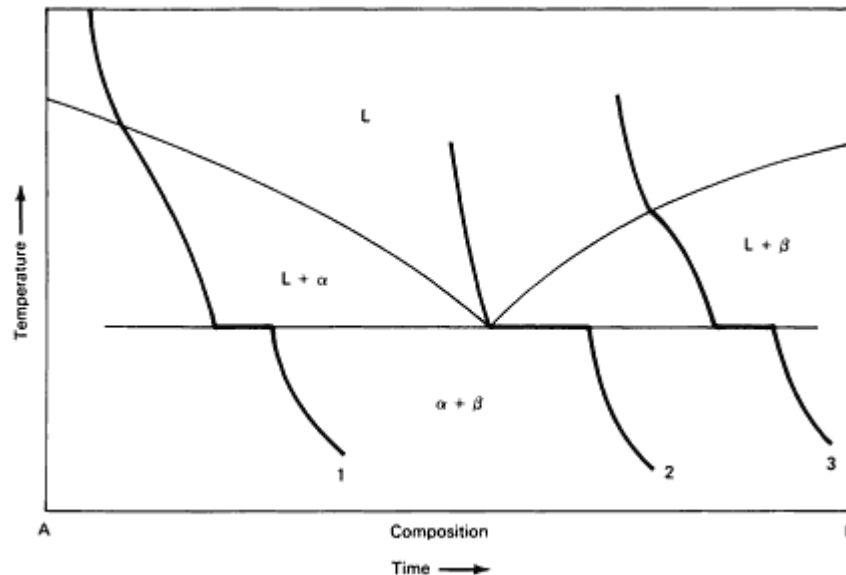


Fig. 28 Ideal freezing curves of (1) a hypoeutectic alloy, (2) a eutectic alloy, and (3) a hypereutectic alloy superimposed on a portion of a eutectic phase diagram. Source: Adapted from 66Pri 4

Differential thermal analysis is a technique used to increase test sensitivity by measuring the difference between the temperature of the sample and a reference material that does not undergo phase transformation in the temperature range being investigated.

Crystal Properties. X-ray diffraction methods are used to determine both crystal structure and lattice parameters of solid phases present in a system at various temperatures (phase identification). Lattice parameter scans across a phase field are useful in determining the limits of homogeneity of the phase; the parameters change with changing composition within the single-phase field, but they remain constant once the boundary is crossed into a two-phase field.

Physical Properties. Phase transformations within a sample are usually accompanied by changes in its physical properties (linear dimensions and specific volume, electrical properties, magnetic properties, hardness, etc.). Plots of these changes versus temperature or composition can be used in a manner similar to cooling curves to locate phase boundaries.

Metallographic Methods. Metallography can be used in many ways to aid in phase diagram determination. The most important problem with metallographic methods is that they usually rely on rapid quenching to preserve (or indicate) elevated-temperature microstructures for room-temperature observation. Hot-stage metallography, however, is an alternative. The application of metallographic techniques is discussed in the section on reading phase diagrams.

Thermodynamic Modeling. Because a phase diagram is a representation of the thermodynamic relationships between competing phases, it is theoretically possible to determine a diagram by considering the behavior of relevant Gibbs energy functions for each phase present in the system and physical models for the reactions in the system. How this can be accomplished is demonstrated for the simple problem of complete solid miscibility shown in Fig. 13. The models required to calculate the possible boundaries in the more complicated diagrams usually encountered are, of course, also more complicated, and involve the use of the equations governing solutions and solution interaction originally developed for physical chemistry. Although modeling alone cannot produce a reliable phase diagram, it is a powerful technique for validating those portions of a phase diagram already derived from experimental data. In addition, modeling can be used to estimate the relations in areas of diagrams where no experimental data exist, allowing much more efficient design of subsequent experiments.

References cited in this section

3. **56Rhi:** F.N. Rhines, *Phase Diagrams in Metallurgy: Their Development and Application*, McGraw-Hill, 1956. *This out-of-print book is a basic text designed for undergraduate students in metallurgy.*
4. **66Pri:** A. Prince, *Alloy Phase Equilibria*, Elsevier, 1966. *This out-of-print book covers the thermodynamic approach to binary, ternary, and quaternary phase diagrams.*

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. Conversions between weight and atomic composition also can be made using the equations given in the following section "Composition Conversions" and standard atomic weights listed in the Appendix.

Composition Conversions. The following equations can be used to make conversions in binary systems:

$$\text{wt\% A} = \frac{\text{at.\% A} \times \text{at. wt of A}}{(\text{at.\% A} \times \text{at. wt of A}) + (\text{at.\% B} \times \text{at. wt of B})} \times 100$$

$$\text{at.\% A} = \frac{\text{wt\% A} / \text{at. wt of A}}{(\text{at.\% A} / \text{at. wt of A}) + (\text{wt\% B} / \text{at. wt of B})} \times 100$$

The equation for converting from atomic percentages to weight percentages in higher-order systems is similar to that for binary systems, except that an additional term is added to the denominator for each additional component. For ternary systems, for example:

$$\text{wt\% A} = \frac{\text{at.\% A} \times \text{at. wt of A}}{(\text{at.\% A} \times \text{at. wt of A}) + (\text{at.\% B} \times \text{at. wt of B}) + (\text{at.\% C} \times \text{at. wt of C})} \times 100$$

$$\text{at.\% A} = \frac{\text{wt\% A} / \text{at. wt of A}}{(\text{wt\% A} / \text{at. wt of A}) + (\text{wt\% B} / \text{at. wt of B}) + (\text{wt\% C} / \text{at. wt of C})} \times 100$$

The conversion from weight to atomic percentages for higher-order systems is easy to accomplish on a computer with a spreadsheet program.

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. (The symbols used for chemical elements are listed in the Appendix.) Allotropes of polymorphic elements are distinguished by small (lower-case) Greek letter prefixes. (The Greek alphabet appears in the Appendix.)

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

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 bcc, ζ or ε for disordered cph, γ for the γ -brass-type structure, and σ for the σ 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. As explained in the section on the features of phase diagrams, 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. 29(a).

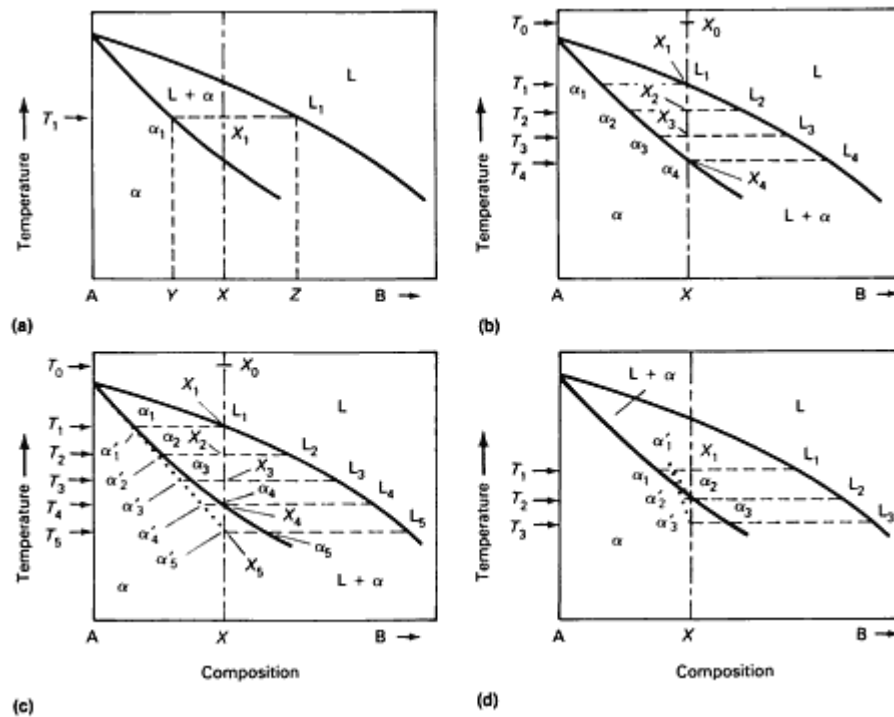


Fig. 29 Portion of a binary phase diagram containing a two-phase liquid-plus-solid field illustrating (a) the lever rule and its application to (b) equilibrium freezing, (c) nonequilibrium freezing and (d) heating of a homogenized sample. Source: 56Rhi 3

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% α 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. According to the lever rule, the percentages of the two phases present can be calculated as follows:

$$\begin{aligned} \% \text{ liquid} &= \frac{\text{length of line } \alpha_1 X_1}{\text{length of line } \alpha_1 L_1} \times 100 \\ \% \text{ solid } \alpha &= \frac{\text{length of line } X_1 L_1}{\text{length of line } \alpha_1 L_1} \times 100 \end{aligned}$$

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

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 areal-fraction values, both in decimal fractions. This conversion can be developed as follows. The weight fraction of the phase is determined from the phase diagram, using the lever rule.

$$\text{Volume portion of the phase} = \frac{\text{weight fraction of the phase}}{\text{phase density}}$$

Total volume of all phases present = sum of the volume portions of each phase.

$$\text{Volume fraction of the phase} = \frac{\text{weight fraction of the phase}}{\text{phase density} \times \text{total volume}}$$

It has been shown by stereology and quantitative metallography that areal fraction is equal to volume fraction [85ASM 13]. (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:

$$\text{Areal fraction of the phase} = \frac{\text{weight fraction of the phase}}{\text{phase density} \times \text{total volume}}$$

The phase density value for the preceding equation can be obtained by measurement 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:

$$\text{Weight of each element} = \text{number of atoms} \times \frac{\text{atomic weight}}{\text{Avogadro's number}}$$

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 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 the phase relationships in many ternary diagram sections (and other types of sections) often can be difficult because of 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 non-parallel tie lines in the two-phase fields of isothermal sections (see Fig. 30a) are replaced with sets of curving lines of equal phase fraction (Fig. 30b). 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. Although this approach to reading diagrams may not seem helpful for such a simple diagram, it can be useful aid in more complicated systems. For more information on this topic, see 84Mor 12 and 91Mor 17.

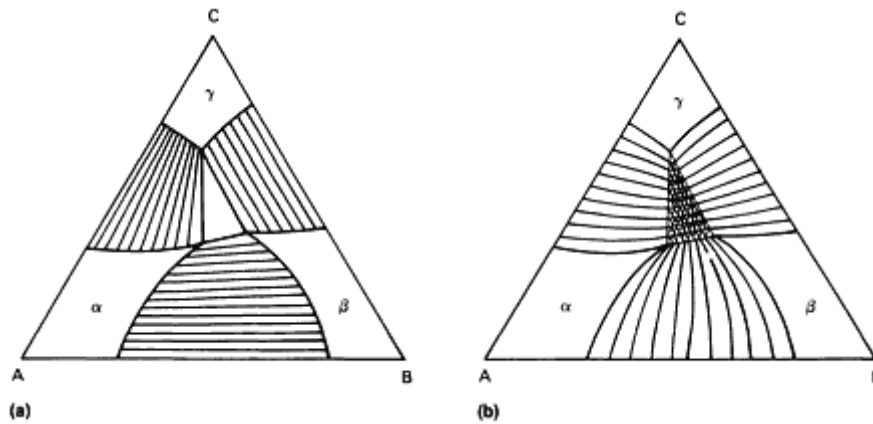


Fig. 30 Alternative systems for showing phase relationships in multiphase regions of ternary diagram isothermal sections. (a) Tie lines. (b) Phase-fraction lines. Source: 84Mor 12

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 temperatures shown in Fig. 29(b), all of which intersect the bulk composition X. The first crystals to freeze have the composition α_1 . 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 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*). The development of this condition is illustrated in Fig. 29(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'_5 . 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. 31.



Fig. 31 Copper alloy C71500 (copper nickel, 30%) ingot. Dendritic structure shows coring: light areas are nickel rich; dark areas are low in nickel. 20 $\times$. Source: 85ASM 13

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 also is 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. 29(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 α_1 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 (such as alloy 2 in Fig. 28) 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. 32). More rapid cooling, however, can affect the microstructure obtained (see Fig. 33). 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.

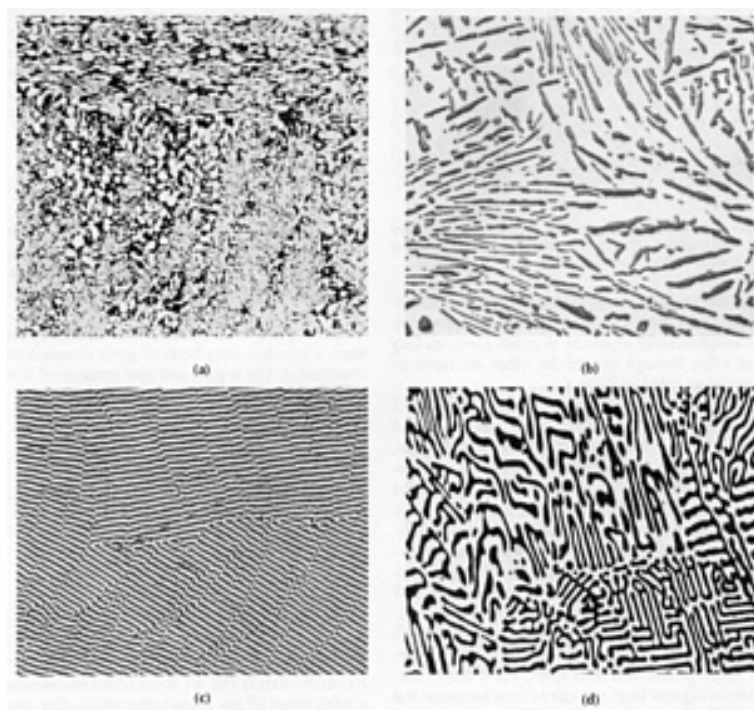


Fig. 32 Examples of characteristic eutectic microstructures in slowly cooled alloys. (a) 50Sn-50In alloy showing globules of tin-rich intermetallic phase (light) in a matrix of dark indium-rich intermetallic phase. 150 $\times$. (b) Al-13Si alloy showing an acicular structure consisting of short, angular particles of silicon (dark) in a matrix of aluminum. 200 $\times$. (c) Al-33Cu alloy showing a lamellar structure consisting of dark platelets of CuAl_2 and light platelets of aluminum solid solution. 180 $\times$. (d) Mg-37Sn alloy showing a lamellar structure consisting of Mg_2Sn "Chinese script" (dark) in a matrix of magnesium solid solution. 250 $\times$. Source: 85ASM 13

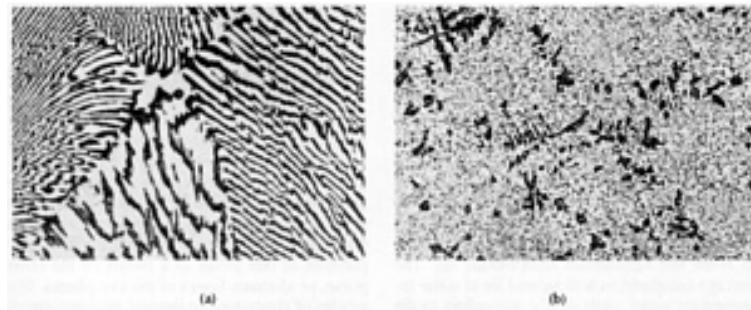


Fig. 33 Effect of cooling rate on the microstructure of Sn-37Pb alloy (eutectic soft solder). (a) Slowly cooled sample shows a lamellar structure consisting of dark platelets of lead-rich solid solution and light platelets of tin. 375 $\times$. (b) More rapidly cooled sample shows globules of lead-rich solid solution, some of which exhibit a slightly dendritic structure, in a matrix of tin. 375 $\times$. Source: 85ASM 13

If the alloy has a composition different from the eutectic composition (such as alloy 1 or 3 in Fig. 28), the alloy will begin to solidify before the eutectic temperature is reached. If the alloy is hypoeutectic (such as alloy 1), some dendrites of α will form in the liquid before the remaining liquid solidifies at the eutectic temperature. If the alloy is hypereutectic (such as alloy 3), 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. 34a). 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. 34b).

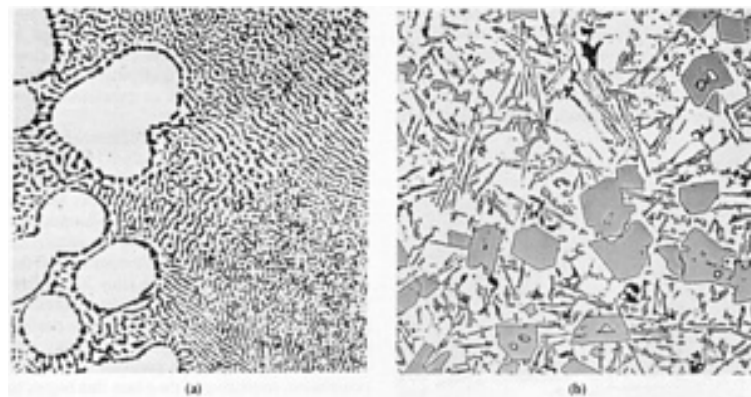


Fig. 34 Examples of primary particle shape. (a) Sn-30Pb hypoeutectic alloy showing dendritic particles of tin-rich solid solution in a matrix of tin-lead eutectic. 500 $\times$. (b) Al-19Si hypereutectic alloy, phosphorus-modified, showing idiomorphic particles of silicon in a matrix of aluminum-silicon eutectic. 100 $\times$. Source: 85ASM 13

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. 35. With relatively rapid cooling of alloy X, the composition of the solid material that forms will follow line α_1 - α'_4 rather than the 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.

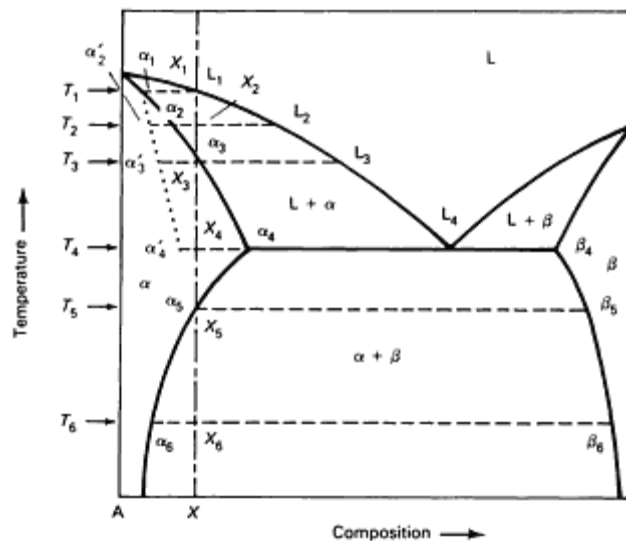


Fig. 35 Schematic binary phase diagram, illustrating the effect of cooling rate on an alloy lying outside the equilibrium eutectic transformation line. Rapid solidification into a terminal phase field can result in some eutectic structure being formed; homogenization at temperatures in the single-phase field will eliminate the eutectic structure; β phase will precipitate out of solution upon slow cooling into the α -plus- β field. Source: Adapted from 56Rhi 3

Eutectoid Microstructures. Because the diffusion rates of atoms are so much lower in solids than in 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. 36, 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. 37). When found in cast irons and steels, this structure is called "pearlite" because of its shiny mother-of-pearl 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."

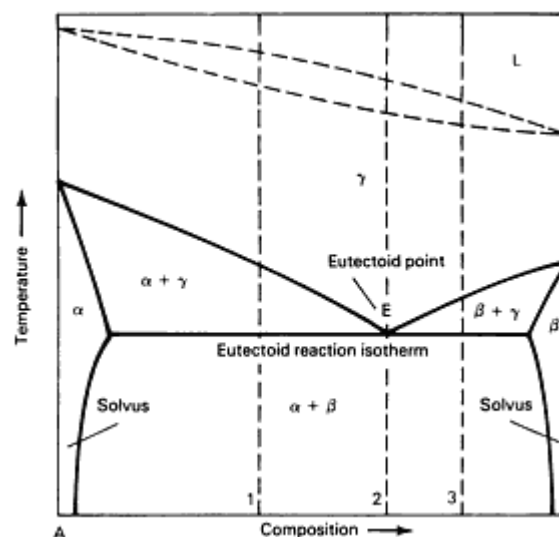


Fig. 36 Schematic binary phase diagram of a eutectoid system. Source: Adapted from 56Rhi 3

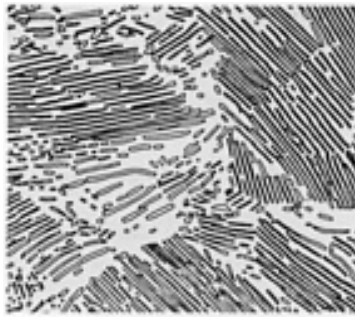


Fig. 37 Fe-0.8C alloy showing a typical pearlite eutectoid structure of alternate layers of light ferrite and dark cementite. 500 $\times$. Source: 85ASM 13

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. 36 is a hypoeutectoid alloy, whereas alloy 3 is hypereutectoid. The solid-state transformation of such alloys takes place in two steps, much like the 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 described 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 1.

Solid-State Precipitation. If alloy X in Fig. 35 is homogenized at a temperature between T_3 and T_5 , it will reach an 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. This process is illustrated for a simple eutectic system, but 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. 38.

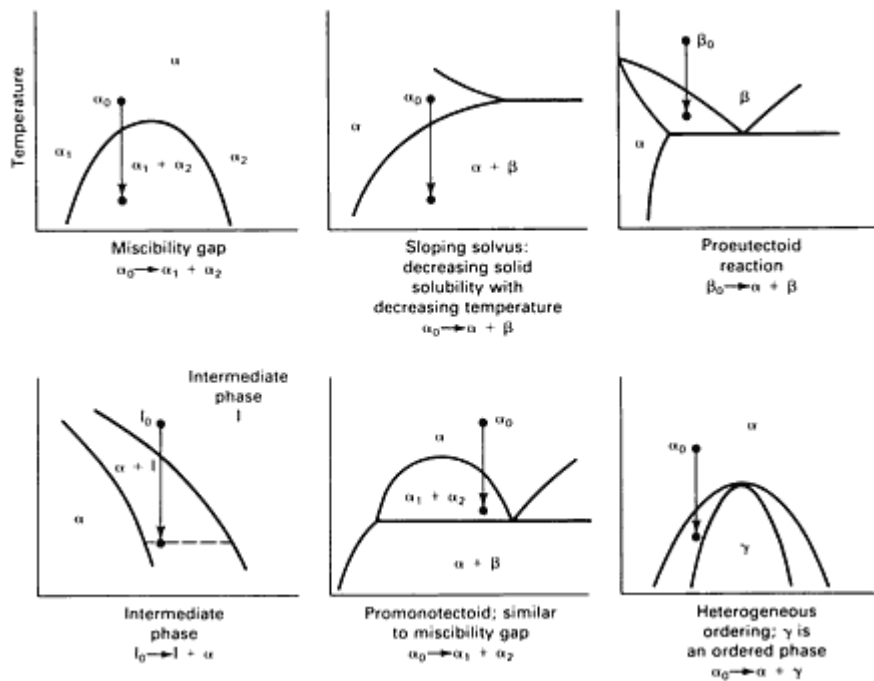


Fig. 38 Examples of binary phase diagrams that give rise to precipitation reactions. Source: 85ASM 13

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 some time, 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. Examples of precipitation microstructures are shown in Fig. 39.

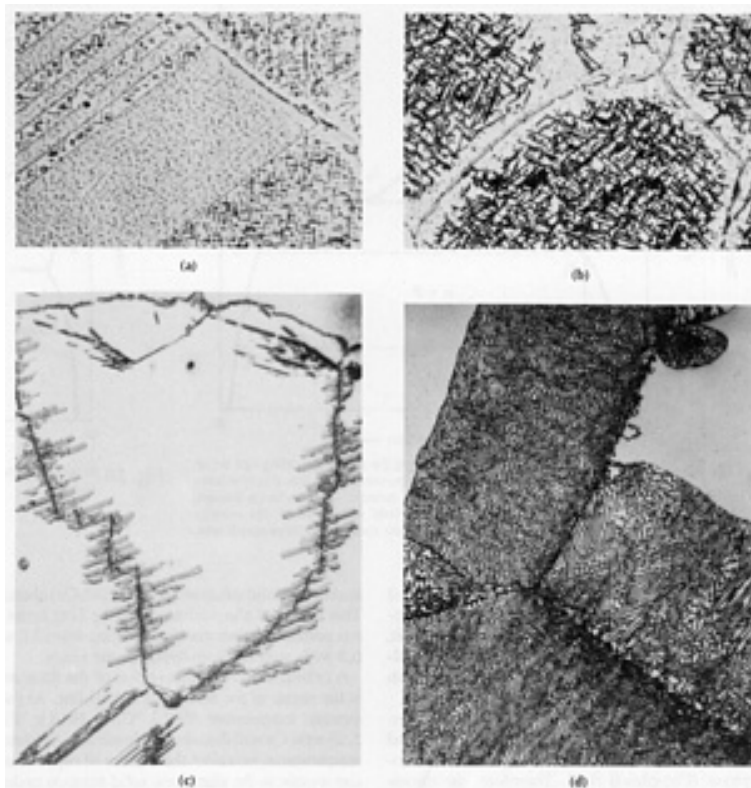


Fig. 39 Examples of characteristic precipitation microstructures. (a) General and grain-boundary precipitation of Co_3Ti (γ' phase) in a Co-12Fe-6Ti alloy aged 3×10^3 min at 800°C (1470°F). $1260\times$. (b) General precipitation (intragranular Widmanstätten) and localized grain-boundary precipitation in an Al-18Ag alloy aged 90 h at 375°C (710°F), with a distinct precipitation-free zone near the grain boundaries. $500\times$. (c) Preferential, or localized, precipitation along grain boundaries in a Ni-20Cr-1Al alloy. $500\times$. (d) Cellular, or discontinuous, precipitation growing out uniformly from the grain boundaries in an Fe-24.8Zn alloy aged 6 min at 600°C (1110°F). $1000\times$. Source: 85ASM 13

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Examples of Phase Diagrams

The general principles of reading alloy phase diagrams are discussed in the preceding section. The application of these principles to actual diagrams for typical alloy systems is illustrated below.

The Copper-Zinc System. The metallurgy of brass alloys has long been of great commercial importance. The copper and zinc contents of five of the most common wrought brasses are:

UNS No.	Common name	Zinc content, wt%	
		Nominal	Range
C23000	Red brass, 85%	15	14.0-16.0
C24000	Low brass, 80%	20	18.5-21.5
C26000	Cartridge brass, 70%	30	28.5-31.5
C27000	Yellow brass, 65%	35	32.5-37.0

As can be seen in Fig. 40, these alloys encompass a wide range of the copper-zinc phase diagram. The alloys on the high-copper end (red brass, low brass, and cartridge brass) lie within the copper solid-solution phase field and are called alpha brasses after the old designation for this field. As expected, the microstructure of these brasses consists solely of grains of copper solid solution (see Fig. 41 a). The strain on the copper crystals caused by the presence of the zinc atoms, however, produces solution hardening in the alloys. As a result, the strength of the brasses, in both the work-hardened and the annealed conditions, increases with increasing zinc content.

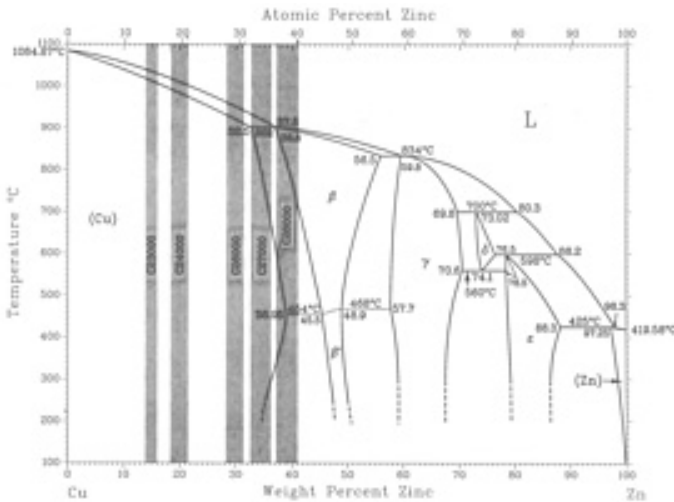


Fig. 40 The copper-zinc phase diagram, showing the composition range for five common brasses. Source: Adapted from 90Mas 15.



Fig. 41 The microstructures of two common brasses. (a) C26000 (cartridge brass, 70%), hot rolled, annealed, cold rolled 70%, and annealed at 638 °C (1180 °F), showing equiaxed grains of copper solid solution. Some grains are twinned. 75×. (b) C28000 (Muntz metal, 60%) ingot, showing dendrites of copper solid solution in a matrix of β . 200×. (c) C28000 (Muntz metal, 60%), showing feathery of copper solid solution that formed at β grain boundaries during quenching of the all- β structure. 100×. Source: 85ASM 13

The composition range for those brasses containing higher amounts of zinc (yellow brass and Muntz metal), however, overlaps into the two-phase (Cu)-plus- β field. Therefore, the microstructure of these so-called alpha-beta alloys shows various amounts of β phase (see. Fig. 41b and c), and their strengths are further increased over those of the alpha brasses.

The Aluminum-Copper System. Another alloy system of great commercial importance is aluminum-copper. Although the phase diagram of this system is fairly complicated (see Fig. 42), the alloys of concern in this discussion are limited to the region at the aluminum side of the diagram where a simple eutectic is formed between the aluminum solid solution and the θ (Al_2Cu) phase. This family of alloys (designated the 2xxx series) has nominal copper contents ranging from 2.3 to 6.3 wt%, making them hypoeutectic alloys.

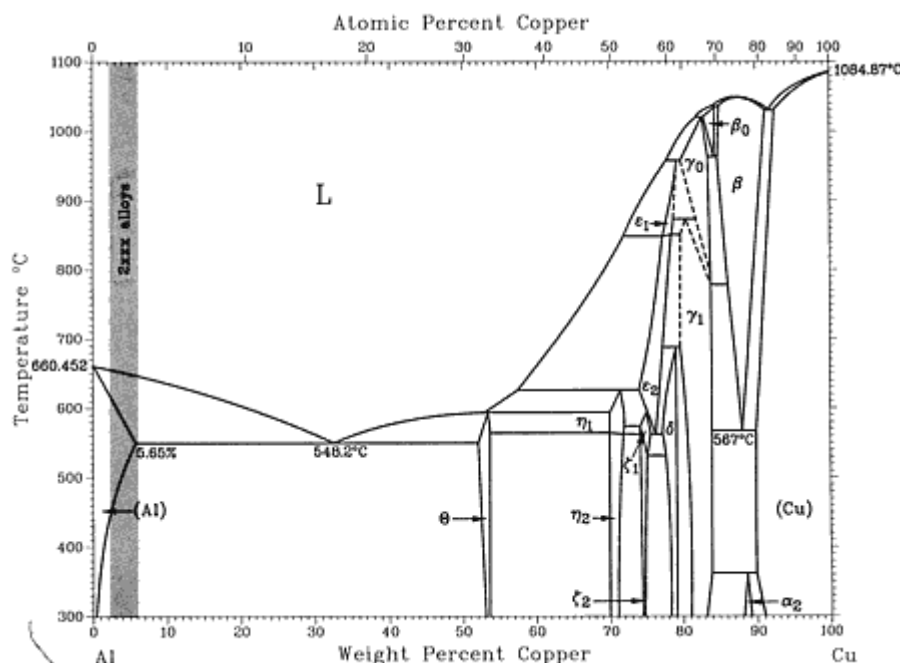


Fig. 42 The aluminum-copper phase diagram, showing the composition range for the 2xxx series of precipitation-hardenable aluminum alloys. Source: 90Mas 15

A critical feature of this region of the diagram is the shape of the aluminum solvus line. At the eutectic temperature (548.2 °C, or 1018.8 °F), 5.65 wt% Cu will dissolve in aluminum. At lower temperatures, however, the amount of copper that can remain in the aluminum solid solution under equilibrium conditions drastically decreases, reaching less than 1% at room temperature. This is the typical shape of the solvus line for precipitation hardening; if any of these alloys are homogenized at temperatures in or near the solid-solution phase field, they can be strengthened by aging at a substantially lower temperature.

The Titanium-Aluminum, Titanium-Chromium, and Titanium-Vanadium Systems. The phase diagrams of titanium systems are dominated by the fact that there are two allotropic forms of solid titanium: cph α Ti is stable at room temperature and up to 882 °C (1620 °F); bcc β Ti is stable from 882 °C (1620 °F) to the melting temperature. Most alloying elements used in commercial titanium alloys can be classified as alpha stabilizers (such as aluminum) or beta stabilizers (such as vanadium and chromium), depending on whether the allotropic transformation temperature is raised or lowered by the alloying addition (see Fig. 43). Beta stabilizers are further classified as those that are completely miscible with β Ti (such as vanadium, molybdenum, tantalum, and niobium) and those that form eutectoid systems with titanium (such as chromium and iron). Tin and zirconium also are often alloyed in titanium, but instead of stabilizing either phase, they have extensive solubilities in both α Ti and β Ti. The microstructures of commercial titanium alloys are complicated, because most contain more than one of these four types of alloying elements.

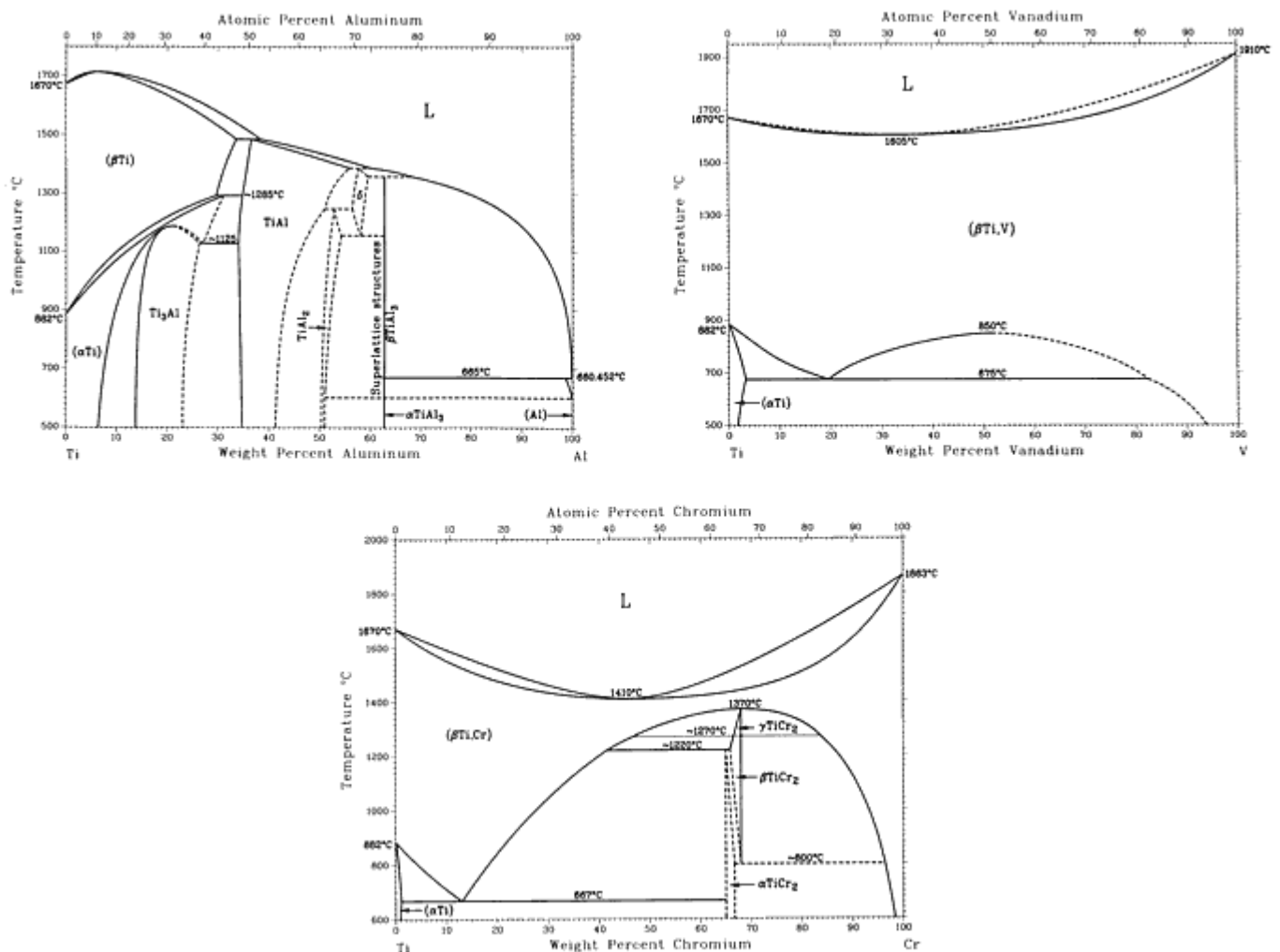


Fig. 43 Three representative binary titanium phase diagrams, showing alpha stabilization (Ti-Al), beta stabilization with complete miscibility (Ti-V), and beta stabilization with a eutectoid reaction (Ti-Cr). Source: 90Mas 15

The Iron-Carbon System. The iron-carbon diagram maps out the stable equilibrium conditions between iron and the graphitic form of carbon (see Fig. 44). Note that there are three allotropic forms of solid iron: the low temperature phase,