Chapter 4

GROWTH KINETICS OF THE SAME CHEMICAL COMPOUND LAYER IN VARIOUS REACTION COUPLES OF A MULTIPHASE BINARY SYSTEM

If a binary system is multiphase, then the layer of the same chemical compound can obviously grow in different reaction couples consisting of elementary substances A and B and their compounds. To show how its growth rate depends on the composition of initial phases, it suffices to consider a system with three compounds A_pB_q, A_rB_s and A_lB_n (see Fig.3.1).

If the A_rB_s layer is the first to occur at the A–B interface, then in a certain range of temperature its growth can readily be observed between

(*i*) elementary substances A and B (reaction couple A–B),

(*ii*) one of the two other compounds and one of the elementary substances (reaction couples A_pB_q–B and A–A_lB_n),

(*iii*) two other compounds (reaction couple A_pB_q–A_lB_n).

Note that in this chapter the A_rB_s layer will be assumed to be the only one in all possible reaction couples of the A–B multiphase binary system under given experimental conditions.

4.1. Growth of the A_rB_s layer in the A–B reaction couple

It is most convenient to compare the growth rates of the layer of the same chemical compound in various reaction couples with the rate of its growth at the interface of elementary substances. Therefore, let us first briefly analyse the case in which the A_rB_s compound layer is formed at the A–B interface (Fig.4.1). To avoid considerable changes in the designations of the reaction-diffusion constants describing the layer-growth kinetics, the numeration of the interfaces of the A_rB_s layer, shown in Fig.3.1, will be retained.

Solid-state growth of the A_rB_s layer at the interface between elementary substances A and B is due to two partial chemical reactions each of which occurs in two consecutive, alternate steps (see Chapter 1). Firstly, the B atoms diffuse across its bulk and then react at the A–A_rB_s interface (interface 2) with the surface A atoms in accordance with the equation

$$sB_{\mathrm{dif}} + rA_{\mathrm{surf}} = A_rB_s. \qquad (4.1)$$

Secondly, the A atoms diffuse in the opposite direction and then react at the A_rB_s–B interface (interface 3) with the surface B atoms

$$rA_{\mathrm{dif}} + sB_{\mathrm{surf}} = A_rB_s. \qquad (4.2)$$

During the time dt, the thickness of the A_rB_s layer increases by dy_{B2} at the A–A_rB_s interface. As a result, this interface moves from position 2′ into position 2. Simultaneously, it increases by dy_{A3} at the A_rB_s–B interface, so that this interface moves from position 3′ into position 3. A kinetic equation describing the growth rate of the A_rB_s layer at the interface of mutually insoluble elementary substances A and B has the form (see Chapter 1)

$$\left(\frac{\mathrm{d}y}{\mathrm{d}t}\right)_{A-B} = \frac{k_{0B2}}{1+\dfrac{k_{0B2}y}{k_{1B2}}} + \frac{k_{0A3}}{1+\dfrac{k_{0A3}y}{k_{1A3}}}. \qquad (4.3)$$

When comparing the chemical constants in the systems A–A_rB_s–B and A–A_pB_q–A_rB_s–A_lB_n–B (see Chapter 3), it should be kept in mind that k_{0B2} is not equal to k'_{0B2} and k_{0A3} is not equal to k'_{0A3} since different partial chemical reactions take place in those systems at the interfaces of the A_rB_s layer with the adjacent phases. Though the rate of

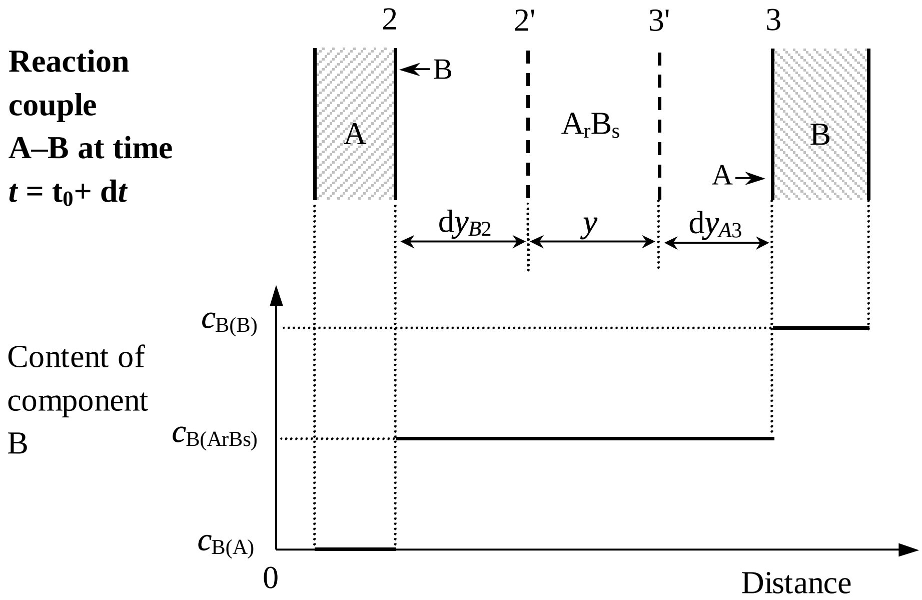

Fig.4.1. Schematic diagram to illustrate the growth process of the A_rB_s layer between mutually insoluble elementary substances A and B at the expense of diffusion of both components.

transport of any component across the bulk of the A_rB_s layer is an intrinsic property of this layer, not depending on the composition of the adjacent phases, the diffusional constants k_{1B2} and k'_{1B2} as well as k_{1A3} and k'_{1A3} are also not identical because in the systems A–A_rB_s–B and A–A_pB_q–A_rB_s–A_lB_n–B different numbers of the A_rB_s molecules are formed per one diffusing atom A or B. Therefore, the constants k_{1B2} and k'_{1B2} differ by a constant multiplier. The same applies to the constants k_{1A3} and k'_{1A3}.

4.2. Growth of the A_rB_s layer in the A_pB_q–B reaction couple

The mechanism of formation of the A_rB_s layer at the A_pB_q–B interface is essentially dependent upon which component (either A or B) has a higher mobility in the crystal lattice of the A_rB_s compound. Comparing the systems A–A_rB_s–B and A_pB_q–A_rB_s–B, it can easily be concluded that the same physicochemical processes take place in both systems at the interface of the A_rB_s and B phases.

It does not mean, however, that if the diffusion of component A prevails in the A_rB_s layer, then the growth rates of this layer in the A_pB_q–B and A–B reaction couples will be identical. Consider this case in more detail.

4.2.1. Growth of the A_rB_s layer between A_pB_q and B at the expense of diffusion of only component A

A schematic diagram to illustrate the growth process of the A_rB_s layer at the interface between the A_pB_q and B phases at the expense of diffusion of component A is shown in Fig.4.2. If the A_pB_q compound has a considerable range of homogeneity, then the content of component A in the initial phase A_pB_q will be assumed to be constant and equal to the lower limit of this range according to the equilibrium phase diagram of the A–B binary system.

During the time dt, the thickness of the A_rB_s layer increases by dy_{A3} at interface 3 as a result of diffusion of the A atoms from interface 2 to interface 3 and their subsequent partial chemical reaction (4.2) with the surface B atoms. In the A_pB_q–B reaction couple the A_pB_q phase acts as a source of diffusing A atoms. It must be clear,