PERIODIC STRUCTURES GENERATED BY MULTICOMPONENT DIFFUSION OF REACTIVE COMPONENTS

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The conditions for the formation of periodic concentrations due to multicomponent diffusion of reactive components are found. These relations are expressed in terms of the diffusion coefficients and the parameters of the reaction kinetics.

In our previous paper[1] we have discussed some possible anomalies in multicomponent diffusion of non-reacting components. The inclusion of the reactions among the components may lead (under well defined conditions) to some unexpected phenomena.

Let us have a system in which a reaction $X_1 + X_2 = X_3$ can take place. The concentration c_1, c_2 satisfy the equations in refs[2,3]

$$\frac{\partial c_1}{\partial t} = D_{11}\nabla^2 c_1 + D_{12}\nabla^2 c_2 + f_1(c_1, c_2), \tag{1}$$

$$\frac{\partial c_2}{\partial t} = D_{21}\nabla^2 c_1 + D_{22}\nabla^2 c_2 + f_2(c_1, c_2),$$

where D_{ij} are the difussion coefficients and f_1, f_2 represent the reaction rates of the components. The concentration of the third component is determined by the respective mass balance. For the sake of further references we remind the inequalities[4]

$$D_{11} > 0, D_{22} > 0 \quad D_{11}D_{22} - D_{12}D_{21} > 0 \tag{2}$$

The Onsager theory of irreversible processes (see e.g. refs[2,3]) yields one reciprocity relation (for a ternary system) among the diffusion coefficients

$$G_{12}D_{11} + G_{22}D_{21} = G_{11}D_{12} + G_{21}D_{22} \tag{3}$$

with known quantities G_{ij}. There are no restrictions on the signs of the interdiffusion coefficients D_{12} and D_{21}.

We shall deal with the reactions represented by the linear functions

$$f_j(c_1, c_2) = -\alpha_{j1}(c_1 - \varkappa_1) - \alpha_{j2}(c_2 - \varkappa_2), \qquad (4)$$

where α_{ij} and $\varkappa_j$ are the characteristic constants. This set corresponds to the decay reactions. The standard reaction formula

$$f - k'_1 c_3 = k_1 c_1 c_2$$

can be reduced to the linear form (see Eq. (*4*)) for small deviations $|c_j - c_j^e| \ll c_j^e$ from the equilibrium concentrations c_j^e. In that case we can neglect small term $(c_1 - c_1^e)(c_2 - c_2^e)$, i.e.

$$c_1 c_2 = [c_1^e + (c_1 - c_1^e)][c_2^e + (c_2 - c_2^e)] \approx c_1^e c_2^e +$$
$$+ c_2^e(c_1 - c_1^e) + c_1^e(c_2 - c_2^e) = c_2^e(c_1 - \tfrac{1}{2}c_1^e) + c_1^e(c_2 - \tfrac{1}{2}c_2^e)$$

This linear approximation corresponds to Eq. (*4*).

The stationary situation is described by the equations

$$D_{11}\nabla^2 c_1 + D_{12}\nabla^2 c_2 - \alpha_{11}(c_1 - \varkappa_1) - \alpha_{12}(c_2 - \varkappa_2) = 0$$
$$D_{21}\nabla^2 c_1 + D_{22}\nabla^2 c_2 - \alpha_{21}(c_1 - \varkappa_1) - \alpha_{22}(c_2 - \varkappa_2) = 0 \qquad (5)$$

RESULTS

We outline the method of calculation of the set (*5*) and summarize the results of practical interest. The most straightforward way is to start with the one-dimensional case, i.e. $c_j \equiv c_j(x)$. The set (*5*) then reads

$$D_{11}u_1''(x) + D_{12}u_2''(x) - \alpha_{11}u_1(x) - \alpha_{12}u_2(x) = 0$$
$$D_{21}u_1''(x) + D_{22}u_2''(x) - \alpha_{21}u_1(x) - \alpha_{22}u_2(x) = 0,$$

where

$$u_1(x) \equiv c_1(x) - \varkappa_1 \quad u_2(x) \equiv c_2(x) - \varkappa_2. \qquad (6)$$

After simple rearrangements we reduce the set to the standard form

$$u_1''(x) = a_{11}u_1(x) + a_{12}u_2(x)$$
$$u_2''(x) = a_{21}u_1(x) + a_{22}u_2(x), \qquad (7)$$

where

$$Da_{11} = \alpha_{11}D_{22} - \alpha_{21}D_{12} \quad Da_{12} = \alpha_{12}D_{22} - \alpha_{22}D_{12}$$
$$Da_{21} = \alpha_{21}D_{11} - \alpha_{11}D_{21} \quad Da_{22} = \alpha_{22}D_{11} - \alpha_{12}D_{21} \tag{8}$$
$$D = D_{11}D_{22} - D_{12}D_{21} > 0\,.$$

Insertion $u_1 = A\,e^{\lambda x}$, $u_2 = B\,e^{\lambda x}$ into Eqs (7) yields the characteristic equation

$$(\lambda^2 - a_{11})(\lambda^2 - a_{22}) - a_{12}a_{21} = 0\,.$$

It is convenient to express the roots in the form

$$\lambda_{1,2,3,4} = \pm(a \pm b)^{1/2}\,, \tag{9}$$

where

$$a = \tfrac{1}{2}(a_{11} + a_{22}) \quad b = \tfrac{1}{2}[(a_{11} - a_{22})^2 + 4a_{12}a_{21}]^{1/2} \tag{9'}$$

The analysis of the solutions depends on the properties of the roots (single, multiple, real or complex). We present here two of the most interesting situations.

If $(a_{11} - a_{22})^2 + 4a_{12}a_{21} > 0$, then b is a real number. In the case

$$a \pm b < 0 \tag{10}$$

all roots in relations (9) are simple and pure imaginary. Let us denote

$$\varrho_1 = (-a - b)^{1/2} \quad \varrho_2 = (-a + b)^{1/2}$$
$$\lambda_1 = i\varrho_1 \quad \lambda_2 = -i\varrho_1 \quad \lambda_3 = i\varrho_2 \quad \lambda_4 = -i\varrho_2\,.$$

We drop the routine calculations and bring the final results

$$c_1(x) = \varkappa_1 + \gamma_1 \sin(\varrho_1 x + \delta_1) + \gamma_2 \sin(\varrho_2 x + \delta_2) \tag{11}$$

$$c_2(x) = \varkappa_2 - (\gamma_1/a_{12})(\varrho_1^2 + a_{11})\sin(\varrho_1 x + \delta_1) - $$
$$- (\gamma_2/a_{12})(\varrho_2^2 + a_{11})\sin(\varrho_2 x + \delta_2)\,, \tag{12}$$

where γ_1, γ_2, δ_1, δ_2 are the integration constants. These constants are usually expressed in terms of the values of concentrations c_1, c_2 and their gradients dc_1/dx, dc_2/dx for some particular point.

The solutions (*11*) and *12*) are represented as a superposition of two periodic (goniometric) functions. Such a superposition is not in general a periodic function.

Nothwithstanding the linear combination of two concentrations

$$L_1(x) = c_2(x) + (1/a_{12})(a_{11} + \varrho_2^2)\,c_1(x) = \varkappa_2 + (\varkappa_1/a_{12})(a_{11} + \varrho_2^2) + (1/a_{12})(\varrho_2^2 - \varrho_1^2)\,\gamma_1 \sin(\varrho_1 x + \delta_1) \qquad (13)$$

is a periodic function with the period $p_1 \equiv 2\pi/\varrho_1$.

The second interesting case occurs when

$$a_{11}a_{22} - a_{12}a_{21} = (1/D)(\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21}) = 0\,. \qquad (14)$$

From (*9'*) one gets

$$b = \tfrac{1}{2}(a_{11} + a_{22})$$

and correspondingly

$$\lambda_{1,2} = \pm(a_{11} + a_{22})^{1/2} \quad \lambda_{3,4} = 0\,.$$

Due to the double root $\lambda_3 = \lambda_4 = 0$ there appears the term $A_4 + A_3x$. If it is (as in the previous case) $a < 0$, then

$$\lambda_{1,2} = \pm \mathrm{i}\varrho \quad \varrho \equiv \sqrt{(-2a)}\,.$$

The general solution then reads

$$c_1(x) = \varkappa_1 + \gamma \sin(\varrho x + \delta) + a_{12}(A_4 + A_3x)$$
$$c_2(x) = \varkappa_2 + \gamma\mu \sin(\varrho x + \delta) - a_{11}(A_4 + A_3x)$$

where $\mu \equiv a_{21}/a_{11} = a_{22}/a_{12}$
and γ, δ, A_3, A_4 are the integration constants. The concentrations remain finite for any x when $A_3 = 0$, i.e.

$$c_1(x) = \varkappa_1 + a_{12}A_4 + \gamma \sin(\varrho x + \delta)$$
$$c_2(x) = \varkappa_2 - a_{11}A_4 + \gamma\mu \sin(\varrho x + \delta)\,. \qquad (15)$$

The concentrations are periodic with the period $p = 2\pi/\varrho$. Let us emphasize that this behaviour anticipates the validity of the relation (*14*).

The three-dimensional solutions of the set (*5*) can be found analogically. We express the concentrations in terms of the three-dimensional Fourier integrals

$$c_j - \varkappa_j = \int \varrho_j(k)\, e^{ikr}\, d^3k, \quad (j = 1, 2)\,.$$

Insertion of these expressions into the set (*5*) yields the equations for ϱ_j and the spectrum k_n. The next step is the construction of the general solutions. We drop these technical calculations and bring the respective final results.

In the case of the validity of the conditions (*10*) one arrives at the solutions

$$\begin{aligned} c_1(r) &= \varkappa_1 + r^{-1}[A\sin(\varrho_1 r) + B\sin(\varrho_2 r)] \\ c_2(r) &= \varkappa_2 - (a_{12}r)^{-1}\,(\varrho_1^2 + a_{11})\,A\sin(\varrho_1 r) + \\ &\quad + (\varrho_2^2 + a_{11})\,B\sin(\varrho_2 r)]\,, \end{aligned} \tag{16}$$

where $r \equiv (x^2 + y^2 + z^2)^{1/2}$. A and B are the integration constants. The concentrations c_1, c_2 are finite for any values of r. The validity of the solutions (*16*) can easily be verified by inserting into the set (*5*).

The concentrations are expressed in the form of the linear combinations of two periodic functions: the coefficients of this combinations are, however, inversely proportional to r.

If the condition (*14*) is satisfied the solutions get the form

$$\begin{aligned} c_1(r) &= \varkappa_1 + a_{12}B + (A/r)\sin(\varrho r) \\ c_2(r) &= \varkappa_2 - a_{11}B + (\mu A/r)\sin(\varrho r)\,. \end{aligned} \tag{17}$$

From the explicit solutions (*11*), (*15*)–(*17*) one can determine the surfaces of the same concentrations (isoconcentration surfaces), particularly the surfaces of the zero concentrations. The condition $c_1(x_0) = c_{ie}$ defines the planes $x = x_0$, and $c_i(r_0) = c_{ie}$ determines the spheres $r = r_0$ of the same concentrations c_{0i}. The very existence and the number of such surfaces is, however, dependent on the values of the integration constants.

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