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Reaction diffusion in heterogeneous binary systems

Part 2 *Growth of the chemical compound layers at the interface between two elementary substances: two compound layers*

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A system of non-linear differential equations describing the growth kinetics of the two compound layers at the interface between two elements is proposed. A number of well-known experimental and theoretical relationships follows from this system in the limiting cases.

1. Introduction

The growth of two compound layers was theoretically treated, from a "diffusional" view-point, by Arkharov [1] Gurov *et al.* [2] Schröder and Leute [3], Fromhold and Sato [4] and other investigators. They arrived at a conclusion that the thickness of each of the two layers, as well as their total thickness, should parabolically increase with time. In general, this is far from being the case. The thickness–time relationship in the case of two compound layers is very complex (see, for example, [5, 6]) and only some portion of the curve is close to a parabola. Moreover, sometimes one of the layers only occurs after a considerable period of time while the other grows from the very beginning of the experiment.

Here, the growth kinetics of two compound layers is treated on the basis of the results obtained in Part 1 [7].

2. Basic ideas and equations

2.1. Model

A schematic diagram to illustrate the growth process is shown in Fig. 1. The elements A and B are considered to be mutually insoluble at the temperature under investigation. It is assumed that the compounds A_pB_q and A_rB_s have very narrow homogeneity ranges.

The A_pB_q layer grows as the B atoms diffuse across its bulk towards interface 1 and react with the surface A atoms:

$$qB + pA = A_pB_q \tag{1}$$

Again, its thickness increases as the A atoms diffuse towards interface 2 and react with A_rB_s to form the A_pB_q compound:

$$(sp - qr)A + qA_rB_s = sA_pB_q \tag{2}$$

The growth of the A_rB_s layer is due to the reactions

$$(sp - qr)B + rA_pB_q = pA_rB_s \tag{3}$$

and

$$rA + sB = A_rB_s \tag{4}$$

which takes place at interfaces 2 and 3, respectively.

It is seen that the compound A_pB_q is the product in Reactions 1 and 2 but at the same time it is the reactant in Reaction 3. The A_rB_s compound is the product in Reactions 3 and 4 and is the reactant in Reaction 2. Hence, the formation, say, of the A_pB_q layer may be imagined as the growth due to Reactions 1 and 2 and the "dissolution" into the adjacent phase A_rB_s due to Reaction 3. Similarly, the A_rB_s layer grows as Reactions 3 and 4 proceed and "dissolves" into the A_pB_q layer in the course of Reaction 2.

2.2. Analytical treatment

During some small period of time, dt, the thickness of the A_pB_q and A_rB_s layers will change from x to $x + \mathrm{d}x$ and from y to $y + \mathrm{d}y$, respectively. The thickness of the A_pB_q layer will increase by

$$\mathrm{d}x_+ = \mathrm{d}x_{B1} + \mathrm{d}x_{A2}, \tag{5}$$

where $\mathrm{d}x_{B1}$ is the increase in the layer thickness at interface 1 due to Reaction 1 and $\mathrm{d}x_{A2}$ is the increase in its thickness at interface 2 due to Reaction 2. The expressions for $\mathrm{d}x_{B1}$ and $\mathrm{d}x_{A2}$ can easily be found using the results of Part 1 (see Equations 11 and 17 to 19); thus

$$\mathrm{d}x_{B1} = \frac{k_{0B1}}{1 + (k_{0B1}x/k_{1B1})}\,\mathrm{d}t, \tag{6}$$

where k_{0B1} is the rate constant of the A_pB_q layer growth under conditions of reaction control and k_{1B1} is the rate constant of its growth under diffusion control conditions. The constant k_{1B1} is a function of the diffusion coefficient, $D_{B(A_pB_q)}$, of B in A_pB_q and the boundary concentrations, $c_{B1(A_pB_q)}$ and $c_{B2(A_pB_q)}$, of component B into the A_pB_q layer:

$$k_{1B1} = \frac{D_{B(A_pB_q)}[c_{B2(A_pB_q)} - c_{B1(A_pB_q)}]}{c_{B1(A_pB_q)}} \tag{7}$$

Similarly,

$$\mathrm{d}x_{A2} = \frac{k_{0A2}}{1 + (k_{0A2}x/k_{1A2})}\,\mathrm{d}t \tag{8}$$

where

$$k_{1A2} = \frac{D_{A(A_pB_q)}[c_{A1(A_pB_q)} - c_{A2(A_pB_q)}]}{c_{A2(A_pB_q)}} \tag{9}$$

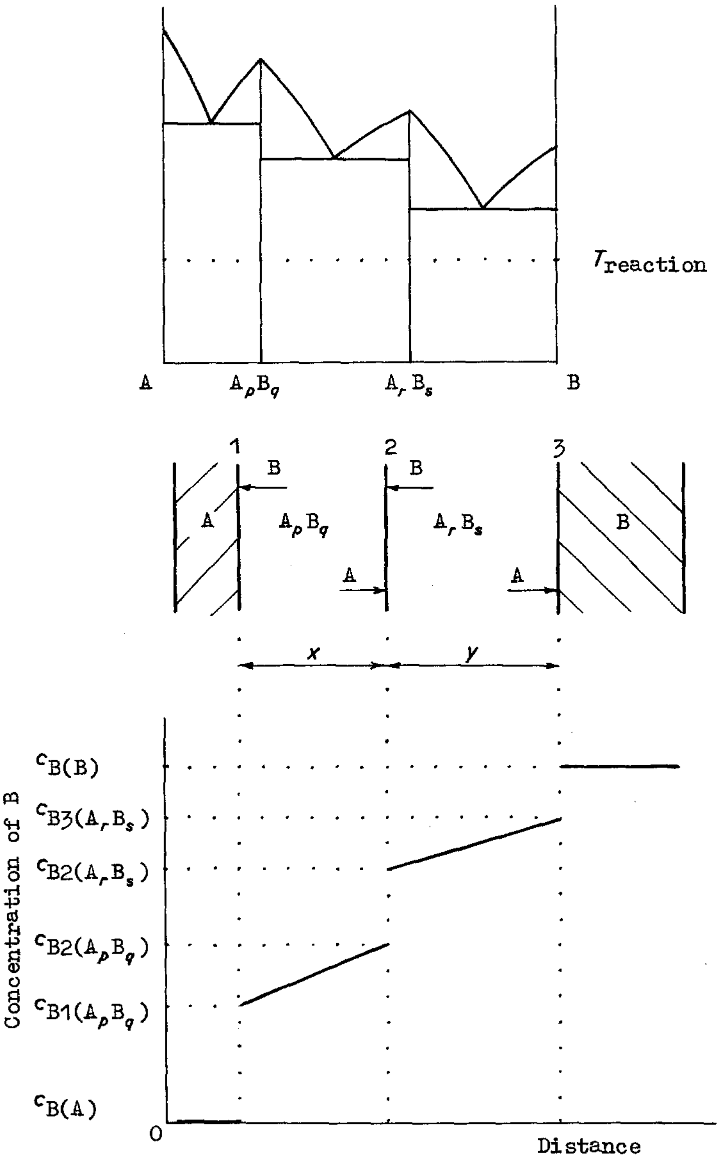

Figure 1 Schematic diagram illustrating the growth of two compound layers at the interface between two elements.

$D_{A(A_pB_q)}$ being the diffusion coefficient of A in A_pB_q, $c_{A1(A_pB_q)}$ and $c_{A2(A_pB_q)}$ the boundary concentrations of A into the A_pB_q layer at interfaces 1 and 2 respectively.

During dt, the A_rB_s layer thickness will increase by

$$\mathrm{d}y_+ = \mathrm{d}y_{B2} + \mathrm{d}y_{A3} \tag{10}$$

where $\mathrm{d}y_{B2}$ is the increase in its thickness at interface 2 due to Reaction 3 and $\mathrm{d}y_{A3}$ is the increase at interface 3 due to Reaction 4. The expressions for $\mathrm{d}y_{B2}$ and $\mathrm{d}y_{A3}$ are

$$\mathrm{d}y_{B2} = \frac{k_{0B2}}{1 + (k_{0B2}y/k_{1B2})}\,\mathrm{d}t \tag{11}$$

and

$$\mathrm{d}y_{A3} = \frac{k_{0A3}}{1 + (k_{0A3}y/k_{1A3})}\,\mathrm{d}t \tag{12}$$

where

$$k_{1B2} = \frac{D_{B(A_rB_s)}[c_{B3(A_rB_s)} - c_{B2(A_rB_s)}]}{c_{B2(A_rB_s)}} \tag{13}$$

$$k_{1A3} = \frac{D_{A(A_rB_s)}[c_{A2(A_rB_s)} - c_{A3(A_rB_s)}]}{c_{A3(A_rB_s)}} \tag{14}$$

D and c being the diffusion coefficients and the boundary concentrations, respectively, of components A and B into the A_rB_s layer.

During the same time, dt, the thickness of the A_pB_q layer will decrease by $\mathrm{d}x_-$ as a result of Reaction 3. This decrease can easily be found from Equation 3. Indeed,

$$\frac{m_{A_pB_q}}{m_{A_rB_s}} = \frac{rM_{A_pB_q}}{pM_{A_rB_s}} \tag{15}$$

where m is the mass and M the molecular mass of the compound. The mass is the product of the density, ϱ, and the volume which in turn is the product of the surface area and the thickness of the layer. Since the surface area is constant,

$$\frac{\varrho_{A_pB_q}\mathrm{d}x_-}{\varrho_{A_rB_s}\mathrm{d}y_{B2}} = \frac{rM_{A_pB_q}}{pM_{A_rB_s}} \tag{16}$$

Hence,

$$\mathrm{d}x_- = \frac{rg}{p}\,\mathrm{d}y_{B2} \tag{17}$$

where the ratio of the molar volume, V, of A_pB_q to that of A_rB_s is denoted by g, i.e. $g = V_{A_pB_q}/V_{A_rB_s}$.

By analogy, from Equation 2 one obtains

$$\mathrm{d}y_{-} = \frac{q}{sg}\,\mathrm{d}x_{A2} \qquad (18)$$

The overall change in the A_pB_q layer thickness during dt is

$$\mathrm{d}x = \mathrm{d}x_{B1} + \mathrm{d}x_{A2} - \mathrm{d}x_{-} \qquad (19)$$

Similarly,

$$\mathrm{d}y = \mathrm{d}y_{B2} + \mathrm{d}y_{A3} - \mathrm{d}y_{-} \qquad (20)$$

Thus, a system of differential equations describing the growth kinetics of two compound layers between the elements A and B is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_{0B1}}{1 + (k_{0B1}x/k_{1B1})} + \frac{k_{0A2}}{1 + (k_{0A2}x/k_{1A2})} - \frac{rg}{p}\frac{k_{0B2}}{1 + (k_{0B2}y/k_{1B2})} \qquad (21a)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{k_{0B2}}{1 + (k_{0B2}y/k_{1B2})} + \frac{k_{0A3}}{1 + (k_{0A3}y/k_{1A3})} - \frac{q}{sg}\frac{k_{0A2}}{1 + (k_{0A2}x/k_{1A2})} \qquad (21b)$$

The system of differential equations set out as Equations 21a and 21b permit some predictions to be made. It should be emphasized, however, that the approach to their solution should not be only mathematical. One must also take into account, besides the initial conditions $x = 0$ and $y = 0$ at $t = 0$, the existence of the critical thickness of the layers (see Equation 16 in Part 1 [7])

$$x_{1/2}^{(B)} = \frac{k_{1B1}}{k_{0B1}} \qquad (22)$$

$$x_{1/2}^{(A)} = \frac{k_{1A2}}{k_{0A2}} \qquad (23)$$

$$y_{1/2}^{(B)} = \frac{k_{1B2}}{k_{0B2}} \qquad (24)$$

$$y_{1/2}^{(A)} = \frac{k_{1A3}}{k_{0A3}} \qquad (25)$$

which divide the $x - t$ and $y - t$ relationships into the reaction and diffusion controlled regions with regard to components A and B (see Section 2 in Part 1 [7]). Here, only some limiting cases of practical interest are treated.

3. Initial stage of the growth process

3.1. Linear growth

Initially, the thicknesses of the layers are small and therefore 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, the terms of the form k_0x/k_1 and k_0y/k_1 can be neglected in comparison with unity. In this case Equations 21a, b simplify to

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{0B1} + k_{0A2} - \frac{rg}{p}k_{0B2} \qquad (26a)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k_{0B2} + k_{0A3} - \frac{q}{sg}k_{0A2} \qquad (26b)$$

If $k_{0B1} + k_{0A2} > (rg/p)k_{0B2}$ and $k_{0B2} + k_{0A3} > (q/sg)k_{0A2}$ then dx/dt and dy/dt are positive and therefore both layers grow linearly with time.

If $k_{0B1} + k_{0A2} = (rg/p)k_{0B2}$ then dx/dt = 0. This means that the thickness of the A_pB_q layer remains constant since the rate of growth of this layer is equal to the rate of its "dissolution" into A_rB_s. Note that at the same time the A_rB_s layer continues to grow linearly.

When the condition

$$k_{0B1} + k_{0A2} < \frac{rg}{p}k_{0B2} \qquad (27)$$

is satisfied then the A_pB_q layer cannot grow at all (dx/dt < 0) and therefore only the A_rB_s layer will grow between the A and B phases. If the A_pB_q layer was initially present in a specimen its thickness would decrease and it may disappear completely. Of course, this does not mean that the A_pB_q layer will never occur between the reacting phases. In general, the rate of the A_pB_q "dissolution" gradually decreases (see Equations 21a, b) and therefore the time will be achieved when dx/dt becomes positive.

Similarly, the A_rB_s layer thickness remains constant or equals zero if $k_{0B2} + k_{0A3} = (q/sg)k_{0A2}$. If

$$k_{0B2} + k_{0A3} < \frac{q}{sg}k_{0A2} \qquad (28)$$

then the A_rB_s layer is absent between the reacting phases.

Note that in the case under consideration both layers grow under reaction controlled regimes with regard to both components as $x \ll x_{1/2}^{(A)}$, $x \ll x_{1/2}^{(B)}$, $y \ll y_{1/2}^{(A)}$ and $y \ll y_{1/2}^{(A)}$ (see Equations 22 to 25 and Section 2 in Part 1 [7]).

3.2. Non-linear–linear growth

Thickening of the layers would result in a change of the regimes of their growth. Suppose that the regime of growth of the A_pB_q layer with regard to component B is diffusion controlled as $x > x_{1/2}^{(B)}$ and consider the case where $x \gg x_{1/2}^{(B)}$. Assume that the regime of the A_pB_q layer growth is reaction controlled with regard to component A so that $x \ll x_{1/2}^{(A)}$. As before, the regime of growth of the A_rB_s layer is regarded as being reaction controlled with regard to both components ($y \ll y_{1/2}^{(A)}, y \ll y_{1/2}^{(B)}$). These conditions can be described as follows: $k_{0B1} \gg k_{1B1}/x$, $k_{0A2} \ll k_{1A2}/x$, $k_{0B2} \ll k_{1B2}/y$ and $k_{0A3} \ll k_{1A3}/y$. Therefore, Equations 21a and b become

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_{1B1}}{x} + k_{0A2} - \frac{rg}{g}k_{0B2} \qquad (29a)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k_{0B2} + k_{0A3} - \frac{q}{sg}k_{0A2} \qquad (29b)$$

From Equation 29b it follows that the A_rB_s layer grows linearly with time. The x–t relationship is somewhat more complicated (parabolic, asymptotic, etc, growth of the A_pB_q layer may be observed).

4. The role of the critical thickness in determining the growth kinetics of the layers

4.1. Departures of the layer thickness–time relationship

Suppose that the regime of the A_pB_q layer growth become diffusion controlled not only with regard to component B but also with regard to component $A(x > x^{(B)}_{1/2},\ x > x^{(A)}_{1/2})$. This case essentially differs from the preceding one. Namely, when the regime of growth of the A_pB_q layer with regard to component A is diffusion controlled then the A_rB_s layer cannot grow at the expense of component A. This is due to the fact that at $x > x^{(A)}_{1/2}$ all the A atoms passing across the A_pB_q layer are combined into the A_pB_q compound at interface 2 according to Reaction 2 (see Section 2 in Part 1 [7]). Moreover, the thicker the A_pB_q layer the greater is a deficit of A atoms in comparison with the reactivity of the A_rB_s layer surface towards these atoms. No A atom is therefore available for Reaction 4. Interface 2 or, more precisely, the surface of the A_rB_s layer acts as an insurmountable barrier for A atoms. Hence, there is no source of A atoms for the A_rB_s layer. At $x > x^{(A)}_{1/2}$ this layer grows only at the expense of component B. In such a case, the term

$$\frac{k_{0A3}}{1 + (k_{0A3}\,y/k_{1A3})}$$

in Equations 21a, b has no physical meaning and therefore it should be omitted whatever y. This results in a perceptible decrease of the rate of growth of the A_rB_s layer. Indeed, at $x < x^{(A)}_{1/2}$ this layer grows at the expense of both components whereas at $x > x^{(A)}_{1/2}$ it grows only at the expense of component B. A departure of the y–t curve from its former course should therefore be observed as shown schematically in Fig. 2.

4.2. "Paralinear" stage of growth of the layers

If $x \gg x^{(B)}_{1/2}$, $x \gg x^{(A)}_{1/2}$ and $y \ll y^{(B)}_{1/2}$ then Equations 21a and b become

$$\frac{dx}{dt} = \frac{k_{1B1} + k_{1A2}}{x} - \frac{rg}{p}k_{0B2} \qquad (30a)$$

$$\frac{dy}{dt} = k_{0B2} - \frac{q}{sg}\frac{k_{1A2}}{x} \qquad (30b)$$

Equation 30a is independent of y and therefore it can be solved separately. It is seen that the A_pB_q layer thickness tends to a limiting value defined by the equation

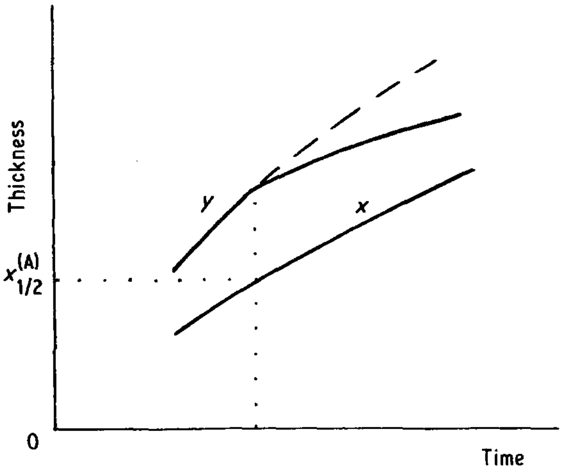

Figure 2 A departure of the A_rB_s layer thickness–time relationship resulting from a change of the regime of growth of the A_pB_q layer.

$$x_{\max} = \frac{(k_{1B1} + k_{1A2})p}{rgk_{0B2}} \qquad (31)$$

while the A_rB_s growth kinetics at fairly large x becomes linear. Thus,

$$\frac{dx}{dt} = \frac{k_{1B1} + k_{1A2}}{x} - \frac{rg}{p}k_{0B2} \qquad (32a)$$

$$\frac{dy}{dt} = k_{0B2} \qquad (32b)$$

The equations of this type were first proposed to describe the growth kinetics of two compound layers, one of which is compact while the other is porous, by Loriers [8–10] (see also Kofstad [11]). In general, Equations 30a, b and 32a, b describe the so-called "paralinear" growth kinetics which is observed in those cases where the diffusion coefficients of the elements in the layers are very different. "Paralinear" growth kinetics are usually observed during oxidation of metals and alloys when a continuous thermogravimetric method is applied to control the run of the process [6, 11–16]. The name "paralinear growth" is due to the fact that some portion of the total specimen mass–time relationship is close to a parabola but then there is a transition to the linear-law kinetics. Indeed, from Equations 30a, b and 32a, b it follows that if

$$\frac{k_{1B1} + k_{1A2}}{x} \gg \frac{rg}{p}k_{0B2}$$

then the mass–time dependence is almost parabolic whereas the more long-time portion is almost linear, Fig. 3.

4.3. Late stage of growth of the layers

Eventually, the regime of growth of the A_rB_s layer becomes diffusional with regard to component B as well ($y > y^{(B)}_{1/2}$, see Equation 24). This change strongly affects the growth rate of the A_pB_q layer. Namely, at $y > y^{(B)}_{1/2}$ the A_pB_q layer has no source of B atoms and therefore its further growth proceeds only at the expense of component A. Thus, at $x > x^{(A)}_{1/2}$ and $y > y^{(B)}_{1/2}$ the growth of both layers is due to Reactions 2 and 3 taking place at interface 2 whereas Reactions 1 and 4 cannot proceed at all. In this case the terms $k_{0B1}/[1 + (k_{0B1}x/k_{1B1})]$ and $k_{0A3}/[1 + (k_{0A3}y/k_{1A3})]$ in Equations 21a, b have no physical meaning and therefore they should be omitted. For the late diffusional region ($x \gg x^{(A)}_{1/2}$ and $y \gg y^{(B)}_{1/2}$), Equations 21a, b become

$$\frac{dx}{dt} = \frac{k_{1A2}}{x} - \frac{rg}{p}\frac{k_{1B2}}{y} \qquad (33a)$$

$$\frac{dy}{dt} = \frac{k_{1B2}}{y} - \frac{q}{sg}\frac{k_{1A2}}{x} \qquad (33b)$$

Analogous systems of differential equations (differing only by coefficients) were obtained by Arkharov [1] Fromhold and Sato [4], Schröder and Leute [3] and others. It should be noted that the solutions of these equations are often based on the assumption that the ratio of the rates of growth of the layers remains constant during the growth, i.e.

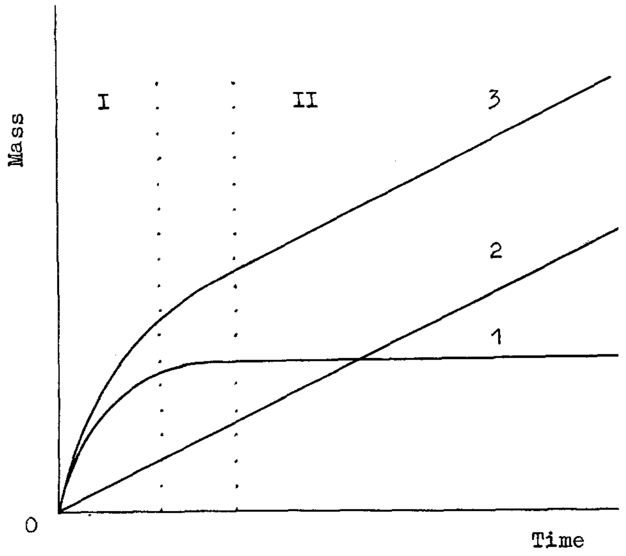

Figure 3 "Paralinear" growth kinetics: 1, mass of the A_pB_q layer; 2, mass of the A_rB_s layer. I, a portion of the total mass–time curve close to a parabola. II, a linear portion.

$$\frac{\mathrm{d}x/\mathrm{d}t}{\mathrm{d}y/\mathrm{d}t} = \text{const.} \tag{34}$$

In general, however, this is not the case. The source of this erroneous assumption can easily be revealed using Equations 33a, b. Indeed, for the layers to grow, $\mathrm{d}x/\mathrm{d}t$ and $\mathrm{d}y/\mathrm{d}t$ must be positive. Hence, Equations 33a, b transform into a system of inequalities of the form

$$\frac{k_{1A2}}{x} - \frac{rgk_{1B2}}{py} > 0 \tag{35a}$$

$$\frac{k_{1B2}}{y} - \frac{qk_{1A2}}{sgx} > 0 \tag{35b}$$

The inequalities should be satisfied simultaneously; thus

$$\frac{q}{sg}\frac{k_{1A2}}{k_{1B2}} < \frac{x}{y} < \frac{p}{rg}\frac{k_{1A2}}{k_{1B2}} \tag{36}$$

It is seen, firstly, that the ratio of the thickness of the A_pB_q layer to the thickness of the A_rB_s layer depends upon: (a) the constants of diffusional growth; (b) the ratio of the molar volumes of the compounds; and (c) the stoichiometry of the compounds. Secondly, it is clear that the x/y ratio varies with time and therefore there is no evidence to suppose that it is constant. On the other hand, it is seen that the closer the compositions of the A_pB_q and A_rB_s compounds the narrower is the range in which the x/y ratio may vary. For example, for compounds of the type AB and AB_2 Inequality 36 becomes

$$\frac{k_{1A2}}{2gk_{1B2}} < \frac{x}{y} < \frac{k_{1A2}}{gk_{1B2}}. \tag{37}$$

This range is fairly wide in comparison with the experimental error of determination of the layer thickness, that usually being 10 to 30%.

For compounds of the type AB_4 and AB_5 this range is

$$\frac{4k_{1A2}}{5gk_{1B2}} < \frac{x}{y} < \frac{k_{1A2}}{gk_{1B2}} \tag{38}$$

From Inequality 38 it is seen that the change in the x/y ratio during the growth of the layers of these compounds is comparable with the experimental error of measuring the layer thickness. In this case from the experimental observations one may conclude that the x/y ratio is "constant".

The law of growth of two compound layers in the late diffusional stage of the interaction can, at least in principle, be found by solving Equations 33a, b at the initial conditions $x = x_0$, $y = y_0$ at $t = 0$ ($x_0 > 0$, $y_0 > 0$) without any assumptions. Indeed, dividing, say, the second of these equations by the first yields an equation of the form $\mathrm{d}y/\mathrm{d}x = f(x, y)$. Solving this equation, one obtains y as a function of x. Substitution of this function into Equation 33a gives a differential equation of the form $\mathrm{d}x/\mathrm{d}t = f(x)$. On integrating this equation, one obtains x as a function of t. The y–t relationship can then be obtained from Equation 33b. It should be emphasized that the problem is so simple only in word, since each step produces very complex expressions and therefore it is hard, if not impossible, to represent the final result in the form of some simple analytical function. However, this difficulty is not an insurmountable obstacle for the use of these equations by experimentalists. Indeed, the values of $(\mathrm{d}x/\mathrm{d}t)_{t=t_0}$ and $(\mathrm{d}y/\mathrm{d}t)_{t=t_0}$ can be found from experimental data (for example, by graphical differentiation of experimental x–t and y–t curves). Then, Equations 33a, b transform into a system of two equations with two unknown quantities, k_{1B2} and k_{1A2}. The constants, k_{1B2} and k_{1A2}, found in such a way are characteristics of the A_pB_q and A_rB_s layers, respectively, i.e. they are the same for any reaction couple where these layers occur.

Note that from Equations 33a, b it follows that the pre-existing layers should not necessarily simultaneously grow during subsequent annealing. If the initial thicknesses, x_0 and y_0, are such that, say, $(\mathrm{d}x/\mathrm{d}t)_{t=0}$ is negative and $(\mathrm{d}y/\mathrm{d}t)_{t=0}$ is positive then the thickness of the A_pB_q layer will decrease while the thickness of the A_rB_s layer will increase during an isothermal anneal of the A–B couple unless the x/y ratio falls into the range defined by Inequality 36. After this, both layers will grow simultaneously.

It should be noted that Equations 33a, b describe the so-called "postlinear" (see [11]) stage of the metal–gas interaction which follows the "paralinear" stage.

5. Discussion

In general, the relationships discussed above continuously transform into each other. This results in a very complicated general relationship which cannot be described by some simple analytical equation. Moreover, it is seen that there may be two more or less considerable departures of the curve describing the time dependence of the total thickness (or mass) of two compound layers as shown schematically in Fig. 4. One of these departures is due to a transition from reaction to diffusion controlled regime of growth of the A_pB_q layer with regard to component A and the other is due to a transition from reaction to diffusion

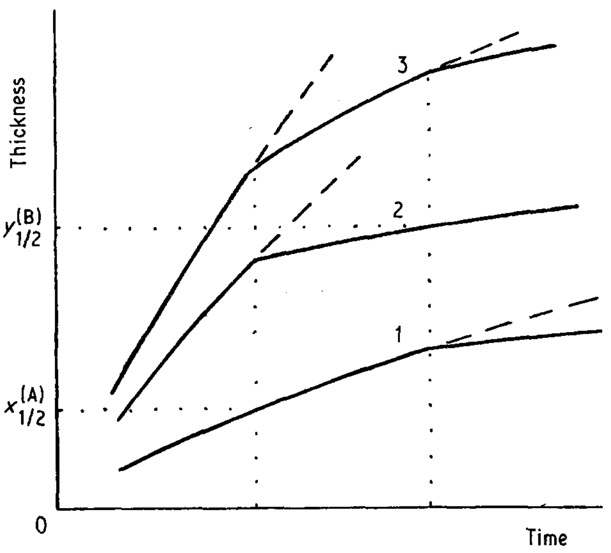

Figure 4 Departures of the thickness (mass)–time relationships due to the existence of the critical thickness of growing compound layers: 1, thickness of the A_pB_q layer; 2, thickness of the A_rB_s layer; 3, total thickness of the layers.

controlled regime of growth of the A_rB_s layer with regard to component B. Such departures may be observed in those cases where the duration of the experiments is very long. It should be emphasized that the appearance of these departures is due only to the quantitative changes in thicknesses of the layers. For such departures to occur, no change in their number, compositions or structures is necessary. This is an example of the transformation of quantity into quality.

It follows that no layer can grow between the A_pB_q and A_rB_s layers if these layers grow under diffusional regimes with regard to component A and B, respectively. In this case all the diffusing A atoms are spent on the growth of the A_pB_q layer (Reaction 2) whereas all the diffusing B atoms are spent on the growth of the A_rB_s layer (Reaction 3).

Any compound lying between A_pB_q and A_rB_s acts only as the reactant in the reactions of formation of the A_pB_q and A_rB_s compounds. Therefore, the thickness of the layer of this compound will decrease until it disappears totally. Hence, the largest number of growing layers in the case under consideration is two. The layer of a new compound will grow only after the total depletion of one of the initial phases, i.e. the growth of compound layers is sequential and not simultaneous. This is in agreement with the experimental observations, the number of layers in the diffusion couples usually being far less than the number of chemical compounds in a given binary system.

6. Conclusions

Contrary to the "diffusional" theory which predicts a parabolic growth for two compound layers, the theory proposed here gives a more complicated relationship. This is in accordance with experiment.

The neglect of a chemical reaction step is the main source of disagreement between the "diffusional" theory and the available experimental data. In fact, the fast chemical reactions taking place at the interfaces between the reacting phases strongly affect the course of the layer growth. They are responsible for the appearance of the barriers to certain kinds of atoms at the critical thicknesses of the layers. This, in turn, results in a restriction of the number of compound layers growing simultaneously under diffusional regimes between the A and B phases. Hence, the rates of chemical transformations play an important, if not decisive, role in determining the direction of the growth process. This assertion is in sharp contradiction with the widespread opinion that the chemical transformations do not influence the growth kinetics except for some small initial period of the layer formation.

In the limiting cases where the rates of chemical transformations are very high compared to the rates of diffusion of the reacting species the theory proposed here and the "diffusional" theory produce the same analytical equations describing the growth kinetics of two compound layers.

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