I. F. Bakhareva

1960

SovietRxiv

Abstract

Full Text

Physical Chemistry

I. F. Bakhareva

On the Nonlinear Thermodynamics of Irreversible Processes

(Presented by Academician V. N. Kondrat' ev, 28 V 1960)

The kinetics of a large group of phenomena can be investigated on the basis of the phenomenological theory of the thermodynamics of irreversible processes, which is based on the Onsager equations

$$\dot{x}_i = \sum_k^n L_{ik} X_k, \quad i = 1, 2, \dots, n; \tag{1}$$

$$L_{ik} = L_{ki}, \tag{2}$$

where $x_1, x_2, \dots, x_n$ is a set of thermodynamic parameters characterizing the degree of deviation of the system from equilibrium; L_{ik} are kinetic coefficients; X_k is the thermodynamic force, which in the case of adiabatic isolation of the system is expressed as

$$X_k = \frac{\partial(-\Delta S)}{\partial x_k}; \tag{3}$$

ΔS is the deviation of the entropy from its equilibrium value.

In the traditional approximation of the thermodynamics of irreversible processes, the expression for the forces X_k is constructed taking into account terms of second order in the expansion of ΔS, so that X_k are linear functions of the thermodynamic parameters

$$X_k = \sum_i^n g_{ik} x_i, \quad k = 1, 2, \dots, n, \tag{4}$$

where it is obvious that

$$g_{ik} = g_{ki}. \tag{5}$$

Taking (4) into account, the system of equations (1) can be represented in the form

$$\dot{x}_i = \sum_{k,l}^{n} L_{ik} g_{il} x_l, \quad i = 1, 2, \dots, n. \tag{6}$$

Thus, the thermodynamic Onsager equations of motion have a linear form both in representation (1) and in representation (6).

The reciprocity relations (2) can be regarded as a consequence of the symmetry of the matrix b_{ik}

$$b_{ik} = b_{ki}, \tag{7}$$

which can be proved statistically ([1]). Its elements enter into the expression for the dissipative function D,

$$D = \frac{1}{2} \sum_{i,k}^{n} b_{ik} \dot{x}_i \dot{x}_k, \tag{8}$$

being, like the "production of entropy," σ

$$\sigma = \frac{d(\Delta S)}{dt} = \sum_{i}^{n} \dot{x}_i X_i, \tag{9}$$

a measure of energy dissipation.

It is easy to see that

$$D = \frac{\sigma}{2}. \tag{10}$$

Taking (7), (8), (9), and (10) into account, we obtain

$$L_{ik} = b_{ik}^{-1}. \tag{11}$$

The linear form of the kinetic law, expressed by the system of equations (6), since it is constructed under condition (4), is valid in the neighborhood of equilibrium. This limitation is not essential only for certain phenomena, such as, for example, transport phenomena. In the general case, however, the linear form (6) cannot be extended to the entire kinetic region of the phenomenon, but begins to operate only from some moment in time close to $t = \infty$, when equilibrium is established in the system.

Let us call the kinetic law expressed by the system of equations (1) under condition (6) linear-linear. We shall show below that in the next approximation the linear form (1) can be preserved, but the linearity of equations (6) is violated.

Let us retain the previous definition for the thermodynamic forces, expressed by conditions (3), but in the expansion of ΔS take into account terms of the third order; then

$$X'_k = \sum_i^n g_{ik} x'_i + \frac{1}{2} \sum_{i,l}^n m_{ikl} x'_i x'_l, \tag{12}$$

where it is obvious that

$$g_{ik} = g_{ki}, \quad m_{ikl} = m_{kil} = m_{nli} = m_{ilk}. \tag{13}$$

It is easy to observe that the form of the function σ is preserved independently of the number of terms in the expansion of ΔS, i.e.

$$\sigma' = \sum_i^n \dot{x}'_i X'_i. \tag{9'}$$

Under this condition the kinetic equations, as before, may be represented in linear form

$$\dot{x}'_i = \sum_k^n L'_{ik} X'_k, \qquad i = 1, 2, \dots, n. \tag{1''}$$

Let us further assume that the dissipative function, since it, like σ, determines the amount of dissipated energy, can be expressed, as before, in the form

$$D' = \frac{1}{2} \sum_{i,k}^n b'_{ik} \dot{x}'_k \dot{x}'_i, \tag{8'}$$

where

$$D' = \frac{\sigma'}{2}. \tag{10'}$$

In order that, as $\dot{x}'_k \to \dot{x}_k$, the function D' should pass into D, it is necessary to set

$$b'_{ik} = b_{ik}. \tag{14}$$

Taking into account (7), (8′), (9′), (10′), and (14), we obtain

$$L'_{ik} = L_{ik}. \tag{15}$$

The kinetic equations (1″) take the form

$$\dot{x}_i = \sum_{k}^{n} L_{ik} X'_k, \tag{1'}$$

where the reciprocity conditions (2) are satisfied for L_{ik}.

Expressing X'_k as functions of the thermodynamic parameters (12), we obtain a system of nonlinear kinetic equations in the form

$$\dot{x}_i = \sum_{k,m}^{n} L_{im} g_{ik} x'_k + \frac{1}{2} \sum_{m,l,k} L_{im} m_{ikl} x'_k x'_l. \tag{6'}$$

We shall call the kinetic law expressed by equations (1′) and (6′) linear-nonlinear.

It is natural to suppose that the linear-nonlinear form of the kinetic law is more general and can encompass the entire kinetic region of certain processes for which the linear-nonlinear form is valid only in a limited region close to the state of equilibrium.

It is easy to see that, in the case when the nonlinear terms may be neglected, (6′) reduces to (6).

As an illustration of the results obtained, let us consider a system in which chemical reactions occur—this is the most typical case of the limited validity of the linear-nonlinear law. For simplicity we shall consider a specific reaction: a sequence of two reversible bimolecular stages:

$$2B_1 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2B_2; \qquad 2B_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} 2B_3;$$

k_i is the rate constant of the i-th reaction;

$$x_i = c_i - c_i^0 = \Delta c_i; \tag{16}$$

c_i is the concentration of the i-th component at the given instant of time; c_i^0 is the concentration of the i-th component at equilibrium.

If the reaction proceeds at constant temperature and volume, then [2]

$$X_i = \frac{\partial(\Delta F)}{\partial(\Delta c_i)}; \tag{17}$$

ΔF is the deviation of the free energy from its equilibrium value.

Taking into account that the superposition effect is absent in the case of chemical reactions [3], i.e.

$$L_{ik} = L_{ki} = 0, \tag{18}$$

we obtain, for independent concentrations, the kinetic equations

$$\frac{1}{2}\frac{d(\Delta c_1)}{dt} = L_1 X_1, \qquad \frac{1}{2}\frac{d(\Delta c_3)}{dt} = L_2 X_2. \tag{19}$$

Under the condition that the chemical potentials are expressed in the form

$$\mu_i = RT \ln \frac{c_i}{c_i^0} + \mu_i^0, \tag{20}$$

Taking into account the third-order terms in the expansion of ΔF, we obtain

$$\begin{aligned} \frac{1}{2}\frac{d(\Delta c_1)}{dt} &= L_1 \left\{ 2\left(\frac{1}{c_2^0} - \frac{1}{c_1^0}\right)\Delta c_1 + \frac{2}{c_2^0}\Delta c_3 + \left[\frac{1}{(c_2^0)^2} - \frac{1}{(c_1^0)^2}\right]\Delta c_1^2 \right. \\ &\qquad \left. + \frac{2}{(c_2^0)^2}\Delta c_1 \Delta c_3 + \frac{1}{(c_2^0)^2}\Delta c_3^2 \right\}; \\ \frac{1}{2}\frac{d(\Delta c_3)}{dt} &= L_2 \left\{ \frac{2}{c_2^0}\Delta c_1 + 2\left(\frac{1}{c_2^0} - \frac{1}{c_3^0}\right)\Delta c_3 + \frac{1}{(c_2^0)^2}\Delta c_1^2 \right. \\ &\qquad \left. + \frac{2}{(c_2^0)^2}\Delta c_1 \Delta c_3 + \left[\frac{1}{(c_2^0)^2} - \frac{1}{(c_3^0)^2}\right]\Delta c_3^2 \right\}. \end{aligned} \tag{21}$$

Taking into account that

$$L_1 = k_1 (c_1^0)^2, \qquad L_2 = k_3 (c_2^0)^2, \tag{22}$$

and reducing system (21) to the variables c_i, with (16) taken into account, we obtain

$$\frac{1}{2}\frac{dc_1}{dt} = -k_1 c_1^2 + k_2 c_2^2,$$

$$\frac{1}{2}\frac{dc_3}{dt} = k_3 c_2^2 - k_4 c_3^2, \tag{23}$$

which is in complete agreement with the law of mass action.

Thus, in the present case the linear-nonlinear form of the law covers the entire kinetic region of the reaction, from its beginning (at $t = 0$, $c_1 = c_0$, $c_2 = c_3 = 0$) up to equilibrium.

It is easy to see that the linear form of the equations in representation (1) is a consequence of the expression for the thermodynamic forces (3). The range of applicability of the thermodynamic method is limited by this definition. The inclusion of the necessary number of terms in the expansion of ΔS is dictated by the conditions of the physical problem. It can be shown that for monomolecular stages, throughout the entire kinetic region, the linear-linear form of the law is valid, obtained by taking into account second-order terms in the expansion of ΔF. Bimolecular stages require the inclusion of third-order terms, and trimolecular stages of fourth-order terms in the expansion of ΔF, in accordance with the law of mass action.

The author takes this opportunity to express deep gratitude to A. D. Stepukhovich for constant attention to the work, valuable advice, and comments.

Saratov State University
named after N. G. Chernyshevsky

Received
26 V 1960

CITED LITERATURE

1. L. Landau, E. Lifshitz, *Statistical Physics*, 1951.
2. K. Popov, DAN, 106, No. 3 (1956).
3. C. R. de Groot, *Thermodynamics of Irreversible Processes*, 1956.

Note: Figure translations are in progress. See original paper for figures.