

OSCILLATIONS OF CONCENTRATIONS IN MULTICOMPONENT DIFFUSION

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While selfdiffusion coefficients D_{ii} are always positive, the stability conditions admit both signs of the interdiffusion coefficients D_{ij} ($i \neq j$). In a multicomponent system ($n > 2$) with opposite signs of interdiffusion (at least within some range of concentrations and temperatures) there might occur anomalous evolution of concentrations, e.g. the damped oscillations of extremal values for some x^2/t .

The partial molar volumes v_i , the molar concentrations c_i , the chemical potentials μ_i and the diffusion current J_i satisfy the relations

$$\sum_{i=1}^n c_i v_i = 1, \quad \sum_{i=1}^n v_i J_i = 0, \quad \sum_{i=1}^n c_i \text{grad } \mu_i = 0 \quad (1)$$

The last condition is a slight modification of the Gibbs–Duhem equation $\sum_{i=1}^n c_i d\mu_i = 0$. We shall not consider the reactions among the components. From (1) we exclude c_n and J_n , so we have to consider $n - 1$ independent concentrations c_1, \dots, c_{n-1} and $n - 1$ independent currents J_1, \dots, J_{n-1} .

In the theory of diffusion the independent currents J_i are usually expressed in the form

$$J_i = - \sum_{j=1}^{n-1} D_{ij} \text{grad } c_j, \quad (i = 1, 2, \dots, n - 1) \quad (2)$$

The time derivatives $\partial c_i / \partial t$ satisfy the equations

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{n-1} \text{div} (D_{ij} \text{grad } c_j). \quad (3)$$

The diffusion coefficients D_{ij} are in general the functions of the concentrations $D_{ij} \equiv D_{ij}(c_1, \dots, c_{n-1})$. The Onsager theory of irreversible processes (see e.g. 1 2) leads to the reciprocity relations among the diffusion coefficients

$$\sum_{j=1}^{n-1} (G_{kj} D_{ji} - G_{ji} D_{jk}) = 0, \quad (4)$$

where

$$G_{kj} = \sum_{r=1}^{n-1} (\delta_{kr} + v_k v_r / c_n v_n) (\partial \mu_r / \partial c_j).$$

From the stability conditions follow the inequalities 3

$$\begin{aligned} D_{11} > 0, D_{22} > 0, \dots, D_{n-1, n-1} > 0 \\ D_{11}D_{22} - D_{12}D_{21} > 0, \dots, \det(D_{ij}) > 0. \end{aligned} \quad (5)$$

One has to emphasize that there are no thermodynamical restrictions on the signs of the interdiffusion coefficients $D_{ij} (i \neq j)$. This is the starting point of our further considerations.

In the case of constant D_{ij} the set (3) has the well-known form

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{n-1} D_{ij} \nabla^2 c_j. \quad (6)$$

Any solutions of this set should respect both sets of conditions (4) and (5).

We shall consider two special cases of (6). Let all concentrations c_i depend on one coordinate only, say x , i.e. $c_i \equiv c_i(x, t)$. The set (6) then reads

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{n-1} D_{ij} \frac{\partial^2 c_j}{\partial x^2}. \quad (7)$$

In the case of spherical symmetry (concentric spherical layers) $c_i \equiv c_i(r, t)$ we express ∇^2 in spherical, coordinates and then by means of the substitutions

$$c_i(r, t) = \frac{1}{r} u_i(r, t)$$

we arrive at the set

$$\frac{\partial u_i}{\partial t} = \sum_{j=1}^{n-1} D_{ij} \frac{\partial^2 u_j}{\partial r^2}$$

formally equivalent to the one-dimensional case (7).

RESULTS

We outline the method of calculation and then summarize the results of practical interest. The detailed calculations are published elsewhere.

We start with the set (7) for ternary system

$$\begin{aligned}\frac{\partial c_1}{\partial t} &= D_{11} \frac{\partial^2 c_1}{\partial x^2} + D_{12} \frac{\partial^2 c_2}{\partial x^2}, \\ \frac{\partial c_2}{\partial t} &= D_{21} \frac{\partial^2 c_1}{\partial x^2} + D_{22} \frac{\partial^2 c_2}{\partial x^2}.\end{aligned}\quad (8)$$

We express c_1, c_2 in terms of Fourier integrals

$$c_i(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f_i(t) e^{ikx} dk, \quad (i = 1, 2). \quad (9)$$

This yields for $f_i(t)$ the equations

$$\begin{aligned}\frac{df_1}{dt} &= -k^2(D_{11}f_1 + D_{12}f_2), \\ \frac{df_2}{dt} &= -k^2(D_{21}f_1 + D_{22}f_2).\end{aligned}\quad (10)$$

This linear set of ordinary equations has particular integrals $f_1 = Ae^{-\lambda t}$, $f_2 = Be^{-\lambda t}$. Insertion of these particular integrals into (10) yields the characteristic equation for λ , i.e.

$$(\lambda - k^2 D_{11})(\lambda - k^2 D_{22}) - k^4 D_{12} D_{21} = 0. \quad (11)$$

The general solution of f_1, f_2 and then of c_1, c_2 depends on the nature of the roots of the characteristic equation (11). We have to distinguish three possibilities.

First case corresponds to real single roots.

$$\lambda_{1,2} = \frac{k^2}{2}(\gamma \pm \mu), \quad (12a)$$

where both

$$\gamma = D_{11} + D_{22}, \quad \mu \equiv [(D_{22} - D_{11})^2 + 4D_{12}D_{21}]^{1/2} \quad (12b)$$

are real positive numbers. This situation occurs in systems where the diffusion coefficients satisfy the inequality

$$4D_{12}D_{21} > -(D_{22} - D_{11})^2. \quad (13)$$

By means of (12) we construct the general solutions of f_1, f_2 and then after insertion into (9) we get the concentrations c_1, c_2 . (The third concentration c_3 is determined

by the normalization conditions $c_1v_1 + c_2v_2 + c_3v_3 = 1$.) We drop the lengthy calculations and bring the respective final results

$$c_1(x, t) = \frac{\int_{-\infty}^{\infty} [(\mu + D_{11} - D_{22})c_{01}(x') + 2D_{12}c_{02}(x')] e^{-Y^2} dx'}{2\mu[2\pi(\gamma + \mu)t]^{1/2}} + \frac{\int_{-\infty}^{\infty} [(D_{22} - D_{11} + \mu)c_{01}(x') - 2D_{12}c_{02}(x')] e^{-Z^2} dx'}{2\mu[2\pi(\gamma - \mu)t]^{1/2}}, \quad (14)$$

$$c_2(x, t) = \frac{\int_{-\infty}^{\infty} [2D_{21}c_{01}(x') + (D_{22} - D_{11} + \mu)c_{02}(x')] e^{-Y^2} dx'}{2\mu[2\pi(\gamma + \mu)t]^{1/2}} - \frac{\int_{-\infty}^{\infty} [2D_{21}c_{01}(x') + (D_{22} - D_{11} - \mu)c_{02}(x')] e^{-Z^2} dx'}{2\mu[2\pi(\gamma - \mu)t]^{1/2}}, \quad (15)$$

where

$$c_{01}(x') = c_1(x', 0), \quad c_{02}(x') = c_2(x', 0)$$

are the initial (at $t = 0$) concentrations, and

$$Y^2 = \frac{(x - x')^2}{2(\gamma + \mu)t}, \quad Z^2 = \frac{(x - x')^2}{2(\gamma - \mu)t}.$$

The equations (14) and (15) solve the problem of the evolution of concentrations in any ternary system with diffusion coefficients satisfying the inequality (13). One has to specify the initial concentrations. For the sake of illustration we shall consider the initial distributions

$$c_{0i}(x') = \begin{cases} a_{0i} & \text{for } x' < 0 \\ b_{0i} & \text{for } x' > 0, \quad i = 1, 2. \end{cases} \quad (16)$$

After performing the respective calculations one gets

$$c_1(x, t) = \frac{1}{2\mu} [2D_{12}a_{02} + (\mu + D_{11} - D_{22})a_{01}] \Phi(-\xi) + \frac{1}{2\mu} [2D_{12}b_{02} + (\mu + D_{11} - D_{22})b_{01}] \Phi(\xi) + \frac{1}{2\mu} [(D_{22} - D_{11} + \mu)a_{01} - 2D_{12}a_{02}] \Phi(-\eta) + \frac{1}{2\mu} [(D_{22} - D_{11} + \mu)b_{01} - 2D_{12}b_{02}] \Omega(\eta), \quad (17)$$

where

$$\xi \equiv \frac{x}{[2(\gamma + \mu)t]^{1/2}}, \quad \eta \equiv \frac{x}{[2(\gamma - \mu)t]^{1/2}}$$

and

$$\Phi(z) = \pi^{-1/2} \int_{-\infty}^z e^{-u^2} du$$

is the well-known Gauss' errorfunction. The concentration $c_2(x, t)$ follows from (17) by the index interchange $1 \leftrightarrow 2$. We see that in a ternary system with diffusion coefficients satisfying the inequality (13) the evolution of concentrations has normal monotonous character.

Let us now turn to the case of complex roots

$$\lambda_{1,2} = \frac{k^2}{2} (\gamma \pm i\nu), \quad (18)$$

where

$$\nu = [-(D_{22} - D_{11})^2 - 4D_{12}D_{21}]^{1/2}. \quad (19)$$

This assumes the inequality

$$4D_{12}D_{21} < -(D_{22} - D_{11})^2, \quad (20)$$

resp.

$$4(D_{11}D_{22} - D_{12}D_{21}) - (D_{11} + D_{22})^2 > 0.$$

In the case under consideration the evolution of $c_1(x, t)$ is determined by the equation

$$\begin{aligned} c_1(x, t) = & \frac{\varrho + 2D_{22}}{2\varrho[\pi(\varrho + \gamma)t]^{1/2}} \int_{-\infty}^{\infty} c_{01}(x') e^{-\gamma X^2} \cos(\gamma X^2) dx' + \\ & + \frac{\varrho - 2D_{22}}{2\varrho[\pi(\varrho - \gamma)t]^{1/2}} \int_{-\infty}^{\infty} c_{01}(x') e^{-\gamma X^2} \sin(\nu X^2) dx' - \\ & - \frac{D_{12}}{\varrho[\pi(\varrho + \gamma)t]^{1/2}} \int_{-\infty}^{\infty} c_{02}(x') e^{-\gamma X^2} \cos(\gamma X^2) dx' + \\ & + \frac{D_{12}}{\varrho[\pi(\varrho - \gamma)t]^{1/2}} \int_{-\infty}^{\infty} c_{02}(x') e^{-\gamma X^2} \cos(\nu X^2) dx', \quad (21) \end{aligned}$$

where

$$\varrho \equiv 2(D_{11}D_{22} - D_{12}D_{21})^{1/2}, \quad X^2 \equiv \frac{(x - x')^2}{2\varrho^2 t}.$$

The corresponding equation for c_2 follows from (21) by index interchange $1 \leftrightarrow 2$.

From (21) one may conclude that there are damped oscillations of the concentrations. To illustrate this anomalous evolution we take the initial point-like distributions

$$c_{01}(x') = \kappa_1 \delta(x' - x_1), \quad c_{02}(x') = \kappa_2 \delta(x' - x_2). \quad (22)$$

where $\delta(z)$ is the well-known Dirac function satisfying the relation

$$\int_{-\infty}^{\infty} f(x') \delta(x' - x_i) dx' = f(x_i).$$

After inserting (22) into (21) we arrive at the equation

$$c_1(x, t) = \frac{\kappa_1 e^{-\gamma X_1^2}}{2\varrho(\pi t)^{1/2}} \left[\frac{\varrho + 2D_{22}}{(\varrho + \gamma)^{1/2}} \cos(\gamma X_1^2) + \frac{\varrho - 2D_{22}}{(\varrho - \gamma)^{1/2}} \sin(\gamma X_1^2) \right] - \frac{D_{12}\kappa_2 e^{-\gamma X_2^2}}{\varrho(\pi t)^{1/2}} \left[\frac{\cos(\gamma X_2^2)}{(\varrho + \gamma)^{1/2}} - \frac{\sin(\gamma X_2^2)}{(\varrho - \gamma)^{1/2}} \right], \quad (23)$$

where

$$X_i^2 \equiv \frac{(x - x_i)^2}{2\varrho^2 t}.$$

It is instructive to compare (23) with the well-known solution

$$c(x, t) = \frac{1}{2(\pi Dt)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (24)$$

of the diffusion equation $(\partial c/\partial t) = D(\partial^2 c/\partial x^2)$. This significant difference between (23) and (24) is due to the inequality (20), i.e. to the opposite interdiffusion.

The generalization of (23) on a more realistic case of the point-like initial distributions (diffusion of the point-like impurities)

$$c_{01}(x') = \sum_i \kappa_{1i} \delta(x' - x_{1i}), \quad c_{02}(x') = \sum_j \kappa_{2j} \delta(x' - x_{2j})$$

is straightforward. And finally some suitable model of the initial random distribution of impurities can be applied.

Let us now turn to the third possible case, i.e. to the case of the double root

$$\lambda = \frac{k^2}{2} \gamma. \quad (25)$$

This situation occur: when $\mu = 0$, what corresponds to

$$4D_{12}D_{21} = -(D_{22} - D_{11})^2 \quad (26)$$

This condition is to be supplemented by the respective reciprocity relation (4) for ternary diffusion

$$G_{12}D_{11} + G_{22}D_{21} = G_{11}D_{12} + G_{21}D_{22} \quad (27)$$

The corresponding solution then reads

$$c_1(x, t) = \frac{1}{(2\pi\gamma t)^{1/2}} \int_{-\infty}^{\infty} c_{01}(x') e^{-U^2} dx' + \\ + \frac{1}{2\gamma(2\pi\gamma t)^{1/2}} \int_{-\infty}^{\infty} [(D_{22} - D_{11})c_{01}(x') - 2D_{12}c_{02}(x')] (1 - 2U^2) e^{-U^2} dx', \quad (28)$$

where

$$U^2 \equiv \frac{(x - x')^2}{2\gamma t}.$$

The corresponding expression for c_2 can be obtained by the same mechanism as above. We apply (28) on the initial distribution (1). After performing the calculations one gets

$$c_1(x, t) = a_{01}\Phi(-\zeta) + b_{01}\Phi(\zeta) + \\ + \frac{1}{2\gamma\sqrt{\pi}} [2(a_{02} - b_{02})D_{12} - (a_{01} - b_{01})(D_{22} - D_{11})] \zeta e^{-\zeta^2}, \quad (28)$$

where

$$\zeta = \frac{x}{(2\gamma t)^{1/2}}.$$

We see that both c_1 and c_2 are the functions of one variable only, $\zeta = x/(2t)^{1/2}$. The extremal values follow from the conditions $(dc_1/d\zeta) = (dc_2/d\zeta) = 0$. Elementary calculations lead to the conclusion that $c_1(\zeta)$ has extremum values at

$$\zeta_1 = \pm \frac{1}{\sqrt{2}} \left[1 - \frac{a_{01} - b_{01}}{A_1} \right],$$

where $(\delta \equiv D_{22} - D_{11})$

$$A_1 = \frac{D_{12}}{\gamma} (a_{02} - b_{02}) - \frac{\delta}{2\gamma} (a_{01} - b_{01}).$$

The inequality $\zeta_1 \Delta_1 < 0$ corresponds to minimum, $\zeta_1 \Delta_1 > 0$ to maximum values of c_1 . Analogical results for c_2 can be obtained by the index interchange $1 \leftrightarrow 2$.

CONCLUSIONS

We have demonstrated three possible evolutions of concentrations in the ternary diffusion. The "normal" monotonous evolution occurs when $\Delta \equiv (D_{22} - C_{11})^2 + 4D_{12}D_{21} < 0$. The opposite inequality $\Delta > 0$ leads to the damped oscillations. The equality $\Delta = 0$ leads to the occurrence of extremum values for particular values of x^2/t . The changes of Δ (e.g. due to the change of concentrations, temperature, etc.) may lead to a subsequent change of the evolution of the diffusion process.

REFERENCES

1. De Groot S. R., Mazur P.: *Non-Equilibrium Thermodynamics*. North-Holland, Amsterdam 1962.
2. Prigogine I.: *Introduction to Thermodynamics of Irreversible Processes*. Interscience, New York 1967.
3. Kvasnica J.: *Czech. J. Phys.* B 32, 19 (1982).

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