

TWO-COMPONENT SYSTEMS

A pressure-temperature diagram is extremely useful when one wishes to discuss a one-component system. A component in this case is an element or compound (for example, Fe, MgO, or H₂O). As long as there is only one component present, the system may be adequately described by the two variables, pressure and temperature. In a two-component system, a third variable is needed; this is composition. The two-component system may be described by a three dimensional pressure - temperature - composition diagram. It is however in the framework of this course not appropriate to deal with the complexities of the 3D phase diagram at this point and, since most materials are used under isobaric (constant pressure) conditions, we will first discuss an isobaric two-dimensional diagram of temperature versus composition. At a later point we will explain how the one component pressure-temperature and the isobaric two-component temperature-composition diagrams may be combined to construct the three-dimensional pressure-temperature-composition diagram of a two-component system.

Temperature-composition diagrams

A two-component temperature-composition diagram at constant pressure is called a binary phase diagram or equilibrium diagram. Temperature is plotted as the ordinate and composition as the abscissa. In the system AB, the composition is usually expressed in terms of the mole fraction of B, x_B , or the weight percent of B, w/o B. (The mole fraction of B is equal to the number of moles of B divided by the sum of the number of moles of A plus the number of moles of B. The weight percent of B is equal to the product of 100 and the weight of B divided by the sum of the weights of A and B.) The composition need not be specified in terms of A since the sum of the mole fraction of B and the mole fraction of A is equal to one, and the sum of the weight percent of A and the weight percent of B is equal to 100. For pure A, both x_B and w/o B are zero; and for pure B they are one and 100, respectively.

A typical binary phase diagram (Figure 1) indicates those phases present in equilibrium at any particular temperature and composition at the constant pressure for which the phase diagram was determined. At low temperatures, the only phase present is the solid designated by S in the phase diagram. Pure A melts at the temperature T_{fA} and pure B melts at the temperature T_{fB} . Alloys of composition between pure A ($x_B = 0$) and pure B ($x_B = 1$) exist only in the solid state of aggregation until the temperature of the

solidus line is reached. The solidus is represented in the phase diagram by the lower curve extending from T_{fA} to T_{fB} . Below the solidus temperature only solid exists; but above the solidus, there is a two-phase region (L + S) in which both liquid and solid phases are in equilibrium. The liquid-plus-solid region extends from the solidus temperature over a finite temperature interval for all alloys of the system AB. The extent of the temperature interval reduces to zero for the pure components A and B, since according to the one-component pressure-temperature diagram, at any particular pressure there is only one temperature at which liquid and solid are in equilibrium.

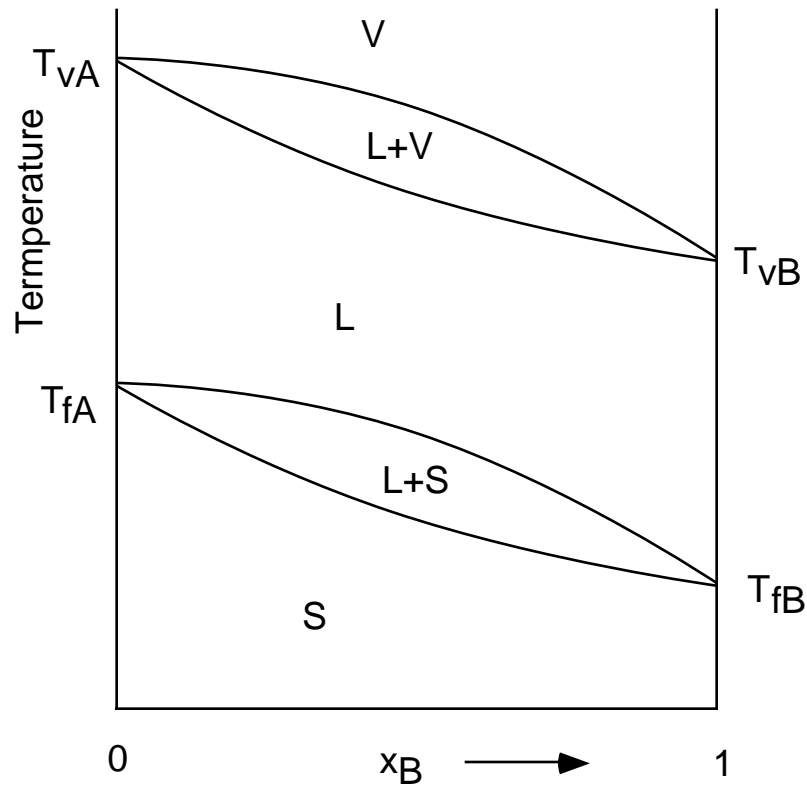


Figure 1 • Binary Phase Diagram. A binary phase diagram is an isobaric temperature-composition diagram. In this case there is complete solubility in the solid, liquid, and vapor states of aggregation, and only one phase is found for each state of aggregation. At low temperatures, the material of any composition is solid; at higher temperatures there is a two-phase liquid-plus-solid region, a liquid region, a liquid-plus-vapor region and, at very high temperatures, an all-vapor region.

The upper boundary of the liquid-plus-solid region is the liquidus temperature. Above this temperature, any alloy of the system exists as a liquid phase until the temperature increases to that level at which vaporization begins. The pure compositions A and B

vaporize completely at T_{VA} and T_{VB} , because the liquid and vapor phases for a pure component at constant pressure can be in equilibrium at only one temperature. Alloys of intermediate composition do not completely vaporize at any one temperature but over a finite temperature interval. This is shown in the phase diagram of Figure 1 by the liquid-plus-vapor (L + V) region. At temperatures above this region, only the vapor phase exists.

Metallurgists or materials scientists are more often concerned with the liquid and solid phases and less often with the vapor phase. For this reason, and the fact that it is difficult to determine vapor phase diagrams, most binary diagrams extend no higher in temperature than the all-liquid region.

Cooling through a two-phase field

Solidification or melting of an intermediate alloy may be illustrated by the enlarged view of a two-phase field shown in Figure 2.

If an alloy of composition x_0 , originally liquid at temperature T_1 , is cooled, it remains liquid until the temperature reaches the liquidus temperature at point 2. At this temperature T_2 , the first particle of solid appears. This solid does not have the same composition as the parent liquid. The composition of the first solid formed at T_2 is found by constructing an isothermal line from 2 to 2'. This isotherm is called a tie-line. The composition of the solid and liquid phases in equilibrium at a particular temperature is given by the intersection of the tie-line at that temperature with the solidus and liquidus curves, respectively. Thus at temperature T_2 , the solid has the composition x_2' and the liquid the composition x_2 (where $x_2 = x_0$).

Upon further cooling to T_3 , the composition of the liquid has shifted to the left along the liquidus to x_3 , and the composition of the solid has shifted to the left along the solidus to x_3' because at T_3 , the only liquid and solid compositions that can be in equilibrium with one another are x_3 and x_3' respectively.

Despite the fact that both liquid and solid have compositions different from the alloy composition, the overall alloy (liquid and solid together) retains its original composition x_0 . As the temperature approaches the solidus temperature T_5 , the solid composition

approaches x_5' , (where $x_5'=x_0$) and the last quantity of liquid of composition x_5 freezes. At temperatures below the solidus, the solid composition remains unchanged, for example, at T_6 the solid composition is x_0 . The above analysis applies only to solidification at such a slow rate of cooling that equilibrium is achieved at every temperature. This is not always the case, however.

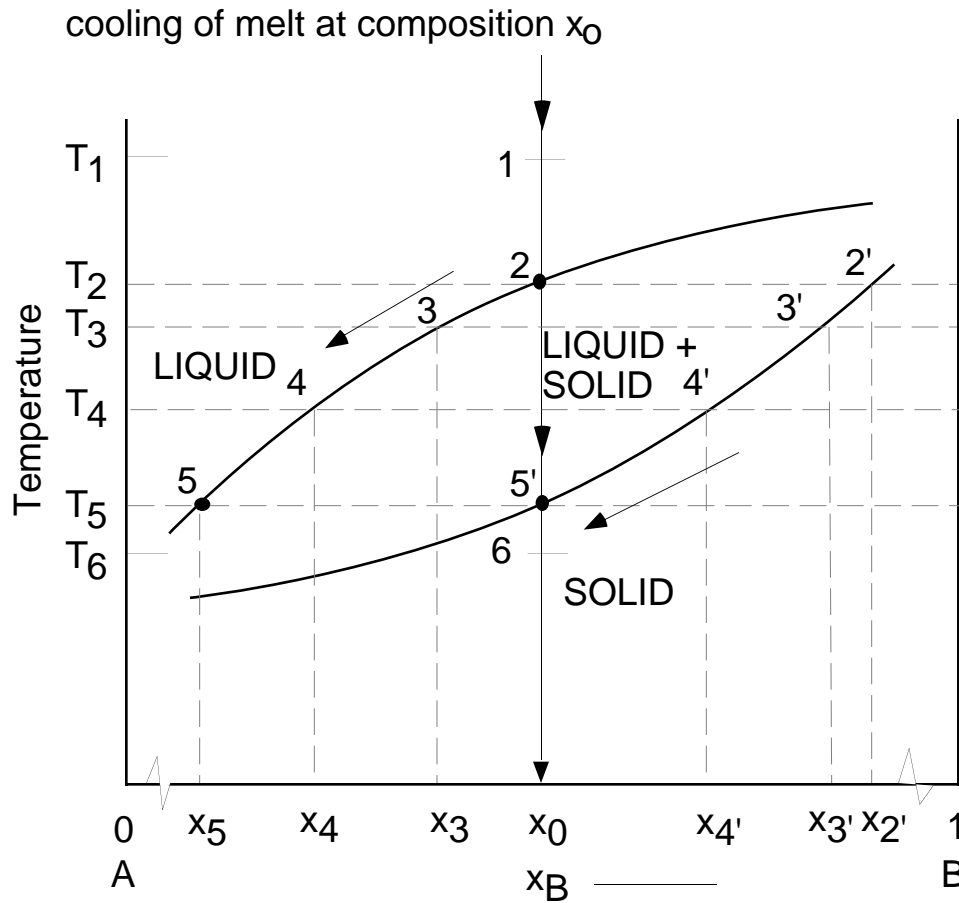


Figure 2 • Cooling Through a Two-Phase Field. As an alloy of composition x_0 is cooled from the liquid region through the two-phase liquid-plus-solid field, the first particle of solid forms at temperature T_2 and is of composition x_2 . The composition of the solid is given by the intersection of the isothermal tie line with the solidus, and the composition of the liquid by the intersection of the tie-line with the liquidus. As the temperature is decreased, the composition of the solid and of the liquid shifts to the left until at T_5 the solid is of composition x_0 and the last of the liquid freezes.

The lever law

To determine exactly how much liquid and solid are present at any given temperature, let us derive a relation known as the "lever law." If one mole of alloy of composition x_0 is chosen as a basis, then, at any temperature T , the fraction of liquid f_L is found as follows: The sum of the fractions of liquid and solid must equal one, that is,

$$f_S + f_L = 1$$

The number of moles of B present in the alloy must be the same as the number of moles of B present in the solid phase plus the number of moles of B present in the liquid phase, that is,

$$x_0 = x_S f_S + x_L f_L$$

Since

$$f_S = 1 - f_L$$

we may substitute and obtain

$$x_0 = x_S - x_S f_L + x_L f_L$$

On rearranging and solving for f_L we find that

$$f_L = (x_S - x_0) / (x_S - x_L).$$

This relation is called the "lever law" because the fraction of one of the two phases present is equal to the opposite side of the tie-line ($x_S - x_0$) divided by the entire tie-line ($x_S - x_L$). In this way the tie-line acts as though it were a lever whose fulcrum is at the point x_0 . In a similar way it is found that

$$f_S = (x_0 - x_L) / (x_S - x_L).$$