4

Liquid-Solid Systems

4.1. Condensed Systems

When considering the transition from liquid to solid for binary systems the effects of pressure can generally be ignored. It has already been stated that while changes in pressure do affect the melting point of a substance the effect is of a very small order. Consequently, the $t-c$ type of diagram is the only type of phase diagram normally considered for liquid—solid systems. Because the effect of pressure is negligible we may consider the system as a condensed system and use a reduced version of the Phase Rule. The reduced Phase Rule may be written

$$P + F = C + 1$$

When two liquids are mixed together, as we have seen already, they may either by completely miscible in one another, be partially soluble in one another, or be completely immiscible. Similarly, when liquids solidify there are several possibilities. The two components of homogeneous liquid solution may be:

(a) totally insoluble in one another when solid;
(b) totally miscible with one another forming a continuous series of solid solutions;
(c) partially soluble in one another when solid;
(d) combine with each other to form one or more compounds.

Temperature—composition phase diagrams are of particular importance in the study of many alloy systems, since most alloys are made in the liquid phase and it is convenient to consider the formation of alloy structures on the basis of the solidification of liquids.
4.2. Total Solid Insolubility

Consider the case of two pure substances, A and B, which are completely soluble in one another in the liquid state, but are totally insoluble in one another in the solid state. If a composition base line and temperature scale is drawn (figure 4.1) certain information can be plotted. The melting point of pure substance A can be marked off as point A on the left-hand temperature axis. Similarly point B on the right-hand axis represents the melting point of pure substance B. At high temperatures any mixture of the two liquids will be a single-phase liquid solution.

In the same way as the presence of dissolved salt depresses the freezing point of water, so the freezing point of a liquid will normally be depressed if the liquid contains some other substance in solution. Line AL in figure 4.1 indicates the depression of freezing point of pure A containing dissolved B. Similarly, line BM is the depression of freezing point curve for pure B containing dissolved A. It is important to note that at any point on line AL it is pure substance A which is freezing, that is during cooling the solid which is forming is crystals of

![Figure 4.1. Freezing point curves for two substances insoluble in the solid state](image-url)