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## TO THE 100th ANNIVERSARY OF THE KARPOV INSTITUTE OF PHYSICAL CHEMISTRY

# Self-Consistency of the Theory of Elementary Stage Rates of Reversible Processes and the Equilibrium Distribution of Reaction Mixture Components

**Yu. K. Tovbin**
*Karpov Institute of Physical Chemistry, Moscow, 105064 Russia*
*e-mail: tovbin@nifhi.ru*

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**Abstract**—An analysis is presented of one of the key concepts of physical chemistry of condensed phases: the theory self-consistency in describing the rates of elementary stages of reversible processes and the equilibrium distribution of components in a reaction mixture. It posits that by equating the rates of forward and backward reactions, we must obtain the same equation for the equilibrium distribution of reaction mixture components, which follows directly from deducing the equation in equilibrium theory. Ideal reaction systems always have this property, since the theory is of a one-particle character. Problems arise in considering interparticle interactions responsible for the nonideal behavior of real systems. The Eyring and Temkin approaches to describing nonideal reaction systems are compared. Conditions for the self-consistency of the theory for mono- and bimolecular processes in different types of interparticle potentials, the degree of deviation from the equilibrium state, allowing for the internal motions of molecules in condensed phases, and the electronic polarization of the reagent environment are considered within the lattice gas model. The inapplicability of the concept of an activated complex coefficient for reaching self-consistency is demonstrated. It is also shown that one-particle approximations for considering intermolecular interactions do not provide a theory of self-consistency for condensed phases. We must at a minimum consider short-range order correlations.

*Keywords:* self-consistency of theory, absolute reaction rate theory, activated complex, non-ideal reaction systems, activity coefficient, interparticle interactions, lattice gas model

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## INTRODUCTION

Upon moving from equilibrium to nonequilibrium thermodynamics for macroscopic unit volumes $dV$, the condition of local equilibrium must be fulfilled and the combined equation of equilibrium thermodynamics $dU = TdS - PdV$ mist be written in the form $dU \leq TdS - PdV$ [1–9]. Here, all of the initial statements of equilibrium thermodynamics are transferred to nonequilibrium processes. To discuss classical thermodynamics from a single point of view, it is logical to consider both types of processes together. The initial statements of classical thermodynamics were therefore supplemented by two refinements in [10]. They were implicitly introduced earlier, but it is essential they be refined for a clearer combined consideration of equilibrium and nonequilibrium processes.

*Refinement 1. The need for a self-consistent description of the kinetics and equilibrium state of a system.* Refinement 1 is implied in the second law of thermodynamics in discussing the possibility for the system to leave and return to the equilibrium state [1–9]. It is also a prerequisite for introducing the concept of affinity in chemical thermodynamics, which is valid in both equilibrium and nonequilibrium states [2, 4]. It also underlies introduction of the concept of thermodynamic functions in nonequilibrium states [6], since when a system transitions to an equilibrium state, these functions are automatically transformed into its equilibrium functions.

*Refinement 2. The need to consider distinctions between characteristic relaxation times $\tau$ in the transfer of different properties: impulse ($\tau_{\text{imp}}$), energy ($\tau_{\text{ener}}$), and mass ($\tau_{\text{mass}}$).* Refinement 2 reflects the experience from experimental studies of dynamic processes near equilibrium and is required for considering relaxation processes in real systems [5, 11].

Refinement 1 is needed to introduce unified unit volume $dV$ in equilibrium and nonequilibrium thermodynamics, and as a criterion for the correct derivation of molecular models of kinetic stages and elementary stages. The value of $dV$ was determined in [12]. In this work, we discuss which models and chemical kinetics equations ensure the self-consistent description of elementary stages in nonequilibrium processes within the microscopic theory for three aggregate states. With equality of rates of reversible reactions in the forward and backward directions, these models should yield the same expressions for equilibrium constants as those for the equilibrium constants within equilibrium distributions. The rates of mass evolution processes are slowest among the three abovementioned properties in Refinement 2, and the possibility of establishing complete equilibrium in a system depends on them.

The concept of a self-consistent description of dynamics and equilibrium states has long been known for ideal reaction systems: It is the law of mass action, which was substantiated for ideal gas mixtures and diluted solutions. For ideal systems, the following expression for the chemical potential can be written $\mu_i = \mu_i^0 + k_B T \ln(c_i)$, where $\mu_i^0$ and $c_i$ are the chemical potential for the standard state and the bulk molar concentration of the $i$ component. The equilibrium constant is then found from the condition

$$\sum_i \nu_i \mu_i \underset{k_2}{\overset{k_1}{\rightleftarrows}} \sum_j \nu_j \mu_j.$$

The collision model was first used to calculate the stage rate constants, but was later replaced by the absolute reaction rate theory (ARRT) [13, 14].

For ideal reaction systems, the rates of elementary stages of mono- and bimolecular reactions are described within the law of mass action:

$$U_i = K_i c_i, \quad U_{ij} = K_{ij} c_i c_j, \tag{1}$$

where $K_i$ and $K_{ij}$ are the rate constants of elementary processes (stages) that characterize the specific rates of elementary processes:

$$\begin{aligned} K_i &= K_i^0 \exp(-E_i/k_B T), \quad K_i^0 = \kappa \frac{kT}{h}\frac{F_i^*}{F_i}, \\ K_{ij} &= K_{ij}^0 \exp(-E_{ij}/k_B T), \quad K_{ij}^0 = \kappa \frac{kT}{h}\frac{F_{ij}^*}{F_i F_j}, \end{aligned} \tag{2}$$

where $K_i^0$ and $K_{ij}^0$ are the preexponentials of rate constants, $E_i$ and $E_{ij}$ are the energies of activation of the reaction $i \to$ product and $i + j \to$ products; $F_i$ and $F_j$ are the statistical sums (the sums over internal states) of the initial molecules; and $F_i^*$ and $F_{ij}^*$ are the statistical sums of the activated complex (AC), calculated over all degrees of freedom except the reaction path.

Let us recall that the self-consistency principle was used in Langmuir's work [15] to obtain an adsorption isotherm from the condition of equality of adsorption and desorption rates. A statistical derivation of the Langmuir isotherm was first made by Temkin [16] and later repeated by Fowler [17]. The authors of the BET isotherm [18] followed in the same way. In the kinetic theory of rarefied gases, the requirement for consistency of new equations developed in gas kinetics with the equations of the equilibrium state of gases is one of its necessary elements [19, 20]. This essential stage was missing from the kinetic theory of condensed phases because (1) in deriving kinetic equations, the principle of detailed equilibrium is assumed from the very beginning (but not checked to what degree it is fulfilled after all averaging procedures) and (2) there are no equations of states for comparison.

*Non-ideal systems.* In a great many experimental systems, the reaction systems cannot be considered to be ideal, and the problem arises of how stage rates can be calculated. Eyring and Temkin proposed two approaches:

According to Eyring's ARRT [14, 21–23], intermolecular interactions in non-ideal reaction systems are considered using thermodynamic relationships known from the theory of non-ideal solutions [4]. This approach is associated with maintaining the concentration factor used as the law of mass action (through the reagent concentration product) in the expression for reaction rates as in formula (1), and with a change in the reaction rate constants in the form

$$K_i^{\mathrm{ef}} = K_i \alpha_i / \alpha_i^*, \quad K_{ij}^{\mathrm{ef}} = K_{ij} \alpha_i \alpha_j / \alpha_{ij}^*, \tag{3}$$

where $\alpha_i$ is the activity coefficient of $i$-sort molecules, $\alpha_i^*$ and $\alpha_{ij}^*$ are the AC activity coefficients at mono- and bimolecular stages; constants $K_i$ and $K_{ij}$ are given in (2). As usual, the activity coefficient is defined through the relation $\alpha_i = a_i/c_i$, where $a_i$ is the activity of the $i$ component in solution, which depends on all concentrations of solution components (under the definition of the total concentration as $c = \sum_i c_i$) and their molecular properties, including their energies of intermolecular interaction.

This means a coefficient of activity analogous to the one for an ordinary solution component is introduced for AC, and we are able to consider the transition from the gas phase to the condensed phase. The internal contradictions of this approach are due to the $a_i$ value depending on all concentrations of solution components and their molecular properties. The rate constant is thus related to all physicochemical properties of the reaction system through the activity coefficients. However, $\alpha_{ij}^*$ cannot be always determined and substantiated. To derive it, we need to average all neighboring molecules over all possible states, and a change in a neighbor alters the conditions of the path of the reaction, which contradicts the concept of the transition state the AC is in. The Eyring interpretation has been widely used in calculating liquid phase reaction rates [21–23].

Temkin's point of view was different [24–26]. He argued it was necessary to directly consider interparticle interactions and their effect on the elementary stage rate, through (among other things) the interaction with the AC stage (the history of considering the non-ideality of reaction systems was presented in detail in [27]). Temkin demonstrated this using the example of heterogeneous reactions [25] at ambient pressures, and he illustrated it vividly by describing the synthesis of ammonia at elevated pressures (above 300 atm) [26]. For high pressures in the gas phase, the pressures themselves must be replaced with volatilities, and the rate constants in the elementary reaction rates must be modified by considering the effect the shift in adsorption equilibrium has on the catalyst's surfaces. In [26], this was done by indirectly considering a change in the equation of state of the adsorbed layer (through the introduction of effective energies of activation associated with the non-ideality of the adsorption layer and its compressibility), but without introducing the concept of an AC activity coefficient. This approach was later developed as an elaboration of the theory of non-ideal reaction systems [28], which is applicable to all three aggregate states of matter [27–30]. This concept is related to the representation of a rapid overcoming of the AC barrier.

The molecular-kinetic theory for the three aggregate states is based on multiparticle distribution functions introduced by Bogolyubov in [31]. It reflects the discrete spatial distribution of molecules on the scale of their size as they form cells, and a continuum description of the molecular distribution inside cells with volume $v_0$. This theory can be applied to matter in three aggregate states, so only it provides equally accurate descriptions of three interfaces. The principles of this theory have been published a number of times [27–30] and are therefore omitted here.

*Reduced system of kinetic equations.* Below, we present a set of kinetic equations of the discrete continuum (Master Equation) approach, obtained after averaging the kinetic equations in the full Liouville phase space over the thermal rates of all components [19, 20, 30, 31] and contains expressions for elementary stage rates $\alpha$ (where $\alpha$ is the number of the process stage) in their right sides. This set consists of equations for the local concentrations of components (reagent and solvent molecules) $\theta_j^i$ (characterizing the molar fraction of $f$-type sites occupied by $i$-sort particles) and the equations for pair distribution functions (DFs) $\theta_{fg}^{ij}(r)$ characterizing the probability of a pair of $i$ and $j$ particles being at distance $r$ at $f$ and $g$ sites [27–30]. Particle concentration $c_i$ is related to numerical density $\theta_i$ (or the molar fraction of the $i$ component on the surface or in the bulk) as $c_i = \theta_i/v_0$. The closed system of equations can be written as

$$\frac{d}{dt}\theta_f^i = \sum_\alpha \left[U_f^b(\alpha) - U_f^i(\alpha)\right] + \sum_r \sum_h \sum_j \sum_\alpha \left[U_{fh}^{bd}(r|\alpha) - U_{fh}^{ij}(r|\alpha)\right], \quad (4)$$

$$\begin{gathered}\frac{d}{dt}\theta_{fg}^{ij}(r) = \sum_\alpha \left[U_{fg}^{bd}(r|\alpha) - U_{fg}^{ij}(r|\alpha)\right] + P_{fg}^{ij}(r) + P_{gf}^{ji}(r),\\ P_{fg}^{ij}(r) = \sum_\alpha \left[U_{fg}^{(b)j}(r|\alpha) - U_{fg}^{(i)j}(r|\alpha)\right] + \sum_h \sum_m \sum_\alpha \left[U_{hfg}^{(cb)j}(\eta|r|\alpha) - U_{hfg}^{(mi)j}(\eta|r|\alpha)\right],\end{gathered} \quad (5)$$

where $U_f^i(\alpha)$ denotes the rates of elementary one-site processes $i \leftrightarrow b$ at an $f$ site, and $U_{fg}^{ij}(r|\alpha)$ are the rates of elementary two-site processes $i + j_\alpha \leftrightarrow b + d_\alpha$ at $f$ and $g$ sites at distance $r$. Equations (5) contain $U_{fg}^{(i)j}(r|\alpha)$ and $U_{hfg}^{(mi)j}(\eta|r|\alpha)$ summands that correspond respectively to one- $(i \leftrightarrow b)$ and two-site $(i + m \leftrightarrow b + c)$ reactions of an $i$ particle in the presence of neighboring $j$ particles. A $j$ particle does not react itself, but it does alter the activation barrier for the interacting $i$ particle in the one-site process or the reacting $i$ and $m$ particles in the two-site process. The second summand in $P_{fg}^{ij}(r)$ describes stage $i + m \leftrightarrow b + c$ at neighboring $f$ and $h$ sites at distance $r$.

The right sides of Eqs. (4) and (5) contain the elementary stage rates of the chemical transformation and the average rates of the thermal translational and rotational motions of molecules. They describe the system's dynamics at the molecular level. Expressions for the rates of elementary processes are written below in the quasi-chemical approximation (QCA) for considering the interactions through unary and pair DFs. The set of equations (4) and (5) describes a wide spectrum of non-equilibrium states of reaction systems. Here, these equations are given to illustrate that despite any degree of a system's nonequilibrium, expressions for elementary reaction rates must always be consistent with its equilibrium state.

## *Rapid Overcoming of the Barrier*

In the molecular theory of non-ideal reaction systems, we must consider the entire spectrum of configurations of neighboring molecules that could affect the course of a reaction for reagents at the central sites under study, and weight the probability of an elementary stage occurring for each configuration of neighbors on the surface [27–30]. Lateral contributions affect the probability of AC formation via a change in the energy of activation, so the number of neighbors and their arrangement are important for the process rate. Figure 1 presents the entire spectrum of configurations of $A$ particles in the first coordination sphere around a central (not shown) particle on lattices $z = 4$ and 6: $A$ are blackened circles; the other sites of the first coordination sphere are vacant (or occupied by

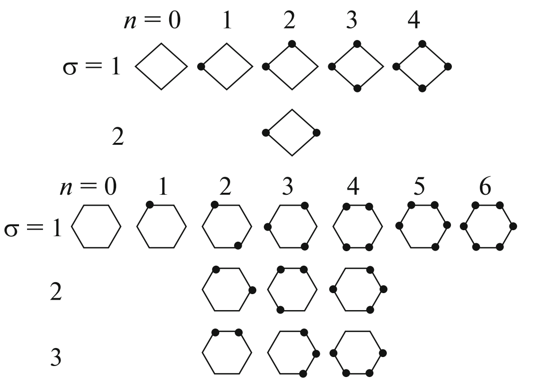

**Fig. 1.** Configurations of $A$ particles in the first coordination sphere around a central particle on lattices $z = 4$ and 6. Black dots are adsorbed $A$ particles; $n$ is the number of $A$ particles; $\sigma(n)$ is the type of configuration at a fixed $n$ value; $R = 1$ [27–30].

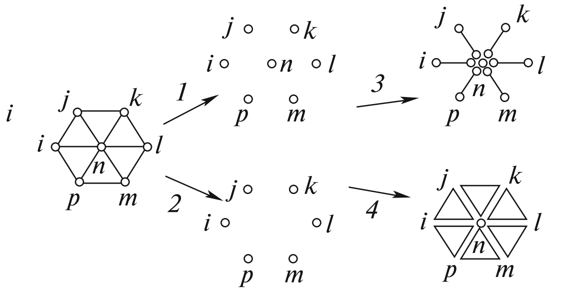

**Fig. 2.** Schemes of approximate calculations of multiparticle configurations of neighboring molecules for lattice $z = 6$: *1* is the mean field and chaotic approximations (through the concentrations of all molecules); *2* is the polynomial approximation (through the concentrations of the neighboring molecules); *3* is the QCA (through the probabilities of pairs of molecules); *4* is considering indirect correlations in the QCA and triple correlations (through the probabilities of triples of molecules) [27–30].

particle $V$). Symbol $\theta_i(n\sigma)$ denotes the probability that $n$ particles $A$ with arrangement $\sigma$ are in the first coordination sphere of the central $i$-sort particle; $i = A$ and $V$.

Lateral interactions are almost always considered approximately (Fig. 2). The first variant of the approximation corresponds to mean field and chaotic approximations when the probability of a multiparticle configuration is expressed through the product of probabilities of a site being occupied by $i$ sort particles $\theta_i$ (or through unary DFs). In this approximation, there are no correlations, and the particle arrangement indicated by $\sigma$ plays no role.

The second variant of the approximation is also one-particle. In it, the multiparticle configuration of the neighbors around the central particle is approximated by the product of unary DFs (a polynomial approximation). A distinction from the first way of disengagement is that the correlations between the central particle and its nearest neighbor are preserved in it.

The third variant of the approximation is that the probabilities of multiparticle configurations $\theta_i(n\sigma)$ are approximated by local probabilities $\theta_i$ of detecting $i$ particles (unary DFs) and pair DFs $\theta_{ij}$. This is the so-called Guggenheim QCA [32] or the Bethe approximation [33]. The correlation effect is explicitly considered through pair DF $\theta_{ij}$. Here, the weights of configurations with different $\sigma$ values (at $n$ = const) are equally probable, or $\sigma$ does not affect the calculations of $\theta_i(n\sigma)$.

The fourth variant of the approximation is the simplest example of considering the correlation effects from three molecules (a discrete variant of the so-called Kirkwood superposition approximation [34]). Within this approximation, $\sigma$ determines the contributions from pairs of particles at different distances. When the superposition approximation is used, the problem is also closed through the equations for unary and pair DFs. The structure of the fourth approximation allows us to go beyond the frames of only pair approximation if we assume that additional equations are deduced for the probabilities of triple configurations. However, this approach drastically increases the dimensionality of the set of equations that must be solved to find the equilibrium particle distribution [27–30].

In the QCA for a mixture with any number of components, we obtain expressions for the rates of mono- and bimolecular elementary processes:

$$U_i = K_i\theta_i S_i^z = K_i\theta_i\Lambda_i^*,\quad S_i = \sum_{k=1}^{s} t_{ik}\exp(\beta\delta\varepsilon_{ik}), \quad (6)$$

$$U_{ij} = K_{ij}\exp(-\beta\varepsilon_{ij})\theta_{ij}(S_iS_j)^{z-1}, \quad (7)$$

where $\delta\varepsilon_{ik} = \varepsilon_{ik}^* - \varepsilon_{ik}$, and $\varepsilon_{ik}^*$ is the parameter of interaction between AC (an $i$ particle at an $f$ site in the transition state) of elementary process $\alpha$ and neighboring particle $k$ at a neighboring $g$ site; where $t_{ij} = \theta_{ij}/\theta_i$ is the conventional probability of a $j$ particle being near the $i$ particle, which is calculated in the QCA. In deducing expressions (6) and (7), rate constants $K_i$ and $K_{ij}$ were assumed to depend weakly on density. In functions $S_i$, summation is performed over all sorts of neighboring particles. Functions $S_i$ are factors of the function of the non-ideality of a reaction system $\Lambda_i^* = S_i^z$ that reflect the effect each neighboring particle has on reaction.

A similar situation is observed for bimolecular reaction (7). The structure of functions $S_i$ is not associated with the type of lateral interaction potential functions or the radius of the potential; it is determined by using the QCA to consider the interactions.

The number of functions $S_i$ in the reaction rate in the form of factors is determined by size $z$ of the coordination sphere. For bimolecular reactions, this number of neighbors virtually doubles around two reagents of $2(z-1)$. A difference between expression (7) and formula (6) is that the effect of intermolecular interactions is exhibited not only through the functions of non-ideality but also through a change in the probability of encountering reagents, described by function $\theta_{ij}$.

### *Self-Consistency of the Rates of One-Site Stages*

Let us consider the elementary stage of chemical transformation $A \leftrightarrow B$, to which the equality of rates in the forward and backward directions $U_A(\alpha) = U_B(\alpha)$ corresponds in equilibrium. The structure of equations for the rates is $U_A(\alpha) = K_A(\alpha)V_A(\alpha)$, where $K_A(\alpha)$ is the reaction rate constant and $V_A(\alpha)$ is the concentration component of the reaction rate. For an ideal reaction system, $V_A(\alpha) = \theta_A$ (1); for a non-ideal reaction system, it is described by formula (6). The ratio of rate constants determined by formulas (2) yields equilibrium constant $K$ and excludes the AC statistical sum from the pre-exponentials of the rate constants of forward and backward reactions [28, 35]. However, AC characteristic $\varepsilon_{ij}^* \equiv \varepsilon_{ij}(\alpha)$ contained in function of non-ideality $S_i(\alpha)$ remains:

$$K_1 = \frac{K_A(\alpha)}{K_B(\alpha)} = \frac{V_B(\alpha)}{V_A(\alpha)} = \frac{\theta_B[S_B(\alpha)]^z}{\theta_A[S_A(\alpha)]^z}. \tag{8}$$

To verify the self-consistency of expressions, it is required that the ratio of non-ideality functions $S_B(\alpha)/S_A(\alpha)$ not depend on the parameters of AC interaction with neighbors $\varepsilon_{ij}^*$. We therefore consider the equations in the QCA for the equilibrium distribution of mixture components [28, 35]:

$$\begin{gathered} \theta_A = \theta_B \exp[\beta(\nu_B - \nu_A)]S_B(A)^z, \\ S_B(A) = \sum_{j=1}^{V} t_{Bj} \exp[\beta(\varepsilon_{Aj} - \varepsilon_{Bj})], \end{gathered} \tag{9}$$

$$\theta_{AC} = \theta_{BC} \exp[\beta(\nu_B - \nu_A + \varepsilon_{AC} - \varepsilon_{BC})]S_B(A)^{z-1}. \tag{10}$$

In $S_B(A)$, the lower index is the sort of the central particle under study, and the symbol in parentheses is the basic sort of the mixture (this symbol often corresponds to a vacancy), and $t_{ij} = \theta_{ij}/\theta_i$.

Excluding exponential $\exp[\beta(\nu_i - \nu_s)]$ from Eqs. (9) and (10), we obtain the relationship between pair and unary DFs:

$$t_{AC} = t_{BC} \exp[\beta(\varepsilon_{AC} - \varepsilon_{BC})]/S_B(A). \tag{11}$$

From this expression, we can see that the denominator does not depend on the sort of neighboring molecule $C$, and the normalization condition is satisfied:

$$\sum_{j=1}^{s} t_{Aj} = \sum_{j=1}^{s} t_{Bj} \exp[\beta(\varepsilon_{Aj} - \varepsilon_{Bj})]/S_B(A) = 1. \tag{12}$$

Using (11), we prove the identity

$$\begin{gathered} \sum_{j=1}^{s} t_{nj} \exp[\beta(\varepsilon_{pj} - \varepsilon_{nj})] \\ = \sum_{j=1}^{s} t_{ij} \exp[\beta(\varepsilon_{pj} - \varepsilon_{ij})] \Big/ \sum_{j=1}^{s} t_{ij} \exp[\beta(\varepsilon_{nj} - \varepsilon_{ij})], \end{gathered} \tag{13}$$

which allows us to move from one sort of central molecule to another. To prove this identity, it is sufficient to insert $A = n$, $B = i$, $C = j$ into (11) and substitute it in the left side of Eq. (13). This identity is compactly written as $S_n(p) = S_i(p)/S_i(n)$. (As a consequence of (13), we find that $S_n(p) = S_p(n)^{-1}$ or $S_n(p)S_p(n) = 1$.)

We rewrite the ratio in formula (8) as

$$\begin{gathered} S_B(\alpha)/S_A(\alpha) = \sum_{j=1}^{s} t_{Bj} \exp[\beta(\varepsilon_{Bj}^* - \varepsilon_{Bj})] \Big/ \sum_{j=1}^{s} t_{Aj} \\ \times \exp[\beta(\varepsilon_{Aj}^* - \varepsilon_{Aj})]. \end{gathered}$$

This involves one AC between reaction products $A$ and $B$, so its properties are identical, or $\varepsilon_{Aj}^* = \varepsilon_{Bj}^* \equiv \varepsilon_{(AB)j}^*$. From identity (13), we then obtain

$$\begin{gathered} \left( \frac{\sum_{j=1}^{s} t_{Bj} \exp[\beta(\varepsilon_{Bj}^* - \varepsilon_{Bj})]}{\sum_{j=1}^{s} t_{Aj} \exp[\beta(\varepsilon_{Aj}^* - \varepsilon_{Aj})]} \right)^z \\ = \left( \sum_{j=1}^{s} t_{Bj} \exp[\beta(\varepsilon_{Aj} - \varepsilon_{Bj})] \right)^z = (S_B(A))^z, \end{gathered} \tag{14}$$

which precisely equals the concentration component of isotherm (9). This shows that despite the path of the process (through a chemical reaction or molecular exchange with the thermostat) the equilibrium state is the same.

In the chaotic approximation, $S_i = \sum_{k=1}^{s} \theta_k \times \exp(\beta\delta\varepsilon_{ik})$, and the analog of Eq. (13) has the form [28, 35]

$$\begin{gathered} \sum_{j=1}^{s} \theta_j \exp[\beta(\varepsilon_{pj} - \varepsilon_{nj})] \\ = \sum_{j=1}^{s} \theta_j \exp[\beta(\varepsilon_{pj} - \varepsilon_{ij})] \Big/ \sum_{j=1}^{s} \theta_j \exp[\beta(\varepsilon_{nj} - \varepsilon_{ij})]. \end{gathered} \tag{15}$$

In the mean field approximation, $S_i = \exp\left(\beta \sum_{k=1}^{s} \delta\varepsilon_{ik}\theta_{ik}\right)$, which is obtained from the chaotic approximation via the limiting transition $\beta\varepsilon_{ij} \to 0$. Without the limiting values of this transition, however, the analog of Eq. (13) is expressed as [28, 35]

$$\exp\left[\sum_{j=1}^{s}\beta(\varepsilon_{pj}-\varepsilon_{nj})\theta_j\right] = \exp\left[\sum_{j=1}^{s}\beta(\varepsilon_{pj}-\varepsilon_{ij})\theta_j\right]/\exp\left[\sum_{j=1}^{s}\exp[\beta(\varepsilon_{nj}-\varepsilon_{ij})\theta_j\right]. \tag{16}$$

These expressions also demonstrate the self-consistency of one-site reactions, due to the identity of AC interactions with the neighbors in the forward and backward reactions, $\varepsilon^*_{Aj}=\varepsilon^*_{Bj}\equiv\varepsilon^*_{(AB)j}$. In the polynomial approximation, the equations for the equilibrium distribution and stage rates are cumbersome, so the their self-consistency can be verified only through numerical comparison [28].

## SELF-CONSISTENCY OF THE RATES OF TWO-SITE STAGES

The proof of the self-consistency of the rates of two-site stages with the equilibrium distribution of molecules differs from the above material by the need to consider the effect of neighboring molecules (through the function of non-ideality), and to relate the probability of encountering the reagent to the law of mass action through its concentration. Let us consider stage $A + C \leftrightarrow B + D$ and verify the self-consistency of the description of the kinetics and equilibrium of non-ideal reaction systems. Here it is essential to follow the course of the elementary process, and to show which product is obtained from the initial reagent (i.e., indicate that $C$ is obtained from $A$ and $D$ is obtained from $B$). This is associated with the structure of the resulting AC, and its properties must not depend on the reaction path. As above, we write $\varepsilon^*_{Aj}=\varepsilon^*_{Cj}\equiv\varepsilon^*_{(AC)j}$ and $\varepsilon^*_{Bj}=\varepsilon^*_{Dj}\equiv\varepsilon^*_{(BD)j}$; the neighbor can be any $1\le j\le s$ [28, 35]. For the two-site stage, the rate is expressed as $U_{AB}(\alpha)=K_{AB}(\alpha)\exp(-\beta\varepsilon_{AB})\times V_{AB}(\alpha)$, where $K_{AB}(\alpha)$ is the pre-exponential of the rate constant and $V_{AB}(\alpha)$ is the concentration component of the two-site reaction rate; $\varepsilon_{AB}$ is the energy of the lateral interaction of the reagents. We must show from equality $U_{AC}(\alpha)=U_{BD}(\alpha)$ that the reaction's equilibrium constant does not depend on the AC parameters:

$$\begin{aligned}K_2 &= \frac{K_{AC}(\alpha)}{K_{BD}(\alpha)}=\frac{V_{BD}(\alpha)}{V_{AC}(\alpha)}\\ &= \frac{\theta_{BD}\exp(-\beta\varepsilon_{BD})[S_B(\alpha)S_D(\alpha)]^{z-1}}{\theta_{AC}\exp(-\beta\varepsilon_{AC})[S_A(\alpha)S_C(\alpha)]^{z-1}}\\ &= \frac{\theta_{BD}\exp(-\beta\varepsilon_{BD})}{\theta_{AC}\exp(-\beta\varepsilon_{AC})}[S_B(A)S_D(C)]^{z-1}.\end{aligned} \tag{17}$$

Identity (13) or (14) is used in the last equation, since it follows from the AC properties that $\varepsilon^*_{Aj}=\varepsilon^*_{Cj}\neq\varepsilon^*_{Bj}=\varepsilon^*_{Dj}$, $1\le j\le s$. Let us examine in detail a separate factor for one of the bonds from $(z-1)$ neighbors around each reagent inside a central dimeric particle. The ratio of concentration factors yields

$$\begin{aligned}&\frac{\sum_{j=1}^{s}t_{Aj}\exp[\beta(\varepsilon^*_{(AC)j}-\varepsilon_{Aj})]\sum_{j=1}^{s}t_{Bj}\exp[\beta(\varepsilon^*_{(BD)j}-\varepsilon_{Bj})]}{\sum_{j=1}^{s}t_{Cj}\exp[\beta(\varepsilon^*_{(AC)j}-\varepsilon_{Cj})]\sum_{j=1}^{s}t_{Dj}\exp[\beta(\varepsilon^*_{(BD)j}-\varepsilon_{Dj})]}\\ &=\sum_{j=1}^{s}t_{Aj}\exp[\beta(\varepsilon_{Cj}-\varepsilon_{Aj})]\sum_{j=1}^{s}t_{Bj}\exp[\beta(\varepsilon_{Dj}-\varepsilon_{Bj})],\end{aligned} \tag{18}$$

which excludes the presence of AC properties in this ratio, as in the case of one-site reactions.

To transform the pair functions in (10), we multiply Eq. (10) on the right- and left-hand side by $\theta_A\theta_B$ and write

$$\begin{aligned}\theta_{AC} &= \theta_{BC}\theta_A\exp[\beta(\varepsilon_{AC}-\varepsilon_{BC})]/(\theta_B S_B(A))\\ &= \theta_{BC}\varphi(A,B,C).\end{aligned} \tag{19}$$

Since $\theta_{nm}=\theta_{mn}$, we represent sought bond $c$ in the form (we see the general case of function $\theta_{nm}$ and $\theta_{kd}$)

$$\theta_{kd}=\theta_{mn}\varphi(k,B,d)/[\varphi(n,d,B)\varphi(m,B,n)], \tag{20}$$

and since $\varepsilon_{nm}=\varepsilon_{mn}$, we again use identity (13) to exclude sort $B$ and obtain

$$\begin{aligned}\theta_{kd} &= \theta_{mn}\frac{\theta_k\theta_d}{\theta_m\theta_n}\exp[\beta(\varepsilon_{kd}-\varepsilon_{mn})]\\ &\times\sum_{j=1}^{s}t_{dj}\exp[\beta(\varepsilon_{nj}-\varepsilon_{dj})]\sum_{j=1}^{s}t_{kj}\exp[\beta(\varepsilon_{mj}-\varepsilon_{kj})].\end{aligned} \tag{21}$$

Finally, the ratio of rate constants of the forward and backward reactions is expressed through (18) and (21):

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$$\begin{aligned}K_2 &= \frac{\theta_{AB}\exp(-\beta\varepsilon_{AB})}{\theta_{CD}\exp(-\beta\varepsilon_{CD})}\left[\frac{\sum_{j=1}^{s}t_{Aj}\exp[\beta(\varepsilon^*_{(AC)j}-\varepsilon_{Aj})]\sum_{j=1}^{s}t_{Bj}\exp[\beta(\varepsilon^*_{(BD)j}-\varepsilon_{Bj})]}{\sum_{j=1}^{s}t_{Cj}\exp[\beta(\varepsilon^*_{(AC)j}-\varepsilon_{Cj})]\sum_{j=1}^{s}t_{Dj}\exp[\beta(\varepsilon^*_{(BD)j}-\varepsilon_{Dj})]}\right]^{z-1}\\ &= \frac{\theta_A\theta_B}{\theta_C\theta_D}\left[\sum_{j=1}^{s}t_{Aj}\exp[\beta(\varepsilon_{Cj}-\varepsilon_{Aj})]\sum_{j=1}^{s}t_{Bj}\exp[\beta(\varepsilon_{Dj}-\varepsilon_{Bj})]\right]^{z}.\end{aligned} \tag{22}$$

With regard to redefining the meaning of the equilibrium constant $K_2$, the course of the two-site reaction can formally be considered as two independent one-site processes at different sites: $A \leftrightarrow C$ and $B \leftrightarrow D$. Expression (22) has the form of a product of two independent processes, each of which is described by equilibrium (8). The condition of reaction equilibrium thus coincides with that of the medium as a whole [28, 35]. In the polynomial approximation, self-consistency can be verified only numerically [28].

*One-particle approximations*. This type of approximation closes the sets of equations for equilibrium and kinetic processes through unary DFs (i.e., only through the concentration of components). All pair functions are in this case expressed as $\theta_{ij} = \theta_i\theta_j$, and they require no additional equations for the pairs. The same is true for DFs with higher dimensionalities. Through derivation, however, the bimolecular reaction rates are still expressed as $U_{AB}(\alpha) = K_{AB}(\alpha)\exp(-\beta\varepsilon_{AB})V_{AB}(\alpha)$, into which $\theta_{ij} = \theta_i\theta_j$ must be substituted. This results in the relations [28, 35]

$$\begin{aligned} K_2 &= \frac{K_{AC}(\alpha)}{K_{BD}(\alpha)} = \frac{V_{BD}(\alpha)}{V_{AC}(\alpha)} \\ &= \frac{\theta_B\theta_D\exp(-\beta\varepsilon_{BD})}{\theta_A\theta_c\exp(-\beta\varepsilon_{AC})}[S_B(A)S_D(C)]^{z-1}, \end{aligned} \tag{23}$$

where non-ideality functions $S_B(A)S_D(C)$ do not contain parameters of $AC$ interaction. The right side of expression (23) (1) is not decomposed into two independent processes with concentration factors $\theta_B S_B(A)^z/\theta_A$ and $\theta_D S_D(C)^z/\theta_C$, as follows from (8), and as it would be for independent one-site stages, and (2) there are energy factors that alter the energies of activation of elementary stages $E_{AC}$ and $E_{BD}$ in the preexponentials of rate constants $K_{AC}$ and $K_{BD}$.

Analysis of the expressions for chaotic and mean field approximations thus shows they do not ensure the self-consistent description of equilibria and kinetics because analogous equations for isotherms are not obtained in the same approximations as a result of equating the reaction rates. These approximations therefore cannot be used to describe kinetic processes. Even in individual instances, migrations according to the vacancy mechanism of an exponential with parameter $\varepsilon_{iV} = 0$ vanish, but this does not compensate for the absence of exponent $(z - 1)$ instead of $z$ [28, 35]. The density functional equations often used for molecular distributions also belong to this type of one-particle approximations. They also lack the correlation effects and do not satisfy the requirement of the self-consistency of expressions for the rates of elementary stages.

## NON-IDEAL HETEROGENEOUS SYSTEMS

In the distributed model of a nonuniform lattice, each site is considered a separate type of the region of a molecule's location; this is the most general type of nonuniform lattices [27–30, 36]. Let us consider the problem of the self-consistency of expressions for the rates of elementary reactions (stages) that proceed at one and two sites, and for the equilibrium state of a reaction system in the QCA with any radius $R$ of the interaction potential between neighbors on the distributed model of a nonuniform lattice system. To do this, we deal with particular individual sites, i.e., before the averaging procedure with DFs of nonuniform surfaces different in compositions and structures. Averaged models are obtained from expressions for the distributed model by weighting with the functions discussed in [27–30].

*One-site reaction*. Consider a reversible reaction between adsorbed particle $A$ and gas particle $B$: $ZA + B \leftrightarrow ZC + D$, occurring at a $q$-type site with number $f$. The equation for the one-site stage rate has the form [27, 37]

$$\begin{aligned} U_{AB} &= \frac{1}{M}\sum_{f=1}^{M} U_f^{AB}, \quad U_f^{AB} = \hat{K}_f^{AB}\theta_f^A S_f^A, \\ S_f^i &= \prod_{r=1}^{R}\prod_{h\in z_f(r)} S_{fh}^i(r), \quad i = A; \\ S_{fh}^i(r) &= \sum_{j=1}^{s}\theta_{fh}^{ij}(r)\exp[\beta\delta\varepsilon_{fh}^{ij}(r)]/\theta_f^i \\ &= 1 + \sum_{j=1}^{s-1}\theta_{fh}^{ij}(r)x_{fh}^{ij}(r)/\theta_f^i, \\ x_{fh}^{ij}(r) &= \exp[\beta\delta\varepsilon_{fh}^{ij}(r)] - 1, \\ \delta\varepsilon_{fh}^{ij}(r) &= \varepsilon_{fh}^{ij*}(r) - \varepsilon_{fh}^{ij}(r), \end{aligned} \tag{24}$$

where $M$ is the number of sites of the distributed system; $\hat{K}_f^{AB}$ is the rate constant of the elementary reaction between adsorbed particle $A$ and gas particle $B$, which involves the product with the partial pressure of component $B$ in the gas phase $P_B$; $\varepsilon_{fh}^{ij*}(r)$ is the parameter of interaction of a neighboring $j$ particle in the ground state at distance $r$ from the AC of the reacting $i$ molecule; the upper index means the expression for the rate includes pressure factor $P_B$ for a particle from the gas phase (not reflected in the symbol of the $f$ site); $\varepsilon_{fh}^{ij}(r)$ is the parameter of interaction between two neighboring particles in the ground state at distance $r$.

In the equilibrium condition, the equations for the forward and backward reaction rates $U_j^{AB} = U_f^{CD}$ yield the relation

$$\hat{K}_f^1 = \hat{K}_f^{AB}/\hat{K}_f^{CD} = \theta_f^C \Psi_f^{CA}/\theta_f^A,$$
$$\Psi_f^{CA} = \prod_{r=1}^{R} \prod_{h \in z_f(r)} S_{fh}^C(r)/S_{fh}^A(r). \tag{25}$$

With no interaction, function $\Psi_f^{CA} = 1$ and $\hat{K}_f^1$ is an effective equilibrium constant for the $f$ site of an ideal adsorption system; $\hat{K}_f^1 = K_f^1 P_B/P_D$, where $K_f^1$ is the true equilibrium constant of the one-site stage $A \leftrightarrow C$.

In the QCA for a nonuniform lattice, we have the following relations for pair DFs instead of (11):

$$\theta_f^i \theta_{fh}^{jk}(r) = \theta_f^j \theta_{fh}^{ik}(r) \exp[\beta\{\varepsilon_{fh}^{jk}(r) - \varepsilon_{fh}^{ik}(r)\}]/S_{fh}^i(j|r), \tag{26}$$

where $S_{fh}^i(j|r) = \sum_{k=1}^{s} \theta_{fh}^{ik}(r) \exp[\beta(\varepsilon_{fh}^{jk}(r) - \varepsilon_{fh}^{ik}(r))]$. Then

$$\theta_{fh}^{kl}(r) = \theta_{fh}^{mn}(r) \exp[\beta\{\varepsilon_{fh}^{kl}(r) - \varepsilon_{fh}^{mn}(r)\}]$$
$$\times S_{fg}^k(m|r) S_{fg}^l(n|r) \theta_f^k \theta_h^l/(\theta_f^m \theta_h^n). \tag{27}$$

Since the AC properties are independent of the reaction's direction ($\varepsilon_{fh}^{Aj*}(r) = \varepsilon_{fh}^{Cj*}(r)$ for any $j$ index), it follows from relations (24) and the equations for the QCA relations (25) that

$$S_{fh}^C(r)/S_{fh}^A(r) = [S_{fh}^A(C|r)]^{-1}, \tag{28}$$

so $\Psi_f^{CA}(r) = [S_{fh}^A(C|r)]^{-1}$; i.e., the right-hand side of expression (25) does not depend on the interaction between the AC and its neighbors, and the effective equilibrium constant is expressed only through the interaction parameters of particles in the ground (rather than transition) state and the equilibrium concentrations of particles. This is entirely consistent with the concept of the equilibrium particle distribution, and expression (25) is the equilibrium constant for a nonuniform system. This means the equilibrium distribution equation is obtained regardless of how it is derived: from kinetic consideration or directly for the equilibrium state of a mixture's molecules.

*Two-site reaction $A + B \leftrightarrow C + D$.* The AC of the reaction occupies two neighboring lattice sites (denoted as $n$ and $k$) and interacts with the neighboring particles in the $r$th coordination sphere ($1 \le r \le R$) with respect to both the $n$ site with the $A$ particle and the $k$ site with the $B$ particle. We introduce the concept of a common $r$th coordination sphere of the dimeric $AB$ molecule as a combination of sites at the same distance $r$ from the nearest $A$ or $B$ site. The coordination spheres of isolated sites overlap, so the common $r$th coordination sphere contains some sites that belong only to the $r$th coordination sphere of one of the $n$ or $k$ sites and a some sites that belong to the $(r + \lambda)$ coordination sphere of the neighboring $k$ or $n$ site. The $\lambda$ value depends on the lattice's dimensionality and the number of nearest neighbors [27, 28, 38].

The set of sites of the common $r$th coordination sphere is divided into equivalent groups of sites that are fixed by their orientation. The site orientation is determined by the angle formed by a straight line connecting the central sites and a straight line between the considered site in the $r$th coordination sphere of a dimeric molecule and the point in between the central sites.

We denote the number of different orientations in the common $r$th coordination sphere as $\pi_r$, and the number of sites with this orientation $\omega_r$ as $\kappa_{\omega r}$ ($1 \le \omega_r \le \kappa_{\omega r}$). Figure 3 shows the site distribution on planar lattices for $R = 2$. The AC interaction potential with the $j$ particle at a site of the $r$th common coordination sphere of the $AB$ dimeric molecule with orientation $\omega_r$ is denoted as $\varepsilon_{ABj}^*(\omega_r)$. The $\varepsilon_{ABj}^*(\omega_r)$ values are expressed through the pair potentials $\varepsilon_{ij}^*(r)$: $\varepsilon_{ABj}^*(\omega_r) = \varepsilon_{Aj}^*(r_{nm}) + \varepsilon_{Bj}^*(r_{rm})$, where $m$ is the number of the site containing the $j$ particle. For instance, for planar lattice $z = 4$ and $R = 2$ we have

$$\varepsilon_{ABj}^*(\omega_1 = 1) = \varepsilon_{Aj}^*(1), \quad \varepsilon_{ABj}^*(\omega_1 = 2) = \varepsilon_{Aj}^*(1) + \varepsilon_{Bj}^*(2),$$

$$\varepsilon_{ABj}^*(\omega_1 = 3) = \varepsilon_{Aj}^*(2) + \varepsilon_{Bj}^*(1), \quad \varepsilon_{ABj}^*(\omega_1 = 4) = \varepsilon_{Bj}^*(1),$$

$$\varepsilon_{ABj}^*(\omega_2 = 1) = \varepsilon_{Aj}^*(2), \quad \varepsilon_{ABj}^*(\omega_2 = 2) = \varepsilon_{Bj}^*(2).$$

The $\varepsilon_{ABj}^*(\omega_r)$ values are deduced in a similar manner for other $z$ and $R$. If $A = B$, the same $\varepsilon_{AAj}^*(\omega_r)$, $1 \le \omega_r \le \pi_r/2$ values to which double $\kappa_{\omega r}$ values correspond also correspond to the symmetric positions of sites of the common $r$th coordination sphere, relative to the plane passing through the middle of the straight line connecting the central sites and perpendicular to this straight line.

The two-site stage rates are written as

$$U_{fg}^{ABC}(1) = \hat{K}_{fg}^{ABC}(fg)\theta_{fg}^{AB}(1)\exp[-\beta\varepsilon_{fg}^{AB}(1)]$$
$$\times \prod_{r=1}^{R} \prod_{\omega_r=1}^{\pi(r|qp)} \prod_{h \in z(\omega_r|qp)} S_{fgh}^{AB}(\omega_r),$$

$$S_{fgh}^{AB}(\omega_r) = \sum_{j=1}^{s} t_{fgh}^{ABj}(\omega_r) \exp[\beta\delta\varepsilon_{fgh}^{ABj}(\omega_r)],$$
$$\delta\varepsilon_{fgh}^{ABj}(\omega_r) = \varepsilon_{fgh}^{ABj*}(\omega_r) - \varepsilon_{fgh}^{ABj}(\omega_r), \tag{29}$$
$$t_{fgh}^{ABj}(\omega_r) = \theta_{fh}^{Aj}(r_1)\theta_{gh}^{Bj}(r_2)/\theta_f^A \theta_g^B \theta_h^j,$$
$$\varepsilon_{fgh}^{ABj}(\omega_r) = \varepsilon_{fh}^{Aj}(r_1) + \varepsilon_{gh}^{Bj}(r_2).$$

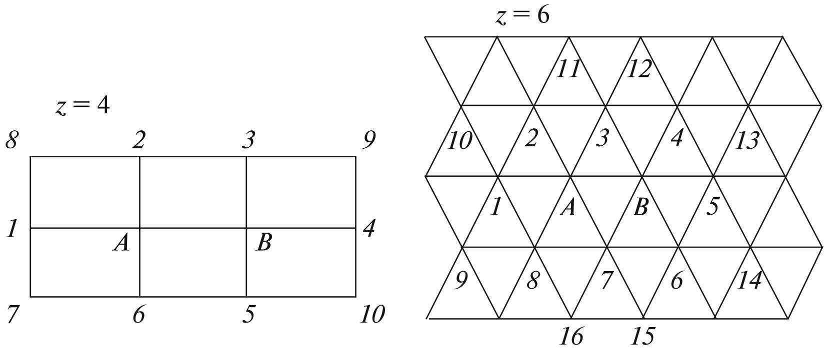

**Fig. 3.** Distributions of planar lattice sites for $z = 4$ and 6 over the equivalent groups of the first two coordination spheres. For $z = 4$, the first coordination sphere contains sites *1–6* ($\pi_1 = 4$); the second, sites 7–10 ($\pi_r = 4$). Site *1* corresponds to $\omega_1 = 1$; sites *2* and *6*, to $\omega_1 = 2$; sites *3* and *5*, to $\omega_1 = 3$; site *4*, to $\omega_4 = 4$; sites *7* and *8*, to $\omega_2 = 1$; sites *9* and *10*, to $\omega_2 = 2$. For $z = 6$, the first coordination sphere contains sites *1–8* ($\pi_1 = 5$); the second, sites *9–16* ($\pi_r = 4$). Site *1* corresponds to $\omega_1 = 1$; sites *2* and *8*, to $\omega_1 = 2$; sites 3 and 7, to $\omega_1 = 3$; sites *4* and *6*, to $\omega_4 = 4$; site *5*, to $\omega_1 = 5$; sites *9* and *10*, to $\omega_2 = 1$; sites *11* and *16*, to $\omega_2 = 2$; sites *12* and *15*, to $\omega_2 = 3$; sites *13* and *14*, to $\omega_2 = 4$.

For large distances $\theta^{ij}_{fh}(r > R) = \theta^i_f\theta^j_h$, which consequently yields $S^{AB}_{fgh}(\omega_r)\big|_{r_1>R} = S^B_{gh}(r_2)$, $\varepsilon^{ABj}_{fgh}(\omega_r) = \varepsilon^{Aj}_{fh}(r_1) + \varepsilon^{Bj}_{gh}(r_2)$.

To confirm the condition of self-consistency, we must prove the relation [27, 30]

$$S^{ED}_{fgh}(\omega_r)/S^{AB}_{fgh}(\omega_r) = S^E_{fh}(r_1)S^D_{gh}(r_2)/[S^A_{fh}(r_1)S^B_{gh}(r_2)], \quad (30)$$

where $\omega_r$, $r_1$, and $r_2$ are clearly related to one another. The equilibrium distribution of molecules is then independent of how it was established: through the kinetics of forward and backward processes or by considering only equilibrium configurations. To prove equality (30), we must remember that $\varepsilon^{Aj*}_{fh}(r_1) = \varepsilon^{Ej*}_{fh}(r_1)$ and $\varepsilon^{Bj*}_{gh}(r_2) = \varepsilon^{Dj*}_{gh}(r_2)$, due to the AC properties being independent of the process's direction. Let us introduce $\tilde\theta^{ij}_{fh}(r) = \theta^{ij}_{fh}(r)\exp[-\beta\varepsilon^{ij}_{fh}(r)]$ and rewrite the left-hand side of formula (30) as $\theta^A_f\theta^B_g\sum_{j=1}^{s} F_j\tilde\theta^{Ej}_{fh}(r_1)\tilde\theta^{Dj}_{gh}(r_2)/\left\{\theta^A_f\theta^B_g\sum_{j=1}^{s} F_j\tilde\theta^{Aj}_{fh}(r_1)\tilde\theta^{Bj}_{gh}(r_2)\right\}$, where $F_j = \exp[\beta\{\varepsilon^{Aj*}_{fh}(r_1) - \varepsilon^{Bj*}_{gh}(r_2)\}]/\theta^j_h$. We must show that ratio $N/L = \tilde\theta^{Ej}_{fh}(r_1)\tilde\theta^{Dj}_{gh}(r_2)/[\tilde\theta^{Aj}_{fh}(r_1)\tilde\theta^{Bj}_{gh}(r_2)]$ is independent of index *j*.

To do this, we express functions $\tilde\theta^{Ej}_{fh}(r_1)$ and $\tilde\theta^{Dj}_{gh}(r_2)$ through $\tilde\theta^{Aj}_{fh}(r_1)$ and $\tilde\theta^{Bj}_{gh}(r_2)$ respectively, using the general QCA relationships for pair functions (e.g., $\tilde\theta^{Ej}_{fh}(r_1) = \tilde\theta^{Aj}_{fh}(r_1)\tilde\theta^{EA}_{fh}(r_1)/\tilde\theta^{AA}_{fh}(r_1)$ and so on). This allows us to write $N/L = \Lambda^{EA}_{fh}(r_1)\Lambda^{DB}_{gh}(r_2)$, where $\Lambda^{ik}_{fh}(r) = \{\tilde\theta^{ii}_{fh}(r)\tilde\theta^{ik}_{fh}(r)/[\tilde\theta^{ki}_{fh}(r)\tilde\theta^{kk}_{fh}(r)]\}^{1/2}$.

Since obvious equality $\sum_{j=1}^{s} F^j_h N/\sum_{j=1}^{s} F^j_h L = N/L$, we can see that the left-hand side of relations (30) is $\theta^A_f\theta^B_g\Lambda^{EA}_{fh}(r_1)\Lambda^{DB}_{gh}(r_2)/\{\theta^E_f\theta^D_g\}$. On the other hand, formulas $S^E_{fh}(r_1)/S^A_{fh}(r_1) = \Lambda^{EA}_{fh}(r_1)\theta^A_f/\theta^E_f$ and $S^D_{gh}(r_2)/S^B_{gh}(r_2) = \Lambda^{DB}_{gh}(r_2)\theta^B_g/\theta^D_g$ can be proved in a similar manner, so by summarizing we obtain the proof for Eq. (30).

The use of approximations that do not consider spatial correlation effects (e.g., the mean field or chaotic approximations) does not correspond to the conditions of self-consistency. This results in particular in the renormalization of the process's energy of activation by the value $\varepsilon^{ij}_{fg}(1)$.

## GENERALIZATIONS OF EQUATIONS (24) AND (29)

Below, we discuss models that consider additional factors in comparison to Eqs. (24) and (29) for reaction rates that consider lattice nonuniformity and interactions between neighbors at distance *R*. We consider the following generalizations associated with considering the effects (1) of a neighboring particle near the reagents at *m* central sites ($m = 1$ and 2) and (2) the internal states of the reagents and AC. The first case requires generalizations of AC states not affecting the equilibrium state of system components (the equilibrium constant is retained). Strongly nonequilibrium systems, the inclusion of the environmental components into the elementary reaction process (or solvent reorganization), and the effect of the reaction being initiated by collisions with an incident particle correspond to the first case. The second involves considering the internal motions of particles, charges, and the electronic polarization of the medium. The general way of proving the self-consistency of the derived expressions remains the same for the first case, so we limit ourselves to reducing these situations to already considered models (24) and (29).

*Strongly non-equilibrium systems*. The first generalization is to consider the self-consistency of expressions for reaction rates in the right-hand sides of equations (5) for pair DFs. Summands $U_{fg}^{(i)j}(r|\alpha)$ and $U_{hfg}^{(mi)j}(r|\alpha)$ appear in them, which respectively correspond to one- ($i \leftrightarrow b$) and two-site ($i + m \leftrightarrow b + c$) reactions of an $i$ particle in the presence of neighboring $j$ particles. The sorts of reacting particles are given in the upper indices in parentheses (as above, the under indices indicate the sites containing these reagents). A neighboring $j$ particle affects the activation barrier value for the reacting $i$ particle.

Expressions for the rates in system (5) are written as

$$U_{fg}^{(i)j}(r|\alpha) = U_f^i(\alpha)t_{fg}^{ij}(r|\alpha)],$$

$$t_{fg}^{ij}(r|\alpha) = t_{fg}^{ij}(r|\alpha)\exp[\beta\delta\varepsilon_{fg}^{ij}(r|\alpha)]/\sum_{k=1}^{s} t_{fg}^{ik}(r|\alpha)$$

$$\times\exp[\beta\delta\varepsilon_{fg}^{ik}(r|\alpha)],$$

$$U_{hfg}^{(mi)j}(\omega_r|\alpha) = U_{hf}^{mi}(\alpha)t_{hfg}^{mij}(\omega_r|\alpha)], \tag{31}$$

$$t_{hfg}^{mij}(\omega_r|\alpha) = t_{hfg}^{mij}(\omega_r|\alpha)$$

$$\times\exp[\beta\delta\varepsilon_{hfg}^{mij}(\omega_r|\alpha)]/\sum_{k=1}^{s} t_{hfg}^{mik}(\omega_r|\alpha)$$

$$\times\exp[\beta\delta\varepsilon_{hfg}^{mik}(\omega_r|\alpha)]$$

through the products of rates of the respective reactions $U_f^i(\alpha)$ for a one-site stage and $U_{hf}^{mi}(\alpha)$ for a two-site stage (these rates and their self-consistency are considered above) and additional factors $t_{fg}^{ij}(r|\alpha)$ and $t_{hfg}^{nij}(\omega_r|\alpha)$, which reflect the effect neighboring particles have on the reaction rate.

Expressions (31) are used at any degree of deviation from the equilibrium state, but they must retain their form in the equilibrium state too. This is confirmed by the zero value of all terms in parentheses in the right-hand sides of (5). The allocation of $U_f^i(\alpha)$ factors reduces the problem to the relations between functions $t_{fg}^{ij}(r|\alpha)$. In a similar manner, the allocation of $U_{hf}^{mi}(\alpha)$ is reduced to relations between functions $t_{hfg}^{nij}(\omega_r|\alpha)$. The proof of the self-consistency is derived like that for reactions in heterogeneous systems. This is done via Eqs. (26) and (30). The ratio of these conventional probabilities under the condition of the equality of the AC properties eliminates the AC characteristics, and the other concentration functions are transformed through (26) and (30) into the non-ideality functions of the respective reaction mixture for particles at fixed sites.

*Third particles*. In the molecular statistical approach, general schemes of elementary processes are considered that can have different physical meanings. The effect of a third particle can thus be attributed to so-called solvent reorganization or a catalytic center. Consider the scheme $F + A \leftrightarrow B + F$, which corresponds to the monomolecular ($m = 1$) stage $A \leftrightarrow B$, and where $F$ is one of the system components. If the $F$ component is not involved in the chemical equilibrium, it could be a process associated with homogeneous or heterogeneous catalysis if it occurs in the surface region [21]. This is also true for $m = 2$. There are other cases as well: the local density depressions described in the LGM as the presence of a neighboring vacancy and allowing the local reorganization of reagent molecules in the form of rotations or rearrangements, or such a change in the local structure that enables the charged particle (electron, proton) transition in accordance with the Franck–Condon principle [22], which was introduced into the kinetics of liquid phase processes from photochemistry. Type (31) summands are in this case present in the right-hand sides of Eqs. (4) (with $F$ instead of $j$).

*Initiation of a reaction by the kinetic energy of an incident molecule*. Close structure of the equations is obtained in considering the effect of external initiation caused by the kinetic energy of an incident molecule on the elementary stage rate. This generally proceeds not only in rarefied gas but also in a dense gas and a relatively rarefied fluid. The incident molecule transfers momentum to the central particle, changing the rate and direction of its motion. The procedure for distinguishing a vacancy region in the dense phase along which the neighboring molecule moves was formulated as the introduction of a ρ-scale to specify the elementary act [39]. This allows us to transfer all derivations of the statistical theory of chemical reactions [40] in dense phases to Master Equations (4) and (5). It allows consideration of all three aggregate states of a system (in dense liquids and solid phases, the contribution from processes is leveled on the ρ-scale) up to rarefied gases within the common set of equations (4) and (5). The equations of the monomolecular stage are written as

$$U_f^{i*} = \sum_{k=1}^{\Phi} U_{\xi f}^{(k)i}(\rho), \quad U_{\xi f}^{(k)i}(\rho) = K_{\xi f}^{(k)i}(\rho)V_{\xi f}^{(k)i}(\rho),$$

$$K_{\xi f}^{(k)i}(\rho) = [F_{\xi f}^{(k)i}/(F_{\xi}^{(k)}F_f^i)]\exp(-\beta E_{\xi f}^{(k)i}(\rho)), \tag{32}$$

$$V_{\xi f}^{(k)i}(\rho) = \theta_f^i\left\langle t_{f\xi}^{ik}\right\rangle\Lambda_{\xi f}^{(k)i}(\rho),$$

where $K_{\xi f}^{(k)i}(\rho)$ is the rate constant of a reaction initiated by a collision with a $k$ particle on the ρ-scale, which is expressed through the statistical sums of AC

$F_{\xi f}^{(k)i}$ and initial particles $F_f^i$ и $F_\xi^{(k)}$, and the energy of activation of this process $E_{\xi f}^{(k)i}(\rho)$. Let us recall that ρ means not only the direction of the bond between the $f$ and ξ sites, but also the magnitude of this bond, which depends on the system's density [41, 42]. The $k$ particle on this bond is nearest to the $f$ site; $V_{\xi f}^{(k)i}$ is the concentration component of the $i \rightarrow$ product one-site reaction rate, which consists of three factors: $\theta_f^i$, the $i$ reagent concentration; $\left\langle t_{f\xi}^{ik} \right\rangle$, the probability of a $k$ particle colliding with the $i$ reagent; and the non-ideality function $\Lambda_{\xi f}^{(k)i}$ for this process, which considers the effect of intermolecular interactions at the AC stage:

$$\begin{gathered} \left\langle t_{f\xi}^{ik} \right\rangle = t_{f\xi}^{ik}(\rho)\exp[\beta\delta\varepsilon_{f\xi}^{ik}(\rho)]/\theta_\xi^k, \\ \Lambda_{\xi f}^{(k)i}(\rho) = \prod_r {\prod_{h_r}}' \sum_m t_{fh}^{im} \exp[\beta\delta\varepsilon_{fh}^{im}(\alpha)]. \end{gathered} \tag{33}$$

In the $h_r$ product, there is no $h_r = \xi$ factor corresponding to the $k$ particle's trajectory along the ρ-scale. It is replaced with factor $\left\langle t_{f\xi}^{ik} \right\rangle$. The emergence of the process initiation source is caused by $i$ particle collisions (on the ρ-scale) with the $k$ particle in the gas phase. This is reflected in a change in the expression for the elementary stage rate. It contains $K_{\xi f}^{(k)i}(\rho)$ factors instead of $K_{\xi f}^{(k)i}(\rho) = (F_f^{i*}/F_f^i)$ and $\left\langle t_{f\xi}^{ik} \right\rangle$ instead of the $\sum_m t_{fh}^{im} \exp[\beta\delta\varepsilon_{fh}^{im}(\alpha)]$ factor from the total function of non-ideality around the central reagents. The difference between rate constants is due to the different energy redistribution during the elementary stage, and it is an intrinsic property of reagent particles weakly associated with the non-ideal behavior of neighbors. The second factor differs in that it has the same exponential part but corresponds to molar fraction $x_\xi$ of the $k$ component at a ξ site instead of numerical density $\theta_\xi$. The condition of self-consistency follows from consideration of Eqs. (31) if we correlate the $k$ particle on the ρ-scale with the $j$ particle in formula (31). For each incident particle, the self-consistency condition is thus satisfied, as was made clear after formula (31). The self-consistency of the expression for two-site elementary stages is proved in exactly the same way. Examples of direct and indirect initiations were considered in [42, 43].

## CONSIDERING THE INTERNAL STATES OF MOLECULES

It was stated above that $F_i$ (the statistical sum of internal motions of the $i$ molecule) differes from the form of a particular configuration of the medium. In the expressions for reaction rate constants $K_A$, $K_{AB}$ (6), (7) the energy is similarly counted from the ideal solvent. All effects of the mutual influence of molecules are formally attributed to the parameters of interparticle interaction.

If we consider that the internal states of molecules affect the equilibrium state of system components, this changes the equations for the equilibrium constant and the elementary stage rates. The internal motions then depend on the particular configuration of the neighbors, and the abovementioned independence of the contributions of lateral interactions from the form of configurations disappears. The equilibrium constants and the elementary stage rate constants become functions of the form of local configurations. These models require a more complex description of particle states inside a reaction cluster [44]. The general idea behind these derivations was presented in [45, 46]. The technical solution to the problem is reduced to organizing a complete enumeration of the configurations of neighbors and the simultaneous tracing of the displacements of the centers of masses inside a discrete cell, the rotational and vibrational states of reagents, and the solvent components or a solid matrix.

For a rarefied gas, any statistical sum of the $i$ molecule is usually written as $F_f^i(\mathbf{r}_i|\alpha) = F_f^i(\mathbf{r}_i|\alpha)_{\text{tr}} F_f^i(\mathbf{r}_i|\alpha)_{\text{rot}} F_f^i(\mathbf{r}_i|\alpha)_{\text{vib}}$ [14, 40]. In dense phases the abovementioned separation of the contributions requires consideration of the effect the neighboring molecules have on each type of motion, and we must derive contributions $F_f^i(\mathbf{r}_i|\alpha)_{\text{tr}}$, $F_f^i(\mathbf{r}_i|\alpha)_{\text{rot}}$, and $F_f^i(\mathbf{r}_i|\alpha)_{\text{vib}}$ for each configuration. Considering the effect of internal motions on the statistical sums of particles in the ground and transition states in the condensed phase is associated with the dependence of statistical sums on the motions of the neighboring molecules in the region of reaction cluster $K_1$. Considering the translational motion depending on the neighboring molecular environment was considered in [30, 47]. Displacements of the center of mass in the cell are expressed through the cell volume accessible to the center of mass. This reflects the effect of the volume of the cell under study being blocked by neighboring particles. This model contains the dependence of the statistical sum of the translational motion $F_f^i(\mathbf{r}_i|\alpha)_{\text{tr}}$ on the conventional probabilities $\theta_{fg}^{l\lambda}(r)/\theta_f^l$ of the presence of different particles λ in the nearest cells. The problems in calculating $F_f^i(\mathbf{r}_i|\alpha)_{\text{rot}}$ were discussed in [46]. It is most difficult to consider the vibrational motions that are collective, so for simplicity and clarity we limit ourselves to considering the local vibrations of molecules. In the approximation of stationary neighbors for the statistical sum of vibrational motion $F_f^i(\mathbf{r}_i|\alpha)_{\text{vib}}$, in [48], expressions for the local Einstein–Mie frequencies were obtained that varied for different configurations of the neighboring particles. Particle vibrations are analogs of vibrational motion or a slight displacement near the equilibrium position. We therefore have a similar dependence on the state of the neighbors. The shift from collective motions to local frequencies is due to rougher dynamic relations and requires verification of their correctness according to the final results for the thermodynamic characteristics of the system.

The cluster approach used to obtain the expressions of averaged characteristics [28] provides the same derivation of distributions for the problems of calculating the equilibrium and stage rates. The radical simplification of the deduced equations is associated with the use of QCA, which considers the effect of short-range order correlations. To close the system in the QCA, we must employ the approximation [27]

$$\theta^i_f(\{n^m_{gr}\}) = \theta^i_f \prod_{r=1}^{R} \prod_{g\in z_f(r)} \prod_{m=1}^{s} [t^{im}_{fg}(r)]^{n^m_{gr}}, \qquad (34)$$
$$t^{im}_{fg}(r) = \theta^{im}_{fg}(r)/\theta^i_f,$$

where $t^{im}_{fg}(r)$ is the conventional probability of the $m$ particle occurrence at the $g_r$ site near the $i$ particle at the $f$ site. Probability of multiparticle configuration $\{n^m_{gr}\}$ is expressed through the product of unary and pair DFs. It is given by a set of values characterizing the numbers of $m$ sort particles at $g$ sites at distance $r$ from the central $i$ particle ($1 \le m \le s$, $1 \le r \le R$). Approximations (34) yield (28) at a constant rate constant. In considering internal motions, rate $\hat{K}^{AB}_f$ is replaced with local rate constants $\hat{K}^{AB}_f(\{n^m_{fg}\})$ corresponding to a particular configuration $\{n^m_{gr}\}$. At the same time, Eq. (9) for the equilibrium constant is rewritten in the form used in [44], since the $\nu_i$ value becomes a function of the form of configuration $\nu_i(\{n^m_{fg}\})$.

For a two-site reaction, the probability of a particular state of a reaction cluster with two central sites at distance $\rho$ is described by the function [27]

$$\theta^{ij}_{fg}(\rho|\{n^m_{h,\omega_r}\}) = \theta^{ij}_{fg}(\rho) \prod_{r=1}^{R} \prod_{\omega_r=1}^{\pi(r|qp)} \prod_{h\in z(\omega_r|qp)} \sum_{m=1}^{s} t^{ijm}_{fgh}(\omega_r|\rho),$$

where the configuration of neighbors $\{n^m_{h,\omega_r}\}$ is determined by the numbers of $m$-type neighboring particles for $h$ sites in analogy with single-center clusters; function $t^{ij}_{fgh}(\omega_r)$ was defined in (29).

The key to proving the self-consistency of expressions for stage rates is that there is a rigorous statistical proof for the discrete particle distribution, and considering the continuum distribution of particles inside cells introduces a relatively small perturbation. The theory self-consistency is preserved if the configurations are completely averaged while maintaining short-range order in the QCA. The components [44] or characteristics of lateral interactions must in this case be averaged over the internal states. Below, we give an example of considering the contributions from induced dipoles to the interaction of system components, in which we obtain the averaged parameters of potential interactions.

Moving to more accurate approximations for considering both internal motions and correlated particle distribution results in much more cumbersome equations. Specific verification of continuum contributions to calculated characteristics is generally needed. The same complication in writing equations compels us to use the quantum chemical energies of clusters instead of atom–atom potentials. Self-consistency is normally verified numerically, in analogy with the above verification of polynomial splitting for nearest neighbors.

## *Slow Reactions*

The characteristic time of an elementary slow reaction is much longer than that of the reorganization of neighboring molecules. The great mobility of neighboring molecules around reagents corresponds to Eyring's hypothesis [14] about the existence of an AC activity coefficient. By introducing the concept of AC activity coefficient $\alpha^*_i$ (or $\alpha^*_{ij}$), we mean averaging over all possible equilibrium states of the environment. It was noted above that a change in the nearest neighbors of reagents always alters the potential relief of a reaction, and other channels for the reaction between the initial reagents to proceed become possible in principle. In addition, there is a purely formal contradiction in the QCA when defining the AC chemical potential as an ordinary particle of a non-ideal mixture through pair DFs $\theta_{ii}(r)$ of neighboring $i$-sort particles [36]:

$$\mu_i = \mu^0_i + \beta^{-1}\sum_{r=1}^{R}\{z_r(\ln[\theta_{ii}(r)/\theta_i^{\,2}] - \beta\varepsilon_{ii}(r)\}/2, \qquad (35)$$

since neighboring pairs $\theta_{ii}(r)$ for the AC of process $\alpha$ are basically not defined in ARRT (summand $\mu^0_i$ describes the internal degrees of freedom of an $i$ component). Altogether, this makes the use of the Eyring approach's thermodynamic concepts contradictory to the dynamics of reaction systems.

Molecular theory allows the derivation of an expression analogous to the Eyring concept [49] by assuming there is an equilibrium distribution of mixture components during the slow formation of an AC (i.e., an AC is long-lived near the barrier top). The expression for one-site elementary process rates is then expressed as

$$\begin{gathered}U_f^i(\alpha) = K_f^{i*}(\alpha)V_f^i(\alpha),\\ V_f^i(\alpha) = \theta_f^i\prod_{r=1}^{R}\prod_{g\in z_f} S_{fg}^i(r|\alpha)R_{fg}^i(r|\alpha),\end{gathered} \tag{36}$$

where all values are defined above, except for factor $R_{fg}^i(r|\alpha)$. It is written using unary and pair DFs, in the form

$$\begin{gathered}R_{fg}^i(r|\alpha) = \exp\sum_{k=1}^{s}[t_{fg}^{ik}(r)\ln\hat{t}_{fg}^{ik}(r)\\ - t_{fg}^{ik*}(r|\alpha)\ln\hat{t}_{fg}^{ik*}(r|\alpha)],\end{gathered} \tag{37}$$

where index $k$ corresponds to rapid mixture components that manage to adjust to the AC. Here we write $\hat{t}_{fg}^{ik}(r) = t_{fg}^{ik}(r)\exp[-\beta\varepsilon_{fg}^{ik}(r)]$ and $\hat{t}_{fg}^{ik*}(r|\alpha) = t_{fg}^{ik*}(r|\alpha)\exp[-\beta\varepsilon_{fg}^{ik*}(r|\alpha)]$.

The rates of two-site elementary processes have the form

$$\begin{gathered}U_{fg}^{ij}(r|\alpha) = K_{fg}^{ij*}(r|\alpha)V_{fg}^{ij}(r|\alpha),\\ V_{fg}^{ij}(r|\alpha) = \theta_{fg}^{ij}(r)\exp[-\beta\varepsilon_{fg}^{ij}(r)]\\ \times\prod_{r=1}^{R}\prod_{\omega_r}^{\pi_r}\prod_{h_r} S_{fgh}^{ij}(\omega_r|\alpha)R_{fgh}^{ij}(\omega_r|\alpha).\end{gathered} \tag{38}$$

All functions here, including $S_{fgh}^{ij}(\omega_r|\alpha)$ and factors $t_{fgh}^{ijm}(\omega_r)$ in them, are defined above. There is also a new factor:

$$\begin{gathered}R_{fgh}^{ij}(\omega_r|\alpha) = \exp\sum_{k=1}^{s}\Big[t_{fgh}^{ijk}(\omega_r)\ln\hat{t}_{fgh}^{ijk}(\omega_r)\\ - t_{fgh}^{ijk*}(\omega_r|\alpha)\ln\hat{t}_{fgh}^{ijk*}(\omega_r|\alpha)\Big],\end{gathered} \tag{39}$$

where $\hat{t}_{fgh}^{ijk}(\omega_r|\alpha) = t_{fgh}^{ijk}(\omega_r|\alpha)\exp[-\beta\varepsilon_{fgh}^{ijk}(\omega_r|\alpha)]$, $\hat{t}_{fgh}^{ijk*}(\omega_r|\alpha) = t_{fgh}^{ijk*}(\omega_r|\alpha)\exp[-\beta\varepsilon_{fgh}^{ijk*}(\omega_r|\alpha)]$.

To calculate factors $R_{fg}^i(r|\alpha)$ and $R_{fgh}^{ij}(\omega_r|\alpha)$, we must solve a set of algebraic equations for the distribution of rapid components in the field of slow components for this time scale. The scale is determined by the derivative in the left-hand side of kinetic equations (4) and (5). Both functions are expressed through a set of $t_{fg}^{ij*}(r|\alpha)$ values. They are found from the equilibrium distributions in the form

$$\begin{gathered}t_{fg}^{ij*}(r|\alpha) = \theta_{fg}^{ij}(r)\exp[\beta\delta\varepsilon_{fg}^{ij}(r|\alpha)]/\Big[\sum_k\theta_{fg}^{ik}(r)\\ \times\exp[\beta\delta\varepsilon_{fg}^{ik}(r|\alpha)]\Big],\end{gathered} \tag{40}$$

where index $k$ denotes only the rapid components. Strong nonequilibrium is considered in the same way as above but only for functions $S_{fg}^i(r|\alpha)$.

It was shown above that the ratios of rate constants and contributions from factors $S_{fg}^i(r|\alpha)$ and $S_{fgh}^{ij}(\omega_r|\alpha)$ do not depend on the AC properties. To prove the self-consistency of expressions (35), (37) it is sufficient to show that when the rates of forward and backward elementary stages are equal, the $R_{fg}^A(r|\alpha)/R_{fg}^B(r|\alpha)$ and $R_{fgh}^{AB}(\omega_r|\alpha)/R_{fgh}^{CD}(\omega_r|\alpha)$ ratios do not depend on the AC properties of stage $\alpha$. To illustrate this, it is sufficient to consider only the expressions for the factors of one-site processes:

$$\begin{gathered}R_{fg}^A(r|\alpha)/R_{fg}^B(r|\alpha) = \exp\sum_{k=1}^{s}[t_{fg}^{Ak}(r)\ln\hat{t}_{fg}^{Ak}(r)\\ - t_{fg}^{Ak*}(r|\alpha)\ln\hat{t}_{fg}^{Ak*}(r|\alpha) - t_{fg}^{Bk}(r)\ln\hat{t}_{fg}^{Bk}(r)\\ + t_{fg}^{Bk*}(r|\alpha)\ln\hat{t}_{fg}^{Bk*}(r|\alpha)].\end{gathered}$$

By definition, the AC values corresponding to the difference between the contributions from forward and backward processes must be reduced. Using relations (26) and (35), the remaining contributions

$$\begin{gathered}R_{fg}^A(r|\alpha)/R_{fg}^B(r|\alpha) = \exp\sum_{k=1}^{s}[t_{fg}^{Ak}(r)\ln\hat{t}_{fg}^{Ak}(r)\\ - t_{fg}^{Bk}(r)\ln\hat{t}_{fg}^{Bk}(r)]\end{gathered}$$

therefore become isothermal relations of type (24) that demonstrate the self-consistency of the theory. For two-site stages, we must additionally use an analog of Eqs. (31). The above also corresponds to other considered generalizations of the theory.

Let us illustrate the character of changes caused by using the analog of the Eyring concept for the simplest process: monomolecular reaction $A \to B$ with regard to nearest neighbors and for two components (when $s = 2$, the system is represented by $A$ and $B$ molecules, and relaxation is the redistribution of molecules around AC during their migration). In the QCA, the following equation was obtained for the rate of a monomolecular reaction by considering the interaction between system components [49, 50]:

$$\begin{gathered}U_i = K_i\theta_i(S_i^*)^z,\\ S_i^* = \exp\sum_{j=1}^{s}\{t_{ij}\ln[t_{ij}\exp(-\beta\varepsilon_{ij})]\\ - t_{ij}^*\ln[t_{ij}^*\exp(-\beta\varepsilon_{ij}^*)]\},\end{gathered} \tag{41}$$

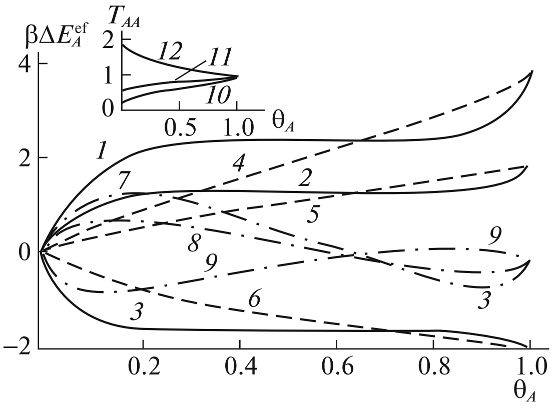

**Fig. 4.** Effective energies of activation for the rates of (*1–3*) slow and (*4–6*) rapid monomolecular reaction, their differences $\beta[\Delta E_A^{\text{ef}}(\text{slow}) - \Delta E_A^{\text{ef}}(\text{rapid})]$ (*7–9*), and the functions $T_{AA} = t^*_{AA}/t_{AA}$ (*10–12*) (insert); $s = 2$, $\beta\varepsilon_{AA} = 1$, $\varepsilon^*_{AA}/\varepsilon_{AA} = 0$ (*1, 4, 7, 10*), 0.5 (*2, 5, 8, 11*), 1.5 (*3, 6, 9, 12*) [50].

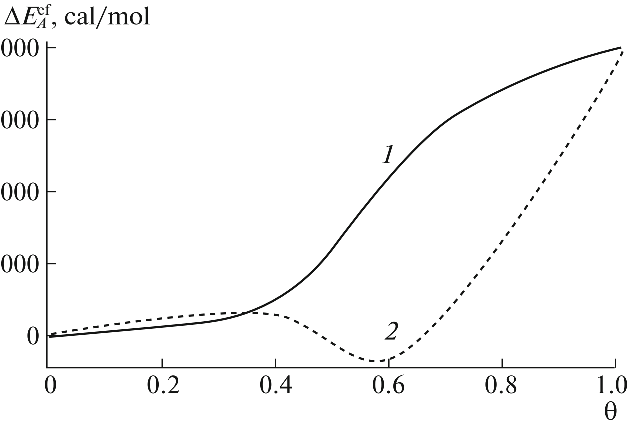

**Fig. 5.** Concentration dependence of the $E_A^{\text{ef}}$ value for monomolecular desorption at $T = 300$ K, calculated for (*1*) rapid and (*2*) slow elementary stages [51].

where $\hat{t}_{ij} = \hat{\theta}_{ij}/\theta_i$ and $t^*_{ij} = t_{ij}\exp(\beta\delta\varepsilon_{ij})/\sum_{k=1}^{s} t_{ik} \times \exp(\beta\delta\varepsilon_{ik})$; energy difference $\delta\varepsilon_{ij}$ was defined in formulas (24). The structure of formulas (24), (29) is retained, but function $S_i$ that considers the non-ideality of the reaction system changes. The formulas show that the elementary process rates depend on difference $\delta\varepsilon_{fg}^{A\lambda}$ between the intermolecular AC and the initial reagent interactions with the environment, which form the activation barriers in each particular local composition. If $\varepsilon_{fg}^{*ij} = \varepsilon_{fg}^{ij}$, then $S_{hg}^{*A} = 1$, and formula (41) for $U_A$ has the same form as for ideal reaction systems: $U_A^{id} = K_A\theta_A$ (1).

It is helpful to consider the role of the relaxation of the medium by considering the rate relations for slow and rapid reactions: $\eta_A = U_A(\text{slow})/U_A(\text{rapid})$, $U_A(\text{slow, rapid}) = K_A\exp[-\beta\Delta E(\text{slow, rapid})]$, $\beta\Delta E_A^{\text{ef}} = -\ln(U_A/U_A^{id})$. The effective energies of activation characterize the degree to which the rate of the reaction deviates from the ideal one in a non-ideal reaction system. Figure 4 presents the calculated rates of rapid and slow monomolecular reactions and the ratio $-\ln(\eta_A)$ for the entire range of $A$ reagent density variation. The insert in Fig. 4 shows the concentration dependences of ratios $T_{AA} = t^*_{AA}/t_{AA}$ that characterize local changes in the $A$ component distributions due to their migration under the AC effect for a slow reaction. This ratio tends to unity when $\theta \Rightarrow 1$. We observe the maximum AC effect at low $\theta$: $T_{AA} = \theta\exp(\beta\delta\varepsilon_{AA})$. For a rapid reaction, $T_{AA} = 1$ at all $\theta$.

Figure 4 illustrates the qualitative difference between the concentration dependences of the reaction rates for various relaxations of the medium. If there is no relaxation, ln $U_A$(rapid) varies in a virtually linear fashion as $\theta$ grows. With equilibrium relaxation of the medium, ln $U_A$(slow) changes abruptly in the regions where $\theta < 0.2$ and $\theta > 0.8$, and remains virtually constant where $0.2 < \theta < 0.8$. This general property of the effect the character of the medium's relaxation has is also observed in other situations, e.g., the mono- and bimolecular stages in solutions that were studied in [50]. It could form the basis for analyzing the experimental concentration dependences of the logarithms of reaction rates in a wide range of concentrations.

The other example in Fig. 5 illustrates the above qualitative difference between the concentration dependences of the reaction rates for different relaxations of the medium at $T$ = const (the curves correspond to the experimental data for a CO–Pt type system [51]). The effective energy of activation of desorption (and thus the rate of the process) grows monotonically along with the degree of occupancy if the calculations are performed using formula (6) (there is no relaxation of the medium). If the calculations are performed using formula (45), the effective energy of activation of desorption changes nonmonotonically for the equilibrium relaxation of the medium. In non-ideal systems, nonmonotonic behavior of the reaction rate is normally possible only if there is an attracting potential (e.g., for Hg–W type systems) [27–29, 51]. The nonmonotonic behavior of the desorption rate contradicts the physics of this process, especially because the chemisorbed particles repel one another at short distances. In addition, the physical sense is contradicted by the sole desorption reaction's negative effective energies of activation.

The examples in Figs. 4 and 5 are typical of the rates of chemical reactions and diffusion processes. In most cases, reactions occur with the AC rapidly overcoming the activation barrier [27, 29]. Equations corresponding to the Eyring concept artificially distort the physical nature of processes, due to incorrect consideration of the procedures for averaging the contributions from atomic–molecular configurations.

*A system with induced dipoles.* One of the few situations in which the Eyring concept can be used seems to be allowing for the effect of electronic polarization. This example was discussed by considering the effect of induced dipole moments in the energy of the system in the expressions for elementary stage rates [52]. It was found that the parameter of lateral interaction between neighboring particles at distance $r$ with regard to discrete dipole orientations $\tilde{\varepsilon}_{fg}^{lm}(r)$ can be written as $\tilde{\varepsilon}_{fg}^{lm}(r_{fg}) = \varepsilon_{fg}^{lm}(r_{fg})_{LD} + \varepsilon_{fg}^{lm}(r_{fg})_{d-d} + \varepsilon_{fg}^{lm}(r_{fg})_{id-id}$, where the contribution from induced dipoles $\varepsilon_{fg}^{lm}(r_{fg})_{id-id}$ consists of all possible types of interaction: the one between the central dipole particle and polarized particles at neighboring $h$ sites, and its polarization under the effect of dipoles of all $n$-sort neighbors at $h$ sites; and the one between an induced dipole on the central particle and induced dipoles on polarized particles at neighboring sites [52]. In deriving $\tilde{\varepsilon}_{fg}^{lm}(r)$, third- and fourth-order correlations emerge that are calculated using the Kirkwood superposition decoupling ($t_{123} = t_{13}t_{23}/\theta_3$) [34] and the Fisher over-superposition approximation ($t_{1234} = t_{13}t_{23}t_{23}t_{24}\theta_{34}/[\theta_{12}(\theta_3\theta_4)^2]$) [53]. The introduced approximation is rigorous at low ratios of interaction parameters $\varepsilon_{fg}^{lm}(r_{fg})_{id-id}$ with respect to the first two summands. In the atom–atom approximation, it is considered that the polarizability of each atomic group is retained in large molecules. Complete AC polarization may in this case be considered as consisting of modified contributions of initial reagents $\alpha_{h\xi}^{*AB} = \alpha_h^{*A} + \alpha_\xi^{*B}$. This assumption is considered in deriving energy parameter $\delta\tilde{\varepsilon}_{h\xi g}^{AB\lambda}(w_r)$ for kinetic stages.

As an example. let us write the expression for the elementary two-site stage rate:

$$U_{AB} = K_{AB}\theta_{h\xi}^{AB}(1)\exp[-\beta\tilde{\varepsilon}_{h\xi}^{AB}(1)]$$
$$\times \prod_{r=1}^{R}\prod_{w_r=1}^{\pi_r}\prod_{g_{wr}} S_{h\xi g}^{*AB}(w_r)R_{h\xi g}^{*AB}(w_r),$$

where all values are defined above in (30) and (32) with $\delta\varepsilon_{h\xi g}^{AB\lambda}(w_r)$ substituted for $\delta\tilde{\varepsilon}_{h\xi g}^{AB\lambda}(w_r)$; i.e., the difference is the presence of renormalized multiparticle interaction potentials instead of the initial potentials. In (30), the superposition approximation is used to describe the probabilities of spatial configurations, as in calculating the energy contributions of induced dipoles. The effects of induced dipoles themselves are reflected in the effective pair energy parameters of function $R_{h\xi g}^{*AB}(w_r)$. It is calculated using formulas (40), in which the state of the AC corresponds to the presence of an intrinsic charge, a constant and induced dipole that differs from the similar properties in the ground state of the reagents.

Analysis of the theory's self-consistency thus shows it is a question of the quality of the approximations that are used (the many bodies problem rarely has an accurate solution, and it is needed to apply approximations). Initial configurations of reagents and the solvent molecule environment, the solid carrier matrix, or those of other reagents always affect the elementary stage rate. The elementary process takes the form of overcoming the activation barrier or that of a sub-barrier transition surrounded by neighbors that make one contribution or another to the formation of the barrier at their particular fixed configuration. Self-consistency is always assumed for a separate configuration, and it is identically included in the full spectrum of configurations in both calculating statistical sums and the probabilities of elementary stages. The problem of self-consistency arises at the stage of simplification in calculating both the probabilities of different configurations and the energy of the elementary reaction stage. Such simplification can result in much rougher probabilities (especially when one-particle approximations, i.e., the law of mass action, is used) or substantial distortion of the properties of the potential barrier, so the derived expressions for the elementary stage rates and equations for the equilibrium distribution of mixture components yield different expressions for the equilibrium constant. This makes it impossible to use the parameters found in kinetic experiments to calculate the equilibrium properties of a system and vice versa.

Apart from the statistical aspects, the problem has a quantum chemical aspect as well. The possibility of more accurately calculating the energy characteristics, and thus the AC and internal motions of particles, depend on the latter. In this respect, the cluster approach to calculating atomic–molecular distributions [28] is naturally related to the cluster approaches in quantum chemistry. Complete statistical averaging involves a large number of configurations; since their direct enumeration is difficult, it requires the introduction of convenient approximations of the potential functions in the system under study.

Experimental data show that in most situations, the AC barrier is rapidly overcome with atomic–molecular stages (the Temkin concept). The Eyring concept can be discussed only in association with electronic polarization processes in a medium.

The theory provides a self-consistent description of dynamics and equilibria on all spatial scales for any densities, temperatures, intensities of lateral interactions, radii of potential, and external fields only when considering the correlation effects, at least for short-range order; otherwise, the self-consistency condition is violated. Therefore, neither molecular DFT nor the mean field and chaotic approximations can be used to describe dynamics in dense phases.

There is generally a strict relationship between kinetics and equilibria in the form of (1) the conditions of local equilibrium underlying all existing equations of nonequilibrium thermodynamics and molecular kinetic equations in all aggregate states; (2) the commonality of potential functions and the relationship between energy characteristics (energies of activation and heats of elementary stages) added by the relationship of the entropy factors in equilibria and kinetics; (3) the self-consistency of the theory in describing kinetics and equilibria. We must therefore completely cease using quasi-thermodynamic expressions for reaction rates in the kinetics of nonideal reaction systems and move to molecular–statistical models the provide self-consistent descriptions of the elementary stage rates and the equilibrium of a reaction system.

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