

It should be emphasised that according to the diffusional theory any chemical compound layer once formed cannot then disappear during isothermal annealing of the $A-B$ reaction couple because its growth rate increases with decreasing thickness: $dx/dt \sim \partial c/\partial x$. It is therefore assumed that the layers do not disappear completely, but their thickness decreases to such an extent that they become unobservable experimentally.

Until recently, when it was only possible to examine compound layers with a thickness of the order of 1 μm or greater, experimentalists were forced to accept this explanation. At present, when the phase composition, the structure and the rate of formation of chemical compound layers, a few nanometers thick, can reliably be determined, this explanation is no longer acceptable. At smaller thicknesses of a growing layer the concept *phase* clearly loses its physical meaning since, in order to be identified as such, any phase must contain at least a few crystal-lattice units across the layer thickness.

Therefore, it seems more reasonable to assume that if the layers of certain compounds cannot be revealed in the $A-B$ reaction couple by means of sufficiently sensitive experimental techniques both in thin films and in massive specimens, then they are simply *missing* from that couple, and to undertake an attempt to find out the reasons for this phenomenon. Such an attempt will be made in this chapter.

3.1. Chemical reactions at phase interfaces in a multiphase binary system

To understand the regularities of multiple layer formation, it suffices to consider the $A-B$ binary system with three chemical compounds A_pB_q , A_rB_s and A_lB_n on the equilibrium phase diagram (Fig.3.1). The scheme of analysis of the process of their occurrence at the $A-B$ interface is analogous to that of two compound layers (see Chapter 2). First of all, the equations of partial chemical reactions taking place at phase interfaces must be written. These are as follows.

Layer	Interface	Partial chemical reaction	
A_pB_q	1	$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q$,	(3.1 ₁)
	2	$(sp - qr)A_{\text{dif}} + qA_rB_s = sA_pB_q$,	(3.1 ₂)
A_rB_s	2	$(sp - qr)B_{\text{dif}} + rA_pB_q = pA_rB_s$,	(3.2 ₁)

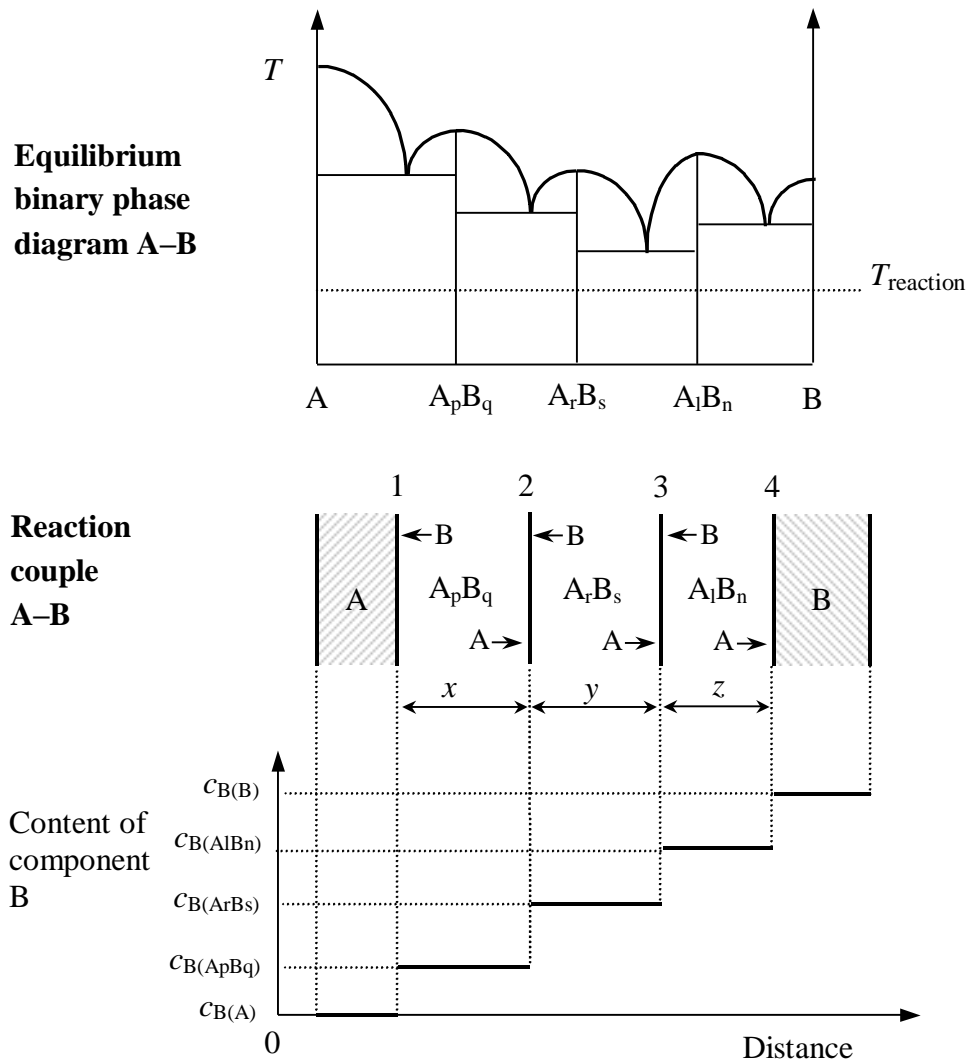


Fig.3.1. Schematic diagram to illustrate the growth process of three chemical compound layers $A_p B_q$, $A_r B_s$ and $A_l B_n$ between mutually insoluble elementary substances A and B .

$$3 \quad (rn - ls)A_{\text{dif}} + sA_lB_n = nA_rB_s, \quad (3.2_2)$$

$$A_lB_n \quad 3 \quad (rn - ls)B_{\text{dif}} + lA_rB_s = rA_lB_n, \quad (3.3_1)$$

$$4 \quad lA_{\text{dif}} + nB_{\text{surf}} = A_lB_n. \quad (3.3_2)$$

As previously, all these reactions are assumed to be independent in the sense that the elementary act of each of them has no effect on the elementary acts of the others.

Partial chemical reactions (3.1₁)-(3.3₂) cause the changes in thickness of appropriate compound layers. During the time dt , reactions (3.1₁) and (3.1₂) lead to the increase of the thickness of the A_pB_q layer respectively by dx_{B1} at interface 1 and by dx_{A2} at interface 2 (Fig.3.2). Reaction (3.2₁) resulting in the increase of the thickness of the A_rB_s layer by dy_{B2} at interface 2, leads simultaneously to the decrease in thickness of the A_pB_q layer by $dx_{-}^{(2)}$ at the same interface 2. The thickness of the A_rB_s layer also increases by dy_{A3} at interface 3 as a result of reaction (3.2₂). At the same time, its thickness decreases by $dy_{-}^{(2)}$ at interface 2 and by $dy_{-}^{(3)}$ at interface 3 since the A_rB_s phase is consumed in the course of reactions (3.1₂) and (3.3₁). Reactions (3.3₁) and (3.3₂) cause the increases of the thickness of the A_lB_n layer during dt by dz_{B3} and dz_{A4} at interfaces 3 and 4, respectively. Again, the thickness of this layer decreases by $dz_{-}^{(3)}$ at interface 3 as a result of reaction (3.2₂).

Position of interface 1 is seen to depend on the occurrence of only one partial chemical reaction (3.1₁). Similarly, position of interface 4 only depends on partial chemical reaction (3.3₂). Position of interface 2 is determined by two partial chemical reactions (3.1₂) and (3.2₁) taking place simultaneously. The same applies to position of interface 3 depending on partial chemical reactions (3.2₂) and (3.3₁).

The thickness of the A_pB_q layer as well as the A_lB_n layer is thus determined by the rate of occurrence of two partial chemical reactions. The thickness of the A_rB_s layer located between them depends on the rate of four partial chemical reactions. The same applies to any other growing layer of a multiphase system, having no direct contact with either of initial phases, if the number of compounds on the phase diagram exceeds three.

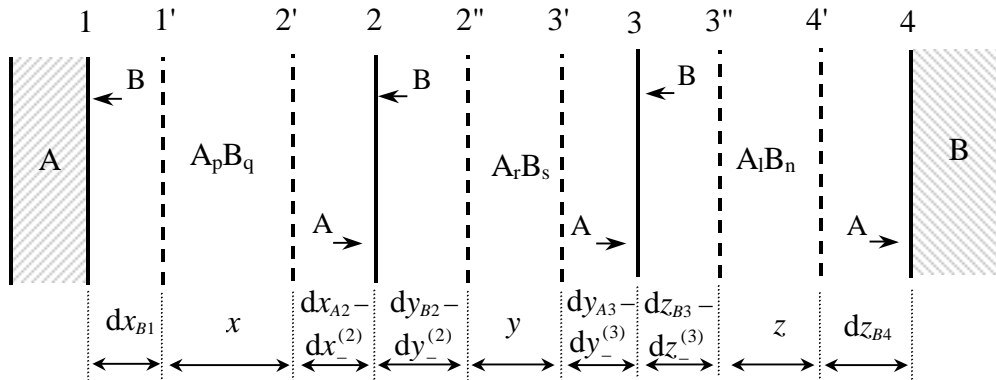


Fig.3.2. Schematic diagram to illustrate the changes in thickness of three chemical compound layers $A_p B_q$, $A_r B_s$ and $A_l B_n$ growing between mutually insoluble elementary substances A and B at the expense of diffusion of both components.