

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:

$$\frac{1}{A} \frac{dn_i}{dt} = -D_i \frac{dc_i}{dx}; \quad \frac{dc_i}{dt} = D_i \frac{d^2c_i}{dx^2}, \quad (1)$$

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]:

$$\frac{1}{A} \frac{dX_i}{dt} = -L_{ii} \frac{d\xi_i}{dx}, \quad (2)$$

where $F_i = d\xi_i/dx$ is the *thermodynamic force* (the local gradient of an intensive state variable ξ_i), $J_i = dX_i/dt$ 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:

$$\mu_i = \mu_i^0 + RT \ln a_i, \quad (3)$$

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:

$$\mu = \frac{G}{n} = G_m; \quad \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq n_i}, \quad (4)$$

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

- [1] G. Kalies: *Back to the roots: The concepts of force and energy*, Z. Phys. Chem. 1–53 (2021); DOI: 0.1515/zpch-2021-3122.
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