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Reaction diffusion in heterogeneous binary systems

Part 3 *Multiphase growth of the chemical compound layers at the interface between two mutually insoluble substances*

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A physicochemical approach to the solid-state growth kinetics of compound layers in multiphase binary heterogeneous systems is proposed. This approach seems to be more adequate than the existing "diffusional" one. At least, it permits one to understand without any speculative suppositions why the number of compound layers in reaction couples is in general far less than the number of chemical compounds in binary phase diagrams at the temperatures under investigation.

1. Introduction

The growth kinetics of one and two compound layers were considered in Parts 1 and 2, respectively, of this paper [1, 2]. Here, the multiphase growth of compound layers is analysed.

The solid-state growth kinetics of chemical compound layers in reaction couples have been treated in a number of works. The results obtained up till now are summarized in books, for example, by Hauffe [3], Gurov *et al.* [4], Geguzin [5] and Kofstad [6], and also in original papers which are too numerous to cite here.

In spite of some differences in details, the theoretical approaches of different authors are similar and represent a further development of Wagner's ideas [3, 7]. Wagner's theory permitted chemists to understand the peculiarities of the kinetics of solid-state heterogeneous reactions which have almost no common features with the kinetics of homogeneous chemical reactions. Indeed, the latter are based mainly on the concept of the order of a chemical reaction (see, for example, [8, 9]) which is clearly inapplicable in the case of heterogeneous reactions. This is due to the fact that for a heterogeneous system consisting of a few immiscible phases it is impossible to define the concept of the concentration of a reacting substance in the same way as for a homogeneous system.

Thanks to the work of Kidson [10], Heumann [11], Gurov *et al.* [4], Geguzin [5], van Loo [12], Schröder and Leute [13], Fromhold and Sato [14], Shatynski *et al.* [15], Williams *et al.* [16], Li and Powell [17] and other researchers, considerable progress in the "diffusional" theory was achieved. However, an adequate explanation of the experimental data available in the literature cannot always be obtained in the framework of the diffusional approach. A disagreement between this theory and experiment is especially conspicuous in the case of compound layers. The experimental data, for example, of van Loo [12], Canali *et al.* [18], Tsaur *et al.* [19], Tu and co-workers [20–22], Hentzell *et al.* [23], Timsit [24], Majni *et al.* [25] and other investigators (see [3, 6, 26]) obtained on thick samples and on thin films clearly show that the simultaneous growth of more than two compound layers in multiphase binary systems is an exception rather than the rule, whereas the "diffusional" theory starts from the quite opposite point of view; namely, that the simultaneous appearance of all compound layers in a reaction couple is a necessary condition for the so-called "local equilibrium". However, no equilibrium can exist even if one phase present in a phase diagram under given conditions is missing at the interface between reacting substances. This is the main point of disagreement between the "diffusional" theory and the experimental data which in turn leads to other difficulties. These difficulties can easily be overcome if one takes into account that in order for a compound layer to form the diffusion of reacting species is a necessary but not sufficient step. In addition, the chemical reaction step should follow the diffusion of the reactants.

The main aim of this work is (a) to show that a restriction on the number of compound layers growing simultaneously in reaction couples under given conditions follows immediately from the nature of the physicochemical processes taking place in multiphase binary systems, and (b) to analyse some thickness–time relationships which may be observed during the layer growth.

2. Reactions and equations

The consideration below is restricted to chemical compounds, i.e. ordered phases with constant or almost constant compositions. To understand the peculiarities of multiphase growth it is enough to consider a binary system with three compounds (Fig. 1). The ranges of homogeneity of the compounds A_pB_q, A_rB_s and A_lB_n, where p, q, r, s, l and n are positive numbers, are considered to be narrow compared to the average contents of Components A and B.

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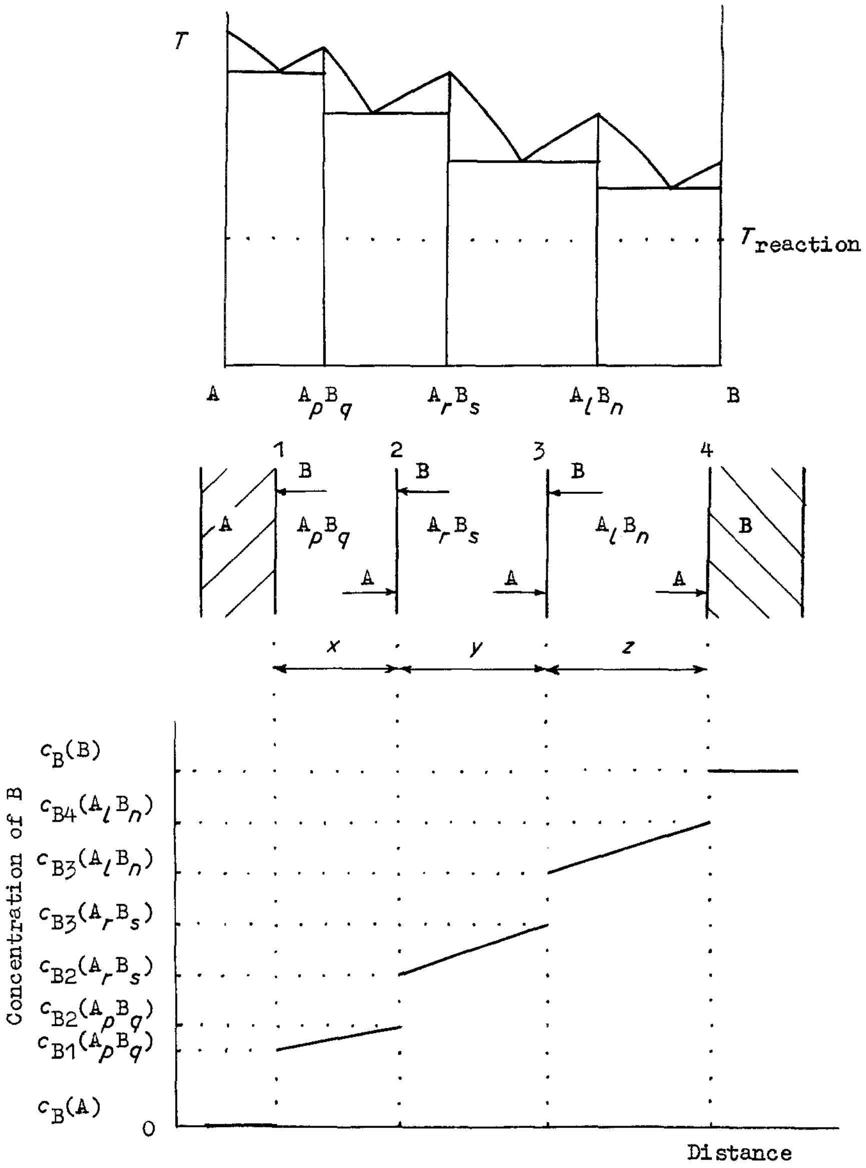

Figure 1 Schematic illustration of the multiphase growth of compound layers in binary systems.

2.1. Reactions

The growth of the layers can be represented by the following scheme:

Layer	*Interface*	*Reaction*	
A_pB_q	1	$q\,B + p\,A = A_pB_q$	(1)
	2	$(sp - qr)\,A + q\,A_rB_s = s\,A_pB_q$	(2)
A_rB_s	2	$(sp - qr)\,B + r\,A_pB_q = p\,A_rB_s$	(3)
	3	$(rn - ls)\,A + s\,A_lB_n = n\,A_rB_s$	(4)
A_lB_n	3	$(rn - ls)\,B + l\,A_rB_s = r\,A_lB_n$	(5)
	4	$lA + nB = A_lB_n$	(6)

All these reactions are considered to proceed independently of one another in the sense that the elementary act of each of them is not affected by elementary acts of the others.

2.2. Equations

Each of the above reactions causes a change in thicknesses of appropriate compound layers. For example, Reactions 1 and 2 lead to an increase in thickness of the A_pB_q layer whereas Reaction 3, causing an increase in thickness of the A_rB_s layer, leads at the same time to a decrease in thickness of the A_pB_q layer, and so on.

The analytical treatment proposed here is based on the following assumptions (see Section 2 in Part 1 [1]):

1. The "differential" time, dt, necessary, for example, for the A_pB_q compound layer to thicken at Interface 1 from x to $x + dx_{B1}$ at the expense of diffusion of Component B (Reaction 1) is the sum of the time, $dt_{\text{diffusion}}$, for diffusion of B atoms and the time, dt_{reaction}, for their further chemical interaction with the surface A atoms.
2. The time of diffusion is directly proportional to both the existing thickness, x, of the A_pB_q layer and the increase, dx_{B1}, in its thickness.
3. The time of reaction is directly proportional to the increase, dx_{B1}, in layer thickness and is independent of its total thickness, x.

Hence, for growth of the A_pB_q layer at Interface 1 at the expense of Component B

$$\mathrm{d}t \;=\; \mathrm{d}t_{\mathrm{reaction}} + \mathrm{d}t_{\mathrm{diffusion}} \;=\; \left(\frac{1}{k_{0\mathrm{B}1}} + \frac{x}{k_{1\mathrm{B}1}}\right)\mathrm{d}x_{\mathrm{B}1} \tag{7}$$

where $k_{0\mathrm{B}1}$ is a chemical constant and $k_{1\mathrm{B}1}$ is a physical (diffusional) constant.

Similarly, for growth of this layer at Interface 2 at the expense of Component A

$$\mathrm{d}t \;=\; \left(\frac{1}{k_{0\mathrm{A}2}} + \frac{x}{k_{1\mathrm{A}2}}\right)\mathrm{d}x_{\mathrm{A}2} \tag{8}$$

Thickening the A_rB_s layer at Interfaces 2 and 3 is described by the equations

$$\mathrm{d}t \;=\; \left(\frac{1}{k_{0\mathrm{B}2}} + \frac{y}{k_{1\mathrm{B}2}}\right)\mathrm{d}y_{\mathrm{B}2} \tag{9}$$

and

$$\mathrm{d}t \;=\; \left(\frac{1}{k_{0\mathrm{A}3}} + \frac{y}{k_{1\mathrm{A}3}}\right)\mathrm{d}y_{\mathrm{A}3} \tag{10}$$

respectively.

By analogy, for the A_lB_n layer

$$\mathrm{d}t \;=\; \left(\frac{1}{k_{0\mathrm{B}3}} + \frac{z}{k_{1\mathrm{B}3}}\right)\mathrm{d}z_{\mathrm{B}3} \tag{11}$$

and

$$\mathrm{d}t \;=\; \left(\frac{1}{k_{0\mathrm{A}4}} + \frac{z}{k_{1\mathrm{A}4}}\right)\mathrm{d}z_{\mathrm{A}4} \tag{12}$$

Equations 7 to 12 are considered to be independent of one another. Therefore, in order to find the increase in thickness, for example, of the A_pB_q layer during $\mathrm{d}t$ it is necessary to find $\mathrm{d}x_{\mathrm{B}1}$ and $\mathrm{d}x_{\mathrm{A}2}$ from Equations 8 and 9, respectively, and to summarize them:

$$\mathrm{d}x_{+} \;=\; \mathrm{d}x_{\mathrm{B}1} + \mathrm{d}x_{\mathrm{A}2} \tag{13}$$

In addition, the decrease, $\mathrm{d}x_{-}$, in the A_pB_q layer thickness during the same time $\mathrm{d}t$ due to Reaction 3 in which the A_pB_q compound acts as a reactant should also be taken into account. From Reaction 3 it follows (see Section 2 in Part 2 [2]) that

$$\mathrm{d}x_{-} \;=\; \frac{rg_1}{p}\,\mathrm{d}y_{\mathrm{B}2} \tag{14}$$

where $g_1 = V_{A_pB_q}/V_{A_rB_s}$, V being the molar volume of a compound. The total change in thickness of the A_pB_q layer during $\mathrm{d}t$ clearly is

$$\mathrm{d}x \;=\; \mathrm{d}x_{+} - \mathrm{d}x_{-} \;=\; \mathrm{d}x_{\mathrm{B}1} + \mathrm{d}x_{\mathrm{A}2} - \mathrm{d}x_{-} \tag{15}$$

Similarly, for the A_rB_s layer

$$\mathrm{d}y_{+} \;=\; \mathrm{d}y_{\mathrm{B}2} + \mathrm{d}y_{\mathrm{A}3} \tag{16}$$

and

$$\mathrm{d}y_{-} \;=\; \frac{q}{sg_1}\,\mathrm{d}x_{\mathrm{A}2} + \frac{lg_2}{r}\,\mathrm{d}z_{\mathrm{B}3} \tag{17}$$

where $g_2 = V_{A_rB_s}/V_{A_lB_n}$.

Equation 17 takes account of the fact that the A_rB_s compound is a reactant in both Reactions 2 and 5. The total change in thickness of the A_rB_s layer during $\mathrm{d}t$ is

$$\mathrm{d}y \;=\; \mathrm{d}y_{\mathrm{B}2} + \mathrm{d}y_{\mathrm{A}3} - \frac{q}{sg_1}\,\mathrm{d}x_{\mathrm{A}2} - \frac{lg_2}{r}\,\mathrm{d}z_{\mathrm{B}3} \tag{18}$$

For the A_lB_n layer

$$\mathrm{d}z_{+} \;=\; \mathrm{d}z_{\mathrm{B}3} + \mathrm{d}z_{\mathrm{A}4} \tag{19}$$

and

$$\mathrm{d}z_{-} \;=\; \frac{s}{ng_2}\,\mathrm{d}y_{\mathrm{A}3} \tag{20}$$

Therefore, during the same time $\mathrm{d}t$ the thickness of the A_lB_n layer will change by

$$\mathrm{d}z \;=\; \mathrm{d}z_{\mathrm{B}3} + \mathrm{d}z_{\mathrm{A}4} - \frac{s}{ng_2}\,\mathrm{d}y_{\mathrm{A}3} \tag{21}$$

Thus, a system of non-linear differential equations describing the growth kinetics of three compound layers at the interface between the mutually insoluble substances A and B is

$$\frac{\mathrm{d}x}{\mathrm{d}t} \;=\; \frac{k_{0\mathrm{B}1}}{1 + (k_{0\mathrm{B}1}x/k_{1\mathrm{B}1})} + \frac{k_{0\mathrm{A}2}}{1 + (k_{0\mathrm{A}2}x/k_{1\mathrm{A}2})} - \frac{rg_1}{p}\,\frac{k_{0\mathrm{B}2}}{1 + (k_{0\mathrm{B}2}y/k_{1\mathrm{B}2})} \tag{22a}$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} \;=\; \frac{k_{0\mathrm{B}2}}{1 + (k_{0\mathrm{B}2}y/k_{1\mathrm{B}2})} + \frac{k_{0\mathrm{A}3}}{1 + (k_{0\mathrm{A}3}y/k_{1\mathrm{A}3})} - \frac{q}{sg_1}\,\frac{k_{0\mathrm{A}2}}{1 + (k_{0\mathrm{A}2}x/k_{1\mathrm{A}2})} - \frac{lg_2}{r}\,\frac{k_{0\mathrm{B}3}}{1 + (k_{0\mathrm{B}3}z/k_{1\mathrm{B}3})} \tag{22b}$$

$$\frac{\mathrm{d}z}{\mathrm{d}t} \;=\; \frac{k_{0\mathrm{B}3}}{1 + (k_{0\mathrm{B}3}z/k_{1\mathrm{B}3})} + \frac{k_{0\mathrm{A}4}}{1 + (k_{0\mathrm{A}4}z/k_{1\mathrm{A}4})} - \frac{s}{ng_2}\,\frac{k_{0\mathrm{A}3}}{1 + (k_{0\mathrm{A}3}y/k_{1\mathrm{A}3})} \tag{22c}$$

If A is a solid in which B is insoluble and B is a liquid undersaturated with A then the term taking into account the rate of dissolution of the A_lB_n layer into the liquid phase should be added with a minus sign to the right-hand side of Equation 22c (see Equations 35 and 38 in Part 1 [1]). The same should be done if B is a gas and the A_lB_n compound is volatile.

Results and discussion

3.1. Initial growth of the layers

In the initial period of time the diffusion of A and B atoms clearly plays no role in determining the layer growth rates; their overall rates of formation are limited only by the rates of chemical reactions at the interfaces. In this case Equations 22a to c take the form

$$\frac{\mathrm{d}x}{\mathrm{d}t} \;=\; k_{0\mathrm{B}1} + k_{0\mathrm{A}2} - \frac{rg_1}{p}\,k_{0\mathrm{B}2} \tag{23a}$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} \;=\; k_{0\mathrm{B}2} + k_{0\mathrm{A}3} - \frac{q}{sg_1}\,k_{0\mathrm{A}2} - \frac{lg_2}{r}\,k_{0\mathrm{B}3} \tag{23b}$$

$$\frac{dz}{dt} = k_{0B3} + k_{0A4} - \frac{s}{ng_2} k_{0A3} \qquad (23c)$$

since the terms of the type k_0x/k_1 at small thicknesses of the layers are negligible compared to unity.

From Equations 23a to c it follows that the following situations may arise:

1. Three layers will grow linearly in the A–B reaction couple if dx/dt, dy/dt and dz/dt are positive.
2. The A_pB_q layer cannot grow if

$$k_{0B1} + k_{0A2} \leqslant \frac{rg_1}{p} k_{0B2}$$

since in this case $dx/dt \leqslant 0$. The product layer will consist of the compounds A_rB_s and A_lB_n. Their growth is described by equations like Equation 26 of Part 2 [2], i.e.

$$\frac{dy}{dt} = k'_{0B2} + k_{0A3} - \frac{lg_2}{r} k_{0B3} \qquad (24a)$$

$$\frac{dz}{dt} = k_{0B3} + k_{0A4} - \frac{s}{ng_2} k_{0A3} \qquad (24b)$$

where $k'_{0B2} \neq k_{0B2}$ because the reactions at Interface 2 are different in the A–A_rB_s–A_lB_n–B and A–A_pB_q–A_rB_s–A_lB_n–B systems (herein, the same numeration of interfaces shown in Fig. 1 is retained for all systems). Indeed, the reaction

$$sB(\text{diffusing}) + rA(\text{surface}) = A_rB_s \qquad (25)$$

proceeds at Interface 2 (i.e. at the interface A/A_rB_s) in the former system instead of Reaction 3 taking place at Interface 2 (A/A_pB_q) in the latter one.

3. If the derivatives, for example dx/dt and dz/dt, are negative, the A_pB_q and A_lB_n layers will not grow and therefore only the A_rB_s layer will occur at the interface between the A and B phases. Its growth in the A–A_rB_s–B system is described by the equation (see Equation 31 in Part 1 [1])

$$\frac{dy}{dt} = k'_{0B2} + k'_{0A3} \qquad (26)$$

where $k'_{0A3} \neq k_{0A3}$.

Thus one, two or three compound layers may start to grow linearly between the A and B phases from the beginning of isothermal annealing. To predict the sequence in which they occur it is necessary to know the values of all chemical constants (see Equations 23a to c). Unfortunately, the phenomenological theory proposed here offers no methods to find these values from the basic properties of the initial elements A and B and/or their compounds. This is its serious drawback. The only consolation is that this drawback is common to all phenomenological descriptions. The only way to find the chemical constants is therefore an experimental one. It should be noted that this is not so easy to do since a number of reaction couples consisting of the elements A and B and their compounds must be investigated. The difficulties are increased by the fact that linear growth is observable mainly in thin compound layers. Some empirical rules predicting the sequence of compound formation from the thermodynamic data or from the peculiarities of binary phase diagrams are therefore of particular value. The rule by Walser and Bene [27] for the first phase to form and that by Tsaur *et al.* [19] for the second should be mentioned. It should be noted, however, that it is necessary to carefully check whether these and other rules are applicable to all binary systems or only to some of them.

3.2. Critical thicknesses of the layers and their influence on the layer-growth kinetics

The layers appearing between the A and B phases thicken continuously with time, and at some thicknesses the terms of the type k_0x/k_1 become important. This may lead to a change in the number of growing layers. Consider the case where the A_pB_q layer was missing in the reaction couple (see Situation 2 in the preceding section). Thickening the A_rB_s layer results in a decrease of the term $(rg_1/p)k_{0B2}/[1 + (k_{0B2}y/k_{1B2})]$ on the right-hand side of Equation 22a. Hence, at some thickness y_0 the equality

$$k_{0B1} + k_{0A2} = \frac{rg_1}{p} \frac{k_{0B2}}{1 + (k_{0B2}y_0/k_{1B2})} \qquad (27)$$

will be satisfied. This means that the A_pB_q layer will grow between the A and A_rB_s phases after some delay (if, of course, Element A has not been consumed completely by this time).

In the above cases all the layers are considered to grow under reaction-controlled regimes with regard to both components (see Section 2 in Part 2 [2]), i.e. $x < x_{1/2}^{(A)}$, $y < y_{1/2}^{(A)}$, $z < z_{1/2}^{(A)}$, $x < x_{1/2}^{(B)}$, $y < y_{1/2}^{(B)}$, $z < z_{1/2}^{(B)}$. The critical thicknesses of the layers, $x_{1/2}^{(A)}$ etc., are defined by the equations

$$x_{1/2}^{(A)} = k_{1A2}/k_{0A2} \qquad x_{1/2}^{(B)} = k_{1B1}/k_{0B1} \qquad (28a)$$

$$y_{1/2}^{(A)} = k_{1A3}/k_{0A3} \qquad y_{1/2}^{(B)} = k_{1B2}/k_{0B2} \qquad (28b)$$

$$z_{1/2}^{(A)} = k_{1A4}/k_{0A4} \qquad z_{1/2}^{(B)} = k_{1B3}/k_{0B3} \qquad (28c)$$

Physically, the existence of critical thicknesses of the layers is quite obvious. Indeed, thickening, for example, the A_pB_q layer results in an increase of the diffusion paths along which the A atoms move from Interface 1 to Interface 2 (see Fig. 1). This leads to a decrease of the flux of A atoms towards Interface 2 where Reaction 2 takes place. On the other hand, the reactivity (or, in other words, the combining ability) of the A_rB_s compound surface towards these atoms remains unchanged since this compound layer is almost uniform macroscopically. Hence, at some single value of the A_pB_q layer thickness the flux of A atoms across this layer and the reactivity of the A_rB_s surface towards these atoms are equal. Note that at the critical thicknesses the equalities $dt_{\text{diffusion}} = dt_{\text{reaction}}$ are fulfilled for appropriate kinds of atoms diffusing across the layers.

At $x = x_{1/2}^{(A)}$ all the A atoms passing across the A_pB_q layer are combined by the A_rB_s surface into the A_pB_q compound at Interface 2 according to Reaction 2. None of them is therefore available for Reaction 3 which leads to the growth of the A_rB_s layer, and the more so for Reaction 6 resulting in the growth of the A_lB_n layer. Thus, these two layers cannot grow at the expense of Component A if the regime of growth of the A_pB_q layer is diffusion-controlled with regard to this component, i.e. if $x > x_{1/2}^{(A)}$. In this case, the second terms in Equations 22b and c and the third term in Equation 22c have no physical meaning and should be omitted. For $x \gg x_{1/2}^{(A)}$ Equations 22a to c reduce to

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + (k_{0B1}x/k_{1B1})} + \frac{k_{1A2}}{x} - \frac{rg_1}{p}\frac{k_{0B2}}{1 + (k_{0B2}y/k_{1B2})} \qquad (29a)$$

$$\frac{dy}{dt} = \frac{k_{0B2}}{1 + (k_{0B2}y/k_{1B2})} - \frac{q}{sg_1}\frac{k_{1A2}}{x} - \frac{lg_2}{r}\frac{k_{0B3}}{1 + (k_{0B3}z/k_{1B3})} \qquad (29b)$$

$$\frac{dz}{dt} = \frac{k_{0B3}}{1 + (k_{0B3}z/k_{1B3})} \qquad (29c)$$

From Equation 29c it follows that the growth of the A_lB_n layer is independent of the growth processes of the other layers. Note that in this case all the layers can yet grow simultaneously (the A_pB_q layer at the expense of both components and the A_rB_s and A_lB_n layers only at the expense of Component B). Another situation arises when the regime of growth of the A_lB_n layer becomes diffusion-controlled with regard to Component B, i.e. when $z > z_{1/2}^{(B)}$. In this case all the B atoms passing across the A_lB_n layer are combined by the A_rB_s surface into the A_lB_n compound at Interface 3. Therefore, the A_rB_s and A_pB_q layers lose a source of B atoms for their growth. But if the A_pB_q layer can yet grow at the expense of Component A, the A_rB_s layer having no source of both A and B atoms cannot grow at all. For $z \gg z_{1/2}^{(B)}$ Equations 29a to c become

$$\frac{dx}{dt} = \frac{k_{1A2}}{x} \qquad (30a)$$

$$\frac{dy}{dt} = -\frac{q}{sg_1}\frac{k_{1A2}}{x} - \frac{lg_2}{r}\frac{k_{1B3}}{z} \qquad (30b)$$

$$\frac{dz}{dt} = \frac{k_{1B3}}{z} \qquad (30c)$$

It is seen that the A_pB_q and A_lB_n layers grow parabolically, whereas the thickness of the A_rB_s layer reduces continuously with time until its total depletion. Note that in this case the diffusional constants k_{1A2} and k_{1B3}, can easily be found from experimental x^2–t and z^2–t relationships, respectively.

After the depletion of the A_rB_s layer the situation changes to A–A_pB_q–A_lB_n–B. During subsequent annealing, the A_pB_q and A_lB_n layers will grow until either A or B depletes completely. After this, the A_rB_s layer will grow in either the A–A_pB_q–A_rB_s–A_lB_n or A_pB_q–A_rB_s–A_lB_n–B system. The sequential occurrence of new compound layers of a multiphase binary system with the simultaneous depletion of the initial phases will proceed until not more than two phases remain at equilibrium as Gibbs' rule requires. This prediction is in good agreement with experimental observations. For example, Hentzell *et al.* [23] found that in Cu–Al samples the $CuAl_2$ compound was the first phase to grow, and only near the end of this reaction was the formation of a new phase layer observed. The sequential growth of silicide layers was observed by Tsaur *et al.* [19] and by Majni *et al.* [25] in transition metal–silicon couples. A number of similar examples can be found [3, 6, 12, 18, 22, 26].

It may seem at first sight that the A_rB_s layer can grow in the A–A_pB_q–A_rB_s–A_lB_n–B system in the same manner as in the A_pB_q–A_rB_s–A_lB_n system, i.e. at the expense of the phase transformation [28, 29]

$$s\,A_pB_q = q\,A_rB_s + (sp - qr)\,\text{A(diffusing)} \qquad (31)$$

This is, however, not the case. Indeed, at $x < x_{1/2}^{(A)}$ ($x_{1/2}^{(A)}$ is defined by Equation 28a) there is an excess of A atoms in comparison with the reactivity of the A_rB_s surface towards these atoms. Under these conditions Reaction 31 will clearly not proceed. At $x \geq x_{1/2}^{(A)}$ the A atoms appearing as a result of Reaction 31 cannot cross the A_pB_q/A_rB_s interface in the A–A_pB_q–A_rB_s–A_lB_n–B system; they will immediately be combined into A_pB_q at this interface according to Reaction 2 which is opposite to Reaction 31. The total result is clearly zero.

The only difference between the two systems under consideration is that the A_pB_q layer is a growing layer in the A–A_pB_q–A_rB_s–A_lB_n–B system and is a non-growing one in the A_pB_q–A_rB_s–A_lB_n system. This is, in turn, due to the two following reasons:

1. In the first system there is a source of A atoms (i.e. Substance A) for the A_pB_q layer to grow whereas in the second system this layer itself is a source of A atoms.
2. A concentration (or activity) gradient exists within the A_pB_q layer in the first system whereas in the second it is absent (compare Figs 1 and 2). Therefore, the same layer behaves quite differently in these two systems.

Similarly, it is easy to show that the A_rB_s layer cannot grow in the A–A_pB_q–A_rB_s–A_lB_n–B system at the expense of Component B in the same manner as in the A_pB_q–A_rB_s–A_lB_n system, i.e. at the expense of the phase transformation

$$r\,A_lB_n = l\,A_rB_s + (rn - ls)\,\text{B(diffusing)} \qquad (32)$$

It is seen that this reaction is opposite to Reaction 5.

To avoid misunderstandings it should be emphasized that it is the *growth* of the third layer *between* the two layers growing under diffusional regimes but not its appearance in the A–B reaction couple that is impossible. For example, if the A_rB_s and A_lB_n layers grow between the A and B phases, the A_pB_q layer may, of course, occur and grow at the A/A_rB_s interface (whatever the regimes of growth of the A_rB_s and A_lB_n layers) as having a direct contact with a source of A atoms, i.e. with Substance A. However, when the regimes of growth of the A_pB_q and A_lB_n layers become diffusion-controlled with regard to Components A and B, respectively, then the A_rB_s layer will be "superfluous". It follows that if A_pB_q is the most A-rich chemical compound and A_lB_n is the most B-

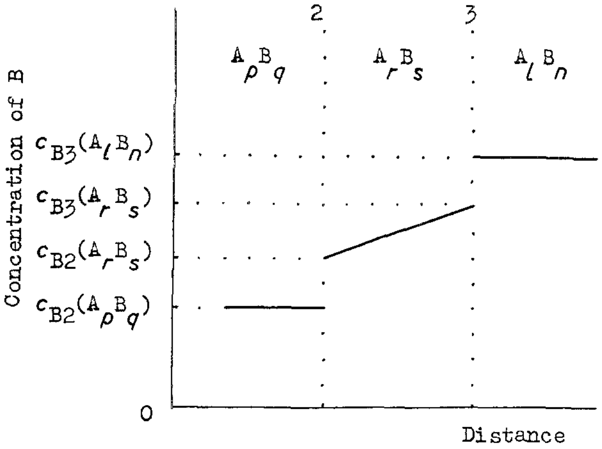

Figure 2 The concentration distribution of Component B in the A_pB_q–A_rB_s–A_lB_n system.

rich one of a multiphase binary system, then no other compound layer can grow in the A–B reaction couple until the full depletion of one of the initial phases if these two layers grow under diffusional regimes with regard to Components A and B, respectively.

It should be noted that the explanation of the absence of some compound layers in a diffusion couple only by their too-slow growth rates (see, for example, [4]) due to small values of $D\Delta c$ (D is the diffusion coefficient and Δc is the range of homogeneity) seems in general to be incorrect. If it was so, the occurrence and growth of these compound layers in a given diffusion couple would be only a matter of time.

Sometimes, more than two layers are observed between the A and B phases. This may be due to the following reasons:

1. If the regimes of growth of the layers are reaction-controlled, at least with regard to one of the two components, then all the layers can grow simultaneously, whatever their number.
2. The layers formed are usually investigated at room temperature, whereas the experiment itself is in most cases performed at elevated temperatures. Additional layers may therefore occur during cooling since the rates of cooling are not always sufficient to arrest the secondary reactions. Therefore, high-temperatures instruments like a hot-stage scanning electron microscope for the continuous observation of the scale–gas interface described by Verma *et al.* [30] are of particular value.
3. The restrictions following from the present consideration are not applicable to phases with wide homogeneity ranges like, for example, the ε-phase in the Ag–Zn system [16]. In the case of such phases the conditions of quasi-stationary concentration distribution (see Section 2 in Part 1 [1]) are not fulfilled. It should be emphasized that whether or not these conditions are fulfilled may in most cases be checked experimentally with the help of electron probe microanalysis.

Note that the theory proposed here (as well as any other phenomenological theory) predicts only a general picture of the layer thickness–time relationships. Therefore, the only way to precisely check this theory in each particular case is to show whether an experimental dependence can be described in terms of the constants k_0 and/or k_1 or whether these "constants" are time-dependent.

It should be emphasized that contrary to Wagner [7], Gurov *et al.* [4] and Ugaste [31], here each of the physical (diffusional) constants is considered as a characteristic of a given compound layer, i.e. it is the same in any reaction couple where this layer occurs. The growth of each compound layer is thus described by the two physical constants and the two chemical constants which, in contrast to the physical constants, depend on the nature of adjacent phases.

4. Concluding remarks

Evans' equation and Arkharov's ideas regarding reaction diffusion in heterogeneous binary systems provide a suitable basis to develop a physicochemical theory of the solid-state growth kinetics of compound layers (see ref. 1). Starting with very simple assumptions it is possible to obtain, from a single view-point, a number of relationships observed during the formation of compound layers in reaction couples.

It should be emphasized that in the case of compound layers growing between immiscible substances the chemical reactions take place onto the surfaces of reacting phases. In such solid-state systems there are no sites where the reacting species can accumulate. Therefore, these reactions proceed in a few consecutive steps by the layer-by-layer consumption of initial substances. For this reason, the times necessary for all steps to complete must be summed. Thus, each elementary chemical reaction can be described in terms of the time as $dt = \Sigma dt_i$ where i is the number of consecutive steps.

Although one may divide the single elementary process leading to an increase in thickness of a given layer by dx into a number of steps, there are only two groups. The first group includes those steps the duration of each of which depends on both the existing layer thickness and the increase in its thickness. The diffusion of atoms within a given compound layer ("internal" diffusion) is clearly the only representative of this group. The second group includes steps the duration of each of which is dependent only on the increase in layer thickness. These are

(a) the transition of a given kind of atoms from one phase into an adjacent one ("external" diffusion),

(b) the redistribution of atomic orbitals of the reacting elements, and

(c) the rearrangement of the lattice of an initial phase into the lattice of a chemical compound.

Here, these steps are grouped together under the name "chemical reaction" (or "chemical interaction").

Although this consideration is developed for "good" chemical compounds, it is also applicable, at least qualitatively, to "bad" compounds having relatively wide ranges of homogeneity. The difference is that in the latter case some part of the diffusing atoms remains within the layer due to the existence of a homogeneity range and takes no part in its growth. For this reason, the diffusional (physical) constants become slightly dependent on the layer thickness. The chemical constants also vary slightly due to the difference in boundary compositions of a layer. This does not mean, of course, that the chemical reaction steps can be ignored in this case; simply a more careful consideration is needed to adequately describe the growth kinetics of such layers.

The analytical treatment proposed here is clearly not exhaustive. Only the simplest situations when the layer thicknesses are very far from the critical values are considered in this work. More careful consideration should be given to the regions near the critical thicknesses of compound layers. It seems quite probable that such experimentally observed layer thickness–time relationships as, for example, cubic, logarithmic, antilogarithmic and some others, are no more than the layer-growth kinetics in the transition regions, and therefore these relationships may possibly be described in the framework of the present considerations. However, in order to show whether this is the case or not much more careful experiments than those performed up till now are necessary.

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