

Mass-Transfer Equation in Multicomponent Mixtures

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Abstract—A multicomponent mass-transfer equation for the distillation of multicomponent mixtures is derived in terms of the thermodynamics of irreversible processes.

It is well known that the notion of time is absent from classical thermodynamics. It usually considers equilibrium states or infinitesimal transitions from one equilibrium state into another. Meanwhile, real-world processes pass through nonequilibrium states, since they are driven by finite driving forces. The thermodynamics of processes far from equilibrium requires a quite complex mathematical apparatus [1].

In 1916, carrying out an experiment with a system containing hydrogen peroxide, formic acid, and sulfuric acid, Morgan observed a periodic generation of carbon monoxide. Somewhat later (1921), Bray detected that the H_2O_2 decomposition in an acidic medium in the presence of the iodate ion has an oscillatory character. In 1930, Frank-Kamenetskii proposed a theory of such oscillatory solutions. The mathematical formalism of these phenomena was borrowed from the Lotka–Volterra model of the periodic coexistence of predator and prey populations. In this model, the numbers of predator and prey individuals are described by nonlinear differential equations, which, as Poincaré (1928) showed, have a totally different solution for oscillatory phenomena. Regardless of their initial state, such systems necessarily come to the same oscillatory motion, which is called the cycle [2].

The nonlinearity of differential equations is a necessary, but not sufficient, condition for oscillatory modes. This is because there are nonlinear processes that cannot occur in oscillatory modes. Among such processes are those whose linear approximation has a symmetric matrix of coefficients. The coefficients can be constants or certain functions of process variables. In the latter case, the symmetric matrix is a functional matrix. If a system is characterized by a nonsymmetric matrix A , it is necessary to determine whether or not this matrix is reduced to a symmetric matrix by the transformation [3]

$$CAC^{-1}, \quad (1)$$

where C and C^{-1} are a matrix and its inverse, respectively. The reduction to a symmetric matrix is possible if the real matrix A has characteristic roots.

Systems for which the first-approximation coefficient matrices are symmetric or can be reduced to symmetric are described in terms of the thermodynamics of linear irreversible processes, which has been sufficiently developed by Onsager and his school of thought. A more general case is the preservation of only the symmetry of the first-approximation coefficient matrices for a number of nonlinear systems. In this case, the first-approximation coefficients are functions of the state variables of the process under consideration [4, 5].

It was previously shown [6] that singular points of the set of paths of continuous distillation can only be generalized nodes or generalized saddles and cannot correspond to eigenvalues among which there are complex, conjugate, or imaginary numbers. Consequently, distillation can be described using the concepts of the thermodynamics of irreversible processes in generalized form.

There can be steady-state and unsteady-state distillation. An example of steady-state distillation is distillation in continuous columns. Examples of unsteady-state distillation are batch distillation and also the startup mode of continuous columns. The latter mode is conveniently represented in a configuration space with $(n-1)(m'+2)$ or $(n-1)(m'+1)$ ordinates, where n is the number of components, m is the number of plates in the rectifying section of a column, and m' is the number of plates in the stripping section of the column. In this case, unlike other representations, the state of the system is described by a point in the $(n-1)(m+2)$ - or $(n-1)(m'+1)$ -dimensional space and, depending on the initial state of the system, all unsteady-state processes are determined by the set of paths. Any of these paths ends at a singular point of the stable-node type. This is the point at which a given steady state takes place.

A system can have several steady states. For example, it can have two stationary points, one of which is an unstable node and the other is a stable node, or three

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