3.2. A system of differential equations describing the growth process of three chemical compound layers between elementary substances *A* and *B*

Again, the use of the postulate about the summation of the time of diffusion of reacting atoms and the time of subsequent chemical transformations with their participation yields

$$\mathrm{d}t = \mathrm{d}t_{\mathrm{dif}}^{(B\to A_pB_q)} + \mathrm{d}t_{\mathrm{chem}}^{(B\to A_pB_q)}, \qquad (3.4_1)$$

$$\mathrm{d}t = \mathrm{d}t_{\mathrm{dif}}^{(A\to A_pB_q)} + \mathrm{d}t_{\mathrm{chem}}^{(A\to A_pB_q)}, \qquad (3.4_2)$$

$$\mathrm{d}t = \mathrm{d}t_{\mathrm{dif}}^{(B\to A_rB_s)} + \mathrm{d}t_{\mathrm{chem}}^{(B\to A_rB_s)}, \qquad (3.5_1)$$

$$\mathrm{d}t = \mathrm{d}t_{\mathrm{dif}}^{(A\to A_rB_s)} + \mathrm{d}t_{\mathrm{chem}}^{(A\to A_rB_s)}, \qquad (3.5_2)$$

$$\mathrm{d}t = \mathrm{d}t_{\mathrm{dif}}^{(B\to A_lB_n)} + \mathrm{d}t_{\mathrm{chem}}^{(B\to A_lB_n)}, \qquad (3.6_1)$$

$$\mathrm{d}t = \mathrm{d}t_{\mathrm{dif}}^{(A\to A_lB_n)} + \mathrm{d}t_{\mathrm{chem}}^{(A\to A_lB_n)}, \qquad (3.6_2)$$

where the subscripts and superscripts have the former meaning (see section 2.2 of Chapter 2).

Assuming that the time of diffusion of the *A* or *B* atoms is directly proportional to both the increase in thickness of the layer and its existing total thickness, while the time of chemical transformations in which these atoms then take part is directly proportional to the increase in thickness of the layer and is independent of its total thickness, one obtains the following relations:

$$\mathrm{d}t_{\mathrm{dif}}^{(B\to A_pB_q)} = \frac{x}{k_{1B1}}\mathrm{d}x_{B1} \quad \text{and} \quad \mathrm{d}t_{\mathrm{chem}}^{(B\to A_pB_q)} = \frac{1}{k_{0B1}}\mathrm{d}x_{B1}, \qquad (3.7_1)$$

$$\mathrm{d}t_{\mathrm{dif}}^{(A\to A_pB_q)} = \frac{x}{k'_{1A2}}\mathrm{d}x_{A2} \quad \text{and} \quad \mathrm{d}t_{\mathrm{chem}}^{(A\to A_pB_q)} = \frac{1}{k'_{0A2}}\mathrm{d}x_{A2}, \qquad (3.7_2)$$

$$\mathrm{d}t_{\mathrm{dif}}^{(B\to A_rB_s)} = \frac{y}{k'_{1B2}}\mathrm{d}y_{B2} \quad \text{and} \quad \mathrm{d}t_{\mathrm{chem}}^{(B\to A_rB_s)} = \frac{1}{k'_{0B2}}\mathrm{d}y_{B2}, \qquad (3.8_1)$$

$$\mathrm{d}t_{\mathrm{dif}}^{(A\to A_rB_s)} = \frac{y}{k'_{1A3}}\mathrm{d}y_{A3} \quad \text{and} \quad \mathrm{d}t_{\mathrm{chem}}^{(A\to A_rB_s)} = \frac{1}{k'_{0A3}}\mathrm{d}y_{A3}, \tag{3.8$_2$}$$

$$\mathrm{d}t_{\mathrm{dif}}^{(B\to A_lB_n)} = \frac{z}{k_{1B3}}\mathrm{d}z_{B3} \quad \text{and} \quad \mathrm{d}t_{\mathrm{chem}}^{(B\to A_lB_n)} = \frac{1}{k_{0B3}}\mathrm{d}z_{B3}, \tag{3.9$_1$}$$

$$\mathrm{d}t_{\mathrm{dif}}^{(A\to A_lB_n)} = \frac{z}{k_{1A4}}\mathrm{d}z_{A4} \quad \text{and} \quad \mathrm{d}t_{\mathrm{chem}}^{(A\to A_lB_n)} = \frac{1}{k_{0A4}}\mathrm{d}z_{A4}. \tag{3.9$_2$}$$

Hence,

$$\mathrm{d}t = \left(\frac{x}{k_{1B1}} + \frac{1}{k_{0B1}}\right)\mathrm{d}x_{B1}, \tag{3.10$_1$}$$

$$\mathrm{d}t = \left(\frac{x}{k'_{1A2}} + \frac{1}{k'_{0A2}}\right)\mathrm{d}x_{A2}, \tag{3.10$_2$}$$

$$\mathrm{d}t = \left(\frac{y}{k'_{1B2}} + \frac{1}{k'_{0B2}}\right)\mathrm{d}y_{B2}, \tag{3.11$_1$}$$

$$\mathrm{d}t = \left(\frac{y}{k'_{1A3}} + \frac{1}{k'_{0A3}}\right)\mathrm{d}y_{A3}, \tag{3.11$_2$}$$

$$\mathrm{d}t = \left(\frac{z}{k_{1B3}} + \frac{1}{k_{0B3}}\right)\mathrm{d}z_{B3}, \tag{3.12$_1$}$$

$$\mathrm{d}t = \left(\frac{z}{k_{1A4}} + \frac{1}{k_{0A4}}\right)\mathrm{d}z_{A4}. \tag{3.12$_2$}$$

Since equations (3.10$_1$)-(3.12$_2$) are assumed to be independent of each other, the increases in thickness of the A_pB_q, A_rB_s and A_lB_n layers can be expressed from them as follows

$$\mathrm{d}x_{B1} = \frac{k_{0B1}}{1 + \dfrac{k_{0B1}x}{k_{1B1}}}\mathrm{d}t, \tag{3.13$_1$}$$

$$\mathrm{d}x_{A2} = \frac{k'_{0A2}}{1+\dfrac{k'_{0A2}x}{k'_{1A2}}}\mathrm{d}t, \tag{3.13$_2$}$$

$$\mathrm{d}y_{B2} = \frac{k'_{0B2}}{1+\dfrac{k'_{0B2}y}{k'_{1B2}}}\mathrm{d}t, \tag{3.14$_1$}$$

$$\mathrm{d}y_{A3} = \frac{k'_{0\mathrm{A}3}}{1+\dfrac{k'_{0\mathrm{A}3}y}{k'_{1\mathrm{A}3}}}\mathrm{d}t, \tag{3.14$_2$}$$

$$\mathrm{d}z_{B3} = \frac{k_{0B3}}{1+\dfrac{k_{0B3}z}{k_{1B3}}}\mathrm{d}t, \tag{3.15$_1$}$$

$$\mathrm{d}z_{A4} = \frac{k_{0A4}}{1+\dfrac{k_{0A4}z}{k_{1A4}}}\mathrm{d}t. \tag{3.15$_2$}$$

The increase of the thickness of the A_pB_q layer during the time dt, due to partial chemical reactions (3.1$_1$) and (3.1$_2$), is (Fig.3.2)

$$\mathrm{d}x_{+} = \mathrm{d}x_{B1} + \mathrm{d}x_{A2}. \tag{3.16}$$

The decrease of the thickness of this layer during the same time dt as a result of partial chemical reaction (3.2$_1$) in which the A_pB_q compound is a reactant, is equal to (see Section 2.2 of Chapter 2)

$$\mathrm{d}x_{-}^{(2)} = \frac{rg_1}{p}\mathrm{d}y_{B2}, \tag{3.17}$$

where $g_1 = V_{A_pB_q}/V_{A_rB_s}$, V is the molar volume of an appropriate compound.

Thus, the total change, dx, of the thickness of the A_pB_q layer during the time dt is

$$\mathrm{d}x = \mathrm{d}x_{+} - \mathrm{d}x_{-}^{(2)} = \mathrm{d}x_{B1} + \mathrm{d}x_{A2} - \frac{rg_1}{p}\mathrm{d}y_{B2}. \tag{3.18}$$

For the A_rB_s layer, the increase of its thickness during the time dt is

$$\mathrm{d}y_{+} = \mathrm{d}y_{B2} + \mathrm{d}y_{A3}. \tag{3.19}$$

Unlike the A_pB_q compound which is only consumed by one partial chemical reaction (3.2_1), the A_rB_s compound is a reactant of two partial chemical reactions (3.1_2) and (3.3_1). Therefore, during dt the thickness of the A_rB_s layer decreases by

$$\mathrm{d}y_{-}^{(2)} = \frac{q}{sg_1}\mathrm{d}x_{A2} \tag{3.20}$$

at interface 2 as a result of reaction (3.1_2) and by

$$\mathrm{d}y_{-}^{(3)} = \frac{lg_2}{r}\mathrm{d}z_{B3} \tag{3.21}$$

at interface 3 as a result of reaction (3.3_1), where $g_2 = V_{A_rB_s}/V_{A_lB_n}$.

Hence, the total change, dy, of the thickness of the A_rB_s layer during the time dt is

$$\mathrm{d}y = \mathrm{d}y_{B2} + \mathrm{d}y_{A3} - \frac{q}{sg_1}\mathrm{d}x_{A2} - \frac{lg_2}{r}\mathrm{d}z_{B3}. \tag{3.22}$$

Evidently, for the A_lB_n layer,

$$\mathrm{d}z_{+} = \mathrm{d}z_{B3} + \mathrm{d}z_{A4} \tag{3.23}$$

and

$$\mathrm{d}z_{-}^{(3)} = \frac{s}{ng_2}\mathrm{d}y_{A3}, \tag{3.24}$$

with the total change, dz, of its thickness during the time dt being

$$\mathrm{d}z = \mathrm{d}z_{B3} + \mathrm{d}z_{A4} - \frac{s}{ng_2}\mathrm{d}y_{A3}. \tag{3.25}$$

The required general system of non-linear differential equations describing the growth rates of three chemical compound layers at the interface between two mutually insoluble solid elementary substances A and B is obtained by inserting the expressions for the layer-thickness changes from equations (3.13_1)-(3.15_2) into equations (3.18), (3.22) and (3.25), giving

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{k_{0B1}}{1+\frac{k_{0B1}x}{k_{1B1}}}+\frac{k'_{0A2}}{1+\frac{k'_{0A2}x}{k'_{1A2}}}-\frac{rg_1}{p}\frac{k'_{0B2}}{1+\frac{k'_{0B2}y}{k'_{1B2}}}, \qquad (3.26_1)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t}=\frac{k'_{0B2}}{1+\frac{k'_{0B2}y}{k'_{1B2}}}+\frac{k'_{0A3}}{1+\frac{k'_{0A3}y}{k'_{1A3}}}-\frac{q}{sg_1}\frac{k'_{0A2}}{1+\frac{k'_{0A2}x}{k'_{1A2}}}-\frac{lg_2}{r}\frac{k_{0B3}}{1+\frac{k_{0B3}z}{k_{1B3}}}, \qquad (3.26_2)$$

$$\frac{\mathrm{d}z}{\mathrm{d}t}=\frac{k_{0B3}}{1+\frac{k_{0B3}z}{k_{1B3}}}+\frac{k_{0A4}}{1+\frac{k_{0A4}z}{k_{1A4}}}-\frac{s}{ng_2}\frac{k'_{0A3}}{1+\frac{k'_{0A3}y}{k'_{1A3}}}. \qquad (3.26_3)$$

Even not making any attempt to find a general solution to this rather complicated system, let us analyse the most important consequences resulting immediately from the differential equations and their solutions in some limiting cases.

3.3. Initial linear growth of three compound layers

During certain initial period of time, the rates of diffusion of the *A* and *B* atoms do not play any significant role in determining the rates of formation of the A_pB_q, A_rB_s and A_lB_n layers. Their growth rates are only restricted by the rates of chemical transformations at the phase interfaces, the diffusing atoms of both types being in great excess for the growth of each of the layers. This does not necessarily mean, however, that they will all occur and grow simultaneously.

At small thicknesses of the A_pB_q, A_rB_s and A_lB_n layers, the terms of the type k_0x/k_1 are evidently negligible in comparison with unity. Hence, the system of equations (3.26) is simplified to