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ON VALIDITY OF LINEAR PHENOMENOLOGICAL NONEQUILIBRIUM THERMODYNAMICS EQUATIONS IN CHEMICAL KINETICS*

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Dedicated to Professor Andrzej Fuliński on the occasion of his 70th birthday

The chemical equilibrium state is treated as a fundamental "reference frame" in description of chemical reaction. In a definition of reactive absolute activities for components in chemical reaction the difference of chemical potential and its value in the equilibrium is used. The chemical reaction rate is shown to be proportional to the force $X_{\rm new}$ defined as the difference of reactive absolute activities of reactants and products. The force $X_{\rm new}$ is shown to be equivalent to the force following from chemical kinetics equations and compared with the reduced affinity X as well as with the force of Ross and Mazur $X_{\rm RM} = 1 - \exp(-X)$. The force $X_{\rm new}$ coincides with X and $X_{\rm RM}$ near to the chemical equilibrium state. A range of the molar fraction of product, in which a difference between the forces $X_{\rm new}$ and X is relatively small, is larger than it would be for the forces $X_{\rm RM}$ and X. It means that for some chemical reactions the formalism of linear nonequilibrium thermodynamics can be used in wider ranges than usually expected. Particular analysis is presented for simple reactions.

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1. Introduction

As shown by Prigogine [1] in nonequilibrium thermodynamic description of proceeding of a simple chemical reaction the source of entropy σ is expressed in the following bilinear form

$$\sigma = JX\,, \tag{1.1}$$

where J is the thermodynamic flux (flow) and X is the thermodynamic force. Additionally, if X is not too large we are restricted to a linear region in which the flux (flow) is in a linear relation with the force

$$J = LX\,. \tag{1.2}$$

In this phenomenological law (phenomenological equation) L is the phenomenological coefficient. From Eqs. (1.1) and (1.2) we obtain

$$\sigma = LXX\,. \tag{1.3}$$

In this quadratic expression, as $\sigma > 0$ also L must be positive [1, 2].

Although we will discuss different chemical reactions, in order to understand the problems discussed in this paper, in this place, it is sufficient to analyze the chemical reaction

$$A + B \rightleftarrows C + D\,, \tag{1.4}$$

where the concentrations of reactants and products are

$$c_A = c_B\,, \quad c_C = c_D\,. \tag{1.5}$$

More complicated reactions can be described similarly. However, we prefer to start analysis from reaction (1.4) because of a possibility of direct comparison with results following from the kinetic theory of gases. We can introduce the flux (flow) J as

$$J = v_A = -\frac{dc_A}{dt} = (v_A)_{\mathrm{f}} + (v_A)_{\mathrm{r}}\,, \tag{1.6}$$

where v_A, $(v_A)_{\mathrm{f}}$, $(v_A)_{\mathrm{r}}$ denote the overall, forward and reverse reaction rates, respectively, and t is the time. The reaction rates can be written as

$$(v_A)_{\mathrm{f}} = k_{\mathrm{f}} c_A c_B\,, \quad (v_A)_{\mathrm{r}} = -k_{\mathrm{r}} c_C c_D\,, \tag{1.7}$$

where k_{f} and k_{r} are the appropriate rate constants. Deriving Eqs. (1.1) and (1.2) Prigogine introduced the thermodynamic force as

$$X_{\mathrm{P}} = \frac{A}{T}\,, \tag{1.8}$$

where T is the temperature and A is the affinity which for reaction (1.4) is expressed as

$$A = \mu_A + \mu_B - (\mu_C + \mu_D)\,, \tag{1.9}$$

where μ_A, μ_B, μ_C and μ_D are the chemical potentials.

As analyzed by Prigogine [3] if the affinity is small enough Eq. (1.8) is not only in agreement with the formalism of linear nonequilibrium thermodynamics (LNT) but also with that of the kinetic theory of gases. This is also in agreement with the description of De Donder [4] who was the first to treat the affinity as the driving force of chemical reaction. The force introduced by De Donder can be written as X_{D}

$$X_{\mathrm{D}} = A\,. \tag{1.10}$$

In order to simplify our description we introduce the dimensionless force X

$$X = \frac{A}{RT} = \frac{X_{\mathrm{P}}}{R} = \frac{X_{\mathrm{D}}}{RT}\,, \tag{1.11}$$

where R is the universal gas constant. Prigogine *et al.* [5] have shown that for few reactions analyzed experimentally close to equilibrium, *i.e.*, for very small A/RT, the reaction rate can be written as

$$v_A = (v_A)_{\mathrm{f}} X\,. \tag{1.12}$$

According to those authors if X is not very small

$$v_A = (v_A)_{\mathrm{f}}[1 - \exp(-X)]\,. \tag{1.13}$$

Glansdorf and Prigogine [6] have also used Eq. (1.13) in phenomenological description of chemical reactions. Ross and Mazur [7] analyzing the nonequilibrium effects in the kinetic theory of reacting gas have emphasized that the following quantity (compare Eq. (1.13))

$$X_{\mathrm{RM}} = 1 - \exp\left(\frac{-A}{RT}\right) = 1 - \exp(-X) \tag{1.14}$$

can be treated as the driving force of chemical reaction. We have introduced the indices RM as the abbreviation of the names Ross and Mazur. After analysis of the results mentioned above, De Groot and Mazur [2] have come to the following conclusions: "Close to equilibrium or more specifically if $A \ll RT$ we may expand the right hand side of equation (such as Eq. (1.14) in this paper) in powers of A retaining only the linear term." and "It turns out that the linear relations of thermodynamics of irreversible processes hold for chemical reactions when the condition $A \ll RT$ is satisfied. In general this condition is only satisfied in the very last stage of reaction". Those authors [2] also have emphasized that the linear relations of thermodynamics are valid in the case of (gas) reactions which do not disturb significantly the Maxwell distribution of the chemical components. However, as emphasized by Ross and Mazur, the law of mass action is sufficient only to the extent that the effect of the perturbed momentum distribution function on the rate of chemical reaction is negligible. Analyzing the entropy production Ross and Mazur [7] have taken into account terms connected with expansion of the velocity distribution function in the perturbation method of solution of the Boltzmann equation. Those authors have shown that it has the expected bilinear form, *i.e.*, the product of the "flux" (the reaction rate) and the force (see Eq. (1.1)). As long as the "flux" can be expressed as a sum of the zero-th and first order terms such a bilinear form exists and linear laws of thermodynamics are valid. Beyond the first order, however, the simple bilinear form is not retained [7]. Although the role of the law of mass action has been emphasized by those authors they have not tried to introduce in the force, in an explicit way, any parameters connected with the chemical equilibrium. Using the law of mass action Baranowski [8] has shown that the linear thermodynamics laws are in agreement with formal kinetic equations if A is small. For this purpose Baranowski has emphasized that near to chemical equilibrium the concentration ratio of products and reactants is nearly constant and differs only slightly from such a ratio in chemical equilibrium. It means that these concentrations are nearly constant if the affinity A is small. In this case both the forces X_{RM} and X coincide. However, we can see that in the limiting case, in the very beginning of chemical reaction when the concentration of product could be negligibly small, the affinity as well as the force X could approach to infinity but for the force X_{RM} we could write

$$\lim_{A\to+\infty} X_{\mathrm{RM}} = 1\,. \tag{1.15}$$

This means that, in this range of a very small concentration of the product, an analysis of the force of X_{RM} does not give information how large this force is and, therefore, how the reaction could proceed. Reactions proceeding far from equilibrium were discussed by many authors (see, *e.g.*, papers presented in [9,10]). In this paper, we would like to introduce a new force for chemical reaction with introduction of a term directly connected with chemical equilibrium to emphasize the role of the law of mass action (already mentioned by Ross and Mazur). Namely, we will introduce additionally the equilibrium constant to the expression for the driving force of chemical reaction.

In order to understand better the proposition of introduction of a new force for chemical reaction it is worthwhile to remind the following results. Within the formalism of statistical as well as phenomenological thermodynamics, in the state of chemical equilibrium, the chemical potentials for reactants and products are equal. For example for the reaction (1.4) we can write

$$\mu_A^{\mathrm{eq}} + \mu_B^{\mathrm{eq}} = \mu_C^{\mathrm{eq}} + \mu_D^{\mathrm{eq}} \,, \tag{1.16}$$

where the index "eq" is introduced to describe the chemical equilibrium state. It is interesting that in this case another quantity, namely the absolute activity introduced and analyzed by Fowler and Guggenheim [11, 12] (see also the analysis presented by Kittel [13]) can be defined as

$$\lambda_I = \exp\left(\frac{\mu_I}{RT}\right) \quad (I = A, B, C, D) \,. \tag{1.17}$$

The state of chemical equilibrium can be described not only by Eq. (1.16) but also [13] by

$$\lambda_A \lambda_B = \lambda_C \lambda_D \,. \tag{1.18}$$

From Eq. (1.17) we can see that

$$\mu_I = RT \ln \lambda_I \quad (I = A, B, C, D) \,. \tag{1.19}$$

The last equation has a similar form to the very known expression

$$\mu_I = \mu_I^0 + RT \ln a_I \quad (I = A, B, C, D) \,, \tag{1.20}$$

where μ_I^0 is the value of μ_I for $a_I = 1$ and a_I is the activity. For the ideal gas Eq. (1.20) can be written in the simplified form

$$\mu_I = \mu_I^0 + RT \ln c_I \quad (I = A, B, C, D) \tag{1.21}$$

Okunev and Parmon looked for a generalization of the thermodynamic force. Those authors [14, 15] suggested to use for the absolute activity also the new name "thermodynamic rush". According to Okunev and Parmon if a chemical reaction proceeds outside the linear region of nonequilibrium thermodynamics its rate is proportional to the difference of thermodynamic rushes of reactants and products. We denote such a force X_{OP} to introduce the names of those authors in the subscript. Such a force for the reaction (1.4) can be written as

$$X_{\mathrm{OP}} = \lambda_A \lambda_B - \lambda_C \lambda_D \,. \tag{1.22}$$

After taking into account Eqs. (1.22), (1.17), (1.21), (1.9), (1.13) and (1.14) we can present this force as

$$X_{\mathrm{OP}} = c_A c_B \, \exp\left(\frac{\mu_A^0 + \mu_B^0}{RT}\right) X_{\mathrm{RM}} \,. \tag{1.23}$$

It should be emphasized that in the definition of Okunev and Parmon the absolute activities (see Eq. (1.17)) are used. Such activities are different from the typical activities (see Eq. (1.20)). If we take into consideration that for a very small values of A/RT the concentrations of reactants are "nearly" constant we can see from Eq. (1.23) that the force X_{OP} is "nearly" proportional to X_{RM} and X only. However, even in this case the force is equal neither to the force X_{RM} nor to the force X. Nevertheless, the force X_{OP} is very useful in analysis of catalytic reactions because for such an analysis it is sufficient for a force to be proportional to A/RT if a reaction proceeds near to the equilibrium.

Recently, continuing analysis of comparison of the forces X and X_{RM} (see [16] and the references cited therein) we have introduced a new definition of force (further denoted in this paper by X_{new}) fulfilling the following conditions:

I. For a very small affinity (near to chemical equilibrium) X_{new}=X_{RM}=X.

II. For a very large affinity (far from equilibrium) X_{new} is not equal to 1 (compare Eq. (1.15)).

The aim of this paper is to show in a more careful way why the introduction of X_{new} permits to evaluate the concentration ranges of products in which the linear laws for chemical reaction described within the formalism of nonequilibrium thermodynamics are in a fairly good agreement with the equations of chemical kinetics, as well as, to show that this force can be expressed by (introduced by Fowler and Guggenheim) absolute activities (after some modifications). Our paper is organized as follows: in Sections 2 and 3 we define the force X_{new} for typical chemical reactions and emphasize a role of chemical equilibrium in this definition and introduce new formulas following from this definition, in Sections 4–7 we present formulas and results for the forces X, X_{new} and X_{RM} and their ratios for some typical reactions chosen, in section 8 we discuss the results for these forces and their ratios and present final summarizing remarks; in Appendix we analyze the consequences following from the invariance of the entropy production.

2. Forces for chemical reactions

We think that in the analysis of proceeding of chemical reaction it is very important to remember that the state of chemical equilibrium is a kind of a typical very important state for each reaction. To be more precise, we can take into consideration that the chemical potential is usually calculated after introduction of a standard state. We think that for a chemical reaction the state of chemical equilibrium should play a more important role than a standard state. That is why we could try to emphasize the role of chemical equilibrium and to introduce few definitions. First, we define the reactive chemical potentials for components in chemical reaction (1.4) as

$$\mu_I^{\mathrm{re}} = \mu_I - \mu_I^{\mathrm{eq}} \quad (I = A, B, C, D)\,, \tag{2.1}$$

where μ_I^{eq} denotes the equilibrium value of μ_I. Next, we define the reactive absolute activities of components in chemical reaction as

$$\lambda_I^{\mathrm{re}} = \exp\left(\frac{\mu_I^{\mathrm{re}}}{RT}\right) \quad (I = A, B, C, D) \tag{2.2}$$

and the reactive absolute activity for reactants R and products P in chemical reaction as

$$\begin{aligned} \lambda_{\mathrm{R}}^{\mathrm{re}} &= \lambda_A^{\mathrm{re}}\lambda_B^{\mathrm{re}} & (2.3)\\ \lambda_{\mathrm{P}}^{\mathrm{re}} &= \lambda_C^{\mathrm{re}}\lambda_D^{\mathrm{re}}\,. & (2.4) \end{aligned}$$

We would like to emphasize that in order to show the problem in a very simple and clear way we restrict in this moment to the reaction (1.4). Naturally, in a description of other reactions appropriate stoichiometric coefficients should be introduced. Additionally, for this purpose we restrict to the simplest "ideal" systems only, *i.e.*, systems composed of reactants and products for which Eq. (1.21) can be used.

For the reaction (1.4) we define the new force X_{new} as the difference of reactive absolute activities of reactants and products.

$$X_{\mathrm{new}} = \lambda_{\mathrm{R}}^{\mathrm{re}} - \lambda_{\mathrm{P}}^{\mathrm{re}}\,. \tag{2.5}$$

We introduce this definition because of two reasons: *(i)* Such a definition used directly for chemical potentials would give only

$$\mu_A^{\mathrm{re}} - \mu_B^{\mathrm{re}} - (\mu_C^{\mathrm{re}} - \mu_D^{\mathrm{re}}) = \mu_A - \mu_B - (\mu_C - \mu_D) = A\,. \tag{2.6}$$

Thus, it would be nothing new. *(ii)* The definition (2.3) looks reasonable because using elementary kinetic equations we can get for the reaction (1.4)

$$v_A = k_{\mathrm{f}} c_A^{\mathrm{eq}} c_B^{\mathrm{eq}} X_{\mathrm{new}}\,. \tag{2.7}$$

Eq. (2.7) can be also written in a form

$$v_A = k_{\mathrm{f}} c_A^{\mathrm{eq}} c_B^{\mathrm{eq}} \frac{c_A c_B}{c_A^{\mathrm{eq}} c_B^{\mathrm{eq}}} X_{\mathrm{RM}} \tag{2.8}$$

because it can be shown that

$$X_{\mathrm{new}} = \frac{c_A c_B}{c_A^{\mathrm{eq}} c_B^{\mathrm{eq}}} X_{\mathrm{RM}}\,. \tag{2.9}$$

Eq. (2.7) can be simply obtained from Eq. (1.13) presented by Glansdorff and Prigogine [7]. We can also see that using Eq. (2.7) we could introduce

$$v_A = J = L' X_{\mathrm{new}} \,, \tag{2.10}$$

where the phenomenological coefficient L' is a constant quantity

$$L' = k_{\mathrm{f}} c_A^{\mathrm{eq}} c_B^{\mathrm{eq}} \,. \tag{2.11}$$

It should be emphasized that, although Eqs. (2.10) and (2.11) can be simply derived from the chemical kinetics equations and the force X_{new} is also obtained from Eq. (2.5), these equations cannot be treated as equations valid within the LNT formalism because Eq. (2.10) has not been derived from the condition for the minimum entropy production. Nevertheless, in the concentration ranges in which X_{new} is nearly equal to X, Eq. (2.10) can be treated as a linear phenomenological equation

$$J = LX \,. \tag{2.12}$$

Such a phenological equation for the force X_{new} could be written, after an introduction of an appropriate "conjugate" flux (flow) J_{new}, and in this case we could also introduce

$$J_{\mathrm{new}} = L_{\mathrm{new}} X_{\mathrm{new}} \,, \tag{2.13}$$

where L_{new} denotes a phenomenological coefficient. As we are interested only in an estimation of a range of X in which X_{new} is nearly equal to X we do not analyze Eq. (2.13) and properties of J_{new} in this section. To make this point clear, we additionally analyze the properties of J_{new} , X_{new} and L_{new} in the Appendix where we show that in the range of X, we are interested in, the phenomenological coefficients L' and L are equal.

It is also interesting that if $c_C = c_D = 0$ we can write

$$\lim_{A \to +\infty} X_{\mathrm{new}} = \frac{c_A^0 c_B^0}{c_A^{\mathrm{eq}} c_B^{\mathrm{eq}}} = (1 + \sqrt{K})^2 \,, \tag{2.14}$$

where c_A^0 and c_B^0 denote the initial concentrations of reactants A and B; K is the thermodynamic equilibrium constant which for reaction (1.4) is

$$K = \frac{c_C^{\mathrm{eq}} c_D^{\mathrm{eq}}}{c_A^{\mathrm{eq}} c_B^{\mathrm{eq}}} = \frac{x_C^{\mathrm{eq}} x_D^{\mathrm{eq}}}{x_A^{\mathrm{eq}} x_B^{\mathrm{eq}}} \,, \tag{2.15}$$

where $x_I (I = A, B, C, D)$ are the molar fractions.

Eq. (2.14) looks better than Eq. (1.15) because in this case the new force is connected with concentration (not with 1 as in Eq. (1.15)). So, Eqs. (2.1)–(2.5) introduced above seem to be reasonable. However, we think that the new force X_{new} could have a practical value only if the ratio X/X_{new} would be nearer to 1 in a larger range of concentration (*e.g.*, in a larger range of the molar fraction of product x_{P}) than the ratio X/X_{RM}. We think that comparisons of these ratios as a function of x_{P} can be a reasonable way of estimation of the concentration ranges in which the nonlinear force-flux relation can be treated as a linear relation.

Eq. (2.9) can be also written in a form

$$X_{\mathrm{new}} = \frac{c_A c_B}{c_A^0 c_B^0}(1+\sqrt{K})^2 \left[1 - \exp\left(\frac{-A}{RT}\right)\right] . \tag{2.16}$$

It is worthwhile to observe that molar fractions can be expressed as functions of K and the affinity A. After taking into account Eqs. (1.9), (1.16), (1.21) and (2.15) we can simply derive

$$x_A = x_B = \frac{0.5\exp(A/2RT)}{\sqrt{K} + \exp(A/2RT)} . \tag{2.17}$$

When the reaction proceeds A diminishes from infinity to 0 and for the chemical equilibrium state Eq. (2.17) simplifies to

$$x_A^{\mathrm{eq}} = x_B^{\mathrm{eq}} = \frac{0.5}{1+\sqrt{K}} . \tag{2.18}$$

From Eqs. (1.14), (2.9), (2.15) and (2.17) we can obtain X_{new} as the following function of A and K:

$$X_{\mathrm{new}} = f(A,K) = \frac{(1+\sqrt{K})^2\exp(A/RT)[1-\exp(-A/RT)]}{[\sqrt{K}+\exp(A/2RT)]^2} . \tag{2.19}$$

From Eq. (2.19) it can be seen that in the beginning of chemical reaction

$$\lim_{A\to+\infty} X_{\mathrm{new}} = (1+\sqrt{K})^2 , \tag{2.20}$$

whereas for the final stages of chemical reaction, *i.e.*, close to equilibrium

$$\lim_{A\to+0} X_{\mathrm{new}} = X_{\mathrm{RM}} = X . \tag{2.21}$$

Only in the limiting case when $K = 0$ Eqs. (2.20) and (1.15) give the same result. However, if K is very large the force X_{new} becomes very large too. In the next sections we will analyze various chemical reactions for some intermediate values of K, *i.e.*, for $0.5 < K < 5$. However, before such an analysis, we will give definitions for a more general reaction.

3. Description of a more general chemical reaction

In this section we show how to introduce the definitions and fundamental formulas for the following chemical reaction

$$aA + bB \rightleftarrows cC + dD \tag{3.1}$$

which represents a generalization of Eq. (1.4). For this reaction we can also use Eq. (1.6) but instead of Eq. (1.7) for this reaction we have

$$(v_A)_{\mathrm{f}} = k_{\mathrm{f}}(c_A)^a(c_B)^b \quad (v_A)_{\mathrm{r}} = -k_{\mathrm{r}}(c_C)^c(c_D)^d \,. \tag{3.2}$$

In this case the forces X , X_{RM} and X_{new} are (compare Eqs. (1.9), (1.11), (1.14), (2.1)–(2.5)):

$$X = \frac{a\mu_A + b\mu_B - (c\mu_C + d\mu_D)}{RT} = \frac{A}{RT} \,, \tag{3.3}$$

$$X_{\mathrm{RM}} = 1 - \exp\left(\frac{-(a\mu_A + b\mu_B - c\mu_C - d\mu_D)}{RT}\right) , \tag{3.4}$$

$$\begin{aligned} X_{\mathrm{new}} &= (\lambda_A^{\mathrm{re}})^a(\lambda_B^{\mathrm{re}})^b - (\lambda_C^{\mathrm{re}})^c(\lambda_D^{\mathrm{re}})^d \\ &= \exp\left[\frac{a(\mu_A - \mu_A^{\mathrm{eq}}) + b(\mu_B - \mu_B^{\mathrm{eq}})}{RT}\right] \\ &\quad - \exp\left[\frac{c(\mu_C - \mu_C^{\mathrm{eq}}) + d(\mu_D - \mu_D^{\mathrm{eq}})}{RT}\right] . \end{aligned} \tag{3.5}$$

In the same way as for the reaction (1.4) we can show that for simple systems in which Eq. (1.21) is used we can obtain

$$X_{\mathrm{new}} = \left(\frac{c_A}{c_A^{\mathrm{eq}}}\right)^a \left(\frac{c_B}{c_B^{\mathrm{eq}}}\right)^b X_{\mathrm{RM}} \,. \tag{3.6}$$

From Eq. (3.6) it follows that in the limiting case when $c_C = c_D = 0$ we can write

$$\lim_{A \to +\infty} X_{\mathrm{new}} = \left(\frac{c_A^0}{c_A^{\mathrm{eq}}}\right)^a \left(\frac{c_B^0}{c_B^{\mathrm{eq}}}\right)^b \,. \tag{3.7}$$

It can be simply shown that for the reaction (3.1) the phenomenological coefficient L' is a constant quantity

$$L' = k_{\mathrm{f}}(c_A^{\mathrm{eq}})^a(c_B^{\mathrm{eq}})^b \,. \tag{3.8}$$

In the next sections we analyze some expressions — especially those for the force X_{new} for some simple reactions chosen.

4. Analysis of properties of the new force for the reaction $A + B \rightleftarrows C + D$

In this section we analyze the reaction (1.4), *i.e.*, $A + B \rightleftarrows C + D$, in a more particular way. As the concentration of product in the equilibrium state depends on the thermodynamic equilibrium constant K we introduce this constant into expression for $X_{\rm new}$. In order to do this we take into consideration that in the chemical equilibrium state $v_A = 0$ (see Eqs. (1.6)) and (1.7). After introducing

$$x = x_{\rm P} = x_C = x_D = 0.5 - x_A = 0.5 - x_B \tag{4.1}$$

and using Eq. (2.15) we can write

$$K = \left(\frac{x^{\rm eq}}{0.5 - x^{\rm eq}}\right)^2 . \tag{4.2}$$

After taking into account Eqs. (1.9), (1.11), (1.14), (1.21), (2.9), (2.15) and (4.2) we can write down the following expressions for the forces for the reaction analyzed

$$X = \frac{A}{RT} = \ln\frac{K(0.5 - x^2)}{x^2} , \tag{4.3}$$

$$X_{\rm RM} = \frac{1 - x^2}{(0.5 - x)^2 K} , \tag{4.4}$$

$$X_{\rm new} = \left(\frac{0.5 - x}{0.5 - x^{\rm eq}}\right)^2 X_{\rm RM} . \tag{4.5}$$

It is worthwhile to observe that when the reaction proceeds the molar fraction x can increase from 0 to $x^{\rm eq}$ which as follows from Eq. (4.2) is

$$x^{\rm eq} = \frac{0.5\sqrt{K}}{1 + \sqrt{K}} . \tag{4.6}$$

Only for a very large value of K this molar fraction can be near to 0.5. From Eqs. (4.5) and (4.6) we get

$$\frac{X_{\rm new}}{X_{\rm RM}} = 4\left(\frac{1 + \sqrt{K}}{0.5 - x}\right)^2 . \tag{4.7}$$

From Eqs. (1.15) and (4.7) it follows

$$\lim_{x \to 0} X_{\rm new} = (1 + \sqrt{K})^2 . \tag{4.8}$$

It means that already in the very beginning of reaction the larger is K (which corresponds to larger x^{eq}) the larger X_{new} is. For the phenomenological coefficient L' we can write

$$L' = k_{\mathrm{f}}(c_A^{\mathrm{eq}})^2(c_B^{\mathrm{eq}})^2\,. \tag{4.9}$$

Now, we analyze the different forces for this reaction to estimate also their ratios. Fig. 1. shows the forces X, X_{RM} and X_{new} as a function of the molar fraction of product x (denoted x_{P}) for the reaction $A + B \rightleftarrows C + D$ for various values of the thermodynamic constant K. Fig. 2. presents such results for reaction $\mathrm{CO_2} + \mathrm{H_2} \rightleftarrows \mathrm{CO} + \mathrm{H_2O}$ proceeding in temperatures 700 K and 1000 K. The values of K for this reaction are 0.534 and 0.719, respectively [18]. Although in proceeding of such reactions also intermediate reactions can appear, we concentrate on description of the total reaction which we treat as the second order reaction because introduction of fluxes connected with some intermediate reactions could be as tedious as the analysis of fluxes of associating components [19]. In the next three sections we present the analysis of the other three reactions in the same way as we have done in this section for the reaction $A + B \rightleftarrows C + D$. In order to avoid unnecessary repetitions and make this presentation in a clear way we introduce the same numbers for the expressions for the same quantities, *e.g.*, Eqs. (4.5), (5.5), (6.5), (7.5) are expressions for the force X_{new}, whereas Eqs. (4.7), (5.7), (6.7), (7.7) — for the ratios of forces X_{new} and X_{RM} for the appropriate reactions.

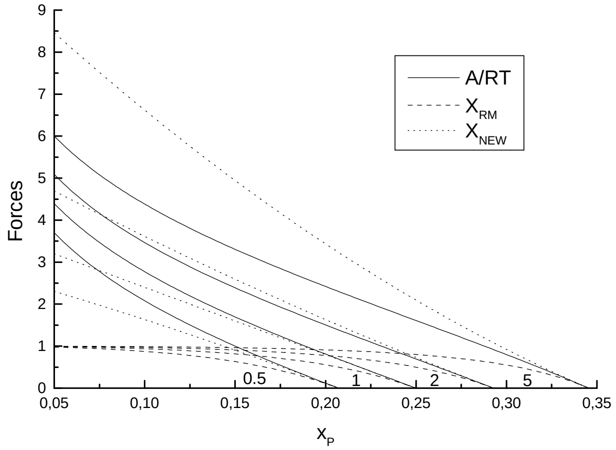

Fig. 1. The forces X, X_{RM} and X_{new} for reaction $A + B \rightleftarrows C + D$ as a function of the molar fraction of product x for four values of the thermodynamic equilibrium constant $K (K = 0.5, 1, 2, 5)$.

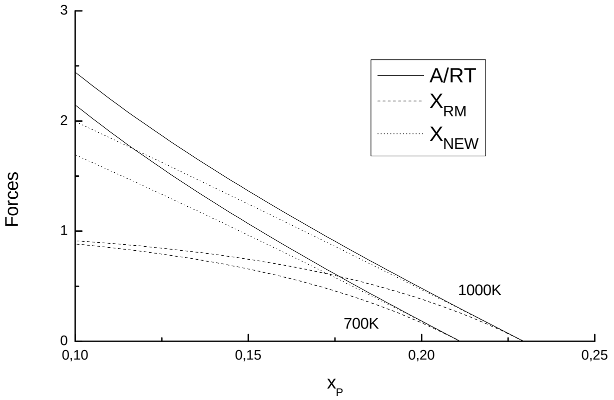

Fig. 2. The forces X, X_{RM} and X_{new} for reaction $\mathrm{CO_2{+}H_2} \rightleftarrows \mathrm{CO{+}H_2O}$ proceeding in temperatures 700 K and 1000 K as a function of x.

5. Analysis of forces for reaction $A + A \rightleftarrows B + B$

It is worthwhile to observe that numerous analysis of nonequilibrium effects have been performed within kinetic theory of reacting gases for this reaction [20–28]. We are interested, however, in such expressions as those presented in Section 4 only. We write down the appropriate equations in the same order as those in Section 4.

$$x = x_{\mathrm{P}} = x_B = 1 - x_A \,, \tag{5.1}$$

$$K = \left(\frac{x^{\mathrm{eq}}}{1 - x^{\mathrm{eq}}}\right)^2 . \tag{5.2}$$

The expressions for the forces are

$$X = \frac{A}{RT} = \ln \frac{K(1-x)^2}{x^2} \,, \tag{5.3}$$

$$X_{\mathrm{RM}} = 1 - \frac{x^2}{(1-x)^2 K} \,, \tag{5.4}$$

$$X_{\mathrm{new}} = \left(\frac{1-x}{1-x^{\mathrm{eq}}}\right)^2 X_{\mathrm{RM}} \,. \tag{5.5}$$

It can be also simply shown that

$$x^{\mathrm{eq}} = \frac{\sqrt{K}}{1 + \sqrt{K}} \,. \tag{5.6}$$

Therefore, we have

$$\frac{X_{\mathrm{new}}}{X_{\mathrm{RM}}} = [(1 + \sqrt{K})(1 - x)]^2 \tag{5.7}$$

and

$$\lim_{x\to 0} X_{\rm new} = (1+\sqrt{K})^2\,. \tag{5.8}$$

For the phenomenological coefficient L' we can write

$$L' = k_{\rm f}(c_A^{\rm eq})^2\,. \tag{5.9}$$

Fig. 3 shows the forces X, $X_{\rm RM}$ and $X_{\rm new}$ for the reaction $A+A \rightleftarrows B+B$.

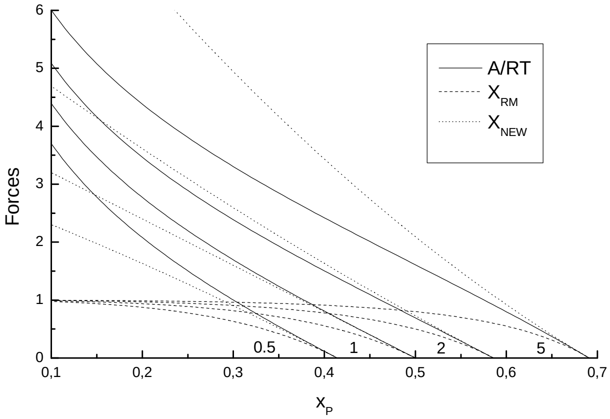

Fig. 3. The forces X, $X_{\rm RM}$ and $X_{\rm new}$ for reaction $A+A \rightleftarrows B+B$ represented in the same way as in Fig. 1.

6. Analysis of forces for reaction $A+A \rightleftarrows B+C$

The corresponding 9 equations for this reaction are:

$$x = x_{\rm P} = x_B = x_C = 0.5(1-x_A)\,, \tag{6.1}$$

$$K = \left(\frac{x^{\rm eq}}{1-2x^{\rm eq}}\right)^2, \tag{6.2}$$

$$X = \frac{A}{RT} = ln\frac{K(1-2x)^2}{x^2}\,, \tag{6.3}$$

$$X_{\rm RM} = 1-\frac{x^2}{(1-2x)^2K}\,, \tag{6.4}$$

$$X_{\rm new} = \left(\frac{1-2x}{1-2x^{\rm eq}}\right)^2 X_{\rm RM}\,, \tag{6.5}$$

$$x^{\rm eq} = \frac{\sqrt{K}}{1+2\sqrt{K}}\,, \tag{6.6}$$

$$\frac{X_{\rm new}}{X_{\rm RM}} = [(1+2\sqrt{K})(1-x)]^2 \,, \tag{6.7}$$

and

$$\lim_{x\to 0} X_{\rm new} = (1+2\sqrt{K})^2 \,, \tag{6.8}$$

$$L' = k_{\rm f}(c_A^{\rm eq})^2 \,. \tag{6.9}$$

In Fig. 4. we present the results for reaction $\mathrm{HI}+\mathrm{HI} \rightleftarrows \mathrm{H_2}+\mathrm{I_2}$ discussed by Glansdorf and Prigogine [7] in analysis of Eqs. (1.12) and (1.13). We have introduced for this reaction proceeding in temperature 900 K the equilibrium constant $K = 0.02292$ [17].

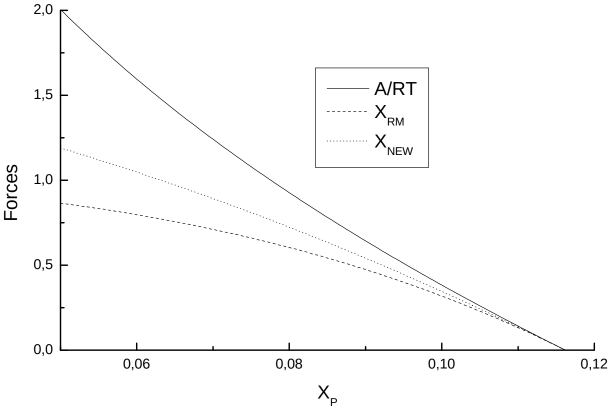

Fig. 4. The forces X, $X_{\rm RM}$ and $X_{\rm new}$ for reaction $\mathrm{HI}+\mathrm{HI} \rightleftarrows \mathrm{H_2}+\mathrm{I_2}$ proceeding in temperature 900 K.

7. Analysis of forces for reaction $A \rightleftarrows B$

Naturally, the corresponding expressions for this reactions are very simple. We present them below

$$x = x_{\rm P} = x_B = 1 - x_A \,, \tag{7.1}$$

$$K = \frac{x^{\rm eq}}{1-x^{\rm eq}} \,. \tag{7.2}$$

For the forces we have

$$X = \frac{A}{RT} = \ln\frac{K(1-x)}{x} \,, \tag{7.3}$$

$$X_{\rm RM} = 1 - \frac{x}{(1-x)K} \,, \tag{7.4}$$

$$X_{\rm new} = \left(\frac{1-x}{1-x^{\rm eq}}\right) X_{\rm RM} \,. \tag{7.5}$$

We can also write

$$x^{\mathrm{eq}} = \frac{K}{1+K}. \tag{7.6}$$

From Eqs. (7.5) and (7.6) it follows

$$\frac{X_{\mathrm{new}}}{X_{\mathrm{RM}}} = (1+K)(1-x) \tag{7.7}$$

and

$$\lim_{x\to 0} X_{\mathrm{new}} = 1+K \tag{7.8}$$

$$L' = k_{\mathrm{f}} c_A^{\mathrm{eq}}\,. \tag{7.9}$$

In Fig. 5. the forces for reaction $A \rightleftarrows B$ are presented in the same way as in Fig. 1.

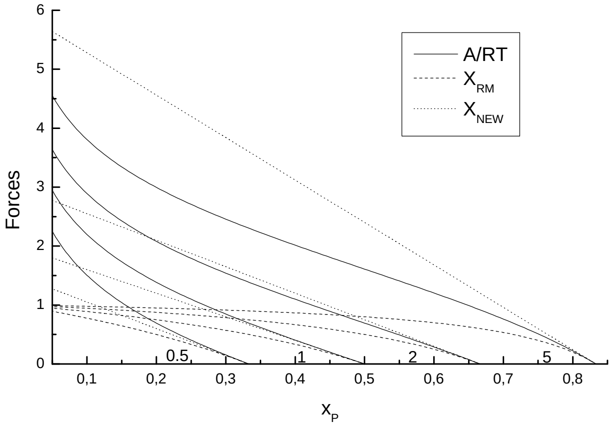

Fig. 5. The forces X, X_{RM} and X_{new} for reaction $A \rightleftarrows B$ represented in the same way as in Fig. 1.

8. Discussion

Basing on concepts presented in Section 2 we have introduced the force X_{new} for some typical reactions (see Eqs. (2.9), (2.19), (3.5), (3.6), (4.5), (5.5), (6.5), (7.5)) and compared with the force X_{RM} introduced by Ross and Mazur (see Eqs. (1.14), (4.4), (5.4), (6.4), (7.4)) as well as with the dimensionless affinity $X = A/RT$ (see Eqs. (4.3), (5.3), (6.3), (7.3)). For the molar fraction of product x slightly differing from its equilibrium value x^{eq} (*i.e.*, in the final stages of chemical reaction) the force X_{new} coincides with the forces X_{RM} and $X = A/RT$. However, for larger values of $x^{\mathrm{eq}} - x$

we can see that with a decrease of x : (1) the force X increases very quickly and for $x \to 0$ the force $X \to \infty$; (2) the force X_{new} also increases but to a finite value only; (3) the force X_{RM} cannot exceed 1, *i.e.* its increase is very limited. The increase of X_{new} with decrease of x can be much more pronounced than such an increase of X_{RM}. As it can be seen from Eqs. (4.8), (5.8), (6.8) and (7.8) X_{new} can be larger than 1 if only K is not equal to 0, *i.e.*, for every chemical reaction. The force X_{new} is an increasing function of K (see, *e.g.*, Eqs. (4.7)–(4.8)). This seems to be reasonable because the larger is the distance from 0 to x^{eq} the larger the force X_{new} is.

Analyzing the reaction (1.4) we can see that the force X_{new} has the largest value $(1+\sqrt{K})^2$ in the beginning of the chemical reaction (see, *e.g.* (2.16)), *i.e.*, for $c_A = c_A^0$ and $c_B = c_B^0$. But when the reaction proceeds $c_A < c_A^0$, $c_B < c_B^0$ and also $1 - \exp(-X)$ becomes smaller than 1. In result X_{new} diminishes step by step from $(1+\sqrt{K})^2$ to 0. For c_A and c_B approaching to c_A^{eq} and c_B^{eq}, respectively, the value of X_{new} is nearly equal to that of X. The less a force differs from the thermodynamic force X the better. That is why comparisons of the ratios X/X_{RM} and X/X_{new} are important. From figures and equations presented in this paper it can be seen that in some ranges of x the ratio X/X_{new} can differ from 1 relatively only a little (*e.g.*, 10%). For the ratio X/X_{RM} such ranges of x are distinctly smaller. The force X quickly increases with a decrease of x and this is why X/X_{RM} increases very quickly with the decrease of x too.

From Fig. 1 and results which can be obtained from Eqs. (4.3)–(4.5) we see that for the reaction $A + B \rightleftarrows C + D$ the ranges of x in which the forces X_{new} and X differ less than 10% are: (a) $0.15 < x < 0.205$ for $K = 0.5$, (b) $0.12 < x < 0.25$ for $K = 1$, (c) $0.05 < x < 0.29$ for $K = 2$, (d) $0.310 < x < 0.345$ (in the range $0.05 < x < 0.310$ the results are worse but still not exceeding 32%) for $K = 5$. The values of X/X_{RM} are significantly larger than those of X/X_{new} in the ranges of x mentioned above (in (a), (b), (c), (d)), *i.e.*, the corresponding maximum values of X/X_{RM} are: (a) 1.56 (these forces differ 56% instead of 10% mentioned above), (b) 2.56, (c) even 5.12, (d) 1.33 (for $0.05 < x < 0.310$ even about 500% instead of 32% mentioned above).

Naturally, such an advantage of introduction of the force X_{new} can be also seen in Fig. 2 for the reaction $CO_2 + H_2 \rightleftarrows CO + H_2O$ proceeding in 700 K and 1000 K (represented by the equilibrium constant $K = 0.534$ and $K = 0.719$, respectively [18] . From Fig. 3 we see that also for the reaction $A + A \rightleftarrows B + B$ the forces X and X_{new} differ visibly less than the forces X and X_{RM}. If we were interested in ranges of x in which the forces X and X_{new} differ less than 10% we would see in Fig. 3. (basing on results obtained from Eqs. (5.3)-(5.5)) the the following ranges of x: (a) $0.307 < x < 0.414$ for $K = 0.5$, (b) $0.25 < x < 0.5$ for $K = 1$, (c) $0.092 < x < 0.585$ for $K = 2$,

(d) $0.628 < x < 0.691$ for $K = 5$. It should be emphasized that in these ranges of x we would have much larger differences between the forces X and X_{RM}. We could observe, for the ranges of x presented above (in (a), (b), (c), (d)) the following maximum values of ratios X/X_{RM}: (a) about 1.5, *i.e.*, corresponding to a difference between these forces equal to about 50%, (b) about 2.5, (c) about 4.25, (d) about 1.3 . All these ratios correspond to differences between the forces X and X_{RM} visibly larger than 10%. Similar advantages of introduction of X_{new} instead of X_{RM} can be easily seen in Fig. 4. for the reaction HI + HI$\rightleftarrows$ H_2 + I_2 and also in Fig. 5 for reaction $A \rightleftarrows B$.

It can be shown that for the reaction $A \rightleftarrows B$ the relation between the phenomenological coefficient L and the forward reaction rate constant k_{f} (see Eq. (7.9)) is equivalent to such a relation presented by Baranowski [6] for a very small A. To see this equivalence it is sufficient to take into consideration that for $A \ll RT$ the concentrations of product c_B and c_B^{eq} are nearly equal. For the reaction $aA + bB \rightleftarrows cC + dD$ the phenomenological coefficient L is a constant quantity related to the forward rate constant and concentrations of reactants in equilibrium (see Eq. (3.8)). The expression for the coefficient L (for concentrations near to those in the equilibrium) has a similar form to that presented by De Groot and Mazur [2]. However, as we have used the dimensionless force X (see the forces in Eqs. (1.16) and (1.19)) we have introduced the constant $1/R$ not in the coefficient L but in the force.

The force X_{RM} introduced by Ross and Mazur is the simplest and reasonable generalization of the force $X = A/RT$ to a nonlinear function of X (see Eqs. (1.13) and (1.14)) which is in agreement with equations of chemical kinetics. The introduction of such a nonlinear function of X by these authors means that the force-flux relation for chemical reaction is nonlinear. As $X_{\mathrm{RM}} \to X$ for a very small X it follows that in this case X_{RM} can be treated as a linear function of X and the formalism of LNT can be used for a very small X only. As shown in this paper it is possible to introduce the force X_{new} which is a function of X and K (see (2.19)). This new function is also in agreement with equations of chemical kinetics and is also a nonlinear function of X. It means that the force-flux relation, after introduction of X_{new} is nonlinear too. We are interested, however, in the ranges of X in which X_{new} (introduced on the basis on simple chemical kinetics equations) is nearly equal to the force X (derived by Prigogine within the formalism of linear nonequilibrium thermodynamics). If only the difference between X_{new} and X is small a description of proceeding of a chemical reaction in a form of a linear phenomenological equation can be treated as a sufficient approximation. Naturally, in a very small range of x near to the equilibrium value x^{eq} the force X_{new} coincides with the forces X_{RM} and the thermodynamic force X. We have introduced the new force X_{new} and shown that the range of the molar fraction of the product x near to the chemical equilibrium state (for which $X_{\rm new}$ is nearly equal to X) is distinctly larger than such a range corresponding to $X_{\rm RM}$ nearly equal to X. It means that using the results presented in this paper we can expect that the linear force-flux relation can be treated as a sufficient approximation in a wider range of X than assumed earlier. We see that in the results presented in Figs. 1–5. we have verified a property for $X/X_{\rm new}$ which we have expected.

We would like to emphasize that we have introduced the new force $X_{\rm new}$ basing on two concepts: *(i)* we looked if the difference between introduced by Fowler and Guggenheim absolute activities, after the modification introduced in this paper, can be treated as a force. As the modification we have replaced the chemical potential in the absolute activity by the difference of thermodynamic potential and its equilibrium value. *(ii)* We looked if such a force can be derived from the equations of chemical kinetics. We have got a positive result in both the cases. It should be emphasized that Okunev and Parmon [14, 15] also performed a kind of a joint thermodynamic-kinetic analysis. The force $X_{\rm OP}$ introduced by Okunev and Parmon is also connected with absolute activities but not with the reactive absolute activities introduced by us. That is why the force $X_{\rm OP}$ even for very small values of A/RT is not equal to $X_{\rm RM}$ but "nearly" proportional only. Naturally, the forces $X_{\rm OP}$ are very convenient for analysis of few simultaneous reactions necessary to describe catalytic processes. In an analysis of parallel catalytic reactions such as, *e.g.*, $A \rightleftarrows B$, $A \rightleftarrows C$ Parmon and Okunev [29] have introduced the forces $\lambda_A - \lambda_B$ and $\lambda_A - \lambda_C$ (see Eq. (1.17)). Those authors have shown that in a description of cross effects for such reactions the Onsager relations are fulfilled. We do not analyze the parallel reactions in this paper. We have concentrated in this paper only on the range of the molar fraction of product in which the forces $X_{\rm new}$ and X are nearly equal. We expect that in such a concentration range the properties of the forces X and $X_{\rm new}$ should be the same. Therefore, as the Onsager relations are fulfilled for the forces X (see, *e.g.*, Ref. [2]) they would be also fulfilled for the forces $X_{\rm new}$ (for parallel chemical reactions) for the concentration range enlarged similar to that analyzed in this paper. Particular analysis of parallel reactions would be tedious similarly as our analysis of the effect of compound formation on diffusion and self-diffusion fluxes [19].

The most important results obtained in this paper are:

1. The force $X_{\rm new}$ which follows from the chemical kinetics is equal to the difference between reactive absolute activities for chemical reaction for reactants and products.

2. The force $X_{\rm new}$ coincides with the reduced affinity $X = A/RT$ (*i.e.*, with the force introduced by De Donder and also derived by Prigogine

within the formalism of LNT) in a fairly large range of the molar fraction of product x in the vicinity of the value of $x = x^{\mathrm{eq}}$ in chemical equilibrium.

3. This range is larger than such a range obtained from the force $X_{\mathrm{RM}} = 1-\exp(-A/RT)$ introduced by Ross and Mazur as the driving force of chemical reaction. In the limiting case of chemical equilibrium state, *i.e.*, for x near to x^{eq}, the forces X_{new}, X_{RM} and A/RT coincide.

4. For some chemical reactions the range of x (near to $x = x^{\mathrm{eq}}$) in which X_{new} is, in fact, nearly equal to A/RT is fairly large, *i.e.*, limited to not too large affinity instead of a very small affinity.

5. It means that the forces for chemical reaction suggested by de Donder and derived by Prigogine (for small affinities, *i.e.*, for x near to x^{eq}) can be used in larger ranges of concentration than expected after looking at the force $X_{\mathrm{RM}} = 1 - \exp(-A/RT)$ only. This is in agreement with general concepts of Ross and Mazur [2, 7] based on analysis of the source of entropy. Those authors have analyzed this problem very thoroughly, however, have introduced a force depending only on the affinity A without taking into consideration the equilibrium constant K. The force X_{new} introduced in this paper is a function of A and K.

6. As the force X_{new} is represented by a simple analytical expression it can be helpful in an evaluation of the possible concentration range in which the linear phenomenological equation for a particular chemical reaction analyzed can be valid.

7. It means that if we base on the chemical kinetics equations we see that the formalism of linear nonequilibrium thermodynamics, also in a case of the scalar thermodynamic force, can be used not only in limited case in which the chemical reactions (analyzed in this article) proceed very close to the chemical equilibrium state. So, as a conclusion we see that similarly as in the other transport phenomena (energy relaxation, transport of mass, transport of energy, transport of momentum, an so on — connected with appropriate vector and tensor forces), also in the case of some chemical reactions limitation to a very small thermodynamic force is not necessary.

8. It should be emphasized that a relatively good agreement (for a wide range of concentration) of the force X_{new} (based on chemical kinetics equations and equivalent to modifications of Fowler's and Guggenheim's definition of the absolute activity) with the force used by De Donder and derived by Prigogine also confirms the conclusion presented above.

9. It is also important that the introduction of the force X_{new} permits to see that the phenomenological coefficient L does not depend on the molar fraction of product (see the analysis in the Appendix and Eqs. (2.11), (3.8), (4.9), (5.9), (6.9), (7.9)). As shown in the Appendix, in the range of X in which X_{new} is nearly equal to X the phenomenological coefficients L and L' are nearly equal; an analysis of a complicated expression for the "conjugate" flux J_{new} following from the invariance of entropy production permits to see that J_{new} is nearly equal to J in this case. It should be emphasized that the force X_{new} has been introduced mainly to see that the linear relation $J = LX$ does not need to be limited to a very small X.

Just to summarize, we have defined the new force X_{new} for chemical reaction in which the role of chemical equilibrium state is emphasized. For this purpose we have defined the reactive absolute activity for chemical reaction in a similar way as Fowler and Guggenheim defined the absolute activity. We have obtained kinetic equation in a form analyzed by Prigogine and Glansdorff. For elementary chemical reactions, we have compared the force X_{new} with dimensionless affinity $X = A/RT$ (based on De Donder's concept) and with the driving force of chemical reaction of Ross and Mazur $X_{\mathrm{RM}} = 1 - \exp(-X)$. According to a general analysis of Ross and Mazur the linear phenomenological equation for chemical reaction can be used in a limited range of affinity and the new force introduced in this paper may be helpful to estimate this range of affinity. We have shown that for some chemical reactions not only near to chemical equilibrium the forces X_{new}, X and X_{RM} coincide but also the ratio X/X_{new} is near to 1 in a relatively larger range of molar fraction of product than it could be expected for the ratio X/X_{RM}. It means that basing on equations of statistical thermodynamics and chemical kinetics we can expect that the formalism of linear nonequilibrium thermodynamics could be used for description of proceeding of some chemical reactions in wider ranges of the molar fraction of product than it was expected before the analysis of the new force introduced in this paper.

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Appendix A

For the sake of simplicity we analyze the flux–force relations for the reaction (1.4) only because for the other chemical reaction the way of arguing would be the same. As it follows from the invariance of entropy production the following condition must be fulfilled

$$JX = J_{\text{new}} X_{\text{new}} \,. \tag{A.1}$$

Basing on this condition and Eq. (2.17) we can obtain

$$J_{\text{new}} = \frac{JX}{X_{\text{new}}} = J \frac{X[\sqrt{K} + \exp(X/2)]^2}{(1+\sqrt{K})^2 \exp(X)[1-\exp(-X)]} \,. \tag{A.2}$$

From Eqs. (2.10) and (2.12) we can get

$$L = \frac{L' X_{\text{new}}}{X} \,. \tag{A.3}$$

From Eqs. (2.13), (A.2), (2.12) and (A.3) we can derive

$$L_{\text{new}} = \frac{J_{\text{new}}}{X_{\text{new}}} = \frac{JX}{X_{\text{new}}^2} = \frac{LX^2}{X_{\text{new}}^2} = \frac{L' X_{\text{new}}}{X} \,. \tag{A.4}$$

If only X is small enough we can obtain from Eqs. (A.2), (A.3) and (A.4)

$$\lim_{X\to 0} J_{\text{new}} = J \,, \tag{A.5}$$

$$\lim_{X\to 0} L = L' \,, \tag{A.6}$$

$$\lim_{X\to 0} L_{\text{new}} = L' \,. \tag{A.7}$$

The property

$$\lim_{X\to 0} X_{\text{new}} = X \tag{A.8}$$

has been widely analyzed and discussed in this paper for various reactions. It should be emphasized that in the range of X in which X_{new} is nearly equal to X the quantities J_{new} and L_{new} are nearly equal to J and L , respectively. For such a range of X the linear phenomenological equation, *i.e.*, Eq. (2.12) can be used. For us it is only important that the range of X in which X_{new} is nearly equal to X is larger than the range of X in which $[1-\exp(-X)]$ is nearly equal to X. The force X_{new} is introduced for a case in which the flux–force relation is nonlinear only as a helpful tool to analyze the range of X for which a linear phenomenological equation is a sufficient approximation in description of a chemical reaction.

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