

4.3.1 Solidification of Single-Phase Alloys

The alloys of interest in this section are those such as X_0 in Fig. 4.19. This phase diagram has been idealized by assuming that the solidus and liquidus are straight lines. It is useful to define a partition coefficient k as

$$k = \frac{X_S}{X_L} \quad (4.32)$$

where X_S and X_L are the mole fractions of solute in the solid and liquid in equilibrium at a given temperature. For the simple case shown in Fig. 4.19, k is independent of temperature.

The way in which such alloys solidify in practice depends in rather a complex way on temperature gradients, cooling rates and growth rates. Therefore let us simplify matters by considering the movement of a planar solid/liquid interface along a bar of alloy as shown in Fig. 4.20a. Such unidirectional solidification can be achieved in practice by passing the alloy in a crucible through a steep temperature gradient in a specially constructed furnace in which heat is confined to flow along the axis of the bar.

Let us examine three limiting cases:

1. Infinitely slow (equilibrium) solidification
2. Solidification with no diffusion in the solid but perfect mixing in the liquid
3. Solidification with no diffusion in the solid and only diffusional mixing in the liquid

Equilibrium Solidification

Alloy X_0 in Fig. 4.19 begins to solidify at T_1 with the formation of a small amount of solid with composition kX_0 . As the temperature is lowered more solid forms and, provided cooling is slow enough to allow extensive solid-state diffusion, the solid and liquid will always be homogeneous with compositions following the solidus and liquidus lines, Fig. 4.20b. The relative amounts of solid and liquid at any temperature are simply given by the lever rule. Note that, since solidification is one-dimensional, conservation of solute requires the two shaded areas in Fig. 4.20b to be equal (ignoring the differences in molar volume between the two phases). At T_3 the last drop of liquid will have a composition X_0/k and the bar of solid will have a composition X_0 along its entire length.

No Diffusion in Solid, Perfect Mixing in Liquid

Very often the rate of cooling will be too rapid to allow substantial diffusion in the solid phase. Therefore let us assume no diffusion takes place in the solid but that the liquid composition is kept homogeneous during solidification by efficient stirring. Again, assuming unidirectional solidification, the first solid will appear when the cooled end of the bar reaches T_1 in Fig. 4.21a, at which stage solid containing kX_0 mol of solute forms. Since $kX_0 < X_0$, this first

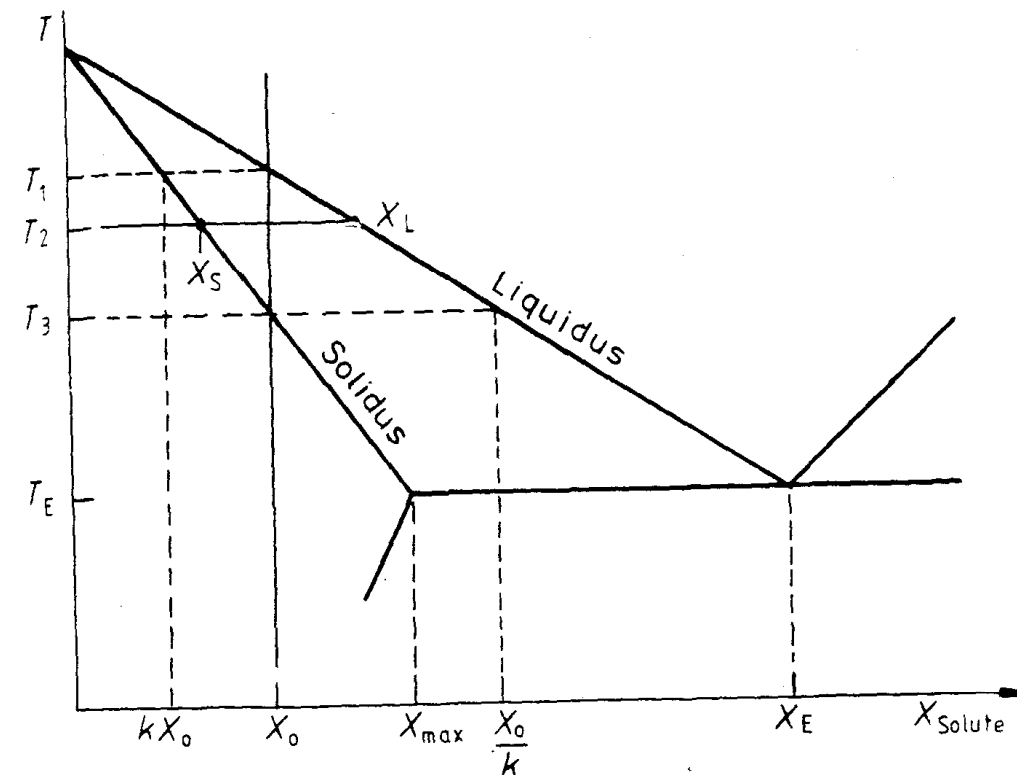


Fig. 4.19 A hypothetical phase diagram. $k = X_S/X_L$ is constant.

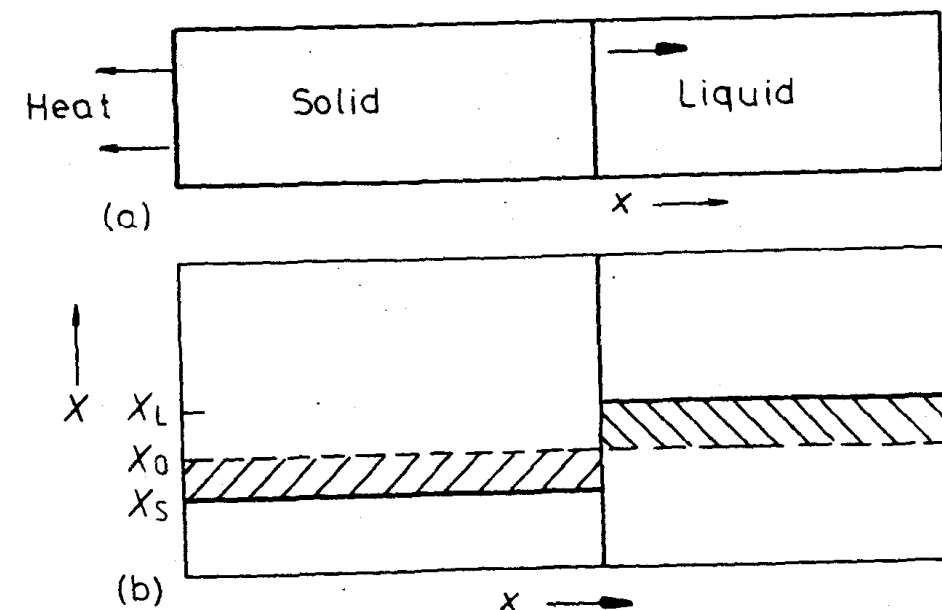


Fig. 4.20 Unidirectional solidification of alloy X_0 in Fig. 4.19. (a) A planar S/L interface and axial heat flow. (b) Corresponding composition profile at T_2 assuming complete equilibrium. Conservation of solute requires the two shaded areas to be equal.

solid will be purer than the liquid from which it forms so that solute is rejected into the liquid and raises its concentration above X_0 , Fig. 4.21b. The temperature of the interface must therefore decrease below T_1 before further solidification can occur, and the next layer of solid will be slightly richer in solute than the first. As this sequence of events continues the liquid becomes progressively richer in solute and solidification takes place at progressively lower temperatures, Fig. 4.21c. At any stage during solidification *local equilibrium* can be assumed to exist at the solid/liquid interface, i.e. for a given interface temperature the compositions of the solid and liquid in contact with one another will be given by the equilibrium phase diagram. However,

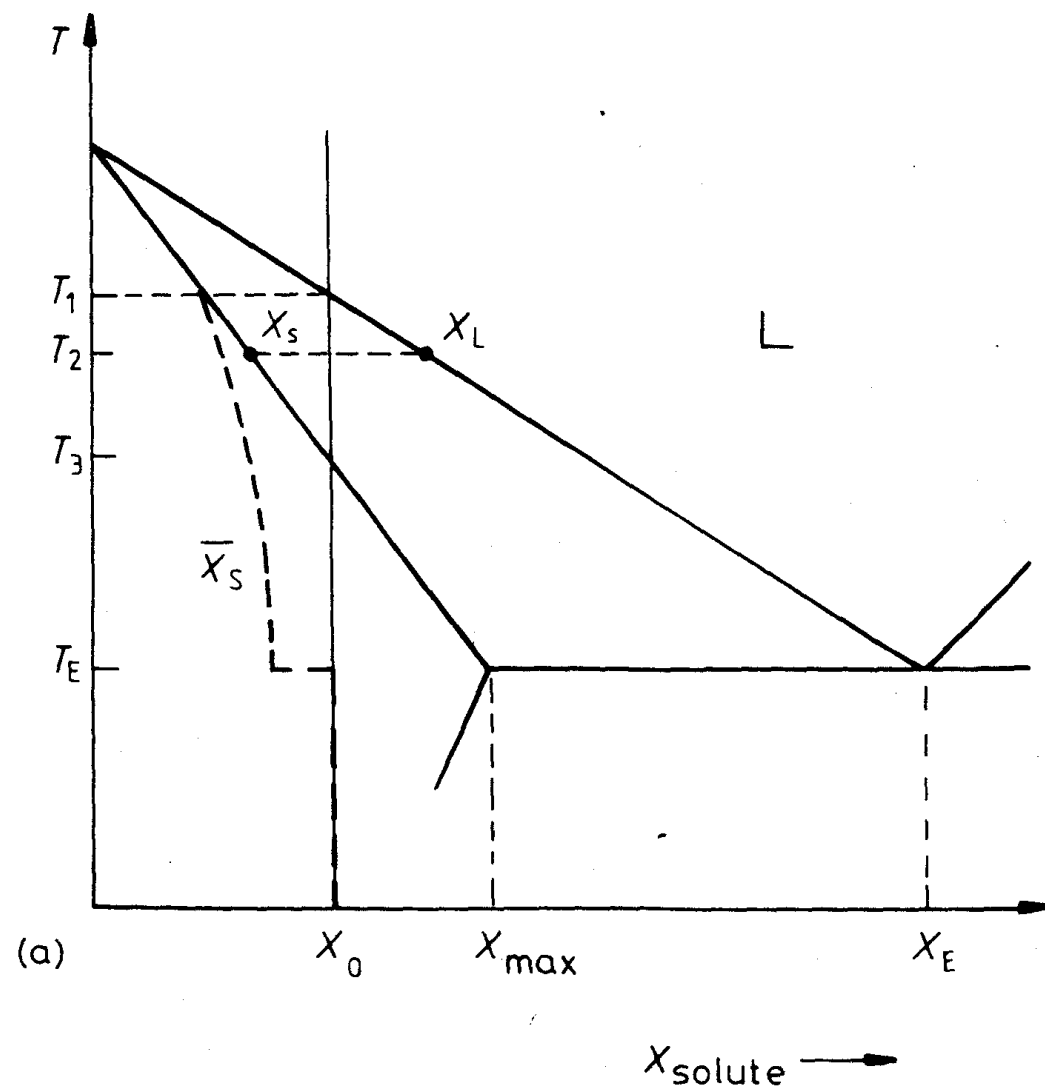


Fig. 4.21 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in the solid, but complete mixing in the liquid. (a) As Fig. 4.19, but including the mean composition of the solid. (b) Composition profile just under T_1 . (c) Composition profile at T_2 (compare with the profile and fraction solidified in Fig. 4.20b). (d) Composition profile at the eutectic temperature and below.

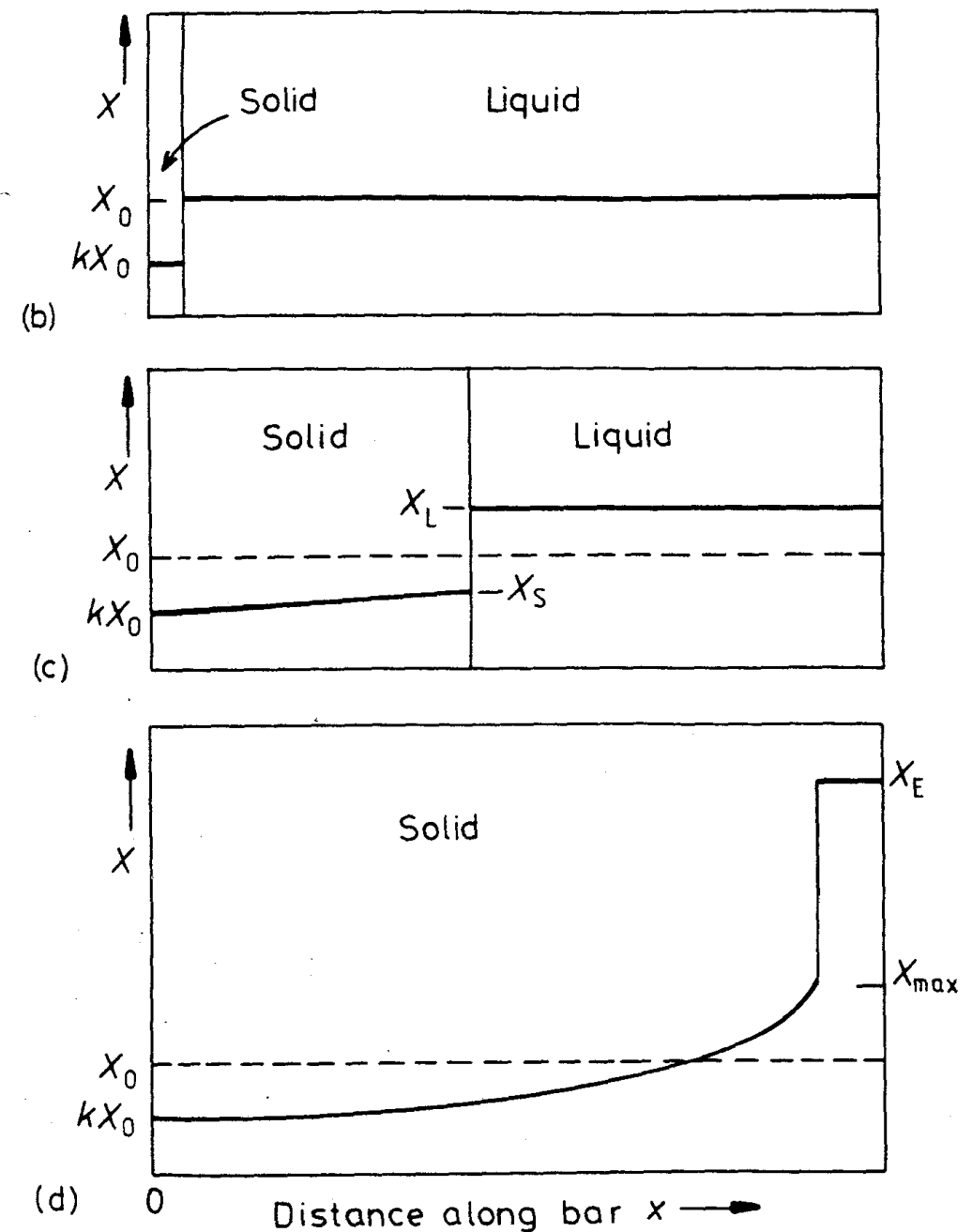


Fig. 4.21 (continued)

since there is no diffusion in the solid, the separate layers of solid retain their original compositions. Thus the mean composition of the solid (\bar{X}_S) is always lower than the composition at the solid/liquid interface, as shown by the dashed line in Fig. 4.21a. The relative amounts of solid and liquid for a given interface temperature are thus given by the lever rule using \bar{X}_S and X_L . It follows that the liquid can become much richer in solute than X_0/k and it may even reach a eutectic composition, X_E , for example. Solidification will thus

tend to terminate close to T_E with the formation of a eutectic structure of $\alpha + \beta$. The completely solidified bar will then have a solute distribution as shown in Fig. 4.21d with $\bar{X}_S = X_0$.

The variation of X_S along the solidified bar can be obtained by equating the solute rejected into the liquid when a small amount of solid forms with the resulting solute increase in the liquid. Ignoring the difference in molar volume between the solid and liquid this gives

$$(X_L - X_S)df_S = (1 - f_S)dX_L$$

where f_S is the volume fraction solidified. Integrating this equation using the boundary condition $X_S = kX_0$ when $f_S = 0$ gives

$$X_S = kX_0(1 - f_S)^{(k-1)}$$

and

$$X_L = X_0 f_L^{(k-1)} \quad (4.33)$$

These equations are known as the *non-equilibrium lever rule* or the *Scheil equations*.

Note that for $k < 1$ these equations predict that when there is no diffusion in the solid there will always be some eutectic in the last drop of liquid to solidify, no matter how little solute is present. Also the equation is quite generally applicable even for non-planar solid/liquid interfaces provided the liquid composition is uniform and that the Gibbs-Thomson effect is negligible.

No Diffusion in Solid, Diffusional Mixing in Liquid

If there is no stirring or convection in the liquid phase the solute rejected from the solid will only be transported away by diffusion. Hence there will be a rapid build up of solute ahead of the solid and a correspondingly rapid increase in the composition of the solid formed, Fig. 4.22a. This is known as the initial transient. If solidification is made to occur at a constant rate, v , it can be shown that a steady state is finally obtained when the interface temperature reaches T_3 in Fig. 4.19⁶. The liquid adjacent to the solid then has a composition X_0/k and the solid forms with the bulk composition X_0 .

During steady-state growth the concentration profile in the liquid must be such that the rate at which solute diffuses down the concentration gradient away from the interface is balanced by the rate at which solute is rejected from the solidifying liquid, i.e.

$$-DC'_L = v(C_L - C_S) \quad (4.34)$$

where D is diffusivity in the liquid, C'_L stands for dC_L/dx at the interface, C_L and C_S are the solute concentrations of the liquid and solid in equilibrium at the interface (units: m^{-3}). Note the similarity of this equation to that describing the rate at which solidification occurs in pure metals, Equation 4.29.

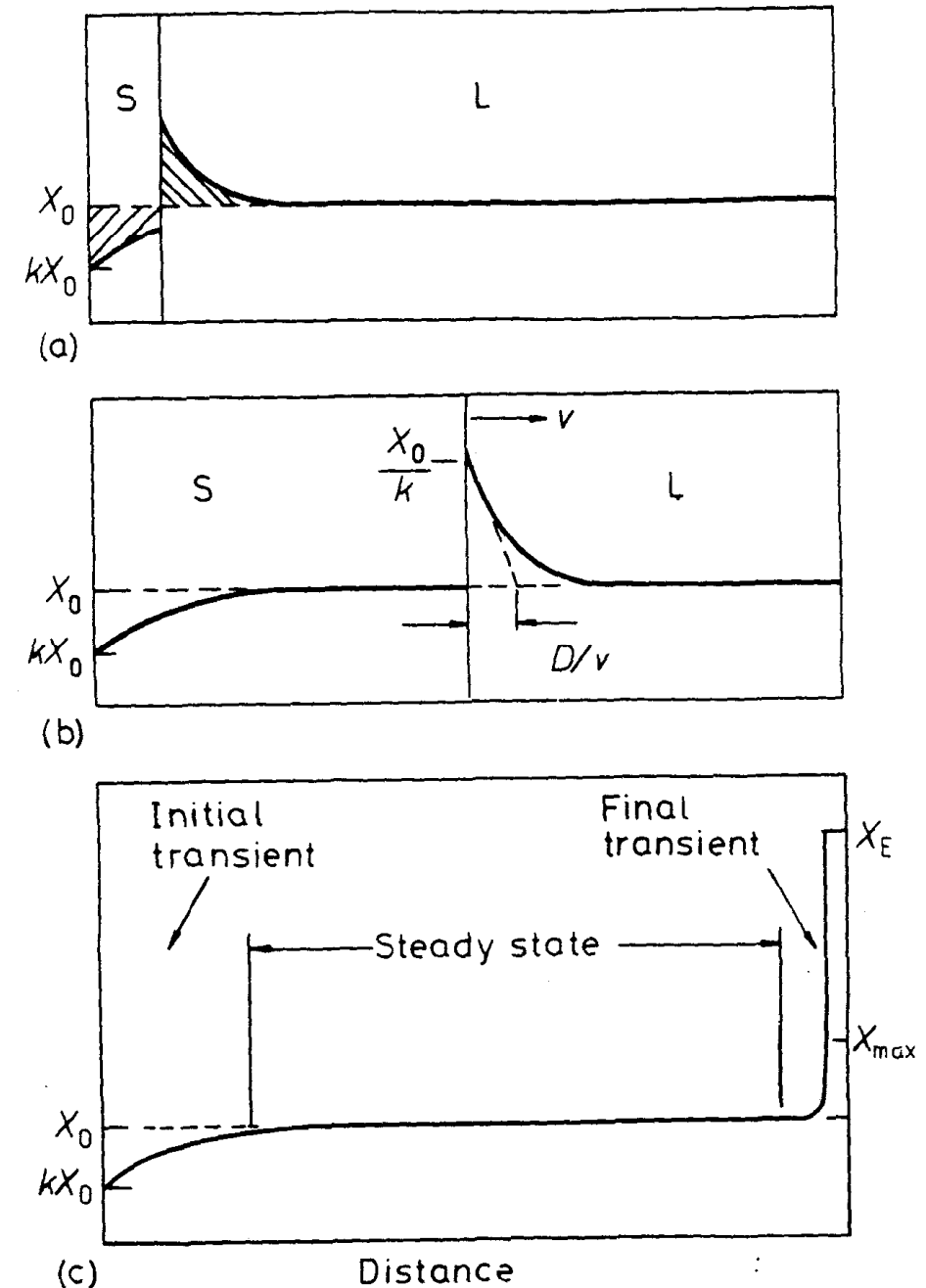


Fig. 4.22 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in the solid and no stirring in the liquid. (a) Composition profile when S/L interface temperature is between T_2 and T_3 in Fig. 4.19. (b) Steady-state solidification at T_3 . The composition solidifying equals the composition of the liquid far ahead of the solid (X_0). (c) Composition profile at T_E and below, showing the final transient.