

Chapter 4

Phase Equilibria

Ceramic materials are inorganic compounds containing at least two, and often many more, elemental constituents. In technological applications they are used in a variety of morphologies including monoliths, fine powders, thin and thick films, and long or short fibers. Each of these may be single crystalline or polycrystalline in nature; they may include one or many phases. Due to the larger number of components, the number of phases which may exist is generally larger than in metal and semiconductor systems. Ceramics are typically heated to high temperatures during processing in order to speed up chemical reactions and to develop desired microstructures. The number, type, and physical distribution of phases are therefore determined by the phase equilibria and the *thermal history* of the material. In this chapter, we develop a primarily graphical description of the high-temperature behavior of multicomponent systems, emphasizing three-component systems. While it is assumed that the reader is somewhat familiar with one- and two-component phase diagrams, we discuss these first in order to ease the transition into multicomponent systems.

4.1 THERMODYNAMIC EQUILIBRIUM

Phase diagrams are most often intended to describe the condition of *equilibrium*. (In some applications "stability diagrams" are used to show the phases that tend to appear, but may not be at equilibrium.) Equilibrium is the state where all chemical

reactions have proceeded to the point where the chemical potential (or *partial molar free energy*) of all components², as well as temperature and pressure, are equal throughout the system. In the terminology of reaction rate theory, the rates of all forward chemical reactions are exactly equal to the rates of all reverse reactions, and this balance is maintained for all time, not being "kinetically limited" by the rate of any process.

In the state of equilibrium, there can exist a number of identifiable *phases* or states of matter. A phase is defined as a physically separable and chemically homogeneous arrangement of atoms, distinguishable from all others which may exist for the composition, temperature, and pressure of the system. The different states of matter—vapors, liquids, glasses, and crystals—are all familiar phases. Crystals that differ in both composition and structure are always distinguishable phases (e.g., MgO and Al₂O₃). Different structural forms of a single composition, such as the liquid and vapor states of water, or the monoclinic, tetragonal, and cubic polymorphs of pure zirconia (see p. 29 in Chapter 1), are also considered distinct phases. A particular structure may also exist over a range of compositions. The different compositions may form separate phases that are *immiscible*; examples include two immiscible liquids (oil and water) or two immiscible solids of the same crystal structure (e.g., MgO and CaO), in which case they are separate phases despite being of like structures.

A phase or assemblage of phases need not represent the most thermodynamically stable condition of the system; if so, however, they are considered equilibrium phases. One frequently encounters *metastable* phases which are not the most stable configuration, but cannot transform into the equilibrium phase due to slow atom transport. A glass is one example of a metastable phase, the equilibrium phase for which is the crystal. Water that is cooled in quiescent conditions in a smooth-walled container to a temperature a few degrees below its freezing point can be easily retained as the metastable liquid phase without having the equilibrium phase, ice, crystallize. Another example of a metastable phase is diamond, which is the equilibrium form of carbon only at high temperatures and pressures (see Special Topic 4.1).

The equilibrium state for a composition of matter at any given temperature and pressure may consist of one or more phases. A principal application of the *phase diagram* is to tell us how many phases, and of what specific compositions, co-exist for a given overall composition, temperature, and pressure. Oil

and water represent two co-existing liquid phases of very different composition, each of which has dissolved in it, at equilibrium, a small amount of the other. An example of multiple solid phases at equilibrium is a geological (rock) formation, in which there are typically several distinguishable crystalline compounds, each of a different composition and crystal structure, co-existing in equilibrium with one another (although arguably they may not be in equilibrium at room temperature, but only at a higher temperature and pressure at which they were formed).

SPECIAL TOPIC 4.1

METASTABILITY IN CARBON: DIAMOND AND DIAMOND-LIKE MATERIALS

The high refractive index of diamond combined with a high dispersion (the variation in refractive index with wavelength, which causes color separation in refracted light) gives this material an extraordinary brilliance and fire, which have made diamonds a popular and valuable gemstone. Because of its extreme hardness, diamond has many important industrial uses as abrasives and cutting tools having a world market of more than a billion dollars. Diamond is not only the hardest material known, but has the highest thermal conductivity at room temperature, is an excellent electrical insulator, is transparent to ultraviolet, infrared, and x-rays as well as visible light. Diamond has the highest elastic modulus of any known material, it is the most incompressible substance known, and has a relatively low thermal expansion coefficient. As a doped semiconductor material, it may have advantages for high temperature electronic applications. With respect to many properties, diamond is superior to all other materials.

There have been efforts to produce synthetic diamonds for more than a century. A Scottish chemist, James Ballantyne Hannay, reported diamond synthesis in 1880 by heating paraffin, bone oil, and lithium in sealed iron tubes. In 1893 the French chemist, Henri Moissan, claimed that he made diamonds from a mixture of carbon and iron heated to a high temperature and then quenched into a water bath. In 1955 F. P. Bundy, H. T. Hall, H. M. Strong and R. H. Wentorf, Jr., announced successful growth of diamonds at high pressure and high temperature at the General Electric Company. The phase equilibrium relationships between diamond and graphite are shown in Fig. ST39. Graphite is the thermodynamic stable form over a wide range of temperature and pressures. Only at high pressures and high temperatures does diamond become the preferred form. The key factor in developing successful diamond synthesis was designing and building high-temperature, high-pressure presses. Graphite in the presence of a liquid metal solvent, such as iron or nickel, is brought to a temperature and pressure range where diamond is the thermodynamic stable phase and at which diamond crystals nucleate and grow. Diamonds are usually formed at pressures of 50–65 kb

²Components are chemical entities. While an elemental constituent can always be regarded as a component, the number of components necessary to describe a system can be less than the total number of elements if there are constraints which prevent all elemental concentrations from being independently varied. For instance, in ionic compounds the valences of all elements are frequently fixed under the range of temperature and atmosphere of interest. Charge neutrality then dictates the relative concentrations of the anions and cations, and a degree of freedom is lost. For example a three element system can be represented as a binary system between two compounds. See also the later discussions of Variable Valence Systems and Reciprocal Salt Diagrams.

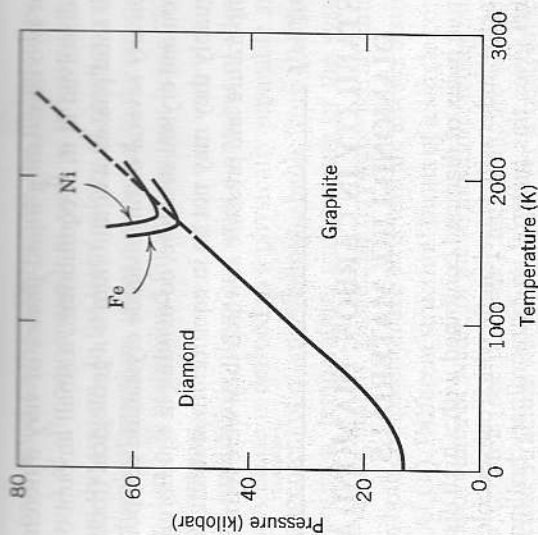


Fig. ST39 Equilibrium phase diagram for the carbon system. The P-T curves for the diamond-iron and diamond-nickel eutectics growth at which a liquid can be produced are also shown.

and at a temperature of about 1800K. More recently, high-temperature, high-pressure cells have been designed with a thermal gradient making it possible for small crystals to dissolve at a higher temperature, diffuse through the liquid, and contribute to the growth of diamond crystals in the lower-temperature part of the reaction cell. Crystals up to 7 mm in diameter are commercially available, and there are reports that crystals as large as 17 mm in diameter and weighing as much as 11 carats have been produced.

The very success of using equilibrium conditions to nucleate and form diamonds turned investigators away from an alternate possibility, metastable diamond synthesis. The likelihood of diamond synthesis in the graphite stable region is suggested by the small free energy difference (500 kcal/mole) between diamond and graphite under ambient conditions. In the late 1950s W. G. Eversole in the United States and B. V. Derjaguin and B. V. Spitsyn in Russia produced metastable diamond growth from a vapor reaction decomposing hydrocarbons. Later, John C. Angus took up the Eversole work and improved the process by using atomic hydrogen to remove graphite that precipitated alongside the new diamond formation; this prepared a graphite-free surface for subsequent diamond growth. The great achievement of the Soviet group looks modest in retrospect. Angus used atomic hydrogen *during* the growth process, which permitted higher growth rates and also the nucleation of new diamond crystallites on non-diamond substrates. Production of atomic hydrogen by the use of hot wire, RF microwave, DC plasma, or thermal plasma generation has been the key to successful diamond growth.

Initial experimental growth rates were very low, but once the barrier to metastable diamond growth was appreciated, modifications of the technique led to spectacular gains. By use of radio frequency induction heating to produce a thermal plasma, growth rates increased from 1 micrometer per hour to more than 1 micrometer per minute. Diamond synthesis at a high rate has also been found to occur in an oxyacetylene combustion torch when the reducing portion of the flame is targeted on a low-temperature substrate.

4.2 THE GIBBS PHASE RULE

The number of phases that can co-exist in equilibrium is concisely described by the *Gibbs phase rule* (sometimes simply referred to as the phase rule). The phase rule relates the number of equilibrium phases (P) and the number of chemical entities in the system (or *components*, C). The number of phases and number of components together define the total degrees of freedom available to the system (F):

$$F = C - P + 2 \quad (4.1)$$

The degrees of freedom is the number of intensive thermodynamic variables (i.e., those not dependent on the mass of the system) that may be changed without changing the number of phases present in equilibrium. Most often we deal with systems of a known number of components C , whereupon the number of phases P becomes constrained by the intensive variables of temperature, pressure, and overall composition. The form of the Gibbs phase rule in Eq. 4.1 assumes that both temperature and pressure are independently variable. However, in much of materials processing, pressure is kept constant at the ambient value, typically near one atmosphere. Under constant pressure conditions the Gibbs phase rule becomes

$$F = C - P + 1 \quad (4.2)$$

This is sometimes referred to as the phase rule for condensed phases. Even under non-isobaric conditions the assumption of constant pressure is sometimes neglected, but results in little error since small changes in total pressure have only a minor effect on condensed phase equilibria.

Before proceeding to illustrate its utility, we present a simple derivation of the Gibbs phase rule. Each phase contains (to some degree, however dilute) a certain concentration X_i of all of the components; the sum of these concentrations in a given phase equals unity:

$$X_1 + X_2 + X_3 + \dots + X_i = 1$$

The chemical potential of each component i , is a function of the concentration X_i according to:

$$\mu_i = \mu_i^0 + RT \ln \gamma_i X_i$$

where μ_i^0 is the chemical potential of the standard state of component i and γ_i is the activity coefficient. There are thus C chemical potentials to be defined for any phase. However, a constraint is presented by the fact that the sum of all concentrations must be unity, which means that we can only independently vary $C-1$ chemical potentials. Counting all P phases present in the system, there are $P(C-1)$ chemical potentials in the system that may be independently varied. Including the intensive additional variables of temperature and pressure, we have:

$$\text{Total variables} = P(C-1) + 2$$

Consider next that equilibrium is defined as the state where the chemical potential of each component, μ_i , is the same in all phases that are present. For example, in a three-phase system the chemical potential of component 1 is the same in phase 1 as in phase 2 as in phase 3: $\mu_1^1 = \mu_1^2$ and $\mu_1^2 = \mu_1^3$. For a system of P phases, this results in $(P-1)$ independent equalities for the chemical potential of component 1. Applying this to all C components, the total number of equations defining the condition of equilibrium is

$$\text{Total equations} = C(P-1)$$

As there are fewer equations than the number of variables, some number of variables need to be independently defined in order to solve the system of equations. These are the degrees of freedom, or number of free variables, defined by the Gibbs phase rule:

$$\text{Degrees of Freedom} = \text{Total variables} - \text{Total equations}$$

$$F = P(C-1) + 2 - C(P-1)$$

$$F = C - P + 2$$

Notice that as one adds more components to a system there is greater chemical freedom, and F increases. On the other hand, as more phases are introduced into a system with a fixed number of components, the state of equilibrium becomes increasingly constrained by the need for equality in chemical potential between all phases, and F decreases.

The utility of the Gibbs phase rule can be illustrated using the pressure-temperature phase diagram for the single-component system H_2O in Fig. 4.1. This phase diagram shows the phases present at equilibrium for a broad range of temperature and pressure. At 1 atmosphere pressure, shown by the horizontal dotted line, the familiar phases are ice, water, and steam, encountered in sequence upon increasing the temperature. Let's apply the Gibbs phase rule for liquid water at

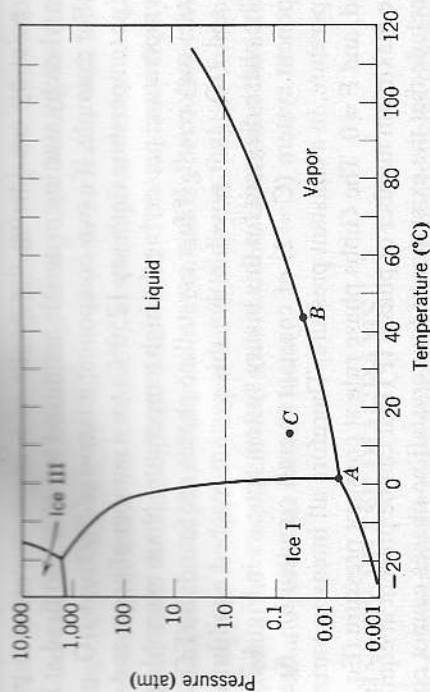


Fig. 4.1 Pressure-temperature phase diagram for water. Behavior at 1 atm pressure is indicated by the horizontal dashed line. The invariant point at which three phases are in equilibrium is labeled "A."

25°C and 1 atmosphere pressure. Since there is one component ($C = 1$) and one phase ($P = 1$), the degrees of freedom F is 2. This means that within the bounds of the phase field for liquid water, we can freely vary both the temperature and pressure and retain liquid as the equilibrium phase.

If we now consider water at 0°C and 1 atmosphere pressure, this point falls directly on the boundary between liquid water and ice. This is the freezing point of water, at which there are two phases in equilibrium for one component. The Gibbs phase rule (Eq. 4.1) states that there is one degree of freedom. This means that we can preserve the two-phase equilibrium between water and ice by varying either temperature or pressure independently, but not both. If we choose to vary one of the variables at will, a two-phase equilibrium can only be maintained if the value of the other is defined by the boundary between the liquid water and ice phase fields in Fig. 4.1. For example, while at 0°C a two-phase equilibrium only exists at a pressure of 1 atmosphere, at -5°C, the ice-water equilibrium exists only at 100 atmospheres. There exists only one combination of temperature and pressure at which all three phases (ice, water, steam) can be in equilibrium, labeled "A". For a one-component system with three phases, according to the Gibbs phase rule there must be zero degrees of freedom. In any phase diagram, a combination of variables at which there are zero degrees of freedom is termed an *invariant point*; for a single-component system such as water this is often referred to as the *triple point* since there are three phases present.

A phase diagram thus provides a graphical depiction of the conditions under which certain phases appear at equilibrium. The determination of a complete phase diagram is, generally speaking, a lot of work. Even in the absence of a detailed phase diagram, however, the Gibbs phase rule is useful for determining the possibility and likelihood that a system of phases is at equilibrium. We illus-

trate this point by considering the results of a common ceramics processing procedure whereby starting materials are mixed together and fired at high temperature. For example, if a two-component mixture of BaO and TiO₂ powders is fired to high temperature (let's say 1250°C) for a number of hours and quenched to room temperature, preserving the high temperature phase assemblage, a number of phases may result. If four crystalline phases are found: BaTiO₃, BaTi₂O₅, BaTi₃O₇, and TiO₂, is it possible that this system reached equilibrium during firing? (The phase diagram for this binary system appears in Fig. 4.7.) This is a two-component system ($C = 2$) of constant overall composition, fired at constant temperature, in a constant pressure. Therefore all intensive variables have been fixed, and $F = 0$. The Gibbs phase rule at constant pressure (Eq. 4.2) tells us that the maximum number of phases (P) that can be present at equilibrium is 3. We conclude that the existence of four crystalline phases cannot constitute a system at equilibrium; most likely the reaction between the starting oxides has not progressed to completion. What if only three of the four crystalline phases (BaTiO₃, BaTi₂O₅, and BaTi₃O₇) are present? Then according to the Gibbs phase rule at constant pressure (Eq. 4.2) this system could, strictly speaking, have been at equilibrium—at an invariant point. However, common sense tells us that the probability that our arbitrarily chosen temperature of 1250°C happened to fall on an invariant point of this system is very low. Thus, while it is thermodynamically *possible* that we reached equilibrium during firing, it is highly unlikely. However, if after quenching we see either two phases or one, according to the phase rule it is certainly possible, and even likely, that the system was at equilibrium.

Let's consider a slightly different experiment where we have fired the sample as before, but then slowly cooled the sample to room temperature. In this instance the overall composition and pressure have both remained constant, but we have independently varied one variable (temperature); hence $F = 1$. How many phases can be present throughout the cooling process if equilibrium is maintained? The Gibbs phase rule for constant pressure (Eq. 4.2) tells us that at most we can have two phases ($P = 2$) present in equilibrium. Thus, if either three or four phases are present in the end product, it is clear that equilibrium during firing was not preserved. If only one or two phases are found after cooling, it is then possible (but not proven) that equilibrium was preserved.

Note that the Gibbs phase rule does not tell us the amount of any phase, or the specific phases that will exist; it only tells us the *number* of phases that can coexist at equilibrium. That is, at 0°C and 1 atmosphere pressure, a minute amount of ice floating in water, and a film of water on ice, are both equally in equilibrium. Heating or cooling processes tend to be arrested in temperature at the boundaries between phase fields while the amounts of the respective phases change. Starting with a small amount of ice in water, if we slowly remove heat from the system additional ice will be formed, but the temperature will remain constant at 0°C until all of the water has solidified to ice. The system can then leave the two-phase

boundary and enter the single phase ice field, allowing the temperature of the system to decrease (cf. Fig. 4.1). Similarly, during slow heating the temperature remains constant at 0°C while the amount of water increases until all the ice is melted (absorbing the latent heat of fusion), at which point we can leave the phase boundary and enter the single-phase water field. This tendency for systems to hesitate in temperature at phase boundaries upon heating or cooling while phases appear or disappear is especially important in binary and higher-component systems. Frequently, the completeness of such reactions determines the actual phases remaining after a particular thermal history.

4.3 BINARY PHASE DIAGRAMS

Binary phase diagrams are representations of the phase fields present in equilibrium mixtures of two components. For the single-component system in Fig. 4.1, we used temperature and pressure as the coordinates. In a two-component system we have an additional variable, which is the overall composition. (In some cases one plots the activity of one component as the chemical variable, but in the majority of phase diagrams composition is used since it is an easily measured experimental variable.) With these three intensive variables (T , P , and composition) being necessary to define the system completely, a complete binary diagram would be a three-dimensional representation of the phases present for every combination of these variables. For simplicity, and because most studies are concerned with phase equilibria at a constant ambient pressure, binary diagrams most often show a constant pressure slice of the three-dimensional diagram, with temperature and composition as the axes. The implicit assumption of a constant pressure is frequently not mentioned, but should be remembered.

Complete Solid Solution

The complexity of binary phase diagrams for solids depends in large part on the similarity of the endmember components. The simplest case is when the two components have the same crystal structure and the constituent atoms or ions are similar in size and chemical properties. An example is MgO-NiO, shown in Fig. 4.2, in which both components crystallize in the rocksalt structure type, share a common ion (oxygen), and have chemically similar cations. The lattice parameters only differ by ~1% (0.4213 nm for MgO, 0.4177 nm for NiO). Complete solid solution of MgO in NiO and vice versa is possible, as indicated by the (Ni,Mg)O solid solution (ss) field. At high temperatures above the melting point of either compound, a single phase liquid solution of MgO and NiO corresponding to the overall composition is found. The lens-shaped region separating the single-liquid phase and single-solid-phase fields is a two-phase field, in which a liquid solution enriched in the lower melting component (NiO) is found in equilibrium with a

solid solution enriched in the higher melting component (MgO). At any temperature and composition within this two-phase field, the compositions of the liquid and solid are given by the endpoints of a horizontal line, known as the *tie line*, which terminates on the boundaries separating the single-phase and two-phase fields. The boundary curve between the single-phase liquid and two-phase field is the *liquidus*; this defines where a given composition becomes completely liquid (i.e., exits the two-phase field) upon heating. The boundary curve between the single-phase solid solution and the two-phase field is termed the *solidus*; upon cooling this is the temperature at which a given composition completely solidifies.

Limited Solid Solubility

Binary Eutectic System Binary systems with complete solid solutions as in Fig. 4.2 are relatively uncommon in ceramics. Figure 4.3 shows a schematic and an actual example of a slightly more complex binary phase diagram, a binary *eutectic*, that frequently results when the two components are less similar. In this example each solid endmember phase dissolves a limited amount of the other component: The single-phase fields are shown shaded, while the two-phase fields are unshaded. In CaO-MgO the endmembers are of the same structure type (rocksalt), but since Ca^{2+} and Mg^{2+} differ substantially in size they do not form a complete solid solution. (CaO has a lattice parameter, 0.4811 nm, which is 14% larger than that of MgO.) The extent of solid solution varies with temperature, with the maximum solid solubility or *solid solution limit* being given by the boundaries of the single phase fields labeled “MgO ss” and “CaO ss” in Fig. 4.3 b. The maximum solubility of CaO in MgO is about 8%, while the maximum solubility of MgO in CaO is about 17%, both occurring at 2370°C. Between these two single-phase solid solution fields lies a field containing two solid phases at temperatures below 2370°C, labeled “MgO ss + CaO ss”. In this field the solid solution limits of both endmember phases have been exceeded, and the compositions of the two solid phases in equilibrium are given by the endpoints of the tie line shown terminating on the solid solution boundary curves.

Let's apply the condensed phase rule ($F = C - P + 1$) to the various fields of this binary phase diagram. For a single phase field in a binary system, $F = 2$, indicating that it is possible to vary both temperature and composition independently without changing the number of phases. In a two-phase field, the phase rule allows only one degree of freedom; this means that if temperature is varied, so must composition if the same two phases are to be maintained. However, an important point is that it is the *phase composition* that must be varied, not the *average composition*. (In a single-phase field, they are one and the same.) Consider the point A in Fig. 4.3 with an average composition of 40% CaO, at 2100°C. This point is in a two-phase field, where the compositions of the two phases in equilibrium are given by the boundary curves between the one- and two-phase fields. The horizontal tie-line at 2100°C joins these compositions, which are at 5% and 90%

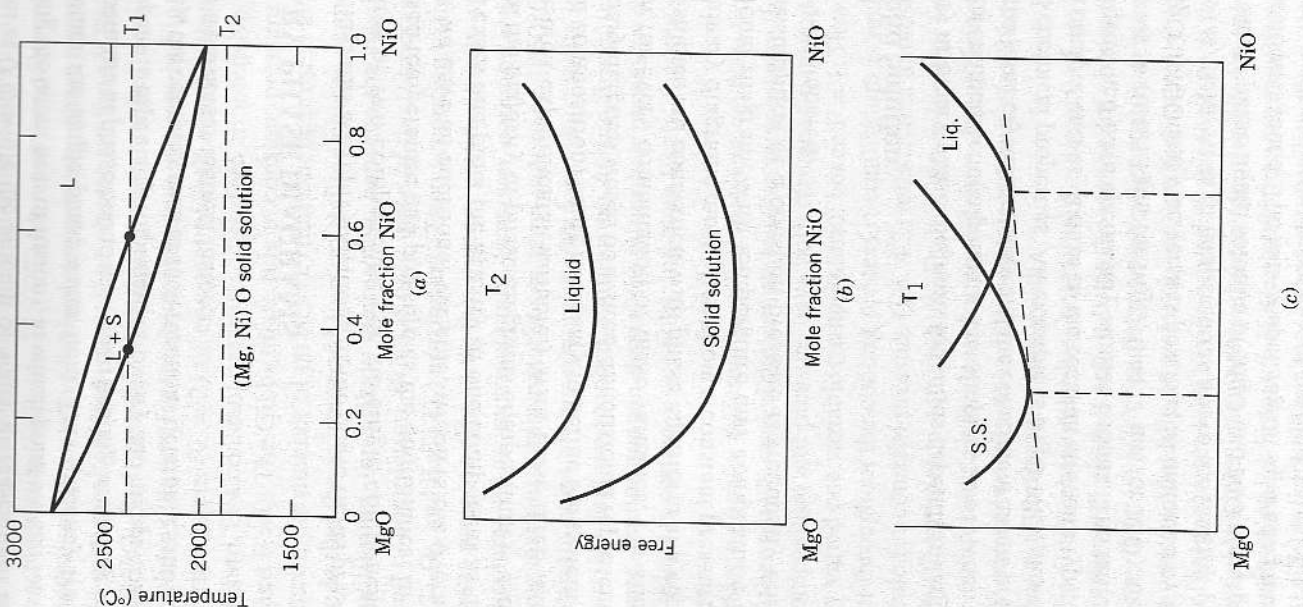


Fig. 4.2 (a) Phase diagram of MgO-NiO. Schematic representation of free energy-composition diagram for (b) $T < 2000^\circ\text{C}$; and (c) $T = 2400^\circ\text{C}$.

CaO, respectively. If temperature is varied up or down the endpoints of the tie-line change accordingly, following the phase boundaries. A change in temperature necessitates a change in the compositions of the individual phases, and therefore the chemical potentials of the constituents, if the two-phase equilibrium is to be maintained. Likewise, an independent variation in the composition of either one of the phases requires a change in temperature if we are to remain on the boundary curves. This demonstrates the one degree of freedom for the two phases in equilibrium. If we instead vary the average composition along the tie-line away from point A, we change the relative amounts of the two phases in equilibrium (according to the binary lever rule discussed later), but not their compositions; those remain at the terminations of the tie-line. Recalling that the Gibbs phase rule does not dictate the relative amounts of phases but only their coexistence, it follows that a change in average composition within the two-phase field does not result in a change in phase equilibrium.

The melting and solidification behavior of a binary eutectic system differs significantly from that in Fig. 4.2. We see that the liquidus curves slope downward toward the center of the diagram, indicating that addition of CaO lowers the melting point of MgO, and vice versa. The two liquidus curves meet at a critical point termed the *eutectic*, labeled E. A liquid of this composition would, upon cooling through the eutectic temperature, solidify directly to two solid phases. At the temperature and composition of the eutectic E, we have three phases of fixed composition co-existing in equilibrium: a liquid of the eutectic composition and the two solid solutions (MgO ss and CaO ss) of compositions corresponding to the solid solution limits at the eutectic temperature (2370°C). For three phases coexisting in equilibrium the Gibbs phase rule yields $F = 0$; hence, the eutectic temperature and composition represent an invariant point where neither temperature nor composition of any of the phases can be varied without causing the disappearance of a phase. In a two-component system, it is not possible to have more than three phases in equilibrium at constant pressure.

Intermediate Compounds

In Fig. 4.3 the endmembers MgO and CaO are of the same structure type, yet are sufficiently mismatched that there is limited solid solution of each in the other. For increasingly dissimilar components, intermediate compounds are often found. Figure 4.4a shows in schematic form a binary system in which the intermediate compound AB forms. The three solid phases: α , β , and ab , have each been drawn as vertical lines to indicate that these are *line compounds* with no visible solid solution range. This diagram has two eutectic points, one between L, A and AB and one between L, AB and B. Typically these will occur at different temperatures. ab is a *congruently melting* compound, which means that it melts to form a liquid of the same composition. For example, the Czochralski technique, widely used in the growth of silicon crystals for semiconductor devices, can only be used for congruently melting compounds. As discussed later, whether or not a com-

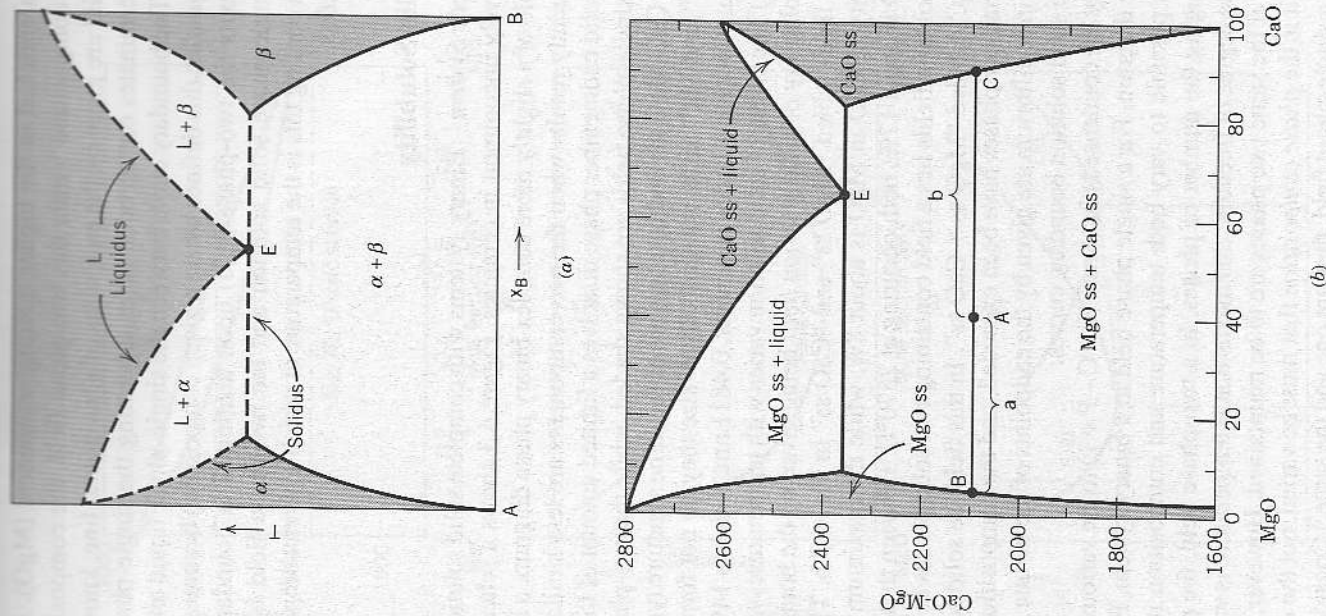


Fig. 4.3 (a) Schematic binary eutectic diagram; (b) CaO-MgO system showing some solid solution of each component in the other endmember phase. Eutectic point is at E. Application of binary lever rule to overall composition A is discussed in text. [adapted from R.C. Doman, J.B. Barr, R.N. McNally, and A.M. Alper, *J. Am. Ceram. Soc.*, **46**(7) 314 (1963).]

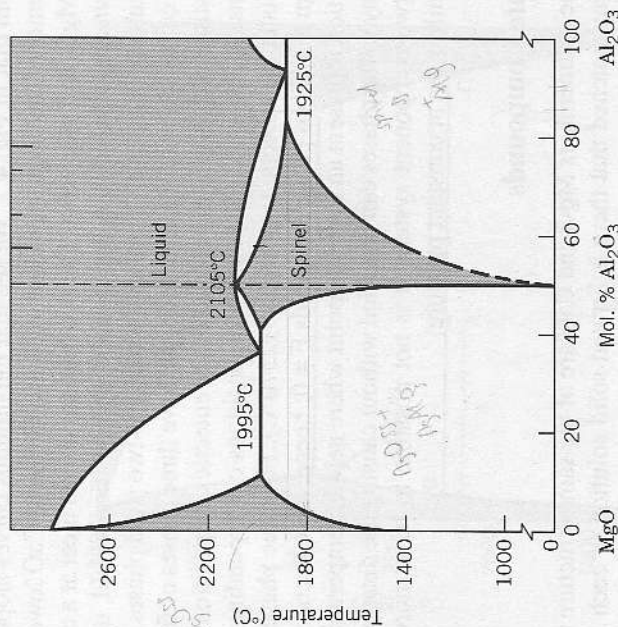
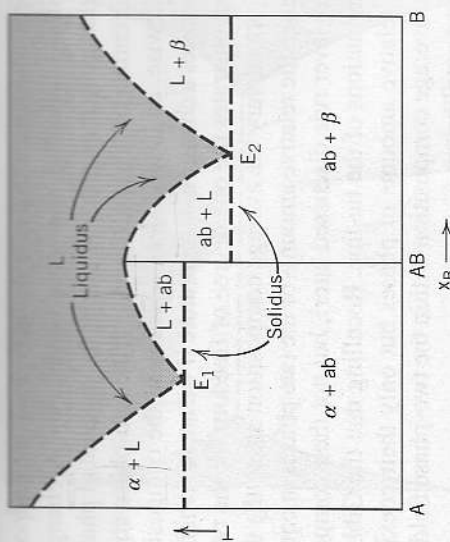


Fig. 4.4 (a) Schematic binary diagram with one intermediate compound ab forming a eutectic with each of the endmembers A and B; all solid phases are line compounds. (b) MgO-Al₂O₃ binary diagram showing two eutectics and an intermediate compound MgAl₂O₄ (spinel). Some range of solid solution exists for periclase and spinel, while corundum dissolves negligible MgO.

ound melts congruently determines the methods that can be used for growth of single crystals.

An example of this kind of phase diagram is shown in Fig. 4.4b for the system MgO - Al₂O₃, in which the intermediate compound is MgAl₂O₄ (spinel). Unlike the schematic in Fig. 4.4a, not all compounds in the system are line compounds. There is an extensive solid solution of Al₂O₃ in spinel that reaches a maximum of about 85 mole% Al₂O₃ at 1860°C, and a more limited solid solution of MgO in spinel reaching 62% Al₂O₃ at 1995°C. The solid solution field of the spinel phase appears as the wide shaded region in Fig. 4.4. There also exists a substantial solid solution of Al₂O₃ in the MgO endmember at elevated temperatures. On the other hand, at the Al₂O₃ endmember no solid solution field is shown for corundum since the solubility of MgO in corundum is at most a few hundred parts-per-million. We may view Fig. 4.4b as either a binary diagram between the components MgO and Al₂O₃ with an intermediate compound, or as two binary diagrams between the components MgO-MgAl₂O₄ and MgAl₂O₄ - Al₂O₃.

SPECIAL TOPIC 4.2

FREE ENERGY CURVES AND THE COMMON TANGENT CONSTRUCTION

The fields and boundaries on a phase diagram depict the phase or combination of phases which represent the minimum free energy for a material of a certain composition and at a given temperature. The origin of these features can be visualized using curves of free energy versus composition for each phase. Figure ST40 shows the free energy for a simple binary solution of two components A and B at a constant temperature. If there is no atomic mixing between the two endmembers, that is, the composition of the whole

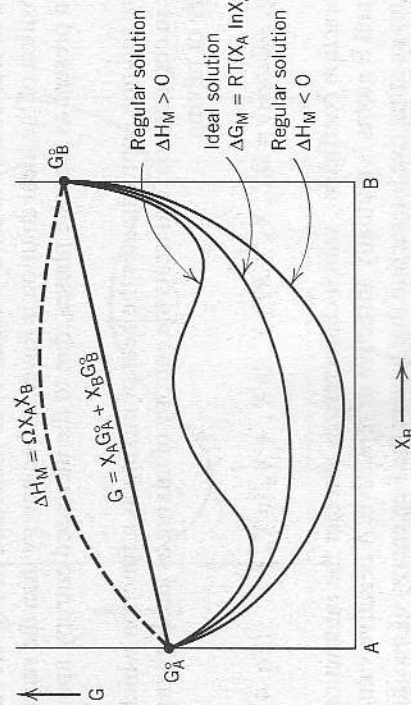


Fig. ST40 Gibbs free energy for a binary solution of A and B.

endmember A and B is shown. At the temperature T_1 , the phases at equilibrium are the solid phases α , AB, and β . The tangents to the free energy curves (solid lines) give the limits of solid solution of α and β (Fig. ST43b). The very limited solid solution range of AB corresponds to a free energy curve that is narrow and steep. The higher free energy curve for the liquid shows that it is metastable, but if the phase AB is difficult to crystallize, the liquid may continue to exist upon cooling as a metastable phase. In this case the common tangents between the liquid free energy curve and the solid phases yield the *metastable extensions* of the liquidus curves, as shown in Fig. ST43a. The phase relations shown by metastable diagrams of this type are most commonly seen in compositions where the liquid phase is viscous and from which crystallization is difficult, such as silicate glasses, or where a liquid has been rapidly quenched. Figure 44 shows a more complex example with several metastable features that have been proposed for the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system. Another form of metastable phase formation is *solid state amorphization*, a phenomenon where two solid phases placed into contact form a metastable glassy solid rather than an equilibrium crystalline intermediate compound.

Peritectic Diagrams and Incongruent Melting

Incongruent melting, whereupon a solid phase melts to form a liquid of a different composition, is the hallmark of *peritectic* diagrams. Figure 4.5 shows a schematic peritectic phase diagram for a two-component system with one intermediate compound, and in which all compounds are line compounds. The compound ab melts incongruently; with increasing temperature, this line compound intersects the $L + \alpha$ two phase field at its melting point. The melting reaction is therefore $ab \rightarrow L + \alpha$. At its melting point, ab is in equilibrium with α and liquid of composition P, constituting a three-phase equilibrium and therefore an invariant point. The peritectic temperature is the melting point of ab, and by convention, the peritectic point "p" is the composition of the liquid that is in equilibrium with the two solids at this temperature. A eutectic also appears in Fig. 4.5, between the compounds ab and β .

We may think of the eutectic and peritectic as being in a sense inverted with respect to one another; the transition from a single-phase to two-phase region occurs upon cooling for the eutectic point, and upon heating for the peritectic point. Peritectic solidification is characterized by the formation of a new solid from the reaction between a pre-existing solid and liquid. In the case of the compound ab, the peritectic solidification reaction is $L + \alpha \rightarrow ab$. Figure 4.6 shows a peritectic phase diagram for a binary system with no intermediate compound, and in which both solid phases have extensive solid solubility. In this instance, the phase β decomposes incongruently upon heating into a mixture of liquid and α .

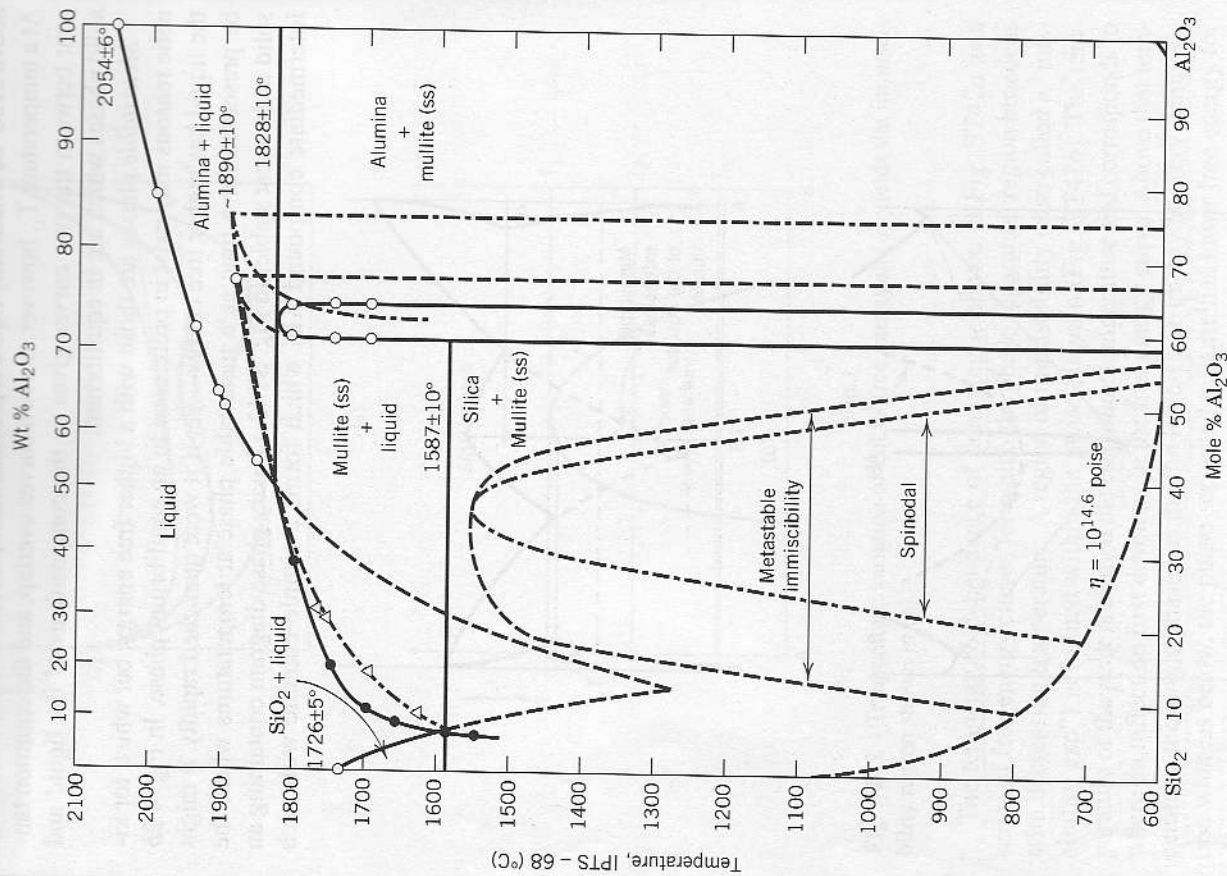


Fig. ST44 $\text{SiO}_2\text{-Al}_2\text{O}_3$ system showing metastable liquidus and solidus extensions and metastable immiscibility region at lower temperature. From S.H. Risbud and J.A. Pask., *J. Mat. Sci.*, 13 [11], 2449 (1978).

An example of a binary system with numerous intermediate compounds and several eutectic and peritectic invariant points is the technologically important system BaO-TiO₂, shown in Fig. 4.7. BaTiO₃ is an important ferroelectric material, as discussed in Chapter 1, and BaTi₄O₉ and Ba₂Ti₉O₂₀ are useful dielectric materials for microwave frequency communications. Most of the intermediate compounds in this system exhibit very limited solid solution. The exceptions are hexagonal and cubic BaTiO₃, both of which appear to have some solid solubility for excess TiO₂ at elevated temperatures. It is left as an exercise to the reader to identify the two eutectic and four peritectic points in this diagram.

Subsolidus Phase Equilibria

Figure 4.8 introduces a new level of complexity, wherein a pure endmember exists as more than one solid phase. This diagram shows the region between ZrO₂ and the intermediate compound ZrCaO₃ in the binary system ZrO₂-CaO. ZrO₂

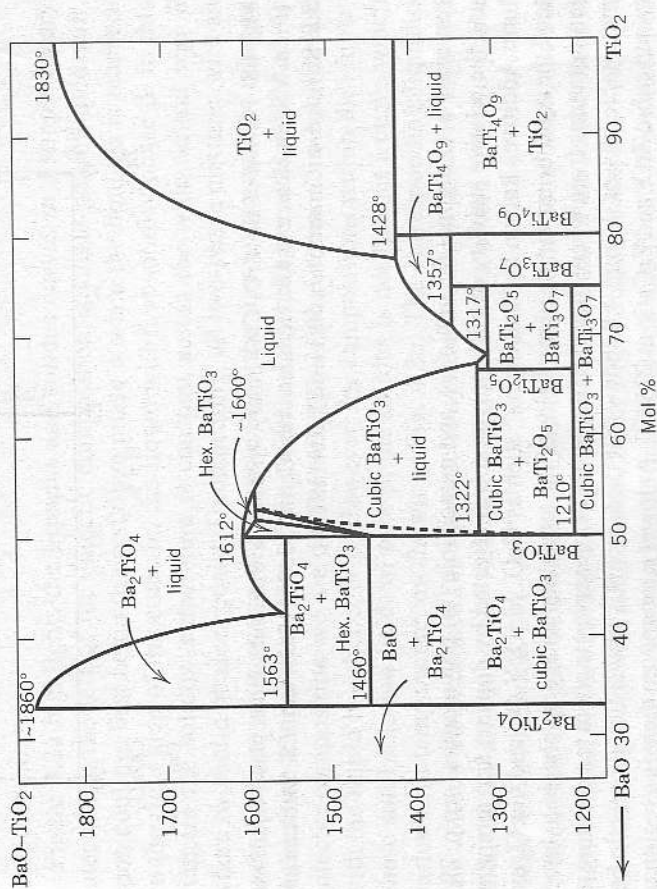


Fig. 4.7 BaO-TiO₂ binary system, showing several intermediate compounds of both congruently and incongruently melting character. (Adapted from Phase Diagrams for Ceramists, The American Ceramic Society, Columbus, Ohio, 1975.)

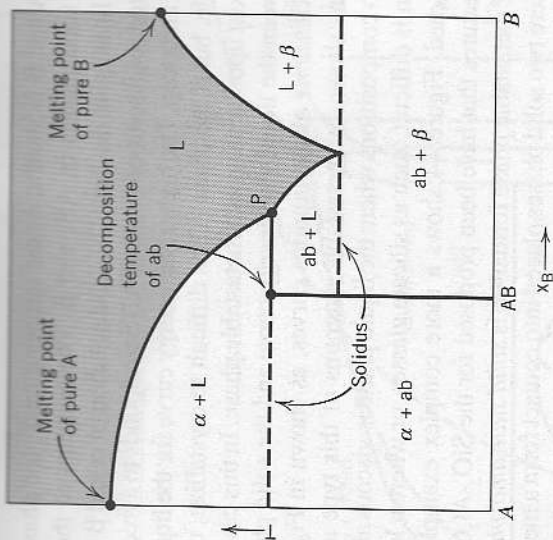


Fig. 4.5 Binary diagram containing an incongruently melting compound *ab*, and containing a peritectic (*P*) and a eutectic invariant point. No solid solution is shown for the solid phases.

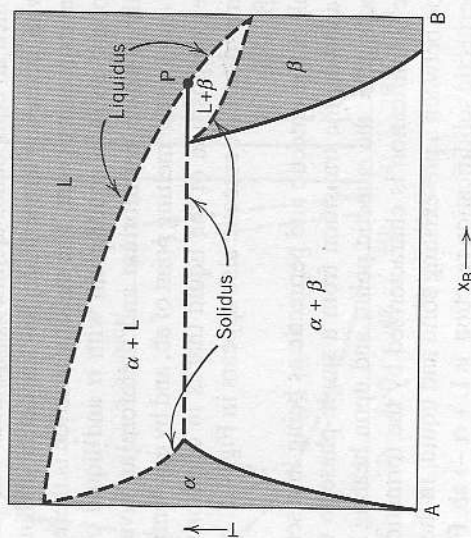


Fig. 4.6 Binary peritectic diagram in which both solid phases have extensive solid solubility. The phase β melts incongruently.

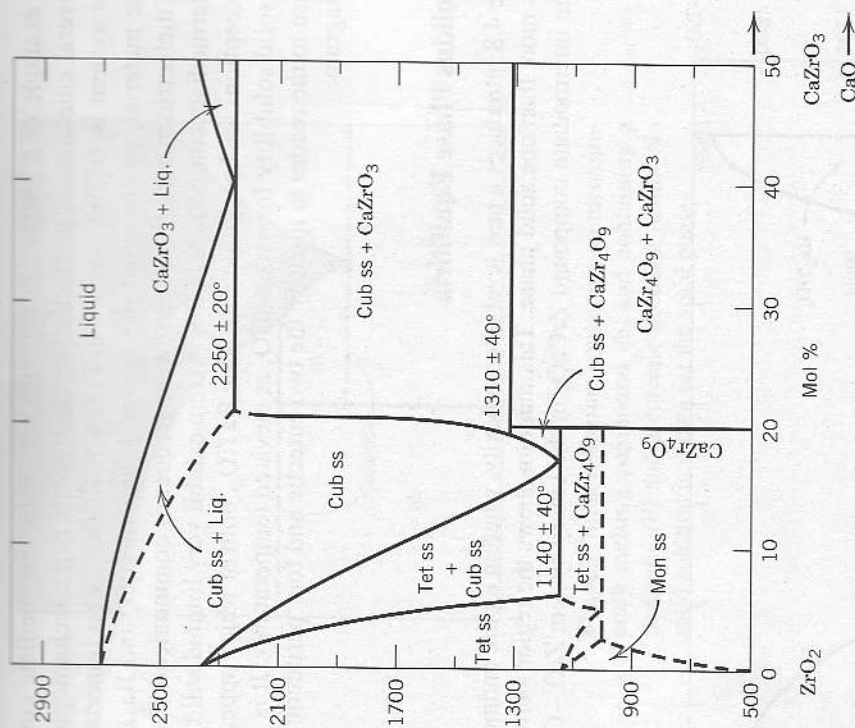


Fig. 4.8 Portion of the ZrO_2 - CaO binary system, showing subsolidus phase equilibria. [From V.S. Stubican and J.R. Hellman, *Adv. Ceram.*, 3, 25 (1981), and V.S. Stubican and S.P. Ray, *J. Am. Ceram. Soc.*, 60[11-12], 534 (1977).]

can exist as tetragonal (*t*), cubic (*c*), and monoclinic (*m*) polymorphs (see p. 29), and the relative stability of each polymorph is affected by dopants and temperature. Additives known as “stabilizers” such as CaO , MgO , Y_2O_3 , and Gd_2O_3 extend the equilibrium single phase fields of the tetragonal and cubic phases to lower temperatures from where they can frequently be preserved to room temperature as metastable phases. Figure 4.8 shows that there exists a conventional eutectic between cubic ZrO_2 and ZrCaO_3 at 2250°C . At lower temperature there is a region of subsolidus phase equilibria where features like those of the eutectic appear between solid phases. At approximately 1140°C and 17% CaO , there is an invariant point termed a *eutectoid* (to indicate only solid phases in equilibrium) where cu-

bic ZrO_2 , tetragonal ZrO_2 , and CaZr_4O_9 are in equilibrium. The cubic phase decomposes to the latter two upon cooling if the kinetics are fast enough. The solid-phase equivalent of the peritectic is the *peritectoid* and can be treated in an analogous manner to these examples. In Fig. 4.7 there also exists a eutectoid at 1210°C between the line compounds BaTi_2O_5 , BaTiO_3 and BaTi_3O_7 . The eutectoid decomposition reaction is $\text{BaTi}_2\text{O}_5 \rightarrow \text{BaTiO}_3 + \text{BaTi}_3\text{O}_7$.

Solidus and Liquidus Temperatures

We referred earlier with respect to Fig. 4.2 to the *liquidus*, defined as the lowest temperature at which a particular composition is completely liquid. This is also, upon heating, the highest temperature at which any remnant of solid exists. The *solidus* is conversely the highest temperature at which a particular composition is completely solid, or the lowest temperature at which any liquid exists. The solidus is an important temperature in the firing process for ceramics, since the presence of a small amount of liquid can dramatically increase diffusional transport, and along with it the rates of chemical reaction, sintering, and grain growth. It is important to emphasize that it is not a single characteristic temperature for a system, but instead varies with the specific composition.

Figure 4.3a highlights the liquidus and solidus curves in a simple binary eutectic. To the left of the eutectic composition, a single-phase liquid will, upon cooling, first begin to crystallize phase α when the liquidus is reached. To the right side of the eutectic, the liquid will first solidify phase β . In this diagram the solidus temperature is constant across the wide central region where two solid phases coexist. Upon heating, all two-phase mixtures with an overall composition within this range exhibit the first appearance of a liquid at the same temperature: that of the eutectic. Depending on which side of the eutectic composition we are on, the solid phase that remains in equilibrium with the liquid is either α or β . However, for compositions within the single-phase solid solution fields of α or β , the solidus is not flat but a curve which varies with temperature, as shown in Fig. 4.3a. The corresponding liquidus and solidus temperatures for a peritectic system are highlighted in Figs. 4.5 and 4.6. In all cases, the liquidus and solidus lines bound the two-phase (solid + liquid) fields.

In eutectic and peritectic systems containing intermediate compounds, such as Figs. 4.4a and 4.5, we have again highlighted the locations of the solidus lines to show that they vary with composition. Using Fig. 4.5 as an example, to the right of the compound *ab*, the two equilibrium solids *ab* and β will first react upon heating at the eutectic temperature to form a liquid of the eutectic composition. The temperature of first melting is considerably higher to the left of *ab*, and occurs at the peritectic temperature.

In the processing of ceramics, starting materials are often those of convenience and economy, rather than solid phases in thermodynamic equilibrium. The critical firing temperature is often the lowest solidus temperature in the system. Let us illustrate by referring again to Fig. 4.5. Consider the starting materials to be the solids α and β , present as finely mixed powders. Upon heating, at microscopic contacts between the powder particles the local composition can span the entire range between pure α and pure β . The first liquid that forms in this material will therefore be of eutectic composition, and will form at the eutectic temperature regardless of whether the overall composition lies to the left or right of the compound ab . Depending on the overall composition this liquid may remain or disappear as the reaction between α and β proceeds toward equilibrium. As another example, consider the BaO-TiO₂ phase diagram in Fig. 4.7. If we heat a mixture of the powders BaO and TiO₂, the first temperature at which a liquid will form, however small the actual amount, is the eutectic at 1317°C. Only after some extent of compositional mixing will equilibrium compositions and phases be achieved. The relation between phase equilibria and processing and microstructure is discussed further in Chapter 5.

Variable Valence Systems: Example in Fe-O

Care must be taken in selecting the correct number of components for a system. In the binary examples Figs. 4.2 through 4.8, we have chosen the respective oxides as the components. In fact there are three elements involved in each instance (two metals and oxygen). Why is this not a three component system? Notice that if the valences of the cations are fixed, the concentration of oxygen in any mixture is dictated by charge balance. This removes one compositional variable—there are only two independently variable chemical potentials. Presuming that the oxygen activity is high enough that the metals remain fully oxidized, it is then convenient and valid to treat these as binary systems between the endmember oxides.

Nonetheless, situations arise in which the metal has more than one stable valence state, as with the transition metal oxides. In these cases oxygen must be considered as one of the components. An important example of a variable valence system is iron-oxygen, the binary diagram for which is shown in Fig. 4.9. The stable valences for iron in oxides are 2+ and 3+. One way to depict the relevant phase equilibria is as a binary diagram between the reduced phase wüstite and the oxidized phase hematite. As the diagram shows, wüstite does not exist at the ideal stoichiometry of FeO that is required of divalent iron, but is always somewhat cation deficient (Fe_{1-x}O) due to a fraction being trivalent. The hematite phase does exist in the ideal stoichiometry Fe₂O₃ corresponding to all iron being in the Fe³⁺ state. There is also an “intermediate compound” Fe₃O₄, magnetite, occurring at the composition FeO·Fe₂O₃, which is narrow in stoichiometry

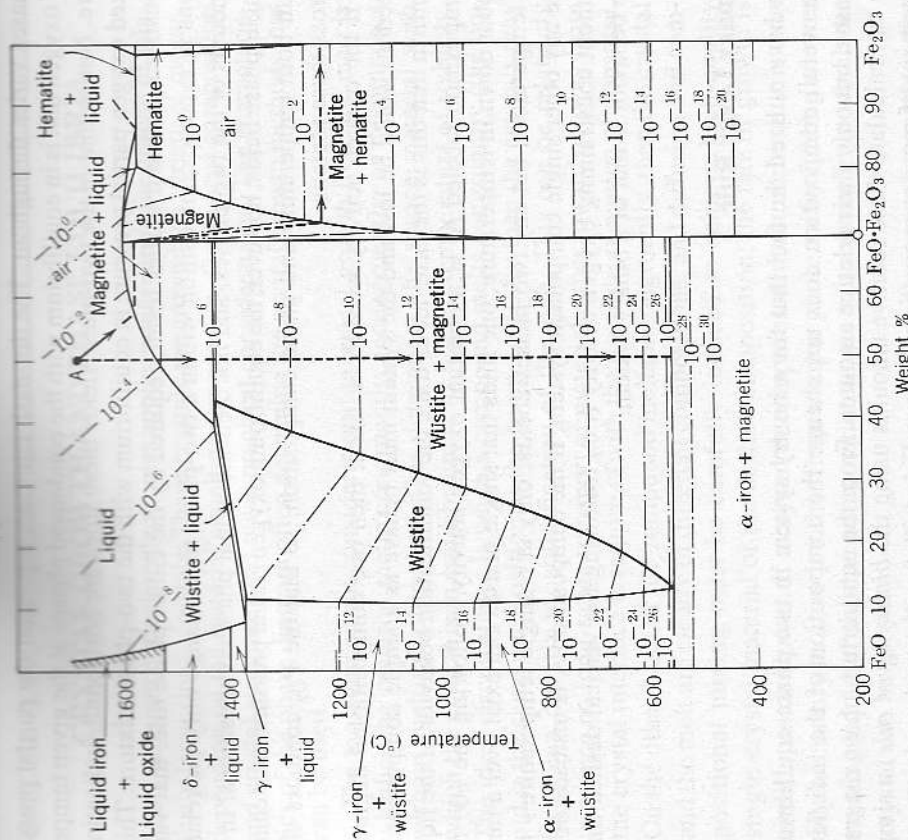


Fig. 4.9 Fe-O diagram, represented as a binary system between FeO and Fe₂O₃ endmembers. Contours of constant oxygen activity in equilibrium with the equilibrium phases are shown.

at temperatures below 1000°C but has a range of solid solution above. The single- and two-phase fields between these three solids and the liquid can be identified by close inspection of Fig. 4.9.

Since the average valence state of the iron is determined by both temperature and oxygen activity, an important aspect of this diagram is the equilibrium between the condensed and vapor phases. The *total pressure* represented in Fig. 4.9 is implied to be one atmosphere, as in the earlier binary diagrams. However, the oxygen *partial pressure* (P_{O₂}) co-existing in equilibrium with the condensed