Nonequilibrium thermodynamics approach to the Brönsted relation

A. P. Grigin

A. N. Frumkin Institute of Electrochemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117071 Moscow, Russian Federation.
Fax: 007 (095) 952 0846

A correlation between the rate of a chemical reaction and the generalized thermodynamic force can be elucidated using the principle of correspondence for the reaction rate expressed in terms of kinetic and thermodynamic variables. The Brönsted relation follows from the dependence obtained.

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Brönsted-type correlation equations establish the relationship between the reaction rate constants and equilibrium constants for a series of reactions of the same type in which the reaction center of the molecule remains virtually the same:[1]

$$k_1 = \varkappa K_0^{\alpha}. \qquad (1)$$

Here k_1 is the reaction rate constant, K_0 is the equilibrium constant, and $\varkappa$ and α are parameters.

The type (1) relation was found empirically by Brönsted and Pederson when they analyzed the experimental data on the kinetics of acid-catalyzed reactions. Later, relations of these sort proved to be valid for many series of reactions of the same type.[1]

At present, the Brönsted equation and other related equations form the basis for correlation analysis in organic chemistry; however, they have not yet received theoretical justification. They belong to the domain of the so-called extrathermodynamic relations, whose proof requires the use of microscopic models of the processes considered. In this study, we showed that relation (1) can be deduced in terms of nonequilibrium thermodynamics, based on the dependence of the reaction rate on the generalized thermodynamic force.

The main problem in nonequilibrium thermodynamics is to find a correlation between currents I and thermodynamic forces x. Thermodynamic current I can be a scalar, a vector, or a tensor of the second or third rank.[2] The $I(x)$ function must be such that the rate of generation of entropy during the process is positive; otherwise, we shall come into conflict with the second law of thermodynamics. In linear nonequilibrium thermodynamics, the Taylor expansion of $I(x)$ is normally used, and consideration is restricted to the first term of the expansion. Dissipative coefficients, *viz.*, diffusion, viscosity, thermal conductivity, and other coefficients, are thus introduced; their signs can be easily found from the condition of the positive determinacy of the rate of entropy generation. Construction of a nonlinear $I(x)$ function involves fundamental difficulties, since the condition of positive determinacy of the rate of entropy generation alone is insufficient to elucidate the $I(x)$ function in explicit form. However, in relation to chemical reactions, this problem can be solved, if it is required in addition that the $I(x)$ function satisfy the principle of correspondence.

From the standpoint of nonequilibrium thermodynamics, the rate of a chemical reaction I is a scalar thermodynamic current varying as a function of the generalized thermodynamic force, which is defined as the difference between the chemical potentials of the initial and final states of a system.[2] To find a nonlinear $I(\Delta\mu)$ function, one can use the correspondence principle, which establishes the relationship between the expressions for I, written in terms of kinetic and thermodynamic variables. In theoretical studies, the correspondence principle is used to find the relationship between various forms of description of the same phenomenon. For example, an analogy between wave geometric optics and Hamiltonian mechanics of mass particles can be established in this way. The possibility of using the correspondence principle in chemical kinetics is due to the fact that the occurrence of a reaction can be considered from two absolutely different standpoints, *viz.*, corpuscular kinetic and thermodynamic standpoints. In the kinetic method, the reaction rate is governed by the probabilities of the forward and back reactions, while in the thermodynamic approach, it is determined by the dependence of I on $\Delta\mu$. Apparently, these two approaches correspond somewhat to each other. It is this correspondence that serves as an additional condition that, together with the condition of positive determinacy of the rate of entropy generation, allows the nonlinear $I(\Delta\mu)$ function to be established in explicit form.

Let us consider application of the principle of correspondence to a reversible elementary association—dissociation reaction (Scheme 1).

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Scheme 1

$$A + B \rightleftharpoons C$$

The rate of the reaction shown in Scheme 1 is

$$I = wn_1n_2 - vm, \qquad (2)$$

where n_1 is the concentration of species A, n_2 is the concentration of species B, m is the concentration of species C, w is the probability of the formation of molecule C from A and B per unit of time, v is the probability of decomposition of molecule C, and I is the reaction rate. Eq. (2) specifies the reaction pathway and expresses the reaction rate in terms of corpuscular kinetic theory.

Now we shall write the rate of the reaction presented in Scheme 1 in terms of nonequilibrium thermodynamics. The occurrence of the reaction is accompanied by generation of entropy S, and the rate of generation is equal to[2]

$$\frac{dS}{dt} = \frac{1}{T}\int I\Delta\mu\, dV, \qquad (3)$$

where $\Delta\mu = \mu_A + \mu_B - \mu_C$ is the difference between the chemical potentials of the initial and final states, and T is the temperature.

The behavior of the system is entirely determined by the dependence of current I on the generalized thermodynamic force $\Delta\mu$. The $I(\Delta\mu)$ function must be such that its substitution in expression (3) would ensure positive determinacy of the rate of entropy generation for any admissible concentration of particles and any thermodynamic force $\Delta\mu$. We shall search for a relation that would express the total current as the product of two functions, one of which would depend on $\Delta\mu$, while the other would be a function of the concentrations of particles.

$$I = R(n_1,n_2,m)f(\Delta\mu) \qquad (4)$$

Let us specify the dependence of the chemical potential on the particle concentration n by a known expression, which is valid for approximation of an ideal gas:

$$\mu = \mu_0 + T\ln n, \qquad (5)$$

where μ_0 is a function of pressure and temperature.

Using Eq. (5), the difference between the chemical potentials of the initial and final states of the system can be represented in the following form:

$$\Delta\mu = \Delta\mu_0 + T\ln(n_1n_2/m). \qquad (6)$$

The question arises of whether the representation of (4), according to which $\Delta\mu$ is a function of the particle concentration, is admissible. From the standpoint of nonequilibrium thermodynamics, the separation of $\Delta\mu$ as an independent variable is quite justified, since it is $\Delta\mu$ that determines the degree to which the system deviates from equilibrium. The concentrations of particles in the system can be changed; however, if $\Delta\mu = 0$, no chemical transformations occur in it.

In order to find a correlation between expressions (2) and (4), we shall try to obtain the $f(\Delta\mu)$ function in the following form:

$$f(\Delta\mu) = \exp\left(\beta_1\frac{\Delta\mu}{T}\right) - \exp\left(\beta_2\frac{\Delta\mu}{T}\right), \qquad (7)$$

where β_1 and β_2 are unknowns.

This form of the $f(\Delta\mu)$ function can be justified by the fact that $\Delta\mu$ follows a logarithmic dependence on the concentration of particles. If we substitute expression (6) in Eq. (7), the dependence of f on the particle concentration will assume the form of an exponential function; therefore, the $R(n_1,n_2,m)$ dependence can also be expressed as an exponential function

$$R = \varkappa(n_1n_2)^{\alpha_1}m^{\alpha_2}, \qquad (8)$$

where α_1 and α_2 are unknown parameters.

By substituting expressions (6)—(8) in Eq. (4), we obtain the following relation for I

$$I = \varkappa\,(n_1n_2)^{\alpha_1}m^{\alpha_2}\left[\left(\frac{n_1n_2}{m}\right)^{\beta_1}\exp\left(\beta_1\frac{\Delta\mu_0}{T}\right) - \left(\frac{n_1n_2}{m}\right)^{\beta_2}\exp\left(\beta_2\frac{\Delta\mu_0}{T}\right)\right], \qquad (9)$$

where $\varkappa$ is the dissipative coefficient.

The correspondence principle in nonequilibrium thermodynamics can be formulated as follows: expressions (2) and (9), which present the rate of the reaction in terms of kinetic and thermodynamic variables, should have identical functional forms with respect to the particle concentrations.[3] By equating the exponents in expressions (2) and (9) with n_1n_2 and m as variables, we obtain set (10) of linear equations for α_1, α_2, β_1, and β_2.

$$\begin{cases} \alpha_1 + 0 + \beta_1 + 0 = 1 \\ 0 + \alpha_2 - \beta_1 + 0 = 0 \\ \alpha_1 + 0 + 0 + \beta_2 = 0 \\ 0 + \alpha_2 + 0 - \beta_2 = 1 \end{cases} \qquad (10)$$

The rank of the matrix of this linear set is 3; therefore the equations in this set are linearly dependent, and one of the unknown quantities is free. Let us choose α_1 as the free variable, introduce the designation $\alpha = \alpha_1$, and exclude the last equation from set (10). By solving the three remaining equations, we obtain

$$\beta_1 = 1 - \alpha;\ \beta_2 = -\alpha;\ \alpha_2 = 1 - \alpha. \qquad (11)$$

Thus, using the principle of correspondence we showed that, with the assumptions made, the nonlinear dependence of the reaction rate on the thermodynamic force is determined by two parameters, *viz.*, dissipative coefficient $\varkappa$ and parameter α. If we substitute expression (11) in Eq. (9), we obtain

$$I(\Delta\mu) = \varkappa (n_1 n_2)^{\alpha} m^{1-\alpha} \left\{ \exp\left[(1-\alpha) \frac{\Delta\mu}{T} \right] - \exp\left(\alpha \frac{\Delta\mu}{T} \right) \right\}. \quad (12)$$

By comparing expressions (12) and (2), we can find the relationship between the kinetic and thermodynamic parameters of the reaction:

$$w = \varkappa \exp\left[(1-\alpha) \frac{\Delta\mu_0}{T} \right]; \; v = \varkappa \exp\left(-\alpha \frac{\Delta\mu_0}{T} \right) . \quad (13)$$

Let us now consider the following question: is it possible to determine the thermodynamic parameters of a system if the probabilities of the forward (w) and back (v) reactions are known? Taking into account expression (13), we obtain

$$\frac{w}{v} = \exp\left(\frac{\Delta\mu_0}{T} \right) . \quad (14)$$

Taking the logarithm of Eq. (13) results in the following set of equations:

$$\begin{cases} \ln\varkappa - \alpha \dfrac{\Delta\mu_0}{T} = \ln v \\ \ln\varkappa + (1-\alpha) \dfrac{\Delta\mu_0}{T} = \ln w \end{cases} . \quad (15)$$

With allowance for relation (14), the equations of set (15) are linearly dependent; therefore, $\varkappa$ and α cannot be determined unambiguously from the specified w and v, *i.e.*, the thermodynamic description of the reaction requires more parameters than the kinetic description.

Let us show that the $I(\Delta\mu)$ function obtained meets the condition of positive determinacy of the rate of entropy generation. The rate of entropy generation (3) can be presented in the following form

$$T \frac{dS}{dt} = \int (w n_1 n_2 - v m) \Delta\mu \, dV . \quad (16)$$

If we substitute expressions (13) in (16), we obtain

$$T \frac{dS}{dt} = \int v m \left[\exp\left(\frac{\Delta\mu_0}{T} \right) \frac{n_1 n_2}{m} - 1 \right] \times \\ \times \ln\left[\exp\left(\frac{\Delta\mu_0}{T} \right) \frac{n_1 n_2}{m} \right] dV . \quad (17)$$

The expression to be integrated in (17) is positively definite, since the $y(x) = (x - 1)\ln x$ function is located entirely in the upper half-plane and touches the ordinate axis only at the $x = 1$ point; therefore, the rate of entropy generation is also positively definite.

Eqs. (13) make it possible to find the relationship between the rate constant and equilibrium constant of a reaction. If we set the left side of Eq. (2) equal to zero and use expression (14), we obtain

$$K_0 = \frac{n_1 n_2}{m} = \exp\left(-\frac{\Delta\mu_0}{T} \right) . \quad (18)$$

By substituting (18) in (13), we find the relationship between the rate constant of dissociation of molecules k_1 and the equilibrium constant K_0:

$$k_1 = \varkappa \exp\left(-\alpha \frac{\Delta\mu_0}{T} \right) = \varkappa K_0^{\alpha} . \quad (19)$$

The most significant point in the derivation of relation (19) is the principle of correspondence between the kinetic and thermodynamic expressions for the rate of the reaction. Using this condition, we obtained the explicit expression (12) for the reaction rate. It should be borne in mind that kinetic expression (2) is applicable for any ratio between the reaction rate and at any time required for local thermodynamic equilibrium to be established, whereas thermodynamic expression (9) can be written only in the approximation of local thermodynamic equilibrium, *i.e.*, under the assumption that the reaction rate is low compared to the time needed for establishment of local thermodynamic equilibrium.

We considered only one reaction in Scheme 1. To apply this theory to a homologous series of similar reactions, parametrization of this series should be introduced, *i.e.*, a parameter should be specified that would vary over this series and thus determine completely each reaction system over this series. Let us denote this parameter by p. Since the arguments presented above for Scheme 1 are also applicable to each member of the given homologous series, Eq. (19) extended to a homologous series has the following form

$$k_1 = \varkappa(p) K_0^{\alpha(p)}. \quad (20)$$

In the general case, not only the equilibrium constant K_0 but also the dissipative coefficients, which now vary as functions of parameter p, change in a homologous series of reactions of the same type. If the reaction centers of molecules change over the homologous series, we can expand the $\varkappa(p)$ and $\alpha(p)$ functions in a Taylor series, restricting consideration to the first l terms of the expansion.

$$\varkappa = \varkappa_0 + \varkappa_1 p + \ldots + \varkappa_l p^l,$$

$$\alpha = \alpha_0 + \alpha_1 p + \ldots + \alpha_l p^l. \quad (21)$$

Thus, for a given series of reactions of the same type parametrized with parameter p, there is a set of phenomenological coefficients such that the relationship between the rate and equilibrium constants in this series is determined by the following dependence

$$k_1 = (\varkappa_0 + \varkappa_1 p + \ \ldots \ + \varkappa_l p^l) K_0^{\alpha_0 + \alpha_1 p + \ldots + \alpha_l p^l} . \quad (22)$$

If the reaction center remains virtually unchanged, we can restrict ourselves only to the main terms in expansion (21): $\varkappa = \varkappa_0$ and $\alpha = \alpha_0$. Then Brönsted relation (1) can be obtained from Eq. (22).

Let us consider as an example the homologous series of reactions presented in Scheme 1 based on the isotope effect, *i.e.*, let us assume that there are a number of systems differing in that several neutrons have been added in the nucleus of one of the atoms of molecule A. The $p = \Delta m_A/m_A$ value, where Δm_A is the change in the mass of the corresponding nucleus, can be chosen as the parameter characterizing this series. The addition of neutrons only slightly changes the reaction center of the molecules. To take this change into account, we will restrict our consideration to two expansion terms in expression (21); then the relationship between the rate and equilibrium constants in this series has the following form

$$k_1 = \left(\varkappa_0 + \varkappa_1 \frac{\Delta m_A}{m_A}\right) K_0^{\alpha_0 + \alpha_1 \frac{\Delta m_A}{m_A}} . \qquad (23)$$

Using a simple chemical reaction as an example, we showed that from the expression for the reaction rate presented in terms of thermodynamic variables, relation (19), which establishes the relationship between the rate and equilibrium constants, can be derived. This result makes it possible to conclude that physical justification of the correlations can be found in the field of nonlinear nonequilibrium thermodynamics.

In chemical kinetics, the logarithmic form of Eq. (1) is normally used:

$$\ln k_1 = \ln \varkappa + \alpha \ln K_0. \qquad (24)$$

Equation (24) can serve as an example of fulfilment of the general relation of linearity of free energies (LFE), according to which changes in the free energies ΔG^0 and activation free energies ΔG^+ in a particular homologous series of reactions are correlated with each other through a linear function

$$\Delta G^0 = b + a\Delta G^+, \qquad (25)$$

where a and b are constants.

Theoretical relation (25) can be justified using methods of quantum statistical physics, *i.e.*, within the framework of microscopic models.[1] In the present study we developed the thermodynamic justification of relation (25).

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