

# Thermodynamics of Natural Systems

Theory and Applications in Geochemistry  
and Environmental Science

Third Edition  
**G.M. ANDERSON**



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# 12

## Phase Diagrams

### 12.1

#### What Is a Phase Diagram?

A phase diagram in the general sense is any diagram that shows what phase or phases are stable as a function of some chosen system variable or variables. Therefore, the  $Eh$ - $pH$ ,  $\log f_{O_2}$ - $pH$ , and activity–activity diagrams we have been looking at are a kind of phase diagram. However, if you mention the subject of phase diagrams to a petrologist, a metallurgist, or a ceramic scientist, they will immediately think of a particular type of diagram that is of great usefulness in these subjects. In these sciences, the compositions of phases and their relationships during phase changes, particularly solid → liquid and liquid → solid changes, are of particular importance, so diagrams that depict this information as a function of temperature and pressure have come to be the subject of “phase diagrams.”

##### 12.1.1

#### Thermodynamics and Phase Diagrams

Though it is true that phase relations can always be described in terms of the thermodynamic principles and equations we have been discussing, and that any phase diagram can in principle be calculated given the appropriate data, the emphasis in this chapter changes from one of calculating what we want to know from numbers in tables of data, to one of simply representing experimentally derived facts in diagrammatic form. The reason for this is that once we get into systems more complex than a single component, and especially when high-temperature melt phases are involved, the calculations are often not possible because the data are not available, or, even if they are available, the results are not very accurate, because they are very sensitive to small inaccuracies in the data. Therefore, in this book, although we will show the relationship between functions such as  $G$  and our diagrams, this will be in an illustrative rather than a quantitative way.

##### 12.1.2

#### Phase Diagrams as Models

Metallurgists and ceramicists quite often deal with simple two- and three-component systems and use phase diagrams to represent their experimental results on the phase relations in these systems. The diagrams therefore truly represent their systems. Petrologists, on the other hand, are interested in the origins of natural rocks, which commonly have 10 or more important components. Systems this complex cannot be represented in simple diagrams and, in fact, can hardly even be thought about in a quantitative way. Experiments can and have been done using natural rocks, but the results are complex and may not be generally

applicable. Therefore, petrologists use simpler systems such as those having two and three components to better understand the principles involved and to investigate simple models of the complex systems in nature.

Phase diagrams represent *equilibrium* relationships. Once these have been depicted, simple *processes* such as melting and crystallization can be considered, but, because as represented on diagrams these involve continuous successions of equilibrium states, they are *reversible processes* in the sense of Section 2.6.1.

## 12.2

### The Phase Rule

The phase rule is a simple but profound relationship, derived by Gibbs (1961a), relating the composition of a system, the number of phases it has, and something called the variance of the system. It requires no thermodynamic data, and although simple in principle, and easily applied to the simple systems usually used to explain it, it can be surprisingly difficult to use when considering geological systems. It is absolutely essential in discussing phase diagrams, and understanding why they look the way they do.



### Phase Rules

The phase rule used or implied in modeling systems having aqueous solutions is somewhat different from the one derived by Gibbs. For example the system NaCl–H<sub>2</sub>O has two components, but this choice of components is not capable of defining the amounts of the aqueous *species* in the system. To do this a different choice of components, a different basis, is required. A typical choice of *basis species* for this system would be Na<sup>+</sup>, Cl<sup>-</sup>, NaCl°, H<sup>+</sup>, OH<sup>-</sup>, NaOH°, and HCl°. See Chapter 11, The Phase Rule, in the online resources.

#### 12.2.1

#### System Variance or Degrees of Freedom

We discussed phases and components in Chapter 2. There remains the concept of *variance* or *degrees of freedom*. A single homogeneous phase such as an aqueous salt solution, say NaCl in water, has a large number of properties, such as temperature, density, NaCl molality, refractive index, heat capacity, absorption spectra, vapor pressure, conductivity, partial molar entropy of water, partial molar enthalpy of NaCl, ionization constant, osmotic coefficient, ionic strength, and so on. We know, however, that these properties are not all independent of one another. Most chemists know instinctively that a solution of NaCl in water will have all its properties fixed if temperature, pressure, and salt concentration are fixed. In other words, there are apparently three independent variables for this two-component system, or three variables that must be fixed before all variables are fixed. Furthermore, there seems to be no fundamental reason for singling out temperature, pressure, and salt concentration from the dozens of properties available – it's just more

convenient; any three would do. The number of variables (system properties) that must be fixed in order to fix *all* system properties is known as the system variance or degrees of freedom.

Now consider two phases at equilibrium, say solid NaCl and a saturated salt solution. Again, intuition or experience tells us that we no longer have three independent variables, but two, because, for example, we cannot choose the composition of the salt solution once *T* and *P* have been fixed – it is fixed for us by the solubility of NaCl in water. If we then consider the possibility of having a vapor phase in equilibrium with the salt and the solution, we see that we lose another independent variable because we can no longer choose the pressure on the system independently once the temperature has been chosen – it is fixed by the vapor pressure of the system. So it would seem that, in general, we restrict the number of independent variables in a system by increasing the number of phases at equilibrium.

#### 12.2.2

#### Mathematical Analogy

The variance of a chemical system is exactly analogous to the variance of a system of linear equations. For example, for the function

$$x + y + z = 0$$

if we choose  $x = 2$ ,  $y = 2$ , then  $z$  is fixed at  $-4$ . The equation could be said to have a variance of two, because two variables must be fixed before all variables are fixed. Three variables minus one relationship between them (one equation) leaves two degrees of freedom. If in addition to this function we have another one involving the same variables, such as

$$2x - y + 4z = -19$$

we now have three variables and two functional relationships, and we are free to choose only one of the three variables, the other two then being fixed. For example, if we choose  $x = 2$ , then there is no further choice:  $y = 3$  and  $z = -5$ . If we choose  $x = 3$ , then  $y = 2.6$  and  $z = -5.6$ . This situation can be said to be *univariant* or to have one degree of freedom.

And, of course, if we have a third functional relationship, for example,

$$-3x + 2y - 7z = 35$$

then we have no choice:  $x$ ,  $y$ , and  $z$  are fixed at 2, 3, and  $-5$ , respectively, and the situation is *invariant*.

The reason why the linear equations analogy for phase relationships is so exact is that there is in fact a thermodynamic equation for each phase (see below), and each of these equations has a number of independent variables equal to the number of components in the system plus two. And this, in turn, is because each component represents a degree of freedom (we can add or subtract each component), and there are two more because we defined our systems at the beginning as being able to exchange energy in only two

ways – heat and one kind of work.<sup>1</sup> If the number of components is  $c$ , then the total number of independent system properties is  $c + 2$ . If there are  $p$  phases in the system, and each phase represents one equation, then there are  $p$  equations in  $c + 2$  variables, or  $c + 2 - p$  degrees of freedom. This is the phase rule:

$$f = c - p + 2 \quad (12.1)$$

where  $f$  is the number of degrees of freedom.

### 12.2.3 Derivation

A more concise derivation uses the Gibbs–Duhem equation,

$$0 = S dT - V dP + \sum_{i=1}^c n_i d\mu_i \quad (4.75)$$

From this equation we can see the number of independent intensive variables in any homogeneous phase. There are  $c$  terms containing  $\mu$ , i.e.,  $c$  independent compositional intensive variables, plus two other intensive terms,  $T$  and  $P$ , for a total of  $c + 2$  intensive variables. In a single homogeneous phase, these  $c + 2$  variables are linked by one equation (4.75), so only  $c + 2 - 1$  of them are independent. If there are  $p$  phases, there are still only  $c + 2$  intensive variables, because they all have the same value in every phase (at equilibrium), but now there is one equation (4.75) for each phase. Each additional equation reduces the number of independent variables by one, so there are now  $c + 2 - p$  independent intensive variables. These independent intensive variables are called degrees of freedom,  $f$ , so

$$f = c - p + 2 \quad (12.2)$$

which is the phase rule. Because we usually consider systems at some fixed values of  $P$  and  $T$ , this “uses up” two degrees of freedom, so the phase rule becomes

$$f = c - p \quad (12.3)$$

which is sometimes called the “mineralogical phase rule.”

To the extent that natural systems approach equilibrium, they obey the phase rule. You might reflect now and then on why natural systems should care about the results of this piece of mathematical reasoning.

## 12.3

### Unary Systems

Figure 12.1 shows a typical although hypothetical unary (one-component) diagram for compound  $\alpha$  ( $\alpha$  stands for the formula of some compound, such as NaCl or CaCO<sub>3</sub>). Although the diagram shows three different *phases* (solid, liquid, and gas), all three have the same composition (whatever the chemical composition of  $\alpha$  is), so the system is unary. This simple diagram contains a surprising amount of information, but you must know how

<sup>1</sup> If we included other kinds of work in our model, there would be an extra degree of freedom for each.

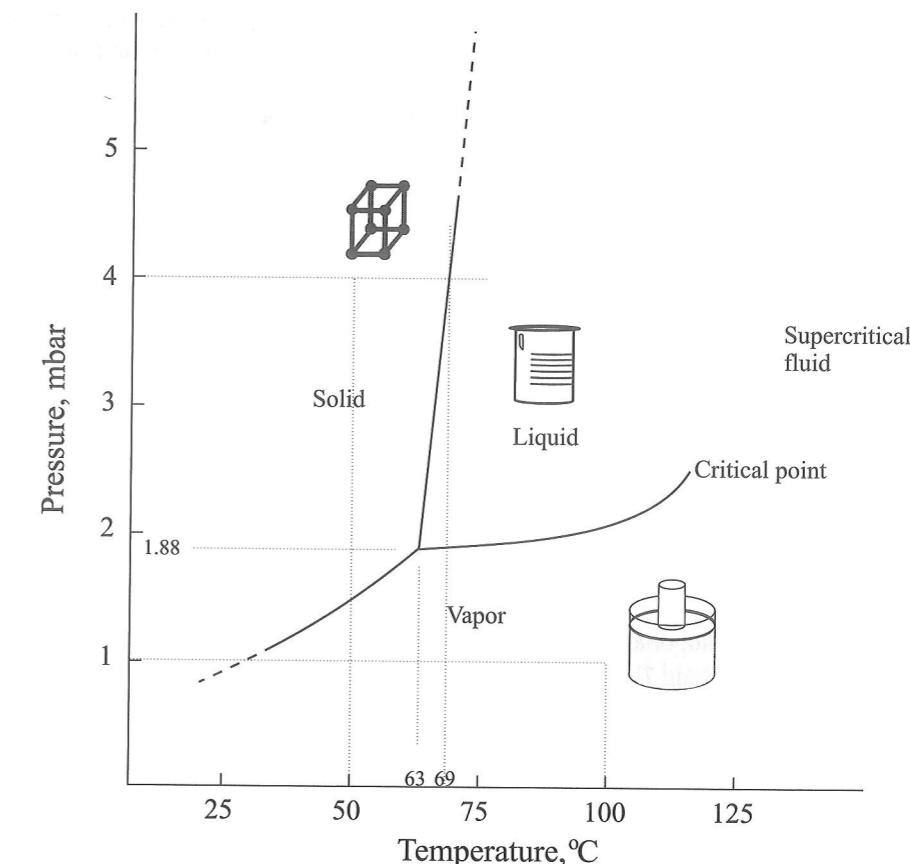


Figure 12.1 Phase diagram for hypothetical compound  $\alpha$ .

to “read” the diagram. First, note that the diagram contains labeled *areas*, *lines* that separate the areas, and *points*. Every location on the diagram has a pair of  $x$ - $y$  coordinates, that is, a pressure and a temperature. For example, a pressure of 4 mbar and a temperature of 50 °C are the coordinates of a point in the area marked “Solid.” Under these conditions, the stable form of compound  $\alpha$  is observed to be a crystalline solid. If the pressure on  $\alpha$  is reduced to 1 mbar, and the temperature increased to 100 °C, the stable form of  $\alpha$  is gaseous. Similarly, for any combination of pressures and temperatures within the area marked “Liquid,” the stable form of  $\alpha$  is liquid. The phase diagram is in fact a record of these experimental observations about the form of  $\alpha$  under various conditions of  $P$  and  $T$ . As mentioned earlier, the vast majority of phase diagrams record the results of experiments – they are not usually the result of theoretical calculations. They are more often a *source* of thermodynamic data than the result of using such data.

Obviously, within these areas,  $P$  and  $T$  could be changed considerably without changing the nature of the phase, although the *properties* of the phase (its density or heat capacity, say) would certainly change with  $P$  and  $T$ . It appears, then, that for  $\alpha$ , and for any pure compound, we must choose *two* variables in order to define the state of the compound.

Thus to answer the question “what is the density (or heat capacity, refractive index, entropy, ...) of  $\alpha$ ?” we must first specify two variables – the  $P$  and the  $T$  we are interested in. One is not enough – at 4 mbar,  $\alpha$  can have quite a range of densities, but at 4 mbar, 50 °C, its density is fixed and determinable, as are all its other properties. So we say that in each of its three forms – solid, liquid, and gas –  $\alpha$  has two *degrees of freedom* – two variables must be specified before *all* are specified. These two variables are in practice usually  $T$  and  $P$ , but in principle any two would do. The phase rule summarizes all this discussion by simply saying

$$\begin{aligned}f &= c - p + 2 \\&= 1 - 1 + 2 \\&= 2\end{aligned}$$

With  $\alpha$  at 4 mbar and 50 °C, consider that we raise the temperature gradually. Nothing much happens, except that the properties of  $\alpha$  change continuously, until we reach 69 °C, which is the temperature of the boundary between the solid and liquid fields. At this  $T$ , solid  $\alpha$  is observed to begin to melt, and at this  $T$ , any proportions of solid and liquid  $\alpha$  are possible (i.e., almost all solid  $\alpha$  with a drop of liquid; or almost all liquid  $\alpha$  with a tiny amount of solid; or anything in between). However, if the temperature is held very slightly above the melting  $T$ ,  $\alpha$  becomes completely liquid. The solid/liquid boundary line then is a locus of  $T$ - $P$  conditions that permit the coexistence of solid and liquid  $\alpha$ . It records the melting temperature of  $\alpha$  as a function of pressure.

Note too that because it is a line rather than an area, or because there are two coexisting phases rather than one, we now have only one degree of freedom. In other words, at 4 mbar we now have no choice of temperature. If solid and liquid coexist at equilibrium, the temperature must be 69 °C – it is chosen for us. We can still choose whatever  $P$  we like (within certain limits), but once we have exercised our one degree of freedom and chosen a pressure, the temperature and all properties of the two phases of  $\alpha$  are fixed. Again, we note that the one degree of freedom can be any property, not just  $T$  or  $P$ . We might choose a certain value for the entropy of solid  $\alpha$ , for example; we would then find that there was only one  $T$  and  $P$  at which solid  $\alpha$  with this particular  $S_\alpha$  could coexist with liquid  $\alpha$ . The phase rule agrees, saying

$$\begin{aligned}f &= c - p + 2 \\&= 1 - 2 + 2 \\&= 1\end{aligned}$$

Similar comments apply to the boundary between the fields of “Liquid” and “Vapor,” which records the *boiling temperatures* of  $\alpha$ , and the boundary between the “Solid” and “Vapor” fields, which records the *sublimation temperatures* of  $\alpha$ . Where these three boundaries come together at about 63 °C, 1.88 mbar (a *triple point*), the three phase fields come together, and solid, liquid, and gaseous  $\alpha$  can coexist in any proportions at this particular  $T$  and  $P$ . Note that for the coexistence of these three phases, we have lost another degree of freedom. In fact we have no choice at all – if we want three phases to coexist, the

$T$  and  $P$  must be 63 °C and 1.88 mbar. As the number of coexisting phases increases, the number of degrees of freedom decreases. Negative numbers of degrees of freedom are not possible, so in a one-component system the phase rule predicts that the *maximum* number of phases at equilibrium is three.

$$\begin{aligned}f &= c - p + 2 \\&= 1 - 3 + 2 \\&= 0\end{aligned}$$

### 12.3.1 Gibbs Energy Sections

Despite the fact, mentioned in Section 12.1.1, that phase diagrams are for the most part experimentally derived, they are controlled by and must conform to fundamental thermodynamic relationships. Understanding phase diagrams is enhanced by examining the relationships between the diagrams and the underlying thermodynamics.

From our study of thermodynamics in previous chapters, we know that the stable state of a system under given conditions is that state having the lowest value of the Gibbs energy,  $G$  (or  $G$ ). If a system does not have the lowest possible value of  $G$ , a spontaneous process will take place (according to our model) until this lowest value has been achieved. Also, we know that if two phases are in equilibrium in a unary system, the Gibbs energy of the component is the same in each phase (Section 6.2.1; Figure 6.1). Therefore, the phase boundaries in Figure 12.1 are places where  $G_\alpha$  is the same in two phases, as shown in Figure 12.2. Note too that we may calculate and plot the Gibbs energy (and other properties) of a liquid phase in regions where it is not the stable phase. When we say, for example, that at 4 mbar, 50 °C in the solid stability field,  $G_\alpha^{\text{solid}} < G_\alpha^{\text{liquid}}$ , we imply that, if liquid  $\alpha$  could exist at 4 mbar, 50 °C, its  $G$  would be greater than that of  $G_\alpha^{\text{solid}}$ . We could, in fact, plot the values of  $G$  for all possible phases over all parts of the diagram. If we did so and looked at a part near the solid/liquid boundary, we would see something like Figure 12.3.

### G-T Sections

Figure 12.4 shows a section through Figure 12.1 at a pressure of 2 mbar. At temperatures below 64 °C at 2 mbar pressure,  $\alpha$  is solid, and the Gibbs energy of this solid ( $G_\alpha^{\text{solid}}$ ) is shown by the line labeled “Solid”. Naturally, as we don’t *know* the absolute Gibbs energy of any substance, we cannot place any absolute numbers on the  $G$ -axis. However, we *do* know the slope of this line (the slope is  $(\partial G_\alpha / \partial T)_P = -S_\alpha$ , and we know  $S$  for most compounds), so we could establish some arbitrary energy divisions on the  $G$ -axis and plot a line with the correct slope. This line would have a gentle downward curvature because  $S$  gradually increases with  $T$ , but to a first approximation it is a straight line. This line continues to the melting temperature, 64 °C, at which point it intersects another line giving the values of  $G_\alpha^{\text{liquid}}$ . This line has a steeper slope, because the entropy of a liquid is always greater than the entropy of a solid of the same composition. At the intersection,  $G_\alpha^{\text{solid}} = G_\alpha^{\text{liquid}}$ , as required by phase equilibrium theory (Sections 6.2.1 and 6.3).

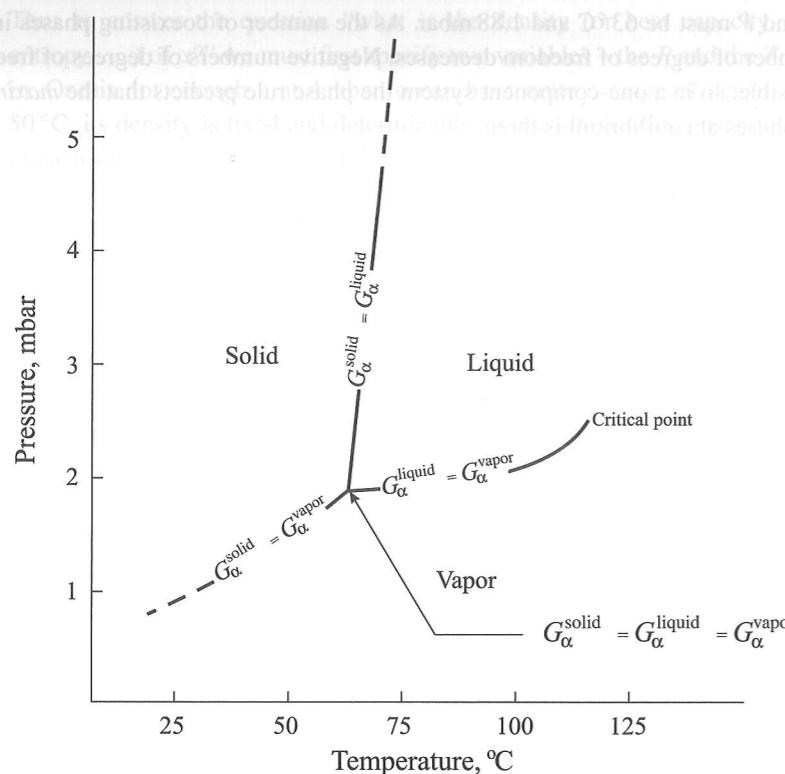


Figure 12.2 Gibbs energy relationships in the phase diagram for compound  $\alpha$ .

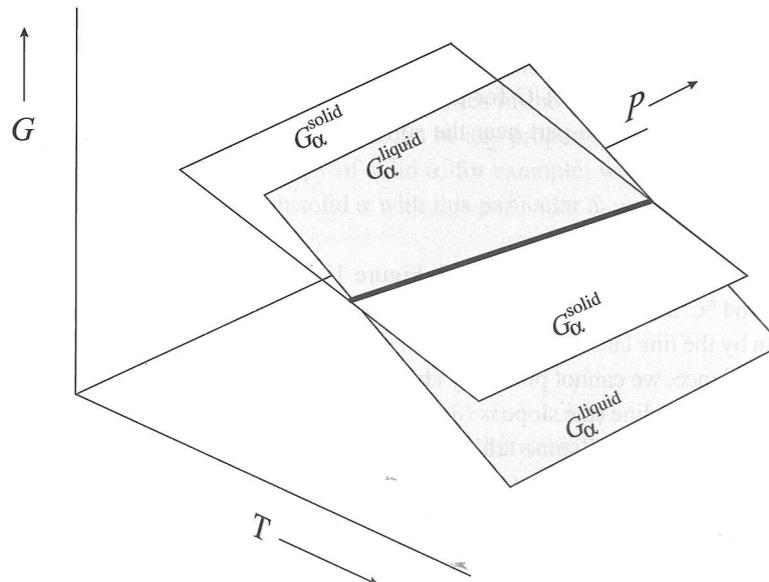


Figure 12.3  $G$ - $T$ - $P$  diagram for part of Figure 12.1. The heavy line at the intersection of the  $G_\alpha^{\text{solid}}$  and  $G_\alpha^{\text{liquid}}$  surfaces is the melting curve.

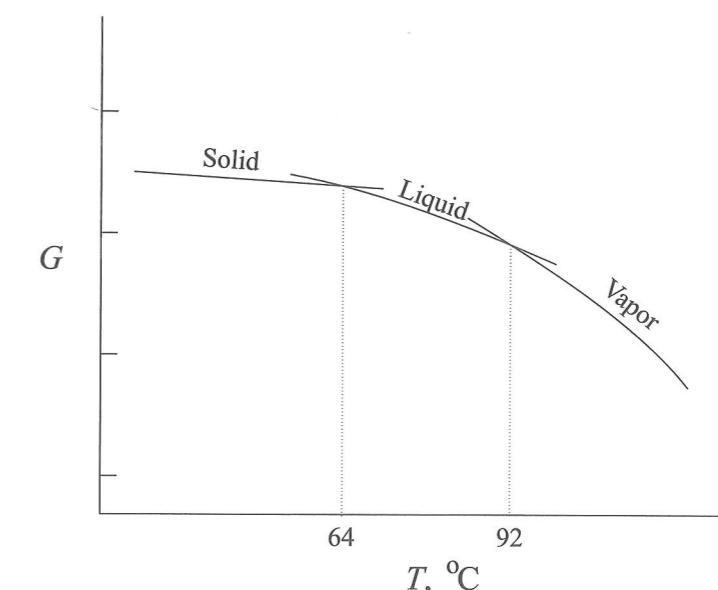


Figure 12.4  $G$ - $T$  section through Figure 12.1 at 2 mbar.

The  $G_\alpha^{\text{liquid}}$  line then continues with a gentle downward curvature through the liquid stability region at 2 mbar until it reaches another phase boundary, the boiling curve, at 92°C. Here it intersects the  $G_\alpha^{\text{vapor}}$  curve, which has a still steeper slope, because the entropy of gases is always much greater than that of liquids.

Note the similarity of this diagram to Figure 6.6, where we considered  $G$ - $T$  sections in a quantitative way, to calculate the positions of phase boundaries.

### $G$ - $P$ Sections

Figure 12.5 shows a  $G$ - $P$  section through Figure 12.1 at a temperature of 69°C. At pressures below 1.89 mbar,  $\alpha$  is gaseous, and the Gibbs energy of this gas is shown by the line labeled "Vapor". The slope of the line is  $(\partial G_\alpha / \partial P)_T = V_\alpha$ , and as the molar volume of gases is large, the line has a steep slope. This line intersects another line, giving the values of  $G_\alpha^{\text{liquid}}$ , having a smaller positive slope, because  $V_\alpha^{\text{liquid}} < V_\alpha^{\text{gas}}$ . This line continues, again with slight downward curvature because the molar volume of the liquid decreases slightly with increasing pressure, until it reaches the freezing curve at 4 mbar, where it intersects the line giving  $G_\alpha^{\text{solid}}$ . Note the similarity between this diagram and Figure 6.2.

### 12.3.2

#### Some Important Unary Systems

Substances whose phase relations are interesting for various reasons include carbon (C), iron (Fe), water ( $H_2O$ ), silica ( $SiO_2$ ), aluminum silicate ( $Al_2SiO_5$ ), and calcium carbonate ( $CaCO_3$ ).

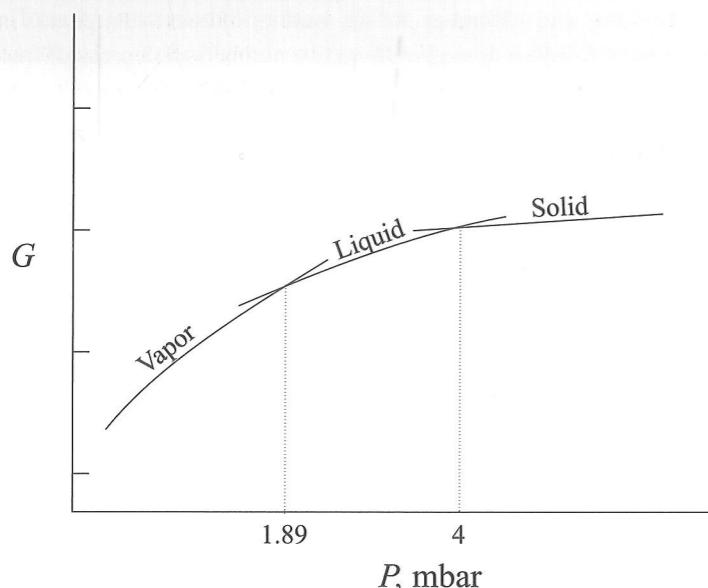


Figure 12.5  $G$ - $P$  section through Figure 12.1 at  $69^\circ\text{C}$ .

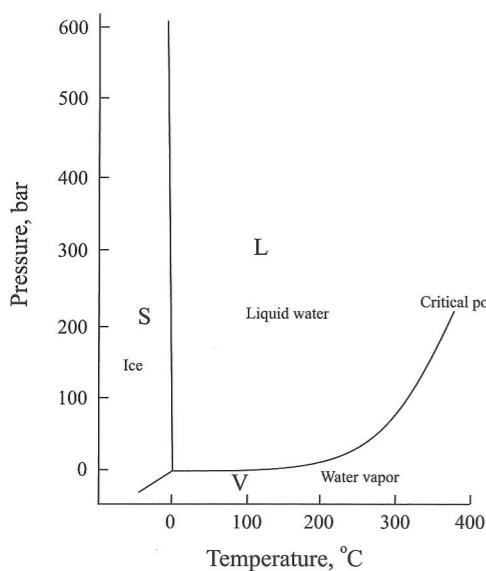


Figure 12.6 Phase diagram for  $\text{H}_2\text{O}$  at relatively low pressures. The solid/liquid boundary is very steep, but in fact has a negative slope.

## $\text{H}_2\text{O}$

The phase diagram for water at relatively low pressures is shown in Figure 12.6. Water is a most unusual substance. It is one of the very few compounds that expands when it freezes, meaning that ice floats. Most substances have solid forms that are denser than their corresponding liquids, and hence will sink during freezing. The fact that ice floats in water is shown in Figure 12.6 by the fact that the liquid/solid boundary (the freezing/melting curve) has a negative slope. In our “typical” unary system (Figure 12.1), this curve has

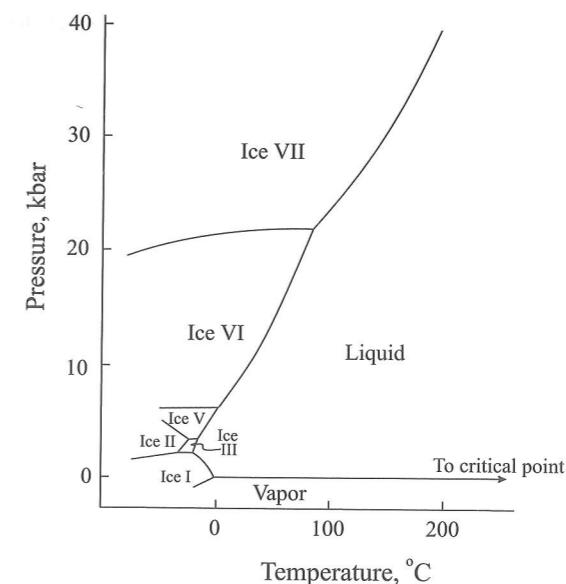


Figure 12.7 Phase diagram for  $\text{H}_2\text{O}$  at high pressures. Ice IV, not shown, is a metastable form of ice in the region of ice V.

a positive slope. In both cases (Figures 12.1 and 12.6), the denser phase lies at higher pressures, as required by Le Chatelier’s principle. The unusual thing is that in the  $\text{H}_2\text{O}$  system, the denser phase is the liquid.

The other term in the slope expression ( $dP/dT = \Delta S/\Delta V$ ) is  $\Delta S$ , which is invariably greater in the liquid than in the solid; therefore, the volume change,  $\Delta V$ , determines whether  $dP/dT$  will be positive or negative.

Figure 12.7 shows the same system over a much greater range of pressures. The striking thing about this diagram is the large number of polymorphs of ice, each with its own stability field. These polymorphs give rise to several *triple points*, showing that the solid–liquid–vapor triple point shown in Figure 12.1, which every unary system has, is often not the only one. We came across this phenomenon (a triple point generated by solid polymorphs) previously (Section 6.4, Figure 6.5). Note the fact that liquid water will freeze (to ice VII) at about 24 kbar at the boiling temperature ( $100^\circ\text{C}$ ). Note too that the negative slope of the freezing curve (between “Ice I” and “Liquid”) extends to only about 2 kbar.

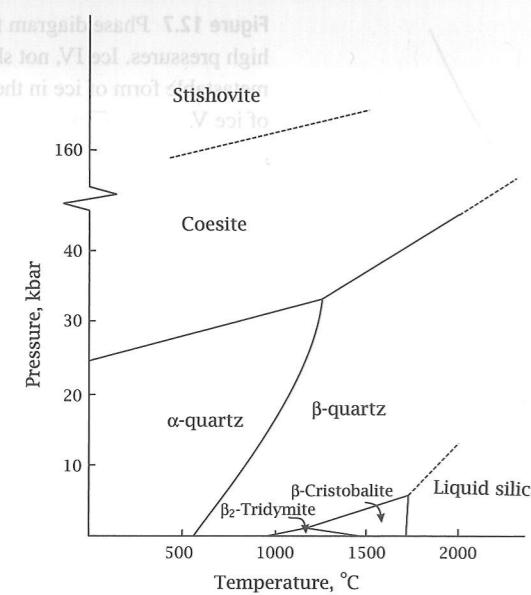
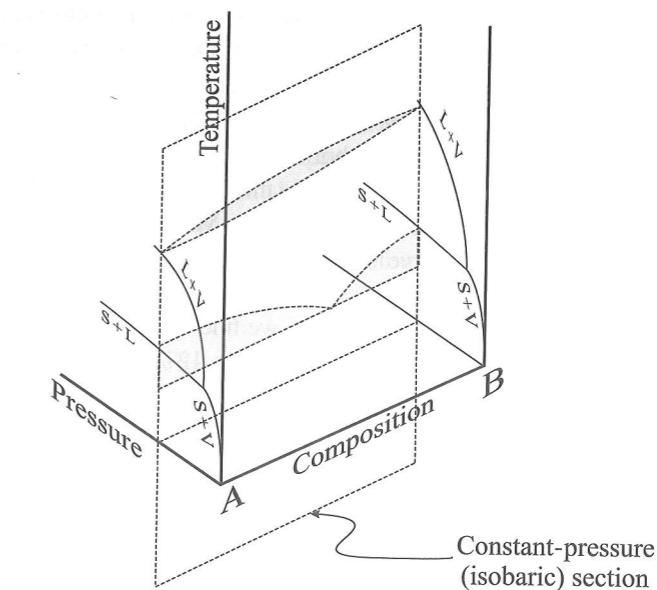
## $\text{SiO}_2$

Silica, one of the most common compounds on Earth, has a number of interesting and complex phase relations, shown in Figure 12.8.

## Binary Systems

### Types of Diagrams

When we consider the phase relations in systems having two components instead of one, we add one dimension to our diagrams. That is, in unary diagrams all phases have the same composition, so we don’t need an axis showing compositions – we can use both

Figure 12.8 Phase diagram for  $\text{SiO}_2$ .

**Figure 12.9** The  $P$ - $T$ - $X$  box.  
Most binary phase diagrams are  $T$ - $X$  sections through this box. The phase relations will, of course, vary with the pressure chosen for the section.  $P = 1$  bar is the commonest choice.

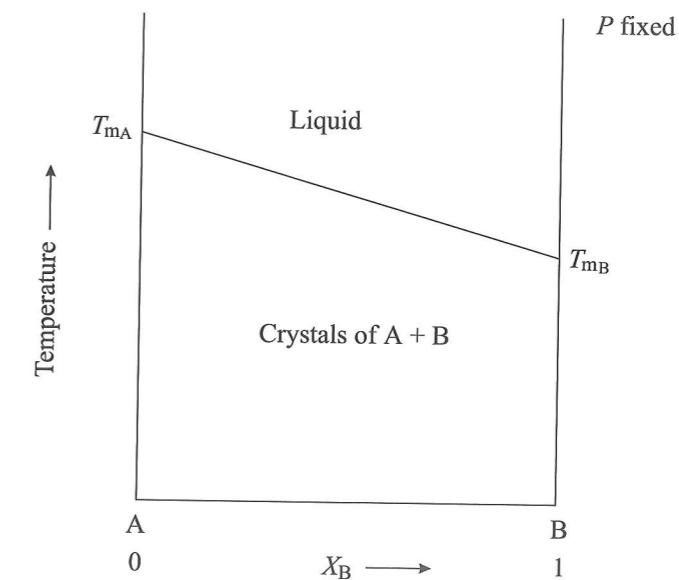


Figure 12.10 An uneducated guess as to the melting temperatures of mixtures of minerals A and B.

It seems very likely that your guess would look like Figure 12.10. In other words, you would probably suppose that the melting temperature of mixtures of A and B would be some kind of average of the melting temperatures of the pure compounds, much in the way that volumes are averages as shown in Figure 7.5(a). But binary systems are not quite that simple. Figure 12.10 is thermodynamically impossible, even if A and B were not separate phases but formed a solid solution, but we will not bother to prove this. Suffice it to say that experiments on hundreds of binary systems have never given results consistent with Figure 12.10.

#### 12.4.2 The Melting Relations of Two Components

Suppose that you now understand unary phase relations very well, but have never encountered binary systems, and you are given the following problem. There are two minerals, A and B. We know the melting point of each mineral,  $T_{mA}$  and  $T_{mB}$ , at atmospheric pressure. We grind samples of A and B together in various proportions, say 25% A, 75% B; 50% A, 50% B; and 75% A, 25% B, and we perform experiments to determine the melting temperature of these mixtures. Your job is to draw a diagram *predicting* the most likely results. The diagram should show temperature as the vertical axis and composition as the horizontal axis, and of course the known melting temperatures of the pure minerals A and B should be plotted on the vertical axes at each end of the composition axis.

<sup>2</sup> We use the “X” in the expressions  $T$ - $X$  or  $P$ - $T$ - $X$  to mean “composition” generally, whether measured as mole fractions or weight percent, or in some other way.

What does happen depends on what compounds A and B actually are. Let's suppose that A is the component  $\text{CaMgSi}_2\text{O}_6$ , and B is the component  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . The stable forms of these components at ordinary temperatures are the minerals diopside ( $\text{CaMgSi}_2\text{O}_6$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), so we will represent the component  $\text{CaMgSi}_2\text{O}_6$  by the symbol Di and the component  $\text{CaAl}_2\text{Si}_2\text{O}_8$  by the symbol An. Diopside melts at  $1392^\circ\text{C}$ , and anorthite melts at  $1553^\circ\text{C}$ . We perform the experiments mentioned above; that is, we grind up both samples into fine powders, then mix the powders in various proportions and heat them up in separate experiments and observe what happens at various temperatures. What a surprise – we find that *all mixtures begin to melt at the same temperature!* And when we analyze the composition of the first liquid to form, we find that *the first liquid to form in all mixtures has the same composition!* The temperature is  $1274^\circ\text{C}$  (called the *eutectic temperature*), and the composition is 42% An, 58% Di (called the *eutectic composition*). On heating to still higher temperatures, another surprise awaits us. For those mixtures having *more* than 42% An, temperatures above  $1274^\circ\text{C}$  result in disappearance of all diopside in the mixtures—we are left with only liquid plus anorthite crystals. For those mixtures having *less* than 42% An, temperatures above  $1274^\circ\text{C}$  result in the disappearance of all anorthite in the mixtures – only liquid plus diopside crystals are left. So *below*  $1274^\circ\text{C}$ , only two phases coexist – crystals of anorthite and diopside. *Above*  $1274^\circ\text{C}$ , again only two phases coexist – either liquid and anorthite, or liquid and diopside. Only at exactly  $1274^\circ\text{C}$  are three phases observed to coexist at equilibrium – anorthite, diopside, and liquid. And note that in the binary system, we have melting far below the melting temperature of either of the pure components. These relationships are summarized in Figure 12.11. They may seem strange at first, but, as we will see, they are one of a rather small set of relationships that satisfy the phase rule.

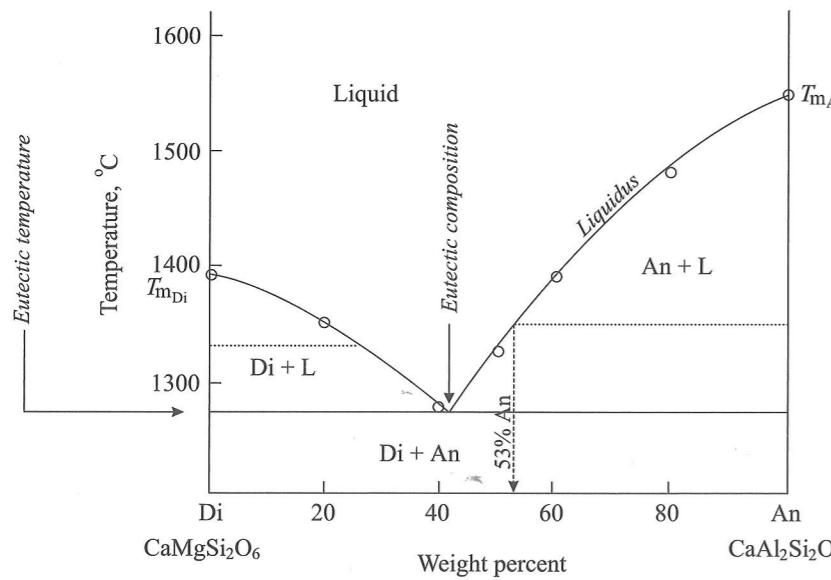


Figure 12.11 The system Di–An at 1 bar pressure. Two representative tie-lines are shown.

## The Isobaric Phase Rule

But, first, we must mention a slight modification of the regular phase rule, Equation (12.1). As shown in Figure 12.9, the experiments we are discussing at a fixed pressure of 1 bar can be represented on a plane or section through  $P$ – $T$ – $X$  space. The general phase rule (11.1) applies to this  $P$ – $T$ – $X$  space. The fact that we confine ourselves to a fixed  $P$  plane within this space means that we have “used” one of our degrees of freedom – we have chosen  $P = 1$  bar, and the same would be true for any other constant- $P$  section (or constant- $T$  section, for that matter). Therefore *on our T–X plane* the phase rule is

$$f = c - p + 1 \quad (12.4)$$

This shows that the maximum number of phases that can coexist at equilibrium in a binary system at an arbitrarily chosen pressure (or temperature) is three ( $p = 3$  for  $c = 2, f = 0$ ), which is consistent with our observations.

### 12.4.3 Reading the Binary Diagram

The main features of the phase relations in Figure 12.11 follow directly from this fact. During the heating of our mixture of Di and An crystals, we have two phases, and

$$\begin{aligned} f &= c - p + 1 \\ &= 2 - 2 + 1 \\ &= 1 \end{aligned}$$

This means that, to fix all the properties of both kinds of crystals, we need only choose the temperature (pressure being already fixed at 1 bar). However, when the first drop of liquid forms,  $p = 3$  (diopside crystals, anorthite crystals, and liquid), and  $f = 0$ . Another word for  $f = 0$  is *invariant*. When  $p = 3$  on an isobaric plane, we have *no* choice as to  $T$ ,  $P$ , or the compositions of the phases – they are all fixed. This explains why all mixtures begin to melt at the same temperature, and why the liquid formed is always of the same composition no matter what the proportions of the two kinds of crystal. No other arrangement would satisfy the phase rule.

A line on a phase diagram joining points representing phases that are at equilibrium with each other is called a *tie-line*. Each of the two-phase regions in Figure 12.11 (Di + L; An + L; Di + An) is filled with imaginary tie-lines joining liquid and solid compositions, or two solid compositions, that are at equilibrium. Only two of these tie-lines are shown. Consider the tie-line at  $1350^\circ\text{C}$  in the region labeled An + L. One end of the line is on the curved line representing liquid compositions (called the *liquidus*), and the other end is on the vertical line representing 100% An composition. The composition scale across the bottom of the diagram applies at any temperature, so we can get the liquid composition by dropping a perpendicular from the liquidus to the composition scale, showing that the liquid composition at  $1350^\circ\text{C}$  in equilibrium with pure anorthite crystals is 53% component An, 47% component Di. The composition of the solid phase is given by the other end of the line, which is at 100% An. In each of these two-phase regions, such as An + L,  $f = 1$ , which means that once we have chosen the temperature, say  $1350^\circ\text{C}$ , all

properties of all phases are fixed. Therefore, all proportions of Di and An in this region will have the same liquid and solid compositions. In other words, *any* starting mixture of diopside and anorthite crystals having more than 53% anorthite would, when heated to 1350 °C, consist of a liquid of composition 53% An, 47% Di, plus crystals of pure anorthite. Mixtures having between about 20% An and 53% An would be completely liquid at this temperature, and mixtures having 0 to 20% An would consist of pure diopside crystals plus a liquid of composition 20% An, 80% Di.

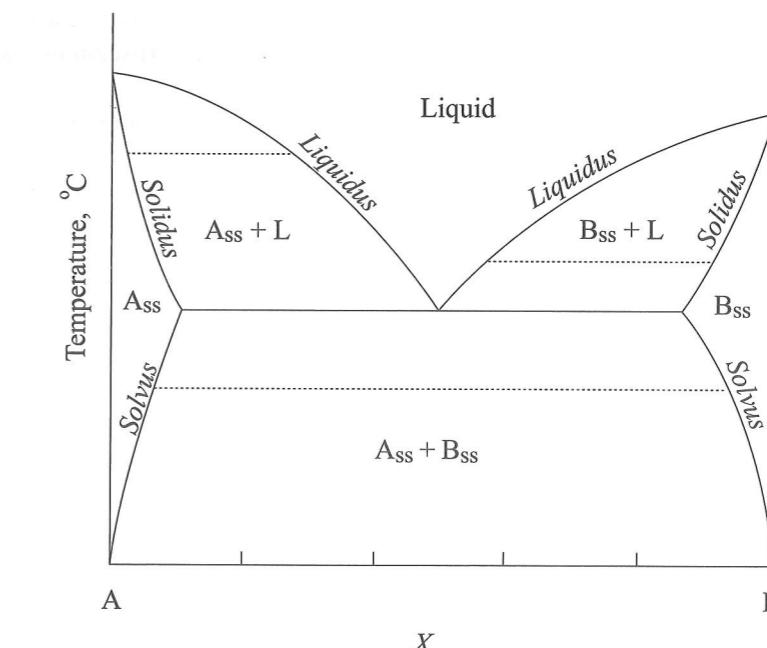
By imagining tie-lines across the An + L region at successively higher temperatures, we see that the composition of the liquid in equilibrium with anorthite crystals gets progressively richer in component An. Similarly, the tie-lines in the Di + L region show that the liquid gets richer in Di as the temperature increases.

Because the temperature of the three-phase tie-line is fixed, it follows that both above and below this temperature there must be regions having only two phases. We already know that below the three-phase line the two phases are Di and An. Above the three-phase line one of the phases must be liquid, because melting has started. Therefore, the liquid can coexist with only one other phase, obviously in this case either Di or An, but not both. As  $T$  increases, the proportion of liquid must increase, eventually becoming 100% liquid. This simple analysis is sufficient to explain the main features of the diagram. "Reading" binary diagrams consists largely of distinguishing between one phase regions, which have no tie-lines (e.g., the "Liquid" region), two-phase regions, which have tie-lines joining two phases at equilibrium, and three-phase tie-lines, which separate two-phase regions, and join three phases at equilibrium.

#### 12.4.4 A More General Example

The system Di–An is misleadingly simple in two respects. For one thing, the diagram shows that both diopside and anorthite remain pure while heated in contact with the other component until the melting temperature is reached (1392 °C for Di, 1553 °C for An). Actually, phases (in theory) never remain perfectly pure when in contact with other phases – some mutual solution always takes place, although as in the case of Di and An it is sometimes small and does not show on the diagram. A more realistic case is shown in Figure 12.12. The diagram is essentially the same as the Di–An diagram, except that there is a field of  $A_{ss}$  and of  $B_{ss}$ , where the subscript ss stands for solid solution.

The other respect in which the Di–An diagram is misleading is that, in fact, it is not strictly speaking a true binary system. This somewhat surprising statement cannot be fully explained without discussing ternary systems. Suffice it to say that just because you choose two components does not necessarily mean that you have a binary system. *To be truly binary, all compositions of all phases must lie on the plane of the diagram.* This must be the case in simple systems such as Cu–Au and with single solution phases such as liquids; but with complex components such as Di and An, although the *bulk composition* must lie on the plane of the diagram, the compositions of coexisting *phases* may each lie "off the plane" of the diagram. Careful work has shown that, in the system Di–An, diopside crystals are not pure but contain some Al. This means that, because bulk compositions lie on the Di–An plane, phases coexisting with diopside must be somewhat deficient in Al. To portray



**Figure 12.12** A more representative binary system. The difference is that both components show solid solution fields. Three representative two-phase tie-lines are shown.

this in a diagram, one needs a three-component triangle. Just remember that not all choices of two components are binary systems – some are planes within ternary systems.

#### Solid Solutions

There is no difference in principle between a solid solution and a liquid or gaseous solution. Substances dissolve into one another, like sugar into tea, or like oxygen into nitrogen, because the Gibbs energy change of such a process is negative – they are spontaneous processes. Consider the system Di–An at a temperature of 1600 °C (Figure 12.11). At this temperature, both pure Di and pure An are liquid phases. If one gram of Di liquid and one gram of An liquid were mixed together, they would dissolve into one another to form a homogeneous liquid solution, represented by a point in the middle of the diagram on the 1600 °C isotherm. If pure diopside crystals are mixed with pure anorthite crystals at 1200 °C, on the other hand, nothing happens – they do not dissolve into each other.

Components A and B in Figure 12.12, on the other hand, behave differently. Liquid A and liquid B still mix to form a homogeneous solution, but when solid A and solid B are mixed together, they dissolve into one another to a limited extent. Salt will dissolve into water, but not without limit – it will dissolve only until the water becomes saturated. Similarly, solid B will dissolve into solid A, but not without limit. It dissolves into A until A is saturated with B, and at the same time A dissolves into B until B is saturated with A. The saturation limit of each component in the other is shown by a line called the *solvus*. The existence of a solvus shows that A and B exhibit *limited miscibility* in the solid state. They exhibit *complete miscibility* in the liquid state. "Miscibility" does not really mean

"mixability," although they sound similar. "Mixability," if it is a word, just means that things can be mixed together – mutual dissolution is not implied. "Miscibility" means the ability to dissolve into something else.

Figure 12.12 shows a eutectic, but the two solid phases in equilibrium with the liquid are not pure A and pure B; A contains some B in solid solution ( $A_{ss}$ ) and B contains some A in solid solution ( $B_{ss}$ ). Similarly, at temperatures above the eutectic, the liquid is not in equilibrium with pure A or pure B, but with  $A_{ss}$  and  $B_{ss}$ . The compositions of the solid solutions in equilibrium with liquid are given by lines called the *solidus*.

#### 12.4.5 Freezing Point Depression

Figure 12.11 shows that mixtures of diopside and anorthite become completely liquid at temperatures lower than the melting temperature of either pure diopside or pure anorthite. This is also shown by the more general system in Figure 12.12 and is, in fact, an extremely common feature of binary systems. It is called *freezing (or melting) point depression* and is, in fact, why we put salt on icy roads in winter. The melting temperature of ice is lowered in the presence of the second component (salt, NaCl), so the ice melts and the resulting salty water corrodes our cars. But why is the freezing point depressed?

The answer is found in the basic thermodynamic relationships between the phases. Figure 12.4 shows the absolute Gibbs energies of the solid, liquid, and vapor phases of our compound  $\alpha$  as a function of temperature at a pressure of 2 mbar. Let's call compound  $\alpha$  component A (just as we called component  $\text{CaMgSi}_2\text{O}_6$  Di). Figure 12.4 therefore shows  $G_A^{\text{solid}}$ ,  $G_A^{\text{liquid}}$ , and  $G_A^{\text{vapor}}$  as functions of  $T$ . If we now add a second component B to A, what happens to these Gibbs energies? To start with the simplest case, we will suppose that B does not dissolve into solid A or into vapor A, but does dissolve into liquid A (if you add NaCl to  $\text{H}_2\text{O}$ , the salt will not dissolve into ice or into steam, but it will dissolve into liquid water). Therefore, the curves for  $G_A^{\text{solid}}$  and  $G_A^{\text{vapor}}$  will not change, because  $A^{\text{solid}}$  and  $A^{\text{vapor}}$  are unchanged in the presence of B. But what is the Gibbs energy of component A in a liquid containing both A and B?

The answer is shown in Figure 7.4, which shows that, when B dissolves into A, the molar Gibbs energy of component A in the solution at a given concentration (which we call  $\mu_A$ ), is *lower* than the molar Gibbs energy of pure A ( $G_A^\circ$ ). This relationship is quite general and without exception, because otherwise A and B would not form a solution. We will be mentioning this relationship at various points throughout this chapter. The consequence of the fact that  $G_A^{\text{liquid}}$  is lowered but  $G_A^{\text{solid}}$  is not is shown in Figure 12.13. The shaded surface in this figure represents the free energy curve from Figure 7.4, extended into a range of temperatures. It shows the lowering of the total Gibbs energy of the liquid phase as component B is added. At the arbitrary amount of 10% B, a tangent surface to the free energy surface extends back to the 0% B plane, which is analogous to the tangent at  $X_B = 0.4$  in Figure 7.4. The trace of this tangent surface on the  $G-T$  section for component A gives  $\mu_A$ , the molar Gibbs energy of A in the solution containing 10% B, 90% A. It of course lies below the curve of  $G_A^{\text{liquid}}$  for pure A. But because the curve for  $G_A^{\text{solid}}$  has not moved, the intersection of the  $G_A^{\text{solid}}$  and  $\mu_A^{\text{liquid}}$  curves is moved to a lower temperature. The intersection of the  $\mu_A^{\text{liquid}}$  and  $G_A^{\text{solid}}$  curves is the point where these two quantities are equal, and it defines the temperature at which A in the solid state and A in the liquid state

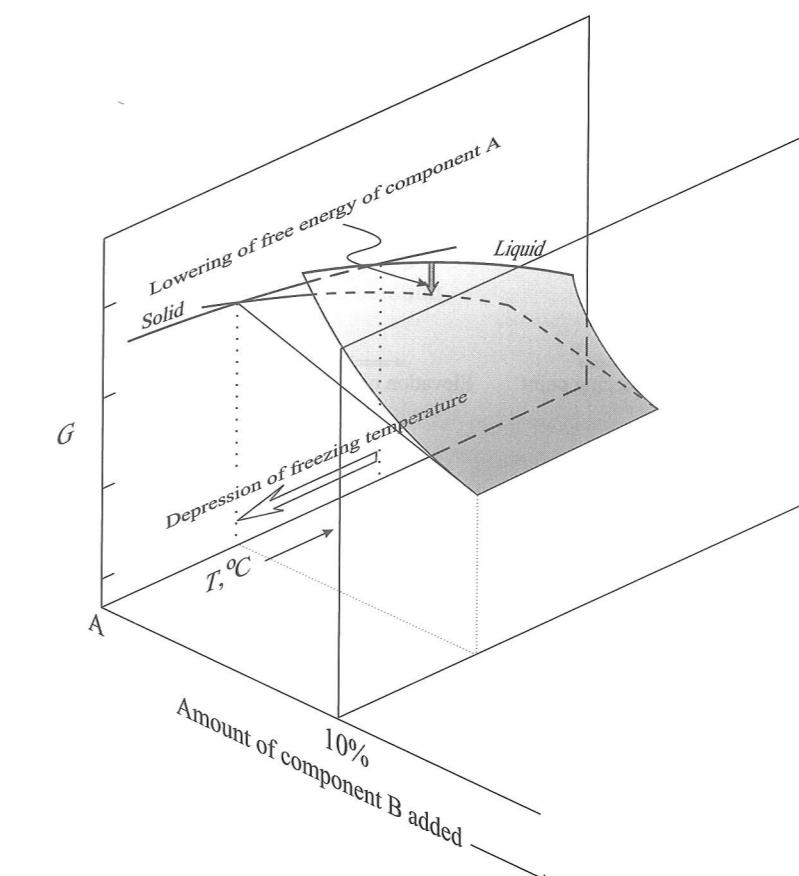


Figure 12.13 The  $G-T$  plane is taken from Figure 12.14. Component B enters the liquid phase and causes a lowering of  $\mu_A^{\text{liquid}}$ , which in turn causes a depression of the freezing temperature.

are in equilibrium. For pure A, this is the melting or freezing temperature; for the system A–B, it defines a point on the liquidus of A and is the result of freezing point depression.

This relationship is shown again in Figure 12.14, this time including the vapor curve. If the vapor curve does not move (no B dissolves into vapor A), depression of  $G_A^{\text{liquid}}$  results in a raising of the boiling temperature as well as a lowering of the freezing temperature. This is also an extremely common effect.

#### 12.4.6 Freezing Point Elevation

But suppose our simplifying assumption that no B enters the solid phase is not true? There is no difference in principle between the thermodynamics of solid and liquid solutions, so if B dissolves into solid A the curve for  $G_A^{\text{solid}}$  will be lowered for the reasons just discussed. Normally, B is less soluble in solid A than in liquid A, so the amount of lowering is less for the solid phase, and the freezing point is still lowered. This is shown by systems like that in Figure 12.12, where the liquidus of A slopes downward, even though B is shown as entering both the liquid and the solid phases of A.

"mixability," although they sound similar, "Mixability," if it is a word, just means that things can be mixed together – mutual dissolution is not implied. "Miscibility" means the ability to dissolve into something else.

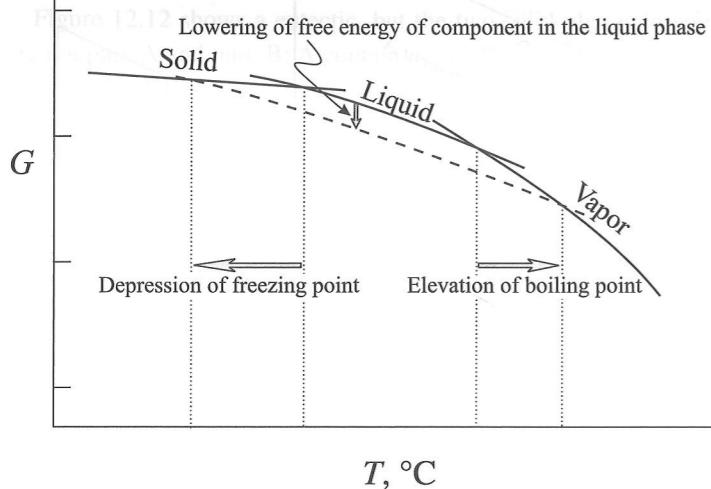


Figure 12.14  $G$ - $T$  section, showing lowering of the Gibbs energy of A in the liquid phase, causing depression of the freezing point and elevation of the boiling point.

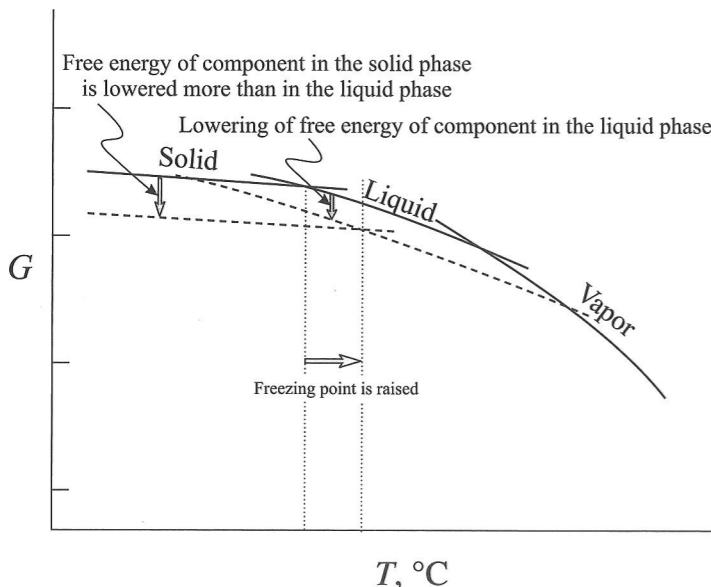


Figure 12.15  $G$ - $T$  section, showing a greater lowering of the solid Gibbs energy than liquid Gibbs energy, causing elevation of the freezing point.

However, what of the possibility that the  $G_A^{\text{solid}}$  curve might be lowered *more* than the  $G_A^{\text{liquid}}$  curve? This would happen if more B dissolved into solid A than into liquid A and would result in a *freezing point elevation* as shown in Figure 12.15. This explains an important feature of many binary systems.

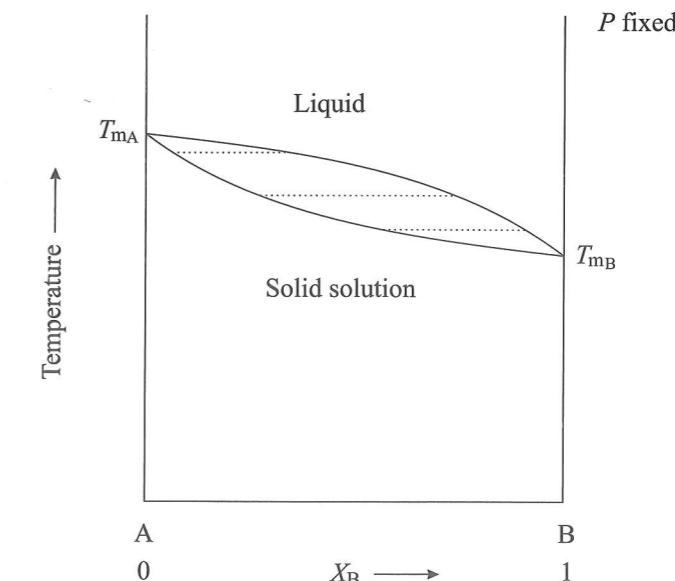


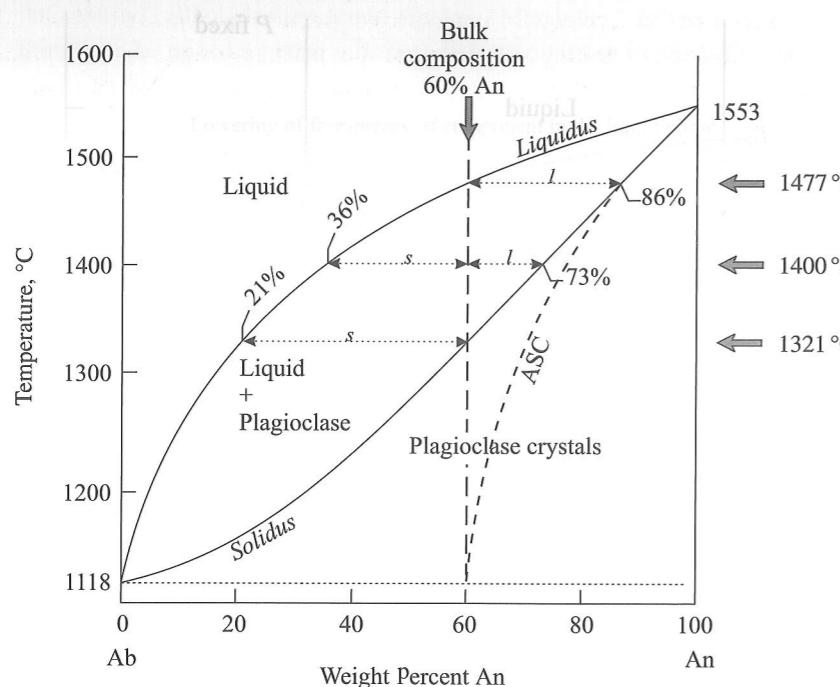
Figure 12.16 A binary system A-B showing complete miscibility both in the solid state and in the liquid state. Three representative tie-lines are shown.

#### 12.4.7 Systems Having Complete Solid Miscibility

A and B in Figure 12.12 show limited solid miscibility, but some important systems show *complete* miscibility in the solid state, giving rise to a diagram that looks quite different, as shown in Figure 12.16. In a sense, it is simpler than the ones we have looked at so far – in fact it looks rather like Figure 12.10, except that the “melting line” in Figure 12.10 is a *melting loop* in Figure 12.16. But the most important difference is that in Figure 12.16 A and B *dissolve completely into one another in the solid state*. This takes some getting used to. We are quite familiar with sugar dissolving into tea, but the idea of placing two solid objects together and observing one disappear into the other is not something in our experience. But this is just another example of something that thermodynamics says *should* happen but in fact does not, because of energy barriers. The thermodynamic model does not consider these barriers, and hence does not always work. These solid solutions do exist, however, because they do not form from solids dissolving into one another at low temperatures. They form at high temperatures, sometimes over long periods of time, and then cool down in their mutually dissolved state. Many important alloys and mineral groups are such complete solid solutions, including the feldspars, olivines, and some pyroxenes and amphiboles.

Note that, in Figure 12.16,  $T_{m_A}$  is lowered by adding B, but  $T_{m_B}$  is raised by adding A. This is because more B enters liquid A than solid A, but more A enters solid B than liquid B, and the free energy consequences of this are shown in Figures 12.14 and 12.15, respectively.

The most important mineralogical example of this type of system is the plagioclase feldspar system, which is shown in Figure 12.17. Plagioclase is a mineral whose



**Figure 12.17** The plagioclase–feldspar system at 1 bar pressure. The curve labeled ASC is the average solid composition during fractional crystallization of the 60% An bulk composition.

composition may vary from virtually pure albite ( $\text{NaAlSi}_3\text{O}_8$ ), or component Ab, to almost pure anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), or component An, depending on the composition of the liquid from which it crystallizes. The melting behavior of a complete solid solution such as this is a simple melting loop – a combined liquidus and solidus that goes from one pure component over to the other. The melting loop is filled with imaginary horizontal tie-lines, three of which are shown in Figure 12.17. They indicate the compositions of liquids, on the liquidus, and the compositions of plagioclase crystals, on the solidus, which are in equilibrium with each other.

#### 12.4.8 Equilibrium vs. Fractional Cooling and Heating

Binary phase diagrams show phase compositions that are at equilibrium – they show what you would obtain if you heated a bulk composition to a certain temperature and waited long enough for equilibrium to be attained. The time required to reach equilibrium after a change in temperature or pressure varies greatly with the system, but equilibrium is *never* achieved instantaneously. Therefore, if we use the diagram to consider what would happen during continuous cooling or heating of a given bulk composition, we cannot be considering what would *really* happen in our system during cooling or heating but are considering *model* processes, as usual.

There are any number of models of processes we could devise involving phase changes in binary systems, but two are especially common – complete equilibrium (reversible)

processes, and “surface equilibrium” (perfect fractional) processes. We will discuss only cooling processes. Heating processes are the exact reverse of cooling processes in the equilibrium case, but they are not always the exact reverse in the case of fractional processes.

#### Perfect Equilibrium Crystallization

Suppose we had a liquid having a composition of 60% An, 40% Ab at a temperature of about 1600 °C (Figure 12.17). On cooling this liquid, nothing much happens (except that the properties of the liquid, such as its density, refractive index, entropy, Gibbs energy, etc., etc., change) until it reaches a temperature of 1477 °C, the liquidus temperature for this composition. At this point, the bulk composition is still 100% liquid, but the first tiny crystal of plagioclase appears. Its composition, given by the solidus, is 86% An, 14% Ab. As cooling continues, plagioclase crystals continue to form, and previously formed crystals change their composition so that all crystals always have the equilibrium composition, with no compositional gradients. When the temperature reaches 1400 °C, the liquid has composition 36% An, and the crystals 73% An. (These compositions are obtained by dropping a perpendicular line from the point of interest to the compositional axis at the bottom of the diagram.) When the composition of the solids reaches the bulk composition of 60% An, the liquid must disappear, and this happens at a temperature of 1321 °C. Further cooling results in no further changes in composition of the crystals.

#### Perfect Fractional Crystallization

Maintaining perfect equilibrium while cooling is one end of a complete spectrum of possibilities. The other end of the spectrum is that crystals form, but always completely out of equilibrium. This end of the spectrum involves an infinite number of cases and so is rather difficult to discuss in a finite number of words. A subset of these possibilities is the case where crystallization produces crystals in equilibrium with the liquid, as required by the diagram, but, after forming, they do not react with the liquid in any way. This is called surface equilibrium (because the liquid is at all times in equilibrium with the surface of the crystals) or fractional crystallization, and is a model process just as much as is equilibrium crystallization. It is also used in connection with liquid–vapor processes (fractional distillation; fractional condensation), as well as isotope fractionation processes.

There are two ways of imagining a process of perfect fractional crystallization.

- As soon as a tiny crystal forms, it is removed from the liquid. This might be by reaching into the liquid with a pair of tweezers and physically removing the crystal, or the crystal might immediately sink to the bottom or float to the top of the liquid, where it becomes covered by other crystals and is removed from contact with the liquid.
- As soon as a tiny crystal with a composition given by the solidus forms, it is covered by a layer of another composition, given by the solidus at a slightly lower temperature. Successive layers are formed, each controlled by the position of the solidus, but, after forming, the various layers do not homogenize in the slightest. The result is a compositionally zoned crystal.

Note that crystals are removed from contact with the liquid in both cases. This is the essential element of fractional crystallization.

Considering the same bulk composition, 60% An, the cooling history is the same as before until the first tiny crystal forms at 1477 °C, having a composition of 86% An. On further cooling, the liquid composition follows the liquidus, as before, and any new crystals that form have compositions given by the solidus at that temperature; but previously formed crystals, being removed from contact with the liquid, do not change their original compositions. The net result is that at any temperature below 1477 °C, the average composition of all solids formed is more An-rich than would be the case in equilibrium crystallization, that is, more An-rich than the solidus at that temperature. Because of this, at each temperature below 1477 °C, there must be a larger proportion of liquid of Ab-rich composition to balance the solid composition, that is, to give the known bulk composition. Therefore, whereas in equilibrium crystallization the last drop of liquid must disappear at 1321 °C, in fractional crystallization it does not, and in fact liquids continue to exist right down to pure Ab composition, where the last liquid crystallizes as pure albite. This is the important aspect of fractional crystallization from a petrological point of view – that a given bulk composition can generate a much wider range of liquid compositions, and hence a wider range of igneous rocks, than can equilibrium crystallization.

It is possible to calculate the average composition of the solids during fractional crystallization, but we will not do this. Just note that a curve indicating the average composition of all solids generated must begin at 1477 °C on the solidus, and it must end at 1118 °C at a bulk composition of 60% An, when the last liquid disappears. This curve is shown in Figure 12.17, labeled “ASC.” For equilibrium cooling, the “ASC” curve is, of course, the same as the solidus.

#### 12.4.9 The Lever Rule and Mass Balances

Phase diagrams contain information not only about phase compositions and their temperatures and pressures, but about the *proportions* of phases for a given bulk composition. This is done using what is called the lever rule. Look at the three tie-lines we have just been discussing in Figure 12.17. Consider first the line extending from the liquidus (36% An) to the solidus (73% An), at 1400 °C. This line is composed of two parts. One part, labeled *l*, represents the proportion of liquid, and the other part, labeled *s*, represents the proportion of solids. The fraction (by weight) of liquid in the bulk composition is thus  $l/(l + s)$ , and the fraction of solids is  $s/(l + s)$ . The easiest way to measure the lengths of *l* and *s* is probably by comparing the compositions of the end points of the tie-line at the liquidus and solidus with the bulk composition. Thus the *s* portion of the tie-line has a length of  $60 - 36 = 24\%$ , and the *l* portion of the tie-line has a length of  $73 - 60 = 13\%$ . The total length of the tie-line is  $73 - 36 = 37\%$ . Therefore the proportion or fraction of solid in the total bulk composition is  $24/37 = 0.65$ , and the fraction of liquid is  $13/37 = 0.35$ , and of course  $0.65 + 0.35 = 1.0$ . If we had a bulk composition weighing 10 g, then at 1400 °C, 1 bar, it would be made up of  $0.65 \times 10 = 6.5$  g of crystals (73% An composition), and  $0.35 \times 10 = 3.5$  g of liquid (composition 36% An). This lever rule can be used in any two-phase region, given the bulk composition, and the lengths of the lines can be