

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

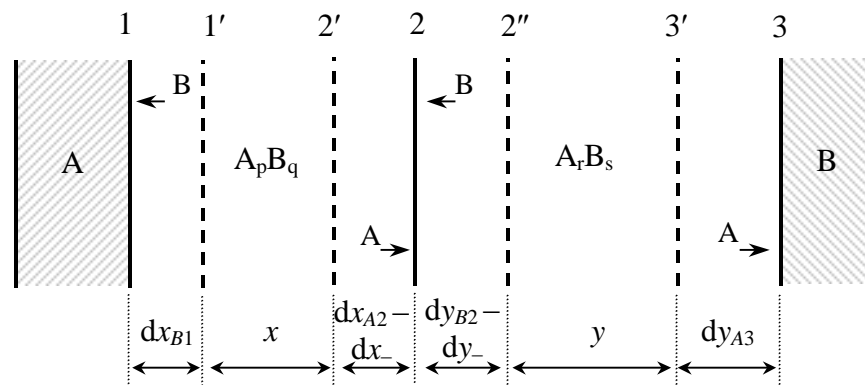


Fig.2.2. Schematic diagram to illustrate the changes, dx_{B1} , dx_{A2} , dy_{B2} , dy_{A3} , dx_- and dy_- , in thicknesses of the A_pB_q and A_rB_s compound layers during the time dt in the general case where both layers grow at the expense of diffusion of both components across their bulks.

$$dt = dt_{\text{dif}}^{(B \rightarrow A_p B_q)} + dt_{\text{chem}}^{(B \rightarrow A_p B_q)}, \quad (2.3_1)$$

$$dt = dt_{\text{dif}}^{(A \rightarrow A_p B_q)} + dt_{\text{chem}}^{(A \rightarrow A_p B_q)}, \quad (2.3_2)$$

$$dt = dt_{\text{dif}}^{(B \rightarrow A_r B_s)} + dt_{\text{chem}}^{(B \rightarrow A_r B_s)}, \quad (2.4_1)$$

$$dt = dt_{\text{dif}}^{(A \rightarrow A_r B_s)} + dt_{\text{chem}}^{(A \rightarrow A_r B_s)}, \quad (2.4_2)$$

where the superscripts of the type $(B \rightarrow A_p B_q)$ in equation (2.3₁) indicate that such a time is required for the diffusion of the B atoms across the bulk of the $A_p B_q$ layer (first term) or for subsequent chemical transformations with their participation (second term). Like the case of formation of the layer of a single chemical compound, it is assumed that the time of diffusion is directly proportional to both the increase of the thickness of a given compound layer and its existing total thickness, whereas the time of chemical transformations is directly proportional to the increase of the thickness of the layer and is quite independent of its total thickness (see Section 1.3). Hence,

$$dt = \left(\frac{x}{k_{1B1}} + \frac{1}{k_{0B1}} \right) dx_{B1}, \quad (2.5_1)$$

$$dt = \left(\frac{x}{k'_{1A2}} + \frac{1}{k'_{0A2}} \right) dx_{A2}, \quad (2.5_2)$$

$$dt = \left(\frac{y}{k'_{1B2}} + \frac{1}{k'_{0B2}} \right) dy_{B2}, \quad (2.6_1)$$

$$dt = \left(\frac{y}{k_{1A3}} + \frac{1}{k_{0A3}} \right) dy_{A3}, \quad (2.6_2)$$

where all k_0 are chemical constants, while all k_1 are physical (diffusional) constants.

Note that the designations with strokes were only introduced to avoid confusion with the results of Chapter 1. Partial chemical reactions at interface 1 are the same in the

$A-A_pB_q-B$ and $A-A_pB_q-A_rB_s-B$ systems, whereas at interface 2 these are different. Therefore, equations (1.6) and (2.5₁) are identical, while equations (1.21) and (2.5₂) are different. Note that not only k'_{0A2} is not equal to k_{0A2} , but also k'_{1A2} is not equal to k_{1A2} , although the diffusion coefficient of the A atoms across the bulk of the A_pB_q layer does not depend on whether this layer borders with phase B or A_rB_s . However, different amounts of the diffusing A atoms are necessary to form one molecule of the A_pB_q chemical compound by reactions (1.2) and (2.1₂). In Section 1.4 k_{1A2} was used to denote the physical (diffusional) constant relating to reaction (1.2). From equations (1.2) and (2.1₂), it follows

$$k'_{1A2} = \frac{sp}{sp - qr} k_{1A2}. \quad (2.7)$$

Relations between different constants will be considered in greater detail, when comparing the growth rates of the same chemical compound layer in various reaction couples of a multiphase binary system (Chapter 4).

On the basis of the principle of independency of the rates of elementary acts of chemical reactions, equations (2.5₁)-(2.6₂) are assumed to be independent of each other. Therefore, the increases of layer thicknesses can explicitly be expressed from these equations as follows:

$$\frac{dx_{B1}}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}}, \quad (2.8_1)$$

$$\frac{dx_{A2}}{dt} = \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}}, \quad (2.8_2)$$

$$\frac{dy_{B2}}{dt} = \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}}, \quad (2.9_1)$$

$$\frac{dy_{A3}}{dt} = \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}}. \quad (2.9_2)$$

The increase in thickness of the A_pB_q layer during the time dt is

$$dx_+ = dx_{B1} + dx_{A2}, \quad (2.10)$$

while that of the A_rB_s layer is

$$dy_+ = dy_{B2} + dy_{A3}. \quad (2.11)$$

During the same period of time, dt , the thickness of the A_pB_q layer decreases by dx_- due to partial chemical reaction (2.2₁). The value of this decrease can easily be found using equation (2.2₁). Calculations are carried out in the conventional manner generally accepted for chemical reactions. The only difference is that the diffusing component must be written in equations (1.1), (1.2), (2.1₁)-(2.2₂) in that form (atom, ion, *etc.*) in which it diffuses across the bulks of growing compound layers and then reacts at an appropriate phase interface, but not in the form in which it exists in an initial substance. Consider a few examples.

The process of growth of the Cu_3Sn and Cu_6Sn_5 intermetallic layers in the $Cu-Cu_3Sn-Cu_6Sn_5-Sn$ system can be represented as follows:

Layer	Interface	Partial chemical reaction	
Cu_3Sn	$Cu-Cu_3Sn$	$Sn_{dif} + 3Cu_{surf} = Cu_3Sn,$	(2.12 ₁)
	$Cu_3Sn-Cu_6Sn_5$	$9Cu_{dif} + Cu_6Sn_5 = 5Cu_3Sn,$	(2.12 ₂)
Cu_6Sn_5	$Cu_6Sn_5-Cu_3Sn$	$3Sn_{dif} + 2Cu_3Sn = Cu_6Sn_5,$	(2.13 ₁)
	Cu_6Sn_5-Sn	$6Cu_{dif} + 5Sn_{surf} = Cu_6Sn_5.$	(2.13 ₂)

In this obvious case, there is no ambiguity in writing partial chemical reactions. It can only be noted that the copper and tin ions, not atoms, are most likely to diffuse across the growing Cu_3Sn and Cu_6Sn_5 intermetallic layers, whereas electrons simply accompany them, so that the final result is such, as if the atoms were the diffusing species. For formal kinetics, such details of the mechanism of atomic transfer are clearly of no importance .

A somewhat different situation arises in the case of formation of the TiO and TiO_2 layers in the $Ti-TiO-TiO_2-O_2$ reaction system. Most probably, oxygen and titanium diffuse across layer bulks in the form of ions or atoms, whereas in the initial

gaseous phase oxygen exists in the form of molecules O_2 . Therefore, the partial chemical reactions taking place at phase interfaces must be written as follows:

Layer	Interface	Partial chemical reaction	
TiO	Ti–TiO	$O_{\text{dif}} + Ti_{\text{surf}} = TiO,$	(2.14 ₁)
	TiO–TiO ₂	$Ti_{\text{dif}} + TiO_2 = 2TiO,$	(2.14 ₂)
TiO ₂	TiO ₂ –TiO	$O_{\text{dif}} + TiO = TiO_2,$	(2.15 ₁)
	TiO ₂ –O ₂ (gas)	$Ti_{\text{dif}} + 2O_{\text{surf}} = TiO_2,$	(2.15 ₂)

but not as



and



The last two reactions may proceed if very porous layers are formed, not preventing the Ti and TiO surfaces from the direct oxygen attack. However, if the layers are compact and have no macroscopic defects, oxygen can only diffuse across their bulks after its molecules have dissociated into atoms or ions onto the surface of the TiO₂ layer bordering with the gaseous phase. Clearly, the time of dissociation of the O₂ molecules into atoms is independent of the thickness of the TiO₂ layer. Therefore, it must be included into the value of the chemical constant corresponding to partial chemical reaction (2.15₂).

If initial phases are chemical compounds, not elementary substances, the growth of the layers of two new chemical compounds in a quasibinary system takes place as a result of counter diffusion of the same-type ions or atoms of smaller size. The common ion usually does not take active part in the growth process. This does not mean, however, that its presence has no effect on the mechanism of formation of the layers. The Rb₂AgI₃ and RbAg₄J₅ layers are known to form in the RbI–AgI system:^{52,200,201} Their formation is due to the following partial chemical reactions:

Layer	Interface	Partial chemical reaction
Rb ₂ AgI ₃	RbI–Rb ₂ AgI ₃	$\text{Ag}^+ + 3\text{RbI} = \text{Rb}_2\text{AgI}_3 + \text{Rb}^+$, (2.18 ₁)
	Rb ₂ AgI ₃ –RbAg ₄ J ₅	$7\text{Rb}^+ + 3\text{RbAg}_4\text{J}_5 = 5\text{Rb}_2\text{AgI}_3 + 7\text{Ag}^+$, (2.18 ₂)
RbAg ₄ J ₅	RbAg ₄ J ₅ –Rb ₂ AgI ₃	$7\text{Ag}^+ + 5\text{Rb}_2\text{AgI}_3 = 3\text{RbAg}_4\text{J}_5 + 7\text{Rb}^+$, (2.19 ₁)
	RbAg ₄ J ₅ –AgJ	$\text{Rb}^+ + 5\text{AgJ} = \text{RbAg}_4\text{J}_5 + \text{Ag}^+$. (2.19 ₂)

It can easily be seen that the total yield of partial chemical reactions (2.18₂) and (2.19₁) is zero. This is caused by the presence of the third, low-mobile component (iodine anions Γ). Because of their presence, rubidium and silver cations are unable to move in the lattices of the growing Rb₂AgI₃ and RbAg₄J₅ compounds independently of each other. The fluxes of these cations should necessarily be balanced since partial chemical reactions (2.18₁) and (2.19₂) are mutually dependent. In this respect, the system under consideration and other similar systems differ from binary ones in which all four partial chemical reactions taking place at layer interfaces are independent of each other unless any diffusional constraints arise (see the next chapter).

Thus, the increase in thickness of the Rb₂AgI₃ layer is due to partial chemical reaction (2.18₁), while that of the RbAg₄J₅ layer to partial chemical reaction (2.19₂). The overall reaction is the sum of these two partial chemical reactions:



Formally, the final result is such, as if the initial phases RbI and AgI reacted immediately, although they have no direct contact. Similar reactions take place during the interaction of oxides and other chemical compounds.^{10,15,16,202}

Let us now return to analysing the process of growth of the A_pB_q and A_rB_s compound layers at the interface between elementary substances A and B . From equation (2.2₁), it follows that the ratio of the mass of the A_pB_q compound entering into partial chemical reaction (2.2₁) to the mass of the A_rB_s compound formed as a result of this reaction is equal to the ratio of the molecular masses of the compounds A_pB_q and

A_rB_s with the factors r and p , respectively:

$$\frac{m_{A_pB_q}}{m_{A_rB_s}} = \frac{rM_{A_pB_q}}{pM_{A_rB_s}}, \quad (2.21)$$

where m is the mass and M is the molecular mass of an appropriate compound. This is a conventional chemical relation.

The mass is equal to the product of the density, ρ , and the volume which in turn is the product of the surface area of the phase interface and the thickness of the growing layer. Since the surface area of the interfaces between all the reacting phases is assumed to be the same and constant during the whole course of layer growth, then

$$\frac{\rho_{A_pB_q} dx_-}{\rho_{A_rB_s} dy_{B2}} = \frac{rM_{A_pB_q}}{pM_{A_rB_s}}. \quad (2.22)$$

Taking into account that the quotient of dividing the molecular mass by the density of a given compound is its molar volume, V , one obtains

$$dx_- = \frac{rg}{p} dy_{B2}, \quad (2.23)$$

where g stands for the ratio of the molar volumes of chemical compounds A_pB_q and A_rB_s : $g = V_{A_pB_q} / V_{A_rB_s}$.

Similarly, from equation (2.12), one finds

$$dy_- = \frac{q}{sg} dx_{A2}. \quad (2.24)$$

Equations (2.23) and (2.24) take account of the mutual consumption of the A_pB_q and A_rB_s layers during their simultaneous formation.

The total change in thickness of the A_pB_q layer during the time dt is equal to the difference between the right-hand parts of equations (2.10) and (2.23):

$$dx = dx_{B1} + dx_{A2} - dx_- . \quad (2.25)$$

For the A_rB_s layer, this value is (see equations (2.11) and (2.24))

$$dy = dy_{B_2} + dy_{A_3} - dy_- . \quad (2.26)$$

Substituting into these equations the expressions (2.8₁)-(2.9₂) for the increases of the thicknesses of the A_pB_q and A_rB_s compound layers, one obtains the required general system of two differential equations describing their growth rates at the $A-B$ interface:

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}} - \frac{rg}{p} \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}}, \quad (2.27_1)$$

$$\frac{dy}{dt} = \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}} + \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}} - \frac{q}{sg} \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}}. \quad (2.27_2)$$

The system of equations (2.27) belongs to the so-called autonomous systems which are analysed in detail, for examples, in Refs 203 and 204. Note, however, that, to avoid misleading conclusions concerning layer growth kinetics, an approach to its solution should by no means be formally mathematical. Namely, besides the initial conditions $x = 0$ and $y = 0$ at $t = 0$, the existence of the critical values of the thicknesses of the A_pB_q and A_rB_s compound layers must necessarily be taken into account. These are as follows (see equations (1.17) and (1.22) in Chapter 1):

$$x_{1/2}^{(B)} = \frac{k_{1B1}}{k_{0B1}}, \quad (2.28_1)$$

$$x_{1/2}^{(A)} = \frac{k'_{1A2}}{k'_{0A2}}, \quad (2.28_2)$$

$$y_{1/2}^{(B)} = \frac{k'_{1B2}}{k'_{0B2}}, \quad (2.29_1)$$

$$y_{1/2}^{(A)} = \frac{k_{1A3}}{k_{0A3}}. \quad (2.29_2)$$

They divide the $x - t$ and $y - t$ kinetic dependences into the reaction controlled and diffusion controlled regions with regard to components A and B (in the theoretical definition given in Section 1.3.2 of Chapter 1).

It should be emphasised that, according to the notations accepted throughout the book, the plus sign only indicates an increase of the thickness of an appropriate compound layer, while the minus sign indicates its decrease, but not the direction of movement of the interfaces of this layer with adjacent phases in some (laboratory) frame of reference. Therefore, the quantities, for example, dx_{B1} and dx_{A2} were taken with the plus sign, although interfaces 1 and 2 (see Fig.2.1) move in the opposite directions during the course of reactions (2.1₁) and (2.1₂). Clearly, in such a case x and y correspond to experimentally measured values of the thicknesses of the A_pB_q and A_rB_s compound layers. This form of writing mathematical equations also makes it possible to easily take account of a change in volume of the system resulting from the formation of chemical compounds, which in many cases is too considerable to be neglected without a noticeable error.

The system of equations (2.27) is seen to be rather complicated. Its solution, if obtainable at all in quadratures, must probably be even more complicated. However, in experiments certain conditions which enable the initial equations to be simplified are usually fulfilled. Consider limiting cases of particular interest from theoretical and practical viewpoints.^{134,136,139,140} The process of growth of the A_pB_q and A_rB_s layers will be analysed in its development with time from the start of the interaction of initial substances A and B to the establishment of equilibrium at which, according to the Gibbs phase rule (see Refs 126-128), no more than two phases should remain in any two-component system at constant temperature and pressure.

2.3. Initial linear growth of the A_pB_q and A_rB_s layers

Evidently, in an initial period of interaction of substances A and B when the thicknesses of the A_pB_q and A_rB_s layers are relatively small the conditions $k_{0B1} \ll k_{1B1}/x$, $k'_{0A2} \ll k'_{1A2}/x$, $k'_{0B2} \ll k'_{1B2}/y$ and $k_{0A3} \ll k_{1A3}/y$ are satisfied. Hence, at low t the terms of the type k_0x/k_1 and k_0y/k_1 can be neglected in comparison with unity. Therefore, the system of equations (2.27) is simplified to