

2.1. Partial chemical reactions at phase interfaces

A schematic diagram illustrating the growth process of the layers of two chemical compounds A_pB_q and A_rB_s , with p , q , r and s being positive numbers, at the A – B interface is shown in Fig.2.1. Note that the lines showing the distribution of the concentration of components A and B in the phases involved in the interaction are parallel to the distance axis since (i) the formation of the layers of chemical compounds which have narrow, if any, ranges of homogeneity is considered and (ii) initial substances are assumed to be mutually insoluble.

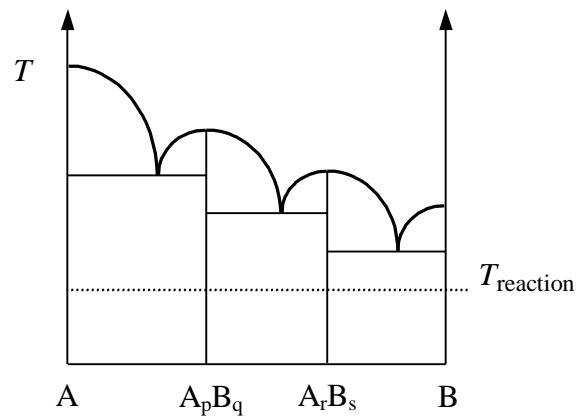
In such a case, immediate application of Fick's laws is clearly impossible. Therefore, it is not surprising that usually smooth concentration distributions characteristic of solid solutions are drawn, while the results obtained are then applied to chemical compounds. Many researchers, especially of physical orientation, even do not use the term *chemical compound*, preferring to analyse the formation of a *new phase*, thus actually making no difference between solid solutions and chemical compounds.

It should be emphasised that, although in many binary systems there is no clear-cut distinction between a chemical compound and a solid solution, it is nonetheless necessary to distinguish between them on the basis of (i) constancy or variability of their composition and (ii) degree of ordering their crystal lattices. Also, usually the chemical compound has a crystal lattice different from crystal lattices of parent phases A and B , while the solid solution has a similar one or the same. It would be a rough mistake resulting, as will be seen later, in far-reaching misleading consequences to ignore these differences.

Whether a particular phase is a chemical compound or a solid solution can hardly be subject to any doubt in obvious cases such as in the Ni–Bi binary system with the intermetallics NiBi (homogeneity range $HR \leq 0.3$ at.%) and NiBi₃ (stoichiometric phase)¹⁴⁸ or in the Ti–Al binary system with the intermetallics Ti₃Al ($HR \approx 12$ at.% at 600°C), TiAl ($HR \approx 7$ at.%), TiAl₂ ($HR \leq 1$ at.%) and TiAl₃ (stoichiometric phase).^{142,145,193} Definitely, NiBi, NiBi₃, TiAl₂ and TiAl₃ are chemical compounds, no less than Bi₂O₃ or TiO₂. Phases like Ti₃Al or TiAl can, of course, be treated ambiguously. This point will be analysed once again in the next chapter.

Also, formation of a solid solution is often considered to be a prerequisite for the occurrence of a chemical compound layer, with the latter being a result of

**Equilibrium
binary phase
diagram A–B**



**Reaction
couple
A–B**

**Content of
component
B**

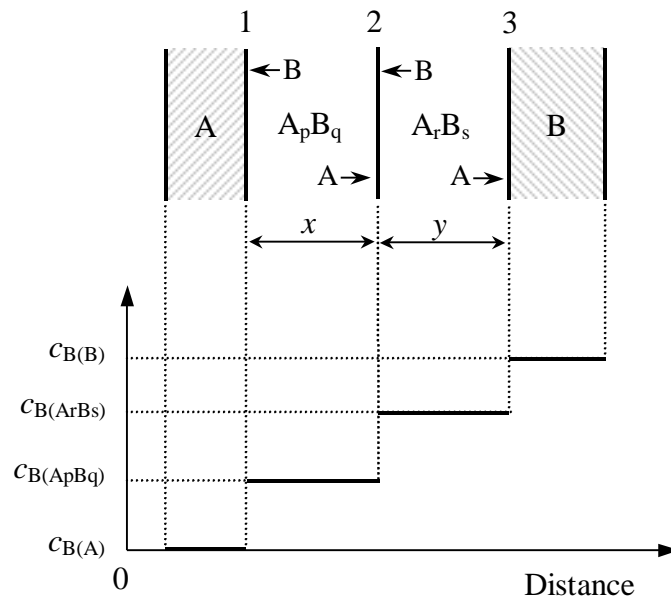


Fig.2.1. Schematic diagram to illustrate the growth process of the layers of two chemical compounds $A_p B_q$ and $A_r B_s$ at the interface between mutually insoluble elementary substances A and B .

supersaturation of the former. In fact, however, these are two concurrent, competing processes, if both solid solutions and chemical compounds are present on the phase diagram of a binary system. In any reaction couple $A-B$ given to itself under conditions of constant temperature and pressure or tending to its equilibrium state from below (from lower to higher temperatures and pressures), no supersaturation is clearly possible.

Direct chemical reaction between elementary substances A and B clearly ceases after the formation of compound layers A_pB_q and A_rB_s , a few crystal-lattice units thick, which separate the reacting phases from each other. Subsequently, four partial chemical reactions take place at the layer interfaces. These are as follows:

Layer	Interface	Partial chemical reaction	
A_pB_q	1	$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q,$	(2.1 ₁)
	2	$(sp - qr)A_{\text{dif}} + qA_rB_s = sA_pB_q,$	(2.1 ₂)
A_rB_s	2	$(sp - qr)B_{\text{dif}} + rA_pB_q = pA_rB_s,$	(2.2 ₁)
	3	$rA_{\text{dif}} + sB_{\text{surf}} = A_rB_s.$	(2.2 ₂)

The A_pB_q compound layer grows at the expense of diffusion of the B atoms to interface 1 where these atoms then enter into reaction (2.1₁) with the surface A atoms. It is seen that the same partial chemical reaction takes place at the $A-A_pB_q$ interface in the $A-A_pB_q-B$ (see Section 1.2) and $A-A_pB_q-A_rB_s-B$ heterogeneous systems. The difference between these two systems is that in the former the B atoms which have crossed only the bulk of the A_pB_q layer enter into the chemical reaction at interface 1, while in the latter the B atoms are to diffuse across the bulks of both layers A_rB_s and A_pB_q before entering into this reaction since the only source of the B atoms in both systems is in fact substance B .

The thickness of the A_pB_q layer also increases at the expense of diffusion of the A atoms to interface 2 and their subsequent partial chemical reaction with the A_rB_s compound in accordance with equation (2.1₂). Thus, another difference between the $A-A_pB_q-B$ and $A-A_pB_q-A_rB_s-B$ systems is that in the former an increase in thickness of the A_pB_q layer at interface 2 is a result of the reaction of the A atoms diffusing across its bulk with phase B , while in the latter with the A_rB_s compound.

Growth of the A_rB_s compound layer is due to both partial chemical reaction (2.2₁) taking place at interface 2 between the diffusing B atoms and the A_pB_q compound and partial chemical reaction (2.2₂) at interface 3 between the diffusing A atoms and the surface B atoms. It must be clear that only the diffusing A atoms which have not entered earlier into reaction (2.1₂) at interface 2 can then enter into reaction (2.2₂) at interface 3.

Note that no reactions proceed within the bulks of both layers. Layer bulks are no more than a transport medium for diffusing atoms. Chemical transformations take place only at the phase interfaces which are regarded as transition regions between the interacting phases, whose widths are not very different from the lattice spacings of those phases.

The A_pB_q chemical compound is seen to be a product of reactions (2.1₁) and (2.1₂). At the same time, it is also a reactant of reaction (2.2₁). The A_rB_s chemical compound is a product of reactions (2.2₁) and (2.2₂) and a reactant of reaction (2.1₂). Thus, each of the two compound layers grows not only at the expense of the A and B atoms diffusing from initial phases A and B , but also partly at the expense of an adjacent compound layer.^{1,46} Hence, the change in thickness of the A_pB_q layer is a result of (i) growth due to reactions (2.1₁) and (2.1₂) and (ii) consumption during the formation of the A_rB_s chemical compound by reaction (2.2₁). Similarly, the A_rB_s layer grows in the course of reactions (2.2₁) and (2.2₂) and is consumed by reaction (2.1₂).

2.2. A system of differential equations describing the rates of formation of two chemical compound layers

During an infinitesimal period of time, dt , the thickness of the A_pB_q layer increases by dx_{B1} at interface 1 as a result of reaction (2.1₁) and by dx_{A2} at interface 2 as a result of reaction (2.1₂), as shown in Fig.2.2. At the same time, the thickness of the A_rB_s layer increases by dy_{B2} at interface 2 and by dy_{A3} at interface 3 due to reactions (2.2₁) and (2.2₂), respectively.

To establish differential equations relating dt to the increases, dx_{B1} , dx_{A2} , dy_{B2} and dy_{A3} , in thicknesses of the A_pB_q and A_rB_s layers, use is again made of the postulate about the summation of the time of diffusion of the A and B atoms and the time of subsequent chemical transformations for each of four partial chemical reactions taking place at phase interfaces 1, 2 and 3. This yields