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The meaning of the state variable *chemical potential* μ

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The theory of diffusion is dominated by the two Fick's laws of diffusion, which are empirical in nature. In Fick's laws, the state variable *concentration c plays* a decisive role:

$$\frac{1}{A}\frac{\mathrm{d}n_i}{\mathrm{d}t} = -D_i\frac{\mathrm{d}c_i}{\mathrm{d}x}; \qquad \frac{\mathrm{d}c_i}{\mathrm{d}t} = D_i\frac{\mathrm{d}^2c_i}{\mathrm{d}x^2}, \tag{1}$$

where n_i denotes the amount of substance of component i, t the time, D_i the diffusion coefficient, c_i the concentration of i, and x the spatial coordinate.

The first Fick's law follows the general structure of linear irreversible transport equations [1]:

$$\frac{1}{A}\frac{\mathrm{d}X_i}{\mathrm{d}t} = -L_{ii}\frac{\mathrm{d}\xi_i}{\mathrm{d}x}, \tag{2}$$

where $F_i = \mathrm{d}\xi_i/\mathrm{d}x$ is the *thermodynamic force* (the local gradient of an intensive state variable ξ_i), $J_i = \mathrm{d}X_i/\mathrm{d}t$ is the *thermodynamic flux* (the temporal transport of an extensive state variable X_i through an area A), and L_{ii} the linear *phenomenological coefficient* that represent a material property. According to Equation (2), the force F_i *causes* a flux J_i, which represents a cause-effect principle.

In case of diffusion (cf. Equation (1)), the local gradient of the concentration c_i causes a transport of amount of substance n_i. Here, it is known from thermodynamics that every material change is actually caused by a local gradient of the *chemical potential* μ. The relationship between the chemical potential μ_i and the concentration c_i of a substance i is well-known:

$$\mu_i = \mu_i^0 + RT\ln a_i, \tag{3}$$

where $\mu_i^0(T)$ is defined at standard pressure, and a_i denotes the activity being for instance a modified concentration or pressure. It is harder to think in terms of μ than in terms of c because until the present day, μ has remained abstract and somewhat mystical. Its abstract definition within Gibbs' thermodynamics:

$$\mu = \frac{G}{n} = G_\mathrm{m}; \qquad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j\neq n_i}, \tag{4}$$

where μ of a pure substance represents the molar Gibbs free energy, and μ_i of a component i in a mixture the partial molar Gibbs free energy, leaves open the question what the abstract energy amount G really *is*.

We show in our work that this question can be answered by a unified formulation of process equations with a clear cause-effect principle [1, 2] leading to a vivid explanation of the chemical potential μ and other basic state variables.

References

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