

Chapter 11

Interpretation of Phase Diagrams

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The subject of phase equilibria and phase diagrams is one of the cornerstones of solid state chemistry. Phase diagrams are plots of temperature (occasionally pressure) against composition. They summarize in graphical form the ranges of temperature and composition over which certain phases or mixtures of phases exist under conditions of thermodynamic equilibrium. Thus the effect of temperature on solids and the reactions that may or may not occur between solids may often be deduced from the appropriate phase diagram. This chapter is concerned primarily with the interpretation of phase diagrams. Thermodynamic background is largely excluded and only a brief outline is given of the methods that are used to determine phase diagrams. Instead, the approach used is to emphasize the interpretation and practical applications of phase diagrams.

The fundamental rule on which phase diagrams are based is the *phase rule*, derived by W. J. Gibbs. The phase rule applies strictly only to conditions of thermodynamic equilibrium but in practice it also has great value in some non-equilibrium situations. The phase rule itself will not be derived but is presented and used as an empirical statement. One big difference from the treatment given

here to that found in many physical chemistry textbooks is that here the solid state is given primary importance whereas in most textbooks attention is focused on the gaseous and liquid states with rather cursory treatment of the solid state. Discussion of the vapour state has been largely omitted from this chapter. This leads to much simplification, and even to a simplified form of the phase rule itself. However, it does mean that certain topics such as the behaviour of systems containing variable valence metal atoms and decomposition reactions have been omitted.

11.1 Definitions

The phase rule is given by the equation

$$P + F = C + 2$$

where P is the number of phases present in equilibrium, C is the number of components needed to describe the system and F is the number of degrees of freedom or independent variables taken from temperature, pressure and composition of the phases present. Each of these terms is now explained more fully.

The number of *phases* is the number of physically distinct and mechanically separable (in principle) portions of a system, each phase being itself homogeneous. The distinction between different *crystalline* phases is usually clear. For example, the differences between chalk, $CaCO_3$, and sand, SiO_2 , are obvious. The distinction between crystalline phases made from the same components but of different composition is also usually clear. Thus, the magnesium silicate minerals enstatite, $MgSiO_3$, and forsterite, Mg_2SiO_4 , are different phases. They have very different composition, structures and properties. With solids it is also possible to get different crystalline phases having the *same* chemical composition. This is known as *polymorphism*. For example, two polymorphs of Ca_2SiO_4 can be prepared at room temperature, the stable γ form and the metastable β form, but these have quite distinct physical and chemical properties and crystal structures (see Chapter 19).

One complicating factor in classifying solid phases is the occurrence of solid solutions (Chapter 10). For example, $\alpha - Al_2O_3$ and Cr_2O_3 have the same crystal structure (corundum) and form a continuous range of solid solutions at high temperature. Any mixture of Al_2O_3 and Cr_2O_3 can react at high temperature to form a single, homogeneous phase whose composition may be altered without changing the integrity or homogeneity of the single phase.

In recent years, with advances in our knowledge of defects in crystals, especially extended defects such as the crystallographic shear structures (Chapter 9), it has become difficult in certain cases to decide exactly what constitutes a separate phase. This is because a minute change in composition can lead to a different arrangement of defects in a structure. In the oxygen-deficient tungsten oxides, WO_{3-x} , what was previously thought to be a range of homogeneous solid solutions is now known to be a large number of phases that

are very close in composition and similar, but distinct, in structure. Some of these phases have formulae belonging to the homologous series W_nO_{3n-1} . Thus $W_{20}O_{59}$ and $W_{19}O_{56}$ are physically distinct phases (Chapter 9). Although these crystallographic shear structures are an interesting new area of solid state chemistry, their occurrence is so far restricted mainly to a small number of transition metal compounds; with by far the majority of solid compounds there is no problem in deciding exactly what constitutes a phase.

In the *liquid* state the number of possible, separate homogeneous phases that can exist is much more limited than in the solid state. This is because single phase liquid solutions form much more readily and over wider compositional ranges than do single phase solid solutions. Take the Na_2O-SiO_2 system for instance. In the liquid state at high temperatures, Na_2O and SiO_2 are completely miscible to give a single, liquid, sodium silicate phase. In the crystalline state, however, the number of phases is quite large. Crystalline sodium silicate phases form at five different compositions and at least one of these shows polymorphism.

In the *gaseous* state, the maximum number of possible phases appears always to be 1; there are no known cases of immiscibility between two gases, if the effects of gravity are ignored.

The number of *components* of a system is rather more difficult to visualize. It is the number of constituents of the system that can undergo independent variation in the different phases; alternatively, it is the *minimum* number of constituents needed in order to describe completely the compositions of the phases present in the particular system. This is best understood with the aid of examples:

- All of the crystalline calcium silicates can be considered to be built from CaO and SiO_2 in varying proportions. $CaO-SiO_2$ is therefore a two-component system even though there are three elements present, Ca, Si and O. Compositions between CaO and SiO_2 can be regarded as forming a binary (i.e. two-component) join in the ternary system Ca-Si-O (Fig. 11.1).
- The system MgO is a unary (one-component) system, at least up to the melting point $2700^\circ C$, because the composition of MgO is always fixed.
- The composition 'FeO' is part of the two-component system, iron-oxygen because wüstite is actually a non-stoichiometric, iron-deficient phase, $Fe_{1-x}O$, caused by having some Fe^{3+} present (Chapter 9). The bulk composition 'FeO' in fact contains a mixture of two phases at equilibrium: $Fe_{1-x}O$ and Fe metal.

The number of *degrees of freedom* of a system is the number of independently variable factors taken from temperature, pressure and composition of phases, i.e. it is the number of these variables that must be specified in order that the system be completely defined. Again, let us see some examples:

- A system that consists of boiling water, i.e. water and steam in equilibrium, does not have a composition variable since both water and steam contain molecules of the same fixed formula, H_2O . To define the system it is necessary

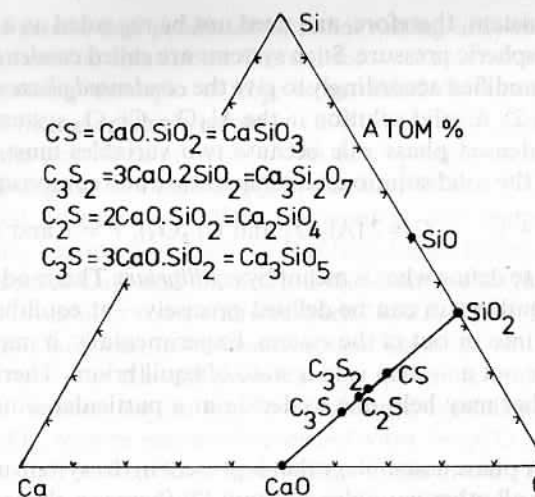


Fig. 11.1 Binary join $CaO-SiO_2$ in the ternary system Ca-Si-O. Note the method used for the labelling of phases, C = CaO , etc. This type of abbreviation is widely used in oxide chemistry

to specify only the steam pressure because then the temperature of boiling is automatically fixed (or vice versa). Application of the phase rule to this system gives:

$$P + F = C + 2; \quad C = 1 \text{ (i.e. } H_2O), P = 2 \text{ (vapour and liquid) and so } F = 1 \text{ (either temperature or pressure but not both).}$$

At sea level, water boils at $100^\circ C$ but at the high altitude of Mexico City atmospheric pressure is only 580 mm Hg and water in equilibrium with steam at this pressure boils at $92^\circ C$. The system water-steam is therefore *univariant* because only one degree of freedom, either P or T , is needed to describe completely the system at equilibrium. It should be emphasized that the relative amounts of water and steam are not given by the phase rule. As long as there is sufficient steam present to maintain the equilibrium pressure, the volume of vapour is unimportant.

- A solid solution in the system $Al_2O_3-Cr_2O_3$ has one composition variable because the $Al_2O_3:Cr_2O_3$ ratio can be varied and the same homogeneous phase obtained. Temperature can also be varied within the single phase solid solution field. In the temperature versus composition phase diagram of the $Al_2O_3-Cr_2O_3$ system the solid solutions occupy an area. Two degrees of freedom are therefore needed in order to characterize a certain solid solution composition and temperature (Fig. 10.6).

In refractory systems with very high melting temperatures, such as $Al_2O_3-Cr_2O_3$, the vapour pressure of the solid phases and even that of the liquid phase is negligible in comparison with atmospheric pressure. The vapour phase is

effectively non-existent, therefore, and need not be regarded as a possible phase for work at atmospheric pressure. Such systems are called *condensed systems* and the phase rule is modified accordingly to give the *condensed phase rule*, $P + F = C + 1$ (instead of $+ 2$). A solid solution in the $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system is *bivariant* in terms of the condensed phase rule because two variables must be specified in order to describe the solid solution, i.e. temperature and composition. Therefore,

$$P + F = C + 1; \quad C = 2 (\text{Al}_2\text{O}_3 \text{ and } \text{Cr}_2\text{O}_3), P = 1 \text{ and so } F = 2.$$

It is important to define what is meant by *equilibrium*. Thermodynamically, the conditions for equilibrium can be defined precisely—at equilibrium, no useful energy may pass into or out of the system. Experimentally, it may be difficult to assess whether or not a system is in a state of equilibrium. There are, however, several criteria that may help one to decide in a particular situation:

(a) Is the phase or phase assemblage that is present in the system unchanged with time, keeping all other variables constant? If there is a change with time, we can definitely say that equilibrium has not been reached, but the converse is not necessarily true. Thus, lime and sand may coexist together indefinitely without reacting but we know from the CaO-SiO_2 phase diagram that they should react to give, at equilibrium, various calcium silicates, depending on the lime: sand ratio. Probably a more thought-provoking example is the thermodynamic instability of the human body in the presence of oxygen; fortunately for us, oxidation of the particular carbon compounds involved is kinetically very slow at room temperature!

Another example of kinetic stability but thermodynamic instability is the occurrence of diamond at room temperature and pressure. From the condensed phase rule, a one-component system, such as carbon, can contain either two phases in equilibrium at a single fixed temperature ($P = 2$, and so $F = 0$), or one phase coexisting over a range of temperatures ($P = 1$, $F = 1$). At ambient temperature and pressure, the equilibrium behaviour of carbon belongs to the second category with graphite as the equilibrium phase. At high pressures, the situation reverses and diamond is stable relative to graphite (Fig. 2.19). However, once diamond has been prepared at high pressures, the pressure can be released without danger of conversion to graphite occurring at measurable rates (and provided the temperature is $\lesssim 900^\circ\text{C}$).

There are countless other examples of phases or materials that coexist together only because reaction between them is kinetically slow. The phase rule tells us absolutely nothing about the kinetics of reaction, only the general direction in which reactions may proceed. Bearing in mind that the phase rule pertains only to equilibrium, there are no known examples of systems in which the phase rule is violated.

(b) For systems that react at observable rates, a useful guideline is to observe the approach to equilibrium from two different directions and see whether the products obtained are identical. For example, at a certain temperature, is the

same phase assemblage produced by either raising or lowering the temperature of the reaction mixture to this value?

An interesting example of this is provided by the crystalline phase Ca_3SiO_5 , which is unstable below $\sim 1250^\circ\text{C}$. Ca_3SiO_5 may be prepared by reacting lime and silica at 1300°C but not by reaction at 1100°C . Is this because the kinetics of reaction are too slow at 1100°C ? This question may be answered by taking Ca_3SiO_5 prepared at, for example, 1300°C and subsequently heating it at 1100°C . It is then found to decompose slowly to give a mixture of CaO and Ca_2SiO_4 . This result proves that Ca_3SiO_5 has a lower limit of stability somewhere between 1100 and 1300°C . Consequently, CaO and Ca_2SiO_4 can never react to form Ca_3SiO_5 at 1100°C .

(c) A related test is to use different starting materials and see whether the products of reaction are the same. For example, crystalline sodium silicates, e.g. $\text{Na}_2\text{Si}_2\text{O}_5$, may be prepared in several ways. Na_2CO_3 and SiO_2 in a 1:2 molar ratio can be heated at subsolidus temperatures (700 to 750°C) for several days to give $\text{Na}_2\text{Si}_2\text{O}_5$. Alternatively, aqueous solutions of a sodium salt and silica (usually as ethyl orthosilicate) may be mixed and dried to give a hydrated gelatinous mixture and fired at $\sim 700^\circ\text{C}$. A third pathway is to melt the starting materials, cool them rapidly to form a glass and crystallize the glass by heating for several hours at $\sim 700^\circ\text{C}$. Since all these methods yield $\text{Na}_2\text{Si}_2\text{O}_5$, it is likely to be a thermodynamically stable phase.

It is important to use different preparative methods where possible, as in the above example, because the processes of reacting together crystalline solids or of crystallizing glasses often occur in several stages (but different stages in the two methods) and the final approach to equilibrium may be slow.

The equilibrium state is always that which has the lowest free energy. It may be thought of as lying at the bottom of a free energy well (Fig. 11.2). The problem in determining whether equilibrium has been reached is that other free energy minima may exist but not be as deep as the equilibrium well. There may be a considerable energy barrier involved in moving from a *metastable* to the *stable* state and under many conditions this barrier may be prohibitively high. Such an example is the metastability of diamond relative to graphite at room tempera-

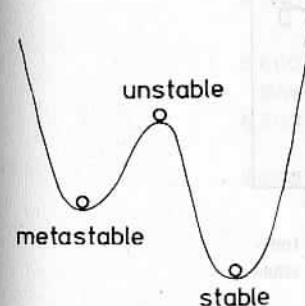


Fig. 11.2 Schematic diagram showing stable, unstable and metastable conditions

ture. The energy barrier or activation energy for the diamond \rightarrow graphite reaction is so high that, once formed, diamond is kinetically stable although thermodynamically metastable.

The thermodynamic meaning of the term *unstable* is shown in Fig. 11.2. If a ball is perched on a hill-top, the slightest movement is sufficient to cause it to start rolling down one side or the other. In the same way, there is no activation energy involved in changing from a thermodynamically unstable to either a stable or a metastable state. Examples of unstable equilibrium are difficult to find (because of their instability!) but one can point to their would-be occurrence. Inside a region of liquid immiscibility (see later and Chapter 18) exists an area bounded by a dome called a *spinodal*. Within the spinodal, a homogeneous liquid would be unstable and would spontaneously separate into two liquids by the process known as *spinodal decomposition*.

11.2 One-component systems

The independent variables in a one-component system are limited to temperature and pressure because the composition is fixed. From the phase rule, $P + F = C + 2 = 3$. The system is *bivariant* ($F = 2$) if one phase is present, *univariant* ($F = 1$) if two are present and *invariant* ($F = 0$) if three are present. Schematic phase relations are given in Fig. 11.3 for a one-component system in which the axes are the independent variables, pressure and temperature. Possible phases are two crystalline modifications or polymorphs (sometimes called allotropes), X and Y, liquid and vapour. Each of these phases occupies an area or *field* on the diagram when $F = 2$ (both pressure and temperature are needed to describe a point in one of these fields). Each single phase region is separated from the neighbouring single phase regions by univariant curves ($P = 2$ and so $F = 1$). Thus if one variable, say pressure, is fixed, then the other, temperature, is automatically fixed. The univariant curves on the diagram represent the following equilibria:

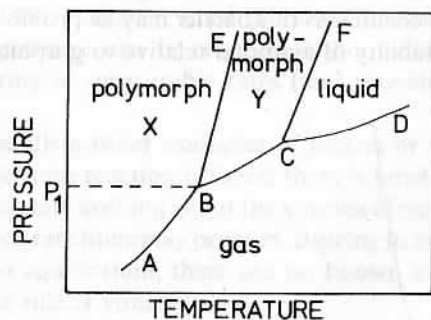


Fig. 11.3 Schematic pressure versus temperature phase diagram of a one-component system

- (a) BE—transition curve for polymorphs X and Y; it gives the change of transition temperature with pressure.
- (b) FC—change of melting point of polymorph Y with pressure.
- (c) AB, BC—sublimation curves for X and Y, respectively.
- (d) CD—vapour pressure curve for the liquid.

From Fig. 11.3, crystals of polymorph X can never melt directly under equilibrium conditions because the fields of X and liquid never meet on the diagram. On heating, crystals of X can either sublime at a pressure below p_1 or transform to polymorph Y at pressures above p_1 . They cannot melt directly. Also present in Fig. 11.3 are two invariant points B and C for which $P = 3$ and $F = 0$. The three phases that coexist at point B are: polymorph X, polymorph Y and vapour. Points B and C are also called *triple points*.

11.2.1 The system H_2O

This important system, shown in Fig. 11.4, gives examples of solid–solid and solid–liquid transitions. Ice I is the polymorph that is stable at atmospheric pressure; several high pressure polymorphs are also known—ice II to ice VI. At first sight, there is little similarity between the diagram for a schematic one-component system (Fig. 11.3) and that for water (Fig. 11.4), but this is mainly because of the location of the univariant curve XY that separates the fields of ice I and water. It is well known that ice I has the unusual property of being less dense than liquid water at 0°C . The effect of pressure on the ice I–water transition temperature can be understood from Le Chatelier's principle which states: 'When a constraint is applied to a system in equilibrium the system adjusts itself so as to nullify the effects of this constraint.' The melting of ice I is accompanied by a decrease in volume; increased pressure makes melting easier and so melting temperatures decrease with increased pressure, in the direction YX. The water system (Fig. 11.4) is also more complex than Fig. 11.3 since additional invariant points exist which correspond to three solid phases in equilibrium (e.g. point Z). The rest of the diagram should be self-explanatory; thus the curves Y X A B C give the variation of melting point with pressure for some of the different ice

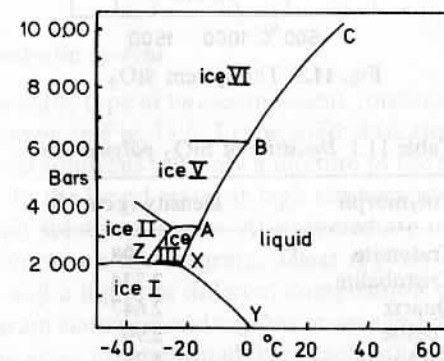
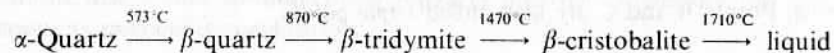


Fig. 11.4 The system H_2O

polymorphs. Liquid–vapour equilibria are omitted from Fig. 11.4 because, with the pressure scale used, these equilibria lie very close to the temperature axis and in the high temperature corner.

11.2.2 The system SiO₂

Silica is the main component of many ceramic materials as well as being the most common oxide, apart from H₂O, in the earth's crust. The polymorphism of SiO₂ is complex with major, first-order phase changes such as quartz–tridymite and minor changes such as α (low)– β (high) quartz. The polymorphism at atmospheric pressure can be summarized by the following sequence of reactions on heating:



With increasing pressure, two main changes are observed (Fig. 11.5); first, the contraction of the field of tridymite and its eventual disappearance, at ~ 900 atm; second, the disappearance of the field of cristobalite at ~ 1600 atm. Above 1600 atm, quartz is the only stable crystalline polymorph and exists up to much higher pressures. The disappearance of tridymite and cristobalite with increasing pressure can be correlated with the lesser density of these phases relative to that of quartz (Table 11.1); the effect of pressure generally is to produce polymorphs that have a higher density and therefore smaller volume. Above 20000 to 40000 atm (depending on temperature), quartz transforms to another polymorph, coesite,

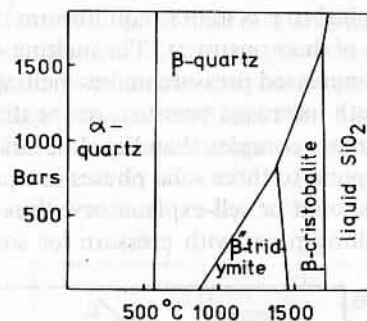


Fig. 11.5 The system SiO₂

Table 11.1 Densities of SiO₂ polymorphs

Polymorph	Density (g cm ⁻³)
Tridymite	2.298
Cristobalite	2.334
Quartz	2.647
Coesite	2.90
Stishovite	4.28

and above 90000 to 120000 atm yet another polymorph, stishovite, is the stable polymorph of SiO₂.

It should be noted that there are many metastable polymorphs of SiO₂ which are absent from Fig. 11.5; e.g. it is very easy to undercool cristobalite and to observe a reversible α (low)– β (high) transformation at $\sim 270^\circ\text{C}$. However, at these temperatures, cristobalite is metastable relative to quartz and so this transformation is omitted from Fig. 11.5.

11.2.3 Condensed one-component systems

For most systems and applications of interest in solid state chemistry, the condensed phase rule is applicable, pressure is not a variable and the vapour phase is not important. The phase diagram for a condensed, one-component system then reduces to a line since temperature is the only degree of freedom. It is not normal practice to represent such a line phase diagram in graphical form, unless it forms part of, say, a binary system. For instance, the condensed phase diagram at 1 atmosphere pressure for SiO₂ would simply be a line showing the polymorphic changes that occur with changing temperature. In such cases it is easier to represent the changes as a 'flow diagram', as indicated above for SiO₂.

11.3 Two-component condensed systems

Two-component or binary systems have three independent variables: pressure, temperature and composition. In most systems of interest in the general sphere of solid state chemistry, the vapour pressure remains low for large variations in temperature and so, for work at atmospheric pressure, the vapour phase and the pressure variable need not be considered. In almost all of what follows, the condensed phase rule $P + F = C + 1$ is used. In binary systems under these conditions an invariant point occurs when three phases coexist in equilibrium: a univariant curve for two phases and a bivariant condition for one phase. Conventionally, temperature is the vertical scale and composition the horizontal one in binary phase diagrams.

11.3.1 A simple eutectic system

The simplest possible type of two-component condensed system is the simple eutectic system shown in Fig. 11.6. In the solid state there are no intermediate compounds or solid solutions but only a mixture of the end-member crystalline phases, A and B. In the liquid state, at high temperatures, a complete range of single phase, liquid solutions occurs. At intermediate temperatures, regions of partial melting appear on the diagram. These regions contain a mixture of a crystalline phase and a liquid of different composition to the crystalline phase.

The phase diagram shows several regions or areas which contain either one or two phases. These areas are separated from each other by solid curves or lines. The area 'liquid' at high temperatures is single phase and bivariant. Every point

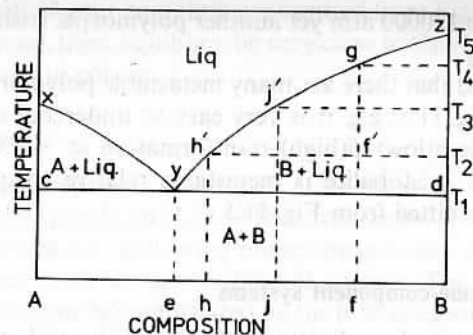


Fig. 11.6 Simple eutectic binary system

within this area represents a different state for the liquid, i.e. a different temperature and composition. In this region, $P = 1$ and $F = 2$. The other three areas shown in Fig. 11.6 contain two phases—A + B, A + liquid, B + liquid—and are univariant, since $P = 2$ and $F = 1$ in these areas. Consider the region B + liquid and let the mixture have overall composition f . Let temperature be the degree of freedom and fix this at T_2 . The compositions of the two coexisting phases, B and liquid, are then automatically fixed, although one would have to determine experimentally what their compositions were.

In order to determine the compositions of these two phases from the phase diagram, construction lines (dashed) are drawn. First, an *isotherm* is drawn at the temperature of interest, T_2 . This is the horizontal dashed line that terminates on the *liquidus* curve at point h' . This point, h' , represents the liquid that is present in the mixture of B + liquid at temperature T_2 . The composition of this liquid is given by drawing a vertical line or *isopleth* which intersects the composition (horizontal) axis at h , at which point the composition of the liquid may be simply read off the composition scale. The other phase that is present in the mixture is B, whose composition is fixed, as pure B, in this example.

An important distinction to be made here is between different meanings of the word 'composition'. It has at least three meanings:

- The composition of a particular phase. In the above example, the liquid phase has composition h .
- The relative amounts of the different phases present in a mixture. This may be referred to as the *phase composition*. In the above example, B and liquid are present in the ratio $\sim 3:2$ (see later for an explanation of the lever rule used to determine phase compositions).
- The overall composition of a mixture, in terms of the components and irrespective of the phases present. This may be termed the *component composition*. In the above example, the component composition of mixture f is $\sim 22\%$ A, 78% B.

Since there is no universally adopted convention over the use of the word 'composition', one can only say, be careful!

In the sense to which the phase rule is applied, composition may be regarded as a degree of freedom only when it refers to the actual compositions of the phases involved, category (a). The relative amounts of the different phases in a mixture, category (b), does not constitute a degree of freedom. Thus, along the isotherm, $h'f/T_2$, the relative amount of the phases B and liquid varies but the compositions of the two individual phases do not vary. The component composition, category (c), is included in the phase rule, not as a degree of freedom but as the number of components.

The liquidus curve, xyz , gives the highest temperature at which crystals can exist as a function of overall composition. Liquids whose compositions lie between A and e cross the liquidus curve between points x and y on cooling and enter the two-phase region: A + liquid. For these compositions A is the *primary phase* because it is the first phase to crystallize on cooling. The line cyd is the *solidus* and gives the lowest temperature at which liquids can exist in equilibrium over this composition range.

Point y is an invariant point at which three phases coexist: A, B and liquid. It is a *eutectic* and its temperature is the lowest temperature at which a composition (in this case e) can be completely liquid. Alternatively, it is the lowest temperature at which liquid may be present for any composition in this system. In simple eutectic systems such as this one, the solidus and eutectic temperatures are the same.

The melting or crystallization behaviour of different mixtures of A and B on heating or cooling can be understood by reference to Fig. 11.6. Consider composition f . It contains a mixture of A and B below temperature T_1 and is completely liquid above T_4 . Between T_1 and T_4 , varying amounts of crystalline B and liquid coexist. Thus at T_2 the liquid composition is at h' . The relative amounts of liquid h' and crystals B, in equilibrium, are given by the *lever rule*. These relative amounts are inversely proportional to their distances on the composition axis from the bulk composition f . The fraction of liquid present at T_2 is given by the ratio fB/Bh and the fraction of B by fh/Bh . The lever rule is the same as the principle of moments but instead of having weights balanced on a beam at different distances from the fulcrum we have different amounts of two phases giving an overall bulk or component composition. The lever rule may be derived by application of the principle of moments, as follows: For composition f at temperature T_2 , the phases present in equilibrium are B and liquid, h' . The relative amounts of B and liquid are given by:

$$(\text{Fractional amount of liquid, } h') \times (\text{distance } hf) = (\text{fractional amount of B}) \times (\text{distance } Bf)$$

i.e.

$$\frac{\text{Fractional amount of liquid, } h'}{\text{Fractional amount of B}} = \frac{\text{fractional amount of liquid, } h'}{1 - \text{fractional amount of liquid, } h'}$$

$$= \frac{Bf}{hf}$$

i.e.

$$\begin{aligned} \text{Fractional amount of liquid, } h' &= \frac{Bf}{Bf + fh} \\ &= \frac{Bf}{Bh} \end{aligned}$$

The lever rule may be used to determine how the relative amounts of phases in a mixture change, if at all, with temperature. Thus at temperature T_2 , the amount of liquid present in composition f is given by Bf/Bh , i.e. ~ 0.38 . At a higher temperature T_3 , the amount of liquid is given by Bf/Bj , i.e. ~ 0.5 . At a lower temperature, just above the solidus T_1 , the amount of liquid is given by Bf/Be , i.e. ~ 0.33 . Clearly, therefore, the effect of raising the temperature above T_1 is to cause an increase in the degree of melting from ~ 0.33 at T_1 to ~ 0.5 at T_3 . The limit is reached at T_4 where the fraction of liquid is 1 and melting is complete. As the degree of melting increases with increasing temperature, so the composition of the liquid phase must change accordingly: since crystals of B disappear into the liquid phase on melting, the liquid must become richer in B. Thus the first liquid that appears on heating, at temperature T_1 , has composition e , i.e. $\sim 33\%$ B, 67% A. As melting continues, the liquid follows the liquidus curve $yh'j'g$ until, when melting is complete at T_4 , the liquid has composition f , i.e. $\sim 78\%$ B, 22% A. On cooling the liquid of composition f , the reverse process should be observed under equilibrium conditions. At T_4 , crystals of B begin to form and with falling temperature the liquid composition moves from g to y as more crystals of B precipitate.

The *eutectic reaction* which occurs on cooling through temperature T_1 gives a good example of the use of the lever rule. Just above T_1 , the fraction of B present is given by fe/Be and is roughly 0.67. Just below T_1 the fraction of B is fA/BA and is roughly 0.78. Thus, the residual liquid, of composition e , has crystallized to a mixture of A and B, i.e. the quantity of B present has increased even further and crystals of A are formed for the first time.

A solid mixture of A and B of overall composition e undergoes complete melting at temperature T_1 and conversely, on cooling, a homogeneous liquid of this composition completely crystallizes to a mixture of A and B at T_1 .

The reactions described above are those that should occur under equilibrium conditions. This usually means that slow rates of heating and, especially, cooling are necessary. Rapid cooling rates often lead to different results, especially in systems which have more complicated phase diagrams. However, the equilibrium diagram can often be very useful in rationalizing these non-equilibrium results (see later).

The liquidus curve xyz may be regarded in various ways. As well as giving the maximum temperature at which crystals can exist, it is also a *saturation solubility curve*. Thus, curve yz could be regarded as giving the solubility limit with temperature for crystals of B dissolved in liquid. Above yz a homogeneous solution occurs but below this curve undissolved crystals of B are present. On cooling, precipitation of crystals B would therefore occur below the temperatures

of curve yz ; otherwise a metastable undercooled, supersaturated solution would be present.

Another interpretation of the liquidus is that it shows the effect of soluble impurities on the melting points of pure compounds. If a specimen of B is held at temperature T_4 and a small amount of A is added, then some liquid of composition g will form. As the amount of added A increases, so the amount of liquid g increases until, when sufficient *flux*, A, has been added to bring the overall composition to g , the solid phase disappears and the sample will be all liquid. Therefore a small amount of soluble impurity A has lowered the melting point of B from T_5 to T_4 . A familiar practical example of this is the addition of salt to icy roads. In the binary system $H_2O-NaCl$, addition of NaCl lowers the melting point of ice below $0^\circ C$; the system contains a low temperature eutectic at $\sim -21^\circ C$.

11.3.2 Binary systems with compounds

Three types of binary system with a compound AB are shown in Fig. 11.7. A stoichiometric binary compound such as AB is represented on the phase diagram by a vertical line. This shows the range of temperatures over which compound AB is stable. Compound AB melts congruently in (a) because it changes directly from solid AB to liquid of the same composition. Figure 11.7(a) may be conveniently divided into two parts, given by the composition ranges A-AB and AB-B; each part may be treated as a simple eutectic system in exactly the same manner as Fig. 11.6. Although the horizontal lines at T_1 and T_2 , corresponding to the two eutectic temperatures, meet the vertical line representing crystalline AB, no changes would be observed at T_1 and T_2 on heating pure AB. This is because these horizontal lines should peter out as composition AB is approached; composition AB, by itself, is a one-component system (but not in Fig. 11.7b and c) and only when another component, A or B, is added are changes observed at T_1 or T_2 .

In Fig. 11.7(b), compound AB melts *incongruently* at T_2 to give a mixture of crystals A and liquid of composition x . The relative amounts of liquid and

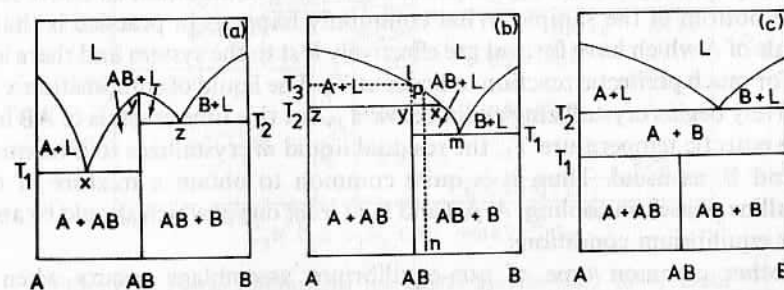


Fig. 11.7 Three types of diagram with a binary compound. AB melts congruently in (a), incongruently in (b) and has an upper limit of stability in (c).

L = liquid

crystals A just above T_2 are given by the lever rule; fraction liquid = yz/xz . On further heating, crystals of A gradually dissolve as the liquid becomes richer in A and moves along the liquidus curve in the direction xl . At T_3 , the liquid composition has reached l and the last A crystals should disappear. Point x is an invariant point at which three phases coexist: A, AB and liquid. It is a *peritectic* point because the composition of the liquid cannot be represented by positive quantities of the two coexisting solid phases, i.e. composition x does not lie between A and AB, as is the case for a eutectic point (Fig. 11.7a). A characteristic feature of a peritectic is that it is not a minimum point on the liquidus, as is a eutectic. Phase AB has a primary phase field. It is the first phase to crystallize on cooling liquids in the composition range $x-m$. However, the composition of AB is separated from its primary phase field. This is different to the case for congruently melting AB in Fig. 11.7(a), where the composition AB lies *within* the range xyz over which AB is the primary phase.

The behaviour of liquid of composition n on cooling is worth describing. At point p , crystals of A start to precipitate; more A crystals form as the temperature drops and the liquid composition moves from p to x . At T_2 , the *peritectic reaction* liquid (x) + A \rightarrow liquid (x) + AB occurs. Thus, the crystalline phase changes from A to AB and the amount of liquid present must diminish. From the lever rule, just above T_2 , the mixture is ~ 90 per cent liquid and just below T_2 only ~ 50 per cent liquid. Therefore, *all* of phase A has reacted with *some* of the liquid to give AB. On further cooling from T_2 to T_1 , more AB crystallizes as the liquid composition moves from x to m ; finally, at T_1 , the residual liquid of composition m crystallizes to a mixture of AB and B. Just above T_1 , the mixture is $\sim 30\%$ liquid and 70% AB and just below T_1 , $\sim 10\%$ B and 90% AB.

The behaviour on cooling of any liquid of composition between A and AB is similar but with one important difference. At T_2 , the peritectic reaction for these compositions involves *some* of A reacting with *all* the liquid to give AB. Below T_2 , a mixture of A and AB coexists and no further changes occur on cooling.

In systems that contain incongruently melting compounds, such as Fig. 11.7(b), it is very easy to get non-equilibrium products on cooling. This is because the peritectic reaction that should occur between A and liquid is slow, especially if the crystals of A are much more dense than the liquid and have settled to the bottom of the sample. What commonly happens in practice is that the crystals of A which have formed are effectively lost to the system and there is not time for much peritectic reaction to occur at T_2 . The liquid of composition x then effectively begins crystallizing again below T_2 , but this time crystals of AB form; at the eutectic temperature T_1 , the residual liquid m crystallizes to a mixture of AB and B, as usual. Thus, it is quite common to obtain a mixture of *three* crystalline phases on cooling: A, AB and B, at least one of which should be absent under equilibrium conditions.

Another common type of non-equilibrium assemblage occurs when the intermediate, incongruently melting compound AB fails completely to crystallize on cooling. If this happened on cooling liquids in Fig. 11.7(b), the crystalline products would be A and B with no AB. Hence the peritectic reaction $A + \text{liquid} \rightarrow AB$ has been suppressed entirely.

In some systems, the liquids may fail to crystallize at all on cooling rapidly. The resulting products are *glasses*. These are effectively supercooled liquids whose viscosity has increased to the extent that the material is rigid and has the mechanical properties of a solid rather than a liquid (Chapter 18).

The first two examples above show how phase diagrams can be applied to non-equilibrium situations. If the equilibrium phase diagram is known the occurrence of non-equilibrium effects may be understood and, in many cases, predicted. Glass formation cannot be predicted from the phase diagram although, in some cases, it is found that glass-forming compositions are in the vicinity of low melting eutectics.

Sometimes, compounds decompose before their melting point is reached, as shown for AB in Fig. 11.7(c). Compound AB has an *upper limit of stability* and at temperature T_1 disproportionates into a mixture of crystalline A and B; at higher temperatures the system is simple eutectic in character.

There are also many examples of systems which contain compounds with a *lower limit of stability*, i.e. below a certain temperature, compound AB decomposes into a mixture of A and B. The behaviour of AB at higher temperatures can then be any of the three types described above.

A phase diagram which contains most of the binary features discussed above and which is one of the most important diagrams in silicate technology is that of

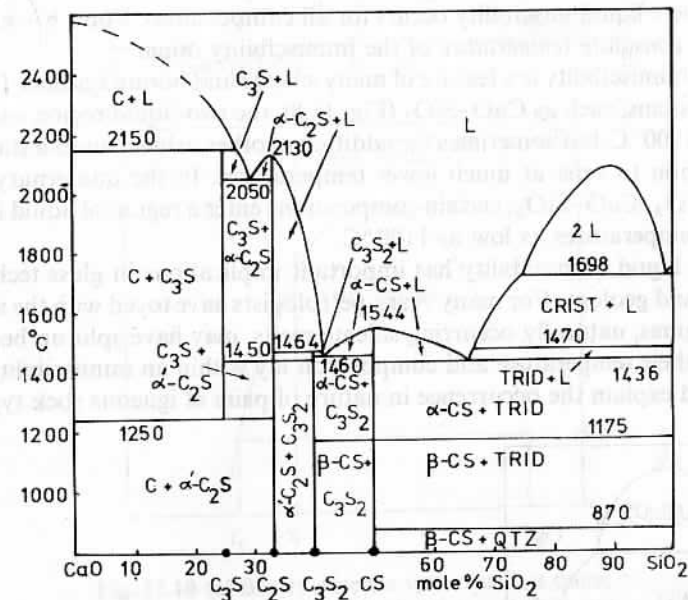


Fig. 11.8 Phase diagram for the binary system CaO-SiO₂. Data from B. Philips and A. Muan, *J. Am. Ceram. Soc.*, **42** 414 (1959) C = CaO, C₃S = Ca₃SiO₅, C₂S = Ca₂SiO₄, C₃S₂ = Ca₃Si₂O₇, CS = CaSiO₃, CRIST = cristobalite, TRID = tridymite, QTZ = quartz, L = liquid

the system CaO-SiO_2 , shown in Fig. 11.8. Two congruently melting compounds are present, $\text{C}_2\text{S}(\text{Ca}_2\text{SiO}_4)$, $\text{CS}(\text{CaSiO}_3)$, and two compounds that melt incongruently, $\text{C}_3\text{S}(\text{Ca}_3\text{SiO}_5)$ and $\text{C}_3\text{S}_2(\text{Ca}_3\text{Si}_2\text{O}_7)$. In addition, C_3S has a lower limit of stability and decomposes to CaO and C_2S below 1250°C . At the silica-rich end of the phase diagram, a range of liquid immiscibility exists between 1698 and $\sim 2100^\circ\text{C}$. Liquid immiscibility is discussed in more detail next.

11.3.3 Binary systems with immiscible liquids

In some systems, two liquid phases can coexist over a range of compositions and temperatures. This usually gives rise to an immiscibility dome, as shown by the area *abc* in Fig. 11.9. The dome has effectively made space for itself on the phase diagram by interrupting the liquidus curve of primary phase A. To see this, imagine the effect of shrinking the immiscibility dome; points *a* and *c* move closer together until, when they meet, the immiscibility dome has disappeared completely and the diagram has the appearance of a simple eutectic system (Fig. 11.6).

Point *a* is an invariant point because three phases are in equilibrium at this point: liquid *a*, liquid *c* and crystals A ($P = 3$, $C = 2$, and so $F = 0$). It is called a *monotectic*.

With increasing temperature, for compositions between *a* and *c*, the two liquids become progressively more soluble in each other until, above temperature T_4 , complete liquid miscibility occurs for all compositions. Point *b* is known as the *upper consolute temperature* of the immiscibility dome.

Liquid immiscibility is a feature of many silicate and borate systems. In binary silicate systems, such as CaO-SiO_2 (Fig. 11.8), the two-liquid region exists only above $\sim 1700^\circ\text{C}$, but sometimes the addition of other oxides causes a stable two-liquid region to exist at much lower temperatures. In the quaternary system $\text{K}_2\text{O-Al}_2\text{O}_3\text{-CaO-SiO}_2$, certain compositions enter a region of liquid immiscibility at temperatures as low as 1100°C .

Silicate liquid immiscibility has important implications in glass technology, ceramics and geology. For many years, petrologists have toyed with the idea that some magmas, naturally occurring silicate melts, may have split up because at one time their temperature and composition lay within an immiscibility dome. This could explain the occurrence in nature of pairs of igneous rock types, one

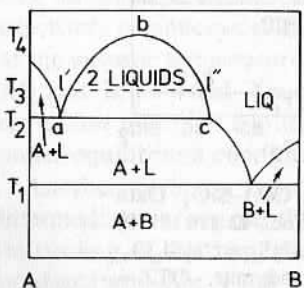


Fig. 11.9 Binary system with liquid immiscibility dome

rich in silica and the other much poorer in silica, with essentially no rocks of intermediate composition present. Irrefutable evidence that liquid immiscibility was the cause of such occurrences has not been found in earth rocks, but was found in lunar samples obtained in the Apollo II mission to the moon. It therefore seems quite likely that liquid immiscibility also played a role in the early history of the earth.

Liquid immiscibility is common in systems of importance as glasses and glass-ceramics. This is because both glass-forming compositions and the compositions over which immiscibility domes exist are usually located at the SiO_2 - rich end of phase diagrams. During the cooling of a liquid to form a glass (Chapter 18), many compositions enter a dome of liquid immiscibility and a process of liquid unmixing or *phase separation* occurs. Often, the immiscibility dome is not present on the equilibrium phase diagram, however, and is an entirely metastable immiscibility dome (Fig. 11.10b). In other cases, the top of the dome is an

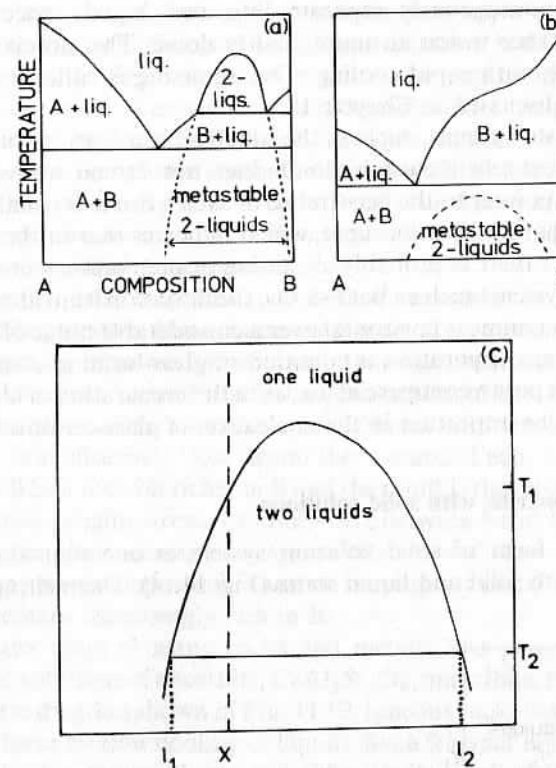


Fig. 11.10 (a) Binary eutectic system with a dome of liquid immiscibility; metastable extension of the stable immiscibility dome is shown by dashed curves. (b) An S-shaped liquidus curve which indicates the presence of a metastable immiscibility dome at lower temperatures. (c) A liquid immiscibility dome

equilibrium feature and is present on the phase diagram, as in Figs. 11.9 and 11.10(a).

The region of two liquids in Fig. 11.10(a) is terminated at its lower temperature end by the precipitation of crystals of B. What would happen if precipitation of B were a kinetically slow process? The two-liquid dome would then extend, metastably, to lower temperatures and in so doing it would probably expand to include a greater range of compositions. This extension is shown by the dashed lines. We therefore have two phase diagrams which are appropriate to different sets of experimental conditions. The equilibrium phase diagram (solid lines) is observed at slow rates of cooling. At faster cooling rates, the only feature to affect a liquid is the dome of liquid immiscibility, part of which is stable and part metastable. This is redrawn in Fig. 11.10(c). Composition x is a single phase liquid above the temperature T_1 , but below T_1 a mixture of two liquids occurs. At T_2 , these liquids have compositions l_1 and l_2 .

Although liquids may avoid crystallizing during cooling and give glasses instead, they spontaneously separate into two liquids once they get an appreciable distance inside an immiscibility dome. This unmixing cannot be suppressed, even with rapid cooling. The unmixing is called *spinodal decomposition* and is discussed in Chapter 18.

In other silicate systems, such as the alkali silicates, an immiscibility dome occurs that is entirely metastable and does not extend above the liquidus (Fig. 11.10b). A pointer to the occurrence of such a dome is usually given by an irregular or S-shaped liquidus curve, which indicates that in the stable melt at high temperature there is probably clustering or premonitory unmixing phenomena. In some systems such as BaO–SiO₂, the deviation from ideality is so great that the liquidus is almost horizontal over a considerable range of compositions. Unmixing or phase separation is common in glass-forming compositions and sometimes this is put to commercial use, as in the preparation of Vycor glass. It is also believed to be important in the nucleation of glass-ceramics (Chapter 18).

11.3.4 Binary systems with solid solutions

The simplest form of solid solution system is one that shows complete miscibility in both solid and liquid states (Fig. 11.11). The melting point of A is

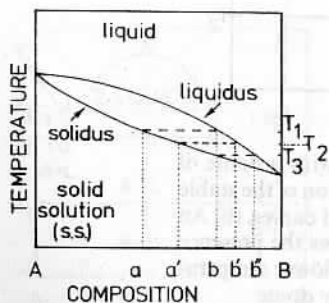


Fig. 11.11 Binary system with a complete range of solid solutions

depressed by the addition of B and that of B is increased by the addition of A. The liquidus and solidus are both smooth curves which meet only at the end-member compositions A and B. At low temperatures, a single phase solid solution exists and is bivariant ($C = 2$, $P = 1$, and so $F = 2$). At high temperatures, a single phase liquid solution exists and is similarly bivariant. At intermediate temperatures, a two-phase region of solid solution + liquid exists. Within this two-phase region, the compositions of the two phases in equilibrium are found by drawing isotherms or *tie-lines* at the temperature of interest, e.g. T_1 . The intersection of the tie-line and the solidus gives the composition of the solid solution, a , and the intersection of the tie-line and the liquidus gives the liquid composition, b .

On cooling liquids in a system such as this, the crystallization pathways are complicated. A liquid of bulk composition b begins to crystallize a solid solution of composition a at temperature T_1 . At a lower temperature, T_2 , and at equilibrium, the amount of solid solution present increases but also its composition changes to a' . The fraction of solid solution a' is given by the lever rule and is equal to $bb'/a'b'$, i.e. the equilibrium mixture is approximately one-third solid solution and two-thirds liquid at T_2 . Crystallization is therefore a complex process because with decreasing temperature, the composition of the solid solution has to change continuously in order to maintain equilibrium. With falling temperature, both crystals and liquid become progressively richer in B but the quantities of the two phases change in accord with the lever rule; the overall composition must obviously always be b . Finally, at temperature T_3 , the solid solution composition reaches the bulk composition b and the last remaining liquid, of composition b'' , disappears.

In systems with phase diagrams such as this, metastable or non-equilibrium products are often produced by a process of *fractional crystallization*. This occurs unless cooling takes place very slowly such that equilibrium is reached at each temperature. The crystals that form first on cooling liquid b have composition a . If these crystals do not have time to re-equilibrate with the liquid on further cooling they are effectively lost from the system. Each new crystal that precipitates will be a little bit richer in B and the result is that crystals form which have composition ranging from a to somewhere between b and B. In practice, the crystals that precipitate during cooling are often 'cored'. The central part that formed first may have composition a and on moving out radially from the centre the crystal becomes increasingly rich in B.

Coring occurs often in many rocks and metals. The plagioclase feldspars, which are solid solutions of anorthite, CaAl₂Si₂O₈, and albite, NaAlSi₃O₈, have the simple phase diagram shown in Fig. 11.12. Igneous rocks contain plagioclase feldspars and form by slow cooling of liquids. Such feldspar liquids and crystals are notoriously slow to equilibrate and although the cooling of melts in nature may have been very slow, it is common nevertheless to find rocks in which fractional crystallization has occurred. In these, the plagioclase crystals have calcium-rich centres and sodium-rich outer regions.

Coring may occur in metals during the manufacture of bars and ingots. The molten metal is poured into moulds (or 'sand cast' in moulds of sand) and allowed

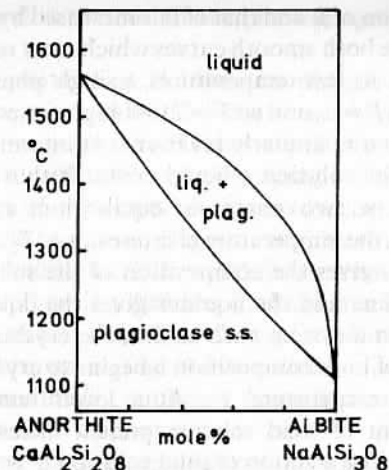


Fig. 11.12 The plagioclase feldspar system, anorthite-albite

to cool. If the metal composition is part of a solid solution then coring may occur. Coring is usually deleterious to the properties of the metal and has to be eliminated. This can be done by subsequently heating the bars to just below the solidus temperature at which homogenization of the metal, with the elimination of coring, occurs rapidly.

It has been noted that the equilibrium subsolidus assemblage is obtained if cooling rates are sufficiently slow, but that with somewhat faster cooling fractional crystallization may occur. This is a property of the phase diagram and can occur with any kind of material, whether it be rocks, metals, or synthetic inorganic or organic materials. At still faster cooling rates, other types of pathway may be followed. With both equilibrium and fractional crystallization, no undercooling or supersaturation of the liquid occurs and crystallization begins as soon as the temperature reaches that of the liquidus. With faster cooling rates, however, undercooling of the liquid is usually possible and this may lead to various products. It may be possible to go directly from a homogeneous liquid to homogeneous single phase crystals of the same composition in one step; e.g. if a liquid of composition 50 per cent albite, 50 per cent anorthite (Fig. 11.12) is cooled quickly to just below the solidus, 1200 to 1250°C, and held at this temperature, homogeneous plagioclase of the same composition may crystallize directly. Alternatively, if the liquid is cooled rapidly to room temperature, there may not be time for any crystallization to occur and a glass forms. Glass formation is common in inorganic materials such as silicates. Recently there has been much scientific and technological interest in glassy semiconductors and metals. These are materials that have unusual electrical and mechanical properties (see Chapters 14 and 18).

The simplest type of solid solution phase diagram is that shown in Fig. 11.11. Other relatively simple types of phase diagram are possible that show complete

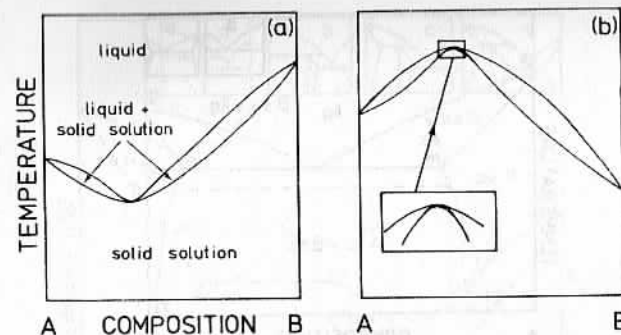


Fig. 11.13 Binary solid solutions with (a) thermal minima and (b) thermal maxima in the liquidus and solidus curves

solubility in both the solid and liquid states but have either a thermal minimum or a thermal maximum in the liquidus and solidus curves (Fig. 11.13). These thermal maxima and minima are called *indifferent points* because they are not true invariant points. For an invariant point, three phases are needed in equilibrium ($F = 0$, $P = C + 1 = 3$), but this condition can never exist in solid solution systems such as these because there are never more than two phases present, i.e. solid solution and liquid solution. The liquidus and solidus are therefore continuous through the thermal maximum or minimum and do not show a discontinuity such as is observed for peritectics and eutectics.

The melting points of congruently melting compounds in binary systems can similarly be regarded as indifferent points because only two phases are present in equilibrium. However, an alternative in these cases is to regard each congruently melting compound as a separate one-component system, in which case the melting point does become an invariant point ($P = 2$, and so $F = 0$). With thermal maxima and minima in solid solution series it is not usual to regard the composition of the solid solution which has the maximum or minimum as a special composition and which can be treated as a one-component system in its own right. This would be done only if this composition had a simple ratio of the components, e.g. 1:1, 1:2, etc., or there was other evidence that this composition was special, e.g. if ordering of the solid solutions occurred, giving evidence of a superstructure in the X-ray diffraction patterns.

Complete solid solubility, such as shown in Figs 11.11 to 11.13, occurs only when the cations or anions that are replacing each other are similar in size, e.g. Al^{3+} and Cr^{3+} . It is far more common to have phase diagrams in which the crystalline phases have only partial solubility in each other. The simplest possible case, shown in Fig. 11.14, is a straightforward extension of the simple eutectic system, shown in inset (a). Crystals of B dissolve in crystals of A to form a solid solution whose maximum extent depends on temperature and is given by the curves xmp . Just below the melting point of A, point p , A cannot form a solid solution (s.s.) with B but melts instead (and enters the region A s.s. + liquid). With falling temperature the range of A solid solution gradually grows; the extent of

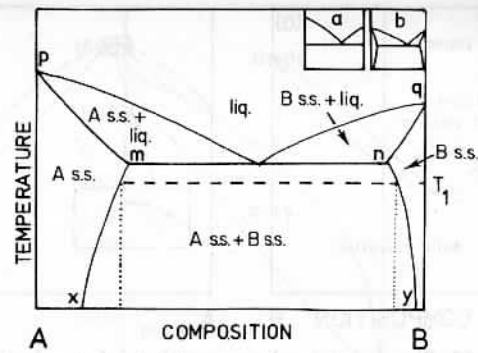


Fig. 11.14 Simple binary eutectic system with partial solid solution formation

the solid solution is a maximum at the solidus temperature, point m . This is usually the case in systems containing a solid solution. At lower temperatures the range of solid solutions diminishes along the curve mx . Crystalline B is also able to dissolve A and its maximum limit of solid solution is given by the curve ynq . The range of B solid solutions is less extensive than that of A solid solutions and, again, the maximum extent occurs at the solidus, point n .

In the two-phase region (A s.s. + B s.s.), the composition of the A s.s. is given by the intersection of the tie-line at the temperature of interest, say T_1 , and the curve $m-x$ which limits the extent of A s.s. The composition of B s.s. is similarly fixed by the intersection of the tie-line and curve $n-y$.

In many phase diagrams, the solid phases are shown as line phases, i.e. as being stoichiometric and without a range of homogeneity or solid solution formation

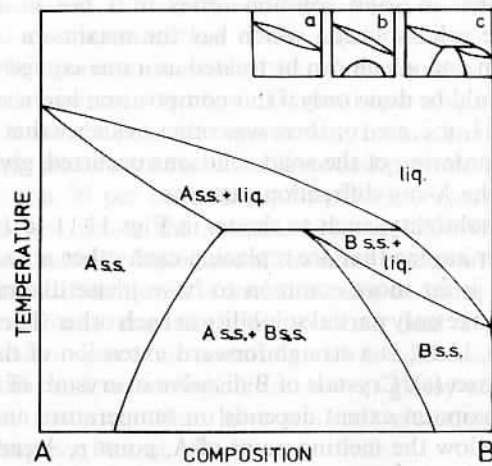


Fig. 11.15 Binary system with partial solid solution formation

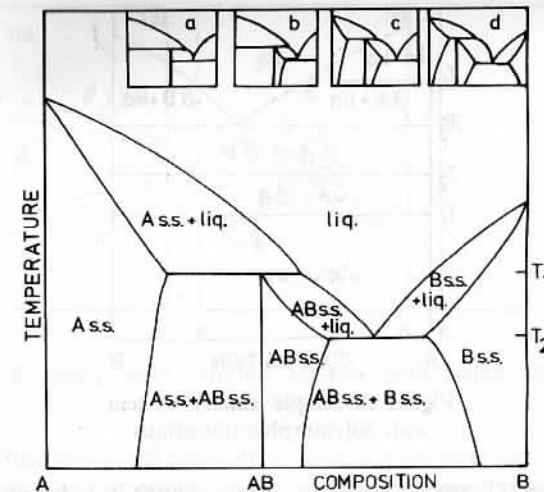


Fig. 11.16 Binary system with incongruently melting compound and partial solid solution formation

(inset a). In practice, however, the phases may have a slightly variable composition, as in inset (b), but it may be difficult to detect or measure this.

Examples of real systems that are similar to Fig. 11.14 are forsterite (Mg_2SiO_4)–willemitte (Zn_2SiO_4), shown in Fig. 10.1, and spinel ($MgAl_2O_4$)–corundum (Al_2O_3), shown in Fig. 10.3.

Another type of simple binary system with partial solid solubility is shown in Fig. 11.15. This rather strange looking diagram can be derived from a simple system showing complete solubility (inset a). First, suppose that an immiscibility dome exists within the solid solutions which has an upper consolute temperature as shown in inset (b). Above the upper consolute temperature, a single phase solid solution exists, but below it a mixture of two phases exists.

Second, let the dome expand to higher temperatures until it intersects the melting curves. The result is shown in inset (c) and on an expanded scale as Fig. 11.15. The phase diagram for silica (SiO_2)–eucryptite ($LiAlSiO_4$), shown in Fig. 10.4, for compositions near the eucryptite end is similar to that in Fig. 11.15. The Al_2O_3 – Cr_2O_3 diagram (Fig. 10.6) is similar to that shown in inset (b).

A more complex phase diagram containing an incongruently melting phase that forms a range of limited solid solutions is shown in Fig. 11.16. The progressive introduction of solid solutions is shown in insets (a), (b), (c) and (d), again working on the principle that the maximum extent of solid solution occurs at the solidus (temperatures T_1 and T_2).

11.3.5 Binary systems with solid–solid phase transitions

The representation of solid–solid phase transitions on phase diagrams depends on the nature of the phase transition. Transitions that thermodynamically

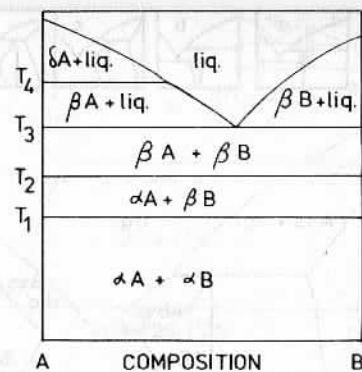


Fig. 11.17 Simple binary system with polymorphic transitions

cally are first order (Chapter 12) and involve a change in some property such as volume or enthalpy, or which, crystallographically, are reconstructive and involve the breaking and forming of many primary bonds, can be treated in much the same way as melting phenomena. In a one-component condensed system, e.g. pure A or pure B, two solid polymorphs may coexist in equilibrium at only one fixed point. In binary systems that do not contain solid solutions, phase transitions in either of the end-member phases are represented by horizontal (i.e. isothermal) lines, there being one line for each phase transition. In Fig. 11.17, the low temperature polymorphs of A and B are labelled αA and αB , respectively. Transition temperatures are $\alpha B \rightleftharpoons \beta B$ at T_1 , $\alpha A \rightleftharpoons \beta A$ at T_2 and $\beta A \rightleftharpoons \delta A$ at T_4 . In the absence of solid solutions, these transition temperatures are the same for the pure phase as for the phase mixed with other phase(s). Several examples of solid-solid phase transitions occur in the CaO-SiO₂ phase diagram (Fig. 11.8); e.g. CaSiO₃(CS) undergoes a transformation between the low temperature β polymorph and the high temperature α polymorph at 1175 °C. This transformation is observed in CaSiO₃ alone or when mixed with either SiO₂ or Ca₃Si₂O₇(C₃S₂).

In systems that exhibit complete solid solubility, as well as phase transitions, three types of phase diagram are possible (Fig. 11.18). For the end-member phases, A and B, the transitions occur at a fixed temperature, as indeed they must according to the phase rule ($C = 1$, $P = 2$, and so $F = 0$). However, for the intermediate compositions, two phases can coexist over a range of temperatures or bulk compositions because there is now one degree of freedom ($C = 2$, $P = 2$, and so $F = 1$). Thus, two-phase regions containing two solid phases, e.g. ($\alpha + \beta$), are generally observed. The treatment of the $\alpha \rightleftharpoons \beta$ change in Fig. 11.18(a) is exactly the same as for the melting of β solid solutions, as discussed in detail for Fig. 11.11. The melting relations in Fig. 11.18(a) are the same as in Fig. 11.11 but in fact could be any of the three types given in Figs 11.11 and 11.13. In Fig. 11.18(a), both end-members A and B and the entire range of solid solutions show both α and β polymorphs.

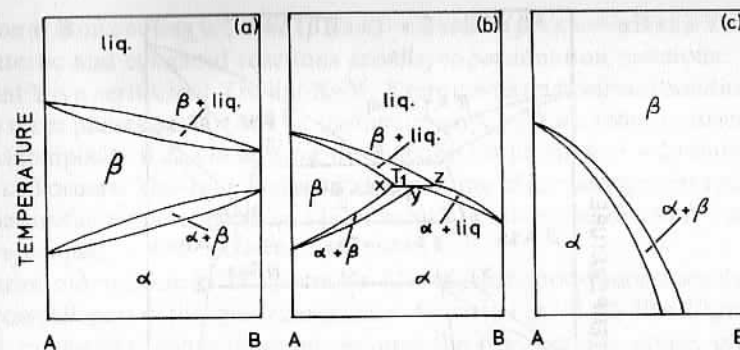


Fig. 11.18 Binary solid solution systems with polymorphic phase transformations

In Fig. 11.18(b), the $\alpha \rightleftharpoons \beta$ phase transition curves intersect the solidus curve because the $\alpha \rightleftharpoons \beta$ transition in B and in solid solutions rich in B now occurs, hypothetically, above the melting point of B and the B-rich solid solutions. The nature of the intersection of the three one-phase fields (α , β and liquid) and the three two-phase regions at T_1 is typical of solid solution systems. Always, two one-phase areas such as α and β must be separated from each other by a two-phase area ($\alpha + \beta$), although in practice the width of the two-phase regions may be difficult to detect experimentally. Three phases can coexist at only one temperature, T_1 , and on the horizontal line xyz . There is an apparent contradiction with the phase rule here because, although three coexisting phases constitute an invariant condition, they coexist over the range of compositions xyz . However, there is no contradiction because the compositions of the individual phases are fixed (as x , y and z for β , α and liquid, respectively). The only variable is the relative amounts of these three phases; these relative amounts are not a degree of freedom in the phase rule.

A similar situation exists in simple eutectic systems (Fig. 11.6). The eutectic is point y but the invariant condition extends along the line cyd .

In Fig. 11.18(c), the temperature of the $\alpha \rightleftharpoons \beta$ transition decreases increasingly rapidly as the solid solutions become more rich in B. For pure B, the α polymorph does not exist at any real temperature. The melting behaviour in (c) is not shown. It could be any of the types shown in Figs 11.11 and 11.13.

A typical binary system that has both phase transitions and partial solid solubility is shown in Fig. 11.19. The $\alpha \rightleftharpoons \beta$ transition occurs at one fixed temperature in pure A and pure B but, in the solid solutions, two-phase regions of ($\alpha A + \beta A$) and ($\alpha B + \beta B$) solid solution exist.

We have already seen that there are analogies between melting behaviour and phase transition behaviour in solid solution systems (Fig. 11.18a). A further analogy exists between the eutectic, E, and the *eutectoid*, B, in Fig. 11.19. The line A-B-C represents an invariant condition over which three phases coexist, βA s.s. (composition A), βB s.s. (composition B) and αB s.s. (composition C). The *eutectic reaction* at E on cooling is 1 liquid \rightarrow 2 solids (βA s.s. + βB s.s.). The *eutectoid*

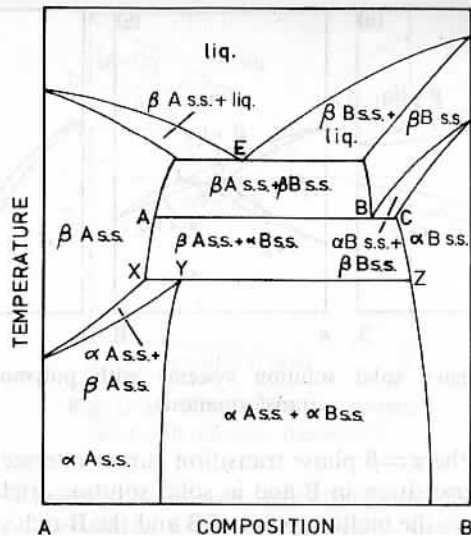


Fig. 11.19 Binary eutectic system with polymorphic phase transformations and partial solid solution formation

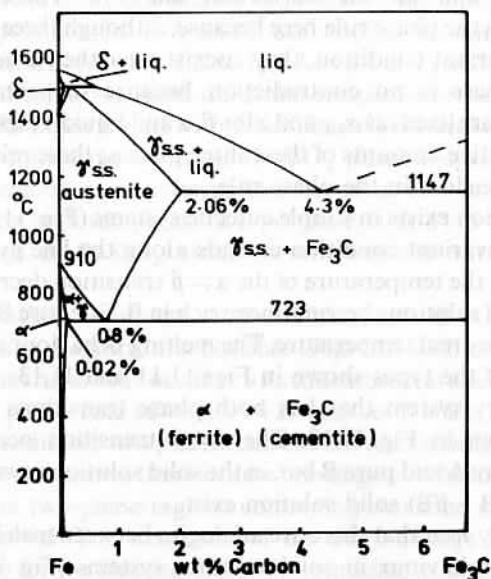


Fig. 11.20 The Fe-C phase diagram. The diagram is not an equilibrium diagram because cementite, Fe₃C, is metastable thermodynamically although kinetically stable

reaction at B on cooling is 1 solid (βB s.s.) \rightarrow 2 solids (βA s.s. + αB s.s.). Thus, both the eutectic and eutectoid reactions are disproportionation reactions.

Point Y is a *peritectoid*. The line X-Y-Z represents an invariant condition over which three phases coexist, αA s.s. (composition Y), βA s.s. (composition X) and αB s.s. (composition Z). On heating, the reaction 1 solid (αA s.s.) \rightarrow 2 solids (βA s.s. + αB s.s.) occurs. This is analogous to the melting of an incongruent compound at a peritectic temperature (Fig. 11.7b), which involves the reaction 1 solid \rightarrow 1 solid + 1 liquid.

A eutectoid reaction in the system Fe-C is of great importance to steel making. The iron-rich part of this phase diagram is shown in Fig. 11.20. The diagram is, in fact, a metastable phase diagram because the iron carbide phase, cementite, Fe₃C, is not an equilibrium phase and should, thermodynamically, decompose to a mixture of iron and graphite. However, kinetically, decomposition of cementite is slow and is not observed under normal conditions of steel making. The changes that occur on thermal cycling of Fe-C alloys can therefore be studied with the aid of Fig. 11.20.

Iron exists in three polymorphic forms: body centred cubic α , stable below 910 °C; face centred cubic γ , stable between 910 and 1400 °C; and body centred cubic (again!) δ , stable between 1400 °C and the melting point 1534 °C. γ -Iron can dissolve appreciable amounts of carbon, up to 2.06 wt%, in solid solution formation, whereas the α and δ forms dissolve very much less carbon, up to a maximum of 0.02 and 0.1 wt%, respectively.

There is a simple explanation for the very different solubilities of carbon in the γ and α polymorphs of iron. Although the face centred cubic γ structure is more densely packed than the body centred cubic α structure, the interstitial holes (suitable for occupation by carbon) are larger although much less numerous in γ -Fe. Unit cells of the two forms are shown in Fig. 11.21 together with the octahedral sites that are available for occupation by carbon. These sites are at the cube face centres in α -Fe and at the body centre in γ -Fe. The iron-carbon distances and, hence, the sizes of the interstitial sites are considerably larger in γ -Fe than in α -Fe. In α -Fe, these sites are distorted. The cubic unit cell edge in α -Fe is 2.866 Å. Two iron-carbon distances would be 1.433 Å. The other four iron-carbon distances would be 2.03 Å. In γ -Fe, the octahedral sites are undistorted and the iron-carbon distance would be half the cell edge, $a = 3.591$ Å. Therefore,

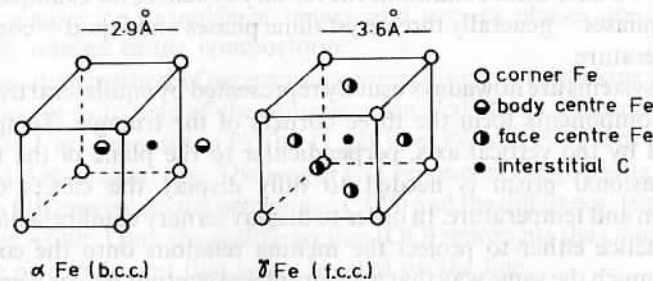


Fig. 11.21 Interstitial sites for carbon in α -Fe and γ -Fe

$Fe-C = 1.796 \text{ \AA}$. (Values are for γ -Fe at 22°C ; values at, for example, 900°C would be a few per cent greater.)

Most carbon steels contain less than 1 wt % carbon, viz. 0.2 to 0.3 per cent for use as structural members. On cooling from the melt, and in the temperature range 800 to 1400°C , these steels form a solid solution of carbon in γ -Fe called austenite (Fig. 11.20). However, the austenite solid solutions are unstable at lower temperatures ($< 723^\circ\text{C}$) because, when the structure changes from that of γ -Fe to α -Fe, exsolution or precipitation of the carbide phase, Fe_3C , occurs. This decomposition starts at the boundaries of the austenite grains; the ferrite (α -Fe) and cementite (Fe_3C) crystals grow side by side to give a lamellar texture known as pearlite.

If the steel is cooled quickly, however, there is not time for decomposition to ferrite and cementite to occur; instead martensite forms. Martensite has a deformed austenite structure in which the carbon atoms are retained in solid solution. It is possible to release these carbon atoms, as cementite, by tempering, i.e. reheating, to give a fine scale pearlite texture.

The hardness of steel depends very much on the cooling conditions and/or tempering treatment. Martensitic steels are hard largely, it seems, because of the stressed state of the martensite crystals which prevents easy motion of dislocations. In steels with pearlite texture, the hardness depends on the size, amount and distribution of the very hard cementite grains; a finer texture with a large number of closely spaced grains gives harder steel. If the steel is cooled slowly or held just below 723°C , the decomposition is slow, giving a coarse pearlite texture. A finer texture is obtained by using a faster cooling rate to produce martensite which is then subsequently tempered at a low temperature, e.g. 200°C .

11.4 Three-component condensed systems

Three-component or ternary systems have four independent variables: pressure, temperature and the composition of two of the components. If the composition or concentration of two of the components in a phase is fixed, the third is automatically fixed by difference. In this chapter, for simplicity, we are not considering volatile systems so we can use the condensed phase rule, i.e. $P + F = C + 1 = 4$. Under these conditions the ternary system is, for example, invariant when four phases—generally three crystalline phases and liquid—coexist at one fixed temperature.

Ternary systems are nowadays usually represented by equilateral triangles and the three components form the three corners of the triangle. Temperature is represented by the vertical axis, perpendicular to the plane of the triangle. A three-dimensional prism is needed to fully display the effects of varying composition and temperature. In order to display ternary equilibria on paper it is normal practice either to project the melting relations onto the composition triangle, in much the same way that a geographical contour map is a projection of

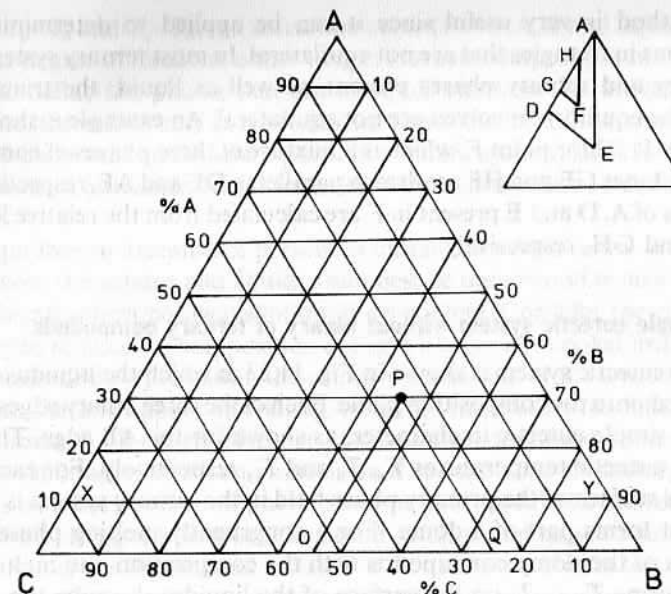


Fig. 11.22 Triangular grid for representing compositions of three component systems

features of the earth's surface, or to construct isothermal sections. Examples of both types of diagram are discussed.

Ternary compositions within equilateral triangles are given by reference to a grid (Fig. 11.22). Each of the three binary edges is divided into a hundred divisions (only ten are shown for clarity). Point A corresponds to 100% A; the edge BC corresponds to 0% A and the line XY to 10% A. Thus, the A content of any ternary composition is given by drawing a line through that composition and parallel to the BC edge. The A content is then read off from the intersection of this line with either the AB or AC edges. The contents of B and C are given similarly by drawing lines parallel to the AC and AB edges, respectively. Point P in Fig. 11.22 has a composition of 30% A, 45% B and 25% C. Compositions can be either in atom per cent, in mole per cent or in weight per cent (but obviously not a mixture). In practice, it is usually preferable to use mole per cent for inorganic systems because the formulae of binary and ternary phases are then clearly and simply related to the composition.

An alternative method of determining composition is, by making appropriate construction lines, to read off the concentration of all three components from one of the edges. For composition P (Fig. 11.22), lines PO and PQ are drawn, parallel to AC and AB, respectively. The length CO represents the percentage of B (45), the length QB represents the percentage C (25) and the difference, length OQ, the percentage A (30). Thus, the middle section (OQ) represents the concentration of the phase or component that is not located on the line.

This method is very useful since it can be applied to determining phase compositions in triangles that are not equilateral. In most ternary systems which have binary and ternary phases present, as well as liquid, the triangles that represent the equilibria involved are not equilateral. An example is shown as an inset to Fig. 11.22 for point F, which is a mixture of three phases of composition A, D and E. Lines GF and HF are drawn parallel to DE and AE, respectively. The percentages of A, D and E present in F are calculated from the relative lengths of DG, AH and GH, respectively.

11.4.1 Simple eutectic system without binary of ternary compounds

A simple eutectic system is shown in Fig. 11.23 in which the liquidus relations are projected onto the composition plane. Each of the three binary edges, AB, AC and BC, is simple eutectic in character, as shown for the AB edge. The binary edges have eutectic temperatures T_a , T_b and T_c , respectively. For each phase, the liquidus surface of the primary phase field in the ternary system is a curved surface that forms part of a dome. For a congruently melting phase such as B, the apex of the dome corresponds with the composition and melting point of B. Isotherms T_1, \dots, T_5 on the surface of the liquidus describe the shape of the dome. The primary phase field of B is bounded by B, T_a , T_d and T_c .

Neighbouring primary phase fields, e.g. of A and B, intersect in a sloping boundary line or valley, in this case $T_a - T_d$. When three neighbouring primary phase fields meet, as at T_d , the point of intersection is a ternary invariant point. As T_d is the lowest temperature at which liquid can exist in this triangle it is a ternary eutectic (at T_d , $P = 4$: A, B, C and liquid; and so $F = 0$). The line $T_a - T_d$, as well as

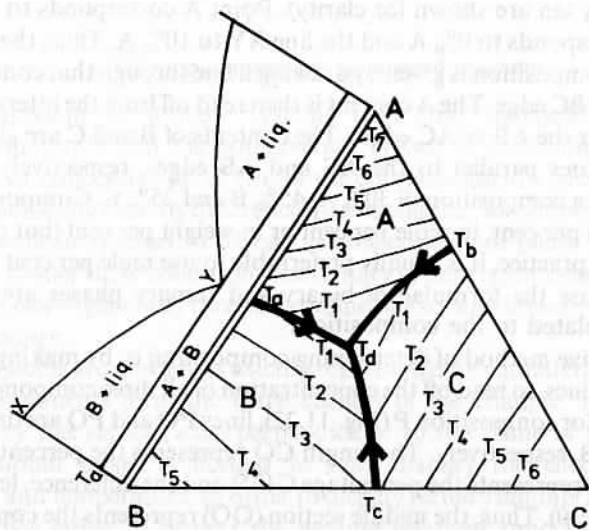


Fig. 11.23 Simple ternary eutectic system showing univariant curves and liquidus isotherms

the lines $T_b - T_d$ and $T_c - T_d$, is a *univariant curve* ($P = 3$: A, B and liquid; and so $F = 1$). One degree of freedom, either temperature or composition of the liquid, is needed to define the phases that are in equilibrium on this univariant curve. Arrows on the univariant curves indicate directions of falling temperature. It should be clear that an invariant point in a binary system, such as the eutectic at y , becomes a univariant curve in the ternary system when a third component is added.

The equilibrium assemblage present in ternary compositions at any temperature between the solidus and liquidus can best be understood from a knowledge of the crystallization pathways followed on cooling. Consider the changes that are expected to occur in composition a (Fig. 11.24) as it is cooled from the liquid state. Composition a lies within the primary phase field of B. Hence B is the first crystalline phase to appear on cooling, once the temperature has fallen inside the liquidus dome. As B progressively crystallizes, the liquid becomes deficient in B and it should be apparent that composition B and the locus of the changing liquid composition must lie on a straight line that passes through the bulk composition a . Thus, with falling temperature, the liquid composition moves away from B, on an extension of the line Ba and towards b . For temperatures in this range, such that the liquid composition is between a and b , the relative amounts of B and liquid are given by a simple lever rule calculation. For instance, when the liquid has almost reached b , the fraction of liquid present is given approximately by aB/bB .

Once the temperature has fallen sufficiently that the liquid composition has reached b , crystals of A begin to form. With a further drop in temperature the liquid composition is constrained to move down the univariant boundary curve bcd and the equilibrium assemblage over this temperature range is (A + B + liquid). The relative quantities of the three phases can be found from a lever rule construction similar to that shown in the inset in Fig. 11.22. For example, with liquid of composition c , the bulk composition a lies in the triangle with A, B and c as corners; lines passing through a and parallel to the Bc and Ac edges may

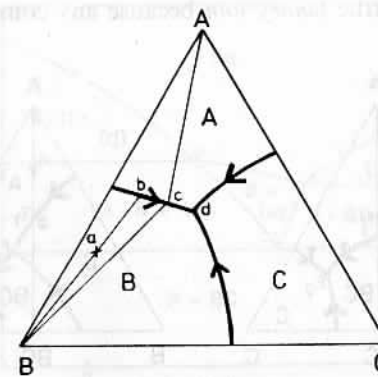


Fig. 11.24 Crystallization pathway in a simple ternary eutectic system

be drawn (not shown) and the phase composition determined from the intercepts of these lines on the AB edge.

In addition to the precipitation of A crystals that occurs as the liquid composition moves from b to d , precipitation of B crystals also continues. This can be checked by making lever rule calculations for different liquid compositions between b and d . Alternatively, it can be seen that if crystals of A precipitate from liquid, say of composition c , then crystals of B must also precipitate in order to maintain the liquid composition on the line cd .

Point d is a ternary eutectic. Its temperature, T_d , is the lowest at which liquid can exist in equilibrium in this system. When this temperature is reached on cooling and the liquid composition has arrived at d , the residual liquid must crystallize to give a mixture of A, B and C. Crystals of C are therefore forming for the first time. The final amounts of A, B and C in equilibrium are determined by lever rule calculations in the triangle A, B, C.

The behaviour of other compositions on cooling can be treated similarly and a sequence of reactions is generally observed. Differences occur only for compositions that happen to coincide with either univariant curves, e.g. c , or invariant points, e.g. d . Thus liquid of composition d must change completely from 100 per cent liquid to a solid mixture of A, B and C at one temperature. The behaviour of solid mixtures on heating is simply the reverse of the crystallization pathway followed on cooling and is not described further.

11.4.2 Ternary systems containing binary compounds

Ternary systems that contain one congruently melting binary compound, but no ternary compounds or solid solutions, can be one of the two types shown in Fig. 11.25. In (a), the triangle ABC can be divided into two smaller triangles, A-B-BC and A-BC-C. Both of these are simple eutectic in character, similar to Figs 11.23 and 11.24. Each triangle can be treated separately and no new principles are involved. The only feature that is worthy of comment is the join A-BC.

The join A-BC is a true *binary join* because any composition on this join,

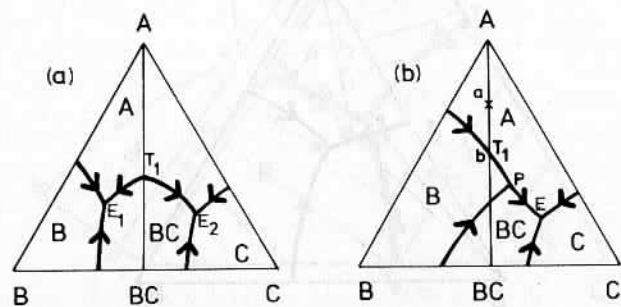


Fig. 11.25 Possible melting relations in ternary systems that contain a congruently melting binary phase

whether solid, liquid or a mixture of solid and liquid, can be represented completely by positive quantities of A and BC alone. The join is simple eutectic in character with a eutectic temperature, T_1 . However, whereas T_1 is the *lowest* temperature at which liquid can exist on the join A-BC, T_1 is in fact a *thermal maximum* on the univariant boundary curve which separates the primary phase fields of A and BC in the ternary A-B-C system, i.e. $T_1 > E_1, E_2$. Drawing an analogy with geographical contour maps, T_1 represents the height of a pass between the two mountains A and BC.

In Fig. 11.25(b), compound BC again melts congruently but the ternary melting behaviour is different for certain compositions. The univariant curves that separate the primary phase fields of (i) A and B and (ii) B and BC now cross the join A-BC, whereas this does not happen in Fig. 11.25(a). As a result, the invariant point located at the intersection of these two univariant curves lies *outside* the triangle A-B-BC. Every triangle, such as A-B-BC has an associated invariant point. The three crystalline phases that coexist at this point are the three phases at the corners of the associated triangle. If an invariant point lies outside its own triangle, automatically it is a ternary peritectic point. If it lies inside its own triangle, it must be a ternary eutectic point. The direction of falling temperature along the univariant curve that separates the fields of A and BC must be in the direction arrowed since the peritectic temperature P must be higher than the eutectic temperature E .

The join A-BC is not a binary join, as it is in the previous example, because over a range of compositions, B is the primary phase and the composition B does not lie on the join A-BC. The join A-BC is shown in Fig. 11.26. It is much more complicated than a simple eutectic system, such as the join A-BC in Fig. 11.25(a). Consider the crystallization of the liquid of composition a on cooling (Figs. 11.25b and 11.26). This composition is within the primary phase field of A and so A is the first crystalline phase to appear. As the temperature drops, A continues to precipitate until temperature T_1 is reached, by which time the liquid composition has arrived at point b . At b , crystals of B begin to form and the liquid

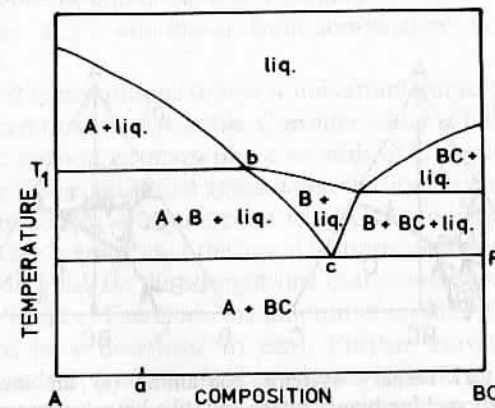


Fig. 11.26 The join A-BC in Fig. 11.25(b)

composition departs from the line A–BC because it is constrained to follow the univariant curve b – P that separates the fields of A and B. In Fig. 11.26 the composition has entered the region, A + B + liquid, although neither B nor the liquid composition (represented by the line bc) lie on the join A–BC. As the temperature drops further, A and B continue to crystallize until the peritectic temperature P is reached. At P , all of B and all of the liquid react (this may be kinetically slow) to give more crystals of A and, for the first time, crystals of BC. Below P no further changes occur as the equilibrium subsolidus assemblage A + BC is now present. Thus, the final subsolidus assemblage has returned to the join A–BC although for most of the crystallization process the compositions of some of the phases present do not lie on the join A–BC.

For all compositions that lie within the triangle A–B–BC (Fig. 11.25b), the processes of crystallization that occur on cooling from the liquid state terminate at temperature P : i.e. P is the solidus temperature for the triangle A–B–BC. For compositions that lie within the triangle A–BC–C, the solidus temperature is the eutectic temperature E .

Two other types of ternary system that contain only one binary compound are shown in Fig. 11.27. The compound BC melts incongruently in Fig. 11.27(a) and the BC edge has a phase diagram that is similar to that shown in Fig. 11.7(b). The ternary diagram A–B–C (Fig. 11.27a) contains one peritectic and one eutectic and is similar to that described above (Fig. 11.25b).

In Fig. 11.27(b), the binary compound BC has an upper temperature limit of stability. The phase diagram of the B–C edge is similar to that shown in Fig. 11.7(c). Above temperature T_1 , BC decomposes to give a solid mixture of B and C; only at the considerably higher solidus temperature, T_2 , does melting begin to occur. The binary eutectic point, T_2 , on the BC edge becomes a univariant curve in the ternary system. This curve separates the primary phase fields of B and C and its temperature falls with increasing A content. When the temperature falls to below T_1 , B and C are no longer stable together but react to give BC. This is true in both binary B–C and ternary A–B–C compositions. As a consequence, a ternary primary phase field for phase BC appears at temperatures

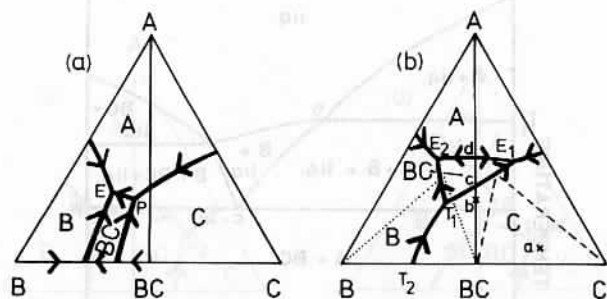
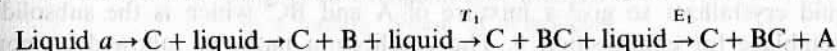


Fig. 11.27 Ternary systems containing (a) an incongruently melting binary phase and (b) a binary phase with an upper limit of stability

below T_1 . Three ternary invariant points are shown in Fig. 11.27(b); two of these are eutectics, E_1 and E_2 , and belong to the triangles A–BC–C and A–B–BC, respectively. The third invariant point at temperature T_1 corresponds to the decomposition of compound BC and at this point the primary phase fields of B, C and BC meet. This invariant point is neither a eutectic nor a peritectic; it does not belong to either of the two triangles but to the straight line B–BC–C. Sometimes, such a point is called a *distribution point*.

Some of the crystallization pathways for compositions within the triangles in Fig. 11.27(b) are quite complicated and involve several stages. For example, on cooling of a liquid of composition a , the crystallization pathway under equilibrium conditions can be summarized in the following scheme of reactions:



As always, the crystallization process ends when the invariant point is reached that belongs to the final, desired subsolidus assemblage, which in this case is A + BC + C. One feature of this sequence that is worth discussing is the reaction that occurs at temperature T_1 . Given that once a liquid composition has arrived at a univariant curve it continues moving down that curve, or another similar univariant curve, with falling temperature (there are exceptions to this, see below), then a liquid arriving at the invariant point and temperature T_1 has apparently a choice of univariant curves to follow. It would appear to be able to go either in the direction of eutectic E_1 or in the direction of eutectic E_2 . However, if the liquid composition followed the univariant curve leading to eutectic E_2 an impossible situation would arise. Clearly the bulk composition a must be represented by positive amounts of the three phases that are in equilibrium at a particular temperature. Suppose the temperature was just below T_1 , but above those of E_1 and E_2 . If the liquid had decided to follow the curve in the direction of E_2 , then the three phases present in equilibrium would be B, BC and liquid. The compositions of these three phases, B, BC and liquid, form a triangle (dotted) and, quite clearly, a lies outside this triangle. This therefore is an impossible situation. The alternative is for the liquid to follow the curve T_1 – E_1 , in which case the three phases present are BC, C and liquid. Bulk composition a does lie within this triangle (dashed).

Although liquid compositions follow a univariant curve on cooling, if at all possible, sometimes this is not possible. Consider liquid of bulk composition b in Fig. 11.27(b). On cooling, primary phase crystals of C appear first. On further cooling, a three-phase equilibrium arises when the liquid composition meets the curve T_1 – E_1 : the phases in equilibrium are BC, C and liquid. This situation continues on further cooling until the liquid composition reaches point c . At this stage, composition b lies on the straight line that connects the compositions of crystals BC and liquid c . Therefore, the amount of crystals C that are present in equilibrium must have decreased to zero. Further movement of the liquid composition towards E_1 is now prohibited because b would lie outside the triangle BC–C–liquid. Instead the liquid composition must depart from the univariant curve T_1 – E_1 and enter the primary phase field of BC.

This effect may be explained with the aid of the phase rule. A liquid is constrained to follow a univariant curve when the reaction mixture is in a condition of univariant equilibrium, i.e. it has only one degree of freedom. This occurs when the liquid composition lies somewhere between T_1 and c . When, however, the liquid composition reaches c , one of the phases, crystalline C, disappears; consequently an extra degree of freedom is created, in accordance with the phase rule. The liquid is therefore no longer constrained to follow the univariant curve.

As the liquid leaves the univariant curve at point c , it enters the primary phase field of BC, i.e. the assemblage present is BC + liquid. As the temperature drops, BC continues to precipitate until the liquid reaches point d . Here, the residual liquid crystallizes to give a mixture of A and BC, which is the subsolidus assemblage for composition b . The equilibrium pathway followed by composition b on cooling may therefore be summarized:



The stage has now been reached where the basic principles of ternary melting behaviour have been set out and illustrated with simple examples. If several binary compounds or one or more ternary compounds are present, the diagrams may be very complicated, but, even so, no new principles are necessary in order to understand the diagrams. It does not seem worth while to try and discuss more complicated systems here; instead it is recommended that the keen reader choose a system and try to work out crystallization pathways for various liquid compositions. In this way, one can begin to find out about a system in much the same manner that a hill-walker can become acquainted with the hills and valleys of a new region by studying an ordinance survey map.

11.4.3 Subsolidus equilibria

The behaviour of systems at subsolidus temperatures is very important, especially in more complicated systems. A system that contains several binary or ternary phases is, at subsolidus temperatures, divided up into a number of smaller triangles. On paper, there is usually more than one possible set of triangles and one of the experimental problems in studying ternary equilibria is to determine the equilibrium arrangement of triangles. The problem is illustrated in Fig. 11.28. Two binary compounds AC and BC are present. The subsolidus triangle AC-BC-C must exist as there are no alternative triangles in this part of the diagram. For the rest of the diagram, however, there is a choice between having either A and BC as *compatible phases* or B and AC. If we assume that A and BC are compatible, a line is drawn between them that indicates their stability in the presence of each other. Two three-phase triangles result, A-B-BC and A-BC-AC. This means that B and AC would be incompatible phases; mixtures of B and AC should therefore react to give a mixture of A and BC, although the reaction rate may be slow.

The compatibility or incompatibility of phase mixtures or assemblages is of

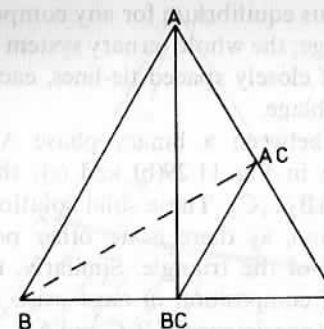


Fig. 11.28 Compatibility triangles in a ternary system at subsolidus temperatures

great practical importance in, for example, cement and refractories. In the manufacture of Portland cement clinker, the desired calcium silicates are Ca_2SiO_4 and Ca_3SiO_5 ; undesired ones are $\text{Ca}_3\text{Si}_2\text{O}_7$ and CaSiO_3 . Additives must clearly be avoided which would react with either Ca_3SiO_5 or Ca_2SiO_4 to produce one of the other calcium silicates. Alternatively, using Fig. 11.28 as an example, if AC is the phase with the desirable properties, it is important to exclude B from the system because B and AC are incompatible. Similar considerations affect the lifetime of refractory bricks, i.e. molten slag and the refractory brick should be compatible.

11.4.4 Ternary systems containing binary solid solutions

Ternary phase equilibria may be quite complicated if solid solutions are present. A full treatment of such systems is not attempted here; instead only some of the more important points in simple systems are highlighted. Subsolidus equilibria for some simple systems are shown in Fig. 11.29. In (a), a complete range of solid solutions between B and C is shown by the hatching of the B-C join. These solid solutions coexist with A but there are never more than two

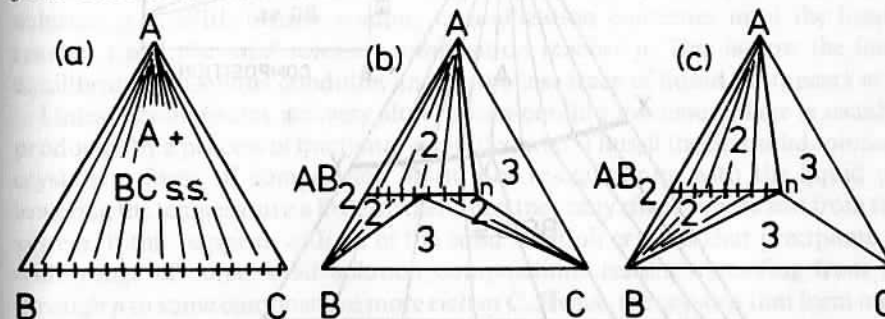


Fig. 11.29 Ternary systems containing ranges of binary solid solution. Numbers refer to the numbers of phases in equilibrium in each region

phases present in subsolidus equilibrium for any composition. Tie-lines radiate from A towards the BC edge; the whole ternary system can therefore be divided into an infinite number of closely spaced tie-lines, each of which represents a different two-phase assemblage.

Partial solid solution between a binary phase AB_2 and a non-existent compound AC_2 is shown in Fig. 11.29(b) and (c); the formula of this solid solution may be written $AB_{2-x}C_x$. These solid solutions must coexist with A, forming a two-phase region, as there is no other possible arrangement for compositions in this part of the triangle. Similarly, the three-phase triangle (A + C + solid solutions of composition n) must exist. For the remaining compositions which involve the coexistence of B, C and AB_2 solid solutions, however, there is more than one possible compatibility arrangement; two of these possibilities are shown in Fig. 11.29(b) and (c). The AB_2 solid solutions may coexist almost entirely with B (Fig. 11.29c) or almost entirely with C (not shown) or partly with B and partly with C (Fig. 11.29b). The correct, equilibrium, arrangement must be determined experimentally.

The presence of solid solutions in a phase diagram complicates melting behaviour. For the subsolidus diagram shown in Fig. 11.29(a), melting relations are typically as shown in Fig. 11.30. The edges AB and AC are simple eutectic in character; the BC edge (Fig. 11.30b) is similar to Fig. 11.11 and has a smoothly changing solidus and liquidus without thermal maxima, minima or invariant points. In the ternary system (Fig. 11.30a), there are no invariant points and only one univariant curve. This separates the primary phase fields of A and BC solid solutions; on this curve, temperatures fall in the direction XY. Liquid on the univariant curve XY coexists with both A and BC solid solutions; each liquid composition coexists with a particular BC solid solution composition. Tie-lines

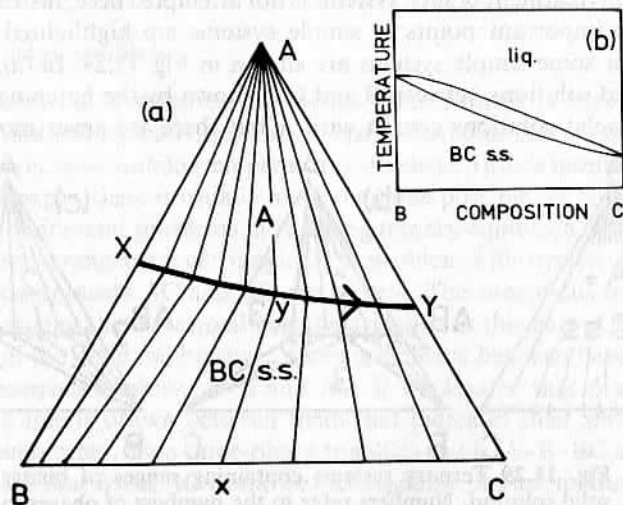


Fig. 11.30 Solid-liquid compatibility relations in ternary systems with binary solid solution

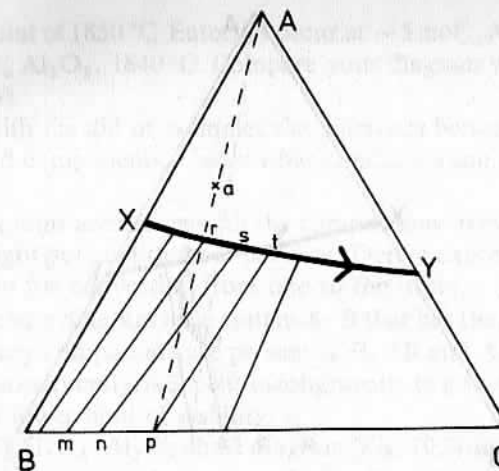


Fig. 11.31 Crystallization pathway in ternary system with binary solid solutions

that connect A and liquid on the curve XY radiate from A; however, tie-lines between BC solid solutions and the same liquids XY do not radiate from either B or C but move smoothly across the diagram. For example, liquid of composition y coexists with A and BC solid solution of composition x .

Consider the cooling of liquid of composition a (Fig. 11.31). The equilibrium subsolidus assemblage is A and solid solution p . On cooling, A starts to precipitate from the liquid and the liquid composition moves away from a on the extension of the line Aa . When the liquid composition reaches r on the univariant curve, BC solid solution crystals start to form; these have composition m . With further cooling, the liquid composition follows the curve XY in the direction rst . As it does so, the composition of the BC solid solution must change continuously at equilibrium and the amount of crystalline material, both A and BC solid solutions, increases. For liquid s the composition of the equilibrium solid solution is n . With further cooling, crystallization continues until the liquid reaches t and the solid solution composition reaches p . This is now the final equilibrium subsolidus condition and so the last trace of liquid disappears at t .

Unless cooling rates are very slow, a non-equilibrium assemblage is usually produced, by a process of fractional crystallization. Thus, if the first solid solution crystals to form, of composition m , do not re-equilibrate with the liquid on lowering the temperature a little further, then they may effectively be lost from the system. If this happens with all of the solid solution crystals that precipitate, a wide range of cored solid solution compositions results, extending from m , through p to some composition more rich in C. Hence, the crystals that form may be inhomogeneous, having B-rich centres and C-rich surfaces. Examples of such zoning or coring in metals and minerals were mentioned in the section on binary systems.

Crystallization of liquids within the primary phase field of BC solid solutions is

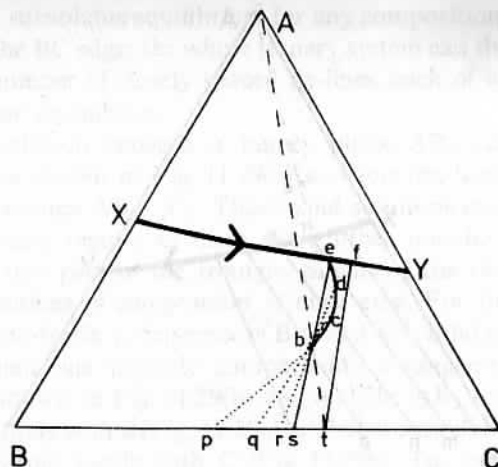


Fig. 11.32 Crystallization pathway in ternary system with binary solid solutions

rather more complex (Fig. 11.32). Consider liquid *b*; the first BC solid solution crystals to form have composition *p*. As the liquid moves down the liquidus surface, precipitation of more C-rich solid solution occurs and also the previously precipitated solid solution, *p*, re-equilibrates with the liquid to become more C-rich. With falling temperature, the liquid composition follows a curved pathway *bcd*e as the solid solution composition moves along *pqr*s. Thus, the liquid and solid solution compositions rotate about the bulk composition, *b*. Each liquid composition that lies on the tie-line *se* follows a unique pathway on cooling, but all of these pathways meet at the common point *e* on the univariant curve *XY*. At point *e*, crystals of *A* start to form and the liquid composition is constrained to follow the curve *XY* until point *f* is reached, at which the last of the liquid disappears. The subsolidus assemblage is *A* + solid solution *t*.

An apparently simple ternary diagram such as shown in Figs 11.30 to 11.32 requires a great deal of experimental work for its complete determination. Each composition within the primary phase field of BC solid solutions has its own particular crystallization pathway (e.g. *bcd*e for composition *b*; see Fig. 11.32) and these pathways have to be determined experimentally. Few systems have therefore been completely evaluated.

Questions

- 11.1 What is (i) the mole per cent and (ii) the weight per cent of (a) Al_2O_3 in mullite, $\text{Al}_6\text{Si}_2\text{O}_{13}$ (b) Na_2O in devitrite, $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ (c) Y_2O_3 in yttrium iron garnet, $\text{Y}_3\text{Fe}_5\text{O}_{12}$?
- 11.2 Sketch the phase diagram for the system Al_2O_3 - SiO_2 using the following information. Al_2O_3 and SiO_2 melt at 2060 and 1720 °C. One congruently melting compound, $\text{Al}_6\text{Si}_2\text{O}_{13}$, forms between Al_2O_3 and SiO_2 with a

melting point of 1850 °C. Eutectics occur at ~ 5 mol% Al_2O_3 , 1595 °C and ~ 67 mol% Al_2O_3 , 1840 °C. Compare your diagram with that shown in Fig. 20.3(a).

- 11.3 Explain with the aid of examples the difference between the concepts of phases and components. Under what conditions can a component be a phase?
- 11.4 Phase diagrams are drawn with the compositions represented usually as either weight per cent or mole per cent. Derive expressions for a binary AB system for converting from one to the other.
- 11.5 Sketch a phase diagram for a system A-B that has the following features. Three binary compounds are present A_2B , AB and AB_2 . Both A_2B and AB_2 melt congruently. AB melts incongruently to give A_2B and liquid. AB also has a lower limit of stability.
- 11.6 For the MgAl_2O_4 - Al_2O_3 phase diagram (Fig. 10.3) describe the reactions that would be expected to occur, under equilibrium conditions, on cooling a liquid of composition 40 mol% MgO, 60% Al_2O_3 . Using rapid cooling rates, how might the product(s) differ?
- 11.7 The system Mg_2SiO_4 - Zn_2SiO_4 is a simple eutectic system in which the two end-member phases form limited ranges of solid solution. Sketch a probable phase diagram for this system. How would you determine experimentally: (i) the compositions of the solid solution limits; (ii) the mechanism of solid solution formation in each case; (iii) the eutectic temperature.
- 11.8 Pure iron undergoes the $\alpha \rightleftharpoons \gamma$ transformation at 910 °C. The effect of added carbon is to reduce the transformation temperature from 910 to 723 °C. Sketch the general appearance of the Fe-rich end of the Fe-C phase diagram using this information.
- 11.9 Construct a triangular grid for representing three-component phase diagrams. Let the three components be Na_2O , CaO and SiO_2 . Mark on your triangle, using a mole% scale, the compositions of the following phases: Na_2SiO_3 , $\text{Na}_2\text{Si}_2\text{O}_5$, CaSiO_3 , $\text{Ca}_3\text{Si}_2\text{O}_7$, Ca_2SiO_4 , Ca_3SiO_5 , $\text{Na}_2\text{CaSiO}_4$, $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$, $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$, $\text{Na}_4\text{CaSi}_3\text{O}_9$, $\text{Na}_2\text{CaSi}_5\text{O}_{12}$.
- 11.10 The ternary system A-B-C contains no binary compounds and only one ternary compound, X. (i) Sketch the layout of the subsolidus compatibility triangles. (ii) Assuming that X melts congruently, sketch the melting relations. Identify three ternary eutectics, three thermal maxima and six univariant curves.

References

- A. M. Alper (Ed.) (1971). *High Temperature Oxides*, Vols 1 to 4, Academic Press, New York.
- A. M. Alper (1976). *Phase Diagrams*, Vols 1 to 5, Academic Press.
- W. G. Ernst (1976). *Petrologic Phase Equilibria*, W. H. Freeman & Co., San Francisco.

- A. Findlay (1951). *The Phase Rule and Its Applications*, 9th Ed Dover N.Y.
 P. Gordon (1968). *Principles of Phase Diagrams in Materials Systems*, McGraw-Hill, New York.
Phase Diagrams for Ceramists 1964 ed., 1969 Suppl., 1975 Suppl., 1981 Suppl., American Ceramic Society, Columbus, Ohio. The standard work of reference for phase diagrams of non-metallic inorganic materials.
 A. Reisman (1970). *Phase Equilibria*, Academic Press, New York.
 J. E. Ricci (1966). *The Phase Rule and Heterogeneous Equilibrium*, Dover, New York.
 F. Tamas and I. Pal (1970). *Phase Equilibria Spatial Diagrams*, Butterworths 1970.

Chapter 12

Phase Transitions

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Phase transitions are important in most areas of solid state science. They are interesting academically, e.g. a considerable slice of current research in solid state physics concerns soft mode theory, which is one aspect of phase transitions, and they are important technologically, e.g. in the synthesis of diamond from graphite, the processes for strengthening of steel and the properties of ferroelectricity and ferromagnetism. This chapter discusses structural, thermodynamic and kinetic aspects of phase transitions and their classification. A few of the more important phase transitions are described; others are mentioned elsewhere in this book.

12.1 What is a phase transition?

If a crystalline material is capable of existing in two or more polymorphic forms (e.g. diamond and graphite), the process of transformation from one polymorph to another is a phase transition. The terms *transition* and *transformation* are both used to describe this and are interchangeable. In the narrowest