Development of the Ideas of M.I. Temkin in Physical Chemistry

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Abstract—This article considers pioneering works by M.I. Temkin in the field of adsorption, the theory of elementary stages of surface processes and general questions describing condensed phases using as examples the processes on surfaces in dense monolayers and in the volume phase. A brief review of the subsequent development of his ideas in these areas is given. The questions of the correct way to take into account the cooperative behavior of adsorbed species in equilibrium and surface reactions and the principle of self-consistent description of the rates of stages and the equilibrium state of the reactants for heterogeneous surfaces and nonideal reaction systems are discussed.

INTRODUCTION

The beginning of the scientific activity of M.I. Temkin (who graduated from the Department of Chemistry of Moscow State University in 1932) coincided with the period of the formation of modern physical chemistry and chemical kinetics. The laws of quantum theory formulated at that time provided a new look at the Gibbs statistical theory, which began to take shape in applications to physical chemistry as statistical thermodynamics.

Temkin's name is usually associated with the following four equations: the Temkin logarithmic isotherm [1, 2], the Temkin−Pyzhev rate equation of ammonia synthesis [3], the model of kinetics on a nonuniform surface [4], and the model of melts of strong electrolytes [5, 6].

He was involved in the following research: statistical thermodynamics of ideal systems, the theory of absolute reaction rates on uniform and nonuniform surfaces, taking into account the nonideality of reaction systems in the mean field approximation on nonuniform surfaces (including the issues of self-consistency in describing the rates of kinetic processes and equilibrium in nonideal and inhomogeneous systems), the theory of ionic melts, the theory of kinetics of heterogeneous catalytic reactions (including multistage processes with a rate-limiting adsorption stage), the kinetics of catalytic complex multistage processes, and the study of the role of outer and inner mass and heat transfer in heterogeneous catalysis.

Of all the works in these areas, this review discusses the main ideas and ways of developing models of physical chemistry (adsorption, solutions, and rates of elementary stages), as well as general principles for describing condensed systems, are discussed below. The focus is on the ideas themselves rather than on the content of individual articles. These ideas were brought to practice in the models of surface processes and processes in the volume phases and expanded the means for taking into account physical properties of reagents as reflected in the mathematical description of these models.

Below I consider adsorption and solutions (section 1), rates of elementary stages (section 2), and the principles of describing condensed systems (section 3). Subsections discuss narrower range of issues.

1. SYSTEMS AT EQUILIBRIUM

The first topic that I would like to discuss is the equilibrium properties of systems. Usually, Temkin considered adsorption systems as analogs of ordinary volume solutions that had specificity due to the presence of a surface. For mixtures of adsorbed substances, as well as those in the volume, it was proposed to use the same terminology—in particular, an ideal adsorption solution [7]. The same generality of concepts was constantly developed by Temkin in chemical kinetics (and by Hill in the thermodynamics of adsorption based on the concept of an inert adsorbent [8]). In the works along these lines, it was common to use the approaches of statistical thermodynamics of noninteracting particles for equilibrium ideal systems.

1.1. Justification of the Langmuir Isotherm

It should be emphasized that Temkin was the first to gave a statistical justification for the Langmuir isotherm [9]: $aP = \theta/(1 - \theta)$, where $\theta = N/M$ is the surface coverage, N is the number of adsorbed species that occupy a single adsorption site, M is the number of adsorption sites per unit surface area, a is the adsorption coefficient or the proportionality coefficient between pressure and the surface coverage at a low coverage, which is called the Henry coefficient in the equation $aP = \theta$ or the Langmuir coefficient.

The Langmuir isotherm was obtained by the kinetic method by equating the rates of adsorption and desorption stages [10]. Obtaining the Langmuir isotherm using a purely equilibrium statistical method showed the relationship between the adsorption—desorption rate constants and the equilibrium constant. The derivation of the Langmuir isotherm from the laws of the statistical distribution of species between the surface and the volume phase of the vapor emphasized the idea of an independent process path to achieve its equilibrium. This fact immediately raised the question of the fundamental importance of a self-consistent description of the properties of the system under study, proceeding from a kinetic and strictly statistical approach. Temkin himself in all his subsequent works consistently adhered to this idea.

The statistical justification of the Langmuir isotherm is usually attributed to Fowler [11, 12], who is one of the founders of statistical thermodynamics [13], but Temkin's work was published 2 years earlier.

1.2. Consideration of the Size of Components in an Adsorption System

A close range of ideas was associated with the need for taking into account the size of the components of an adsorption system. In the Langmuir isotherm, each species occupies one adsorption site on the surface. Obviously, different molecules adsorb differently on the same surface, and this be primarily affected by the size of a molecule relative to the size of an adsorption site, the number of which per unit of surface area is fixed. For the first time, Temkin derived the adsorption isotherm of dimeric molecules on a one-dimensional structure of sites [14]. A dimeric molecule occupies two adjacent sites and this fact determines the surface coverage: $\theta = 2N/M$, and the isotherm takes the form $aP = \dfrac{(2 - \theta)\theta}{4(1 - \theta)^2}$. Apparently, this isotherm appeared under the influence of article by Fowler and Rushbrooke [15] for solutions in two- and three-dimensional systems, but for adsorption it was a kind of a initiation, after which the theory of adsorption of multi-site species began to develop rapidly.

At the same time, works [16, 17] appeared, and later [18—20] for structures of various dimensions, including one-dimensional ideal [21] and nonideal [22, 23] adsorption systems. Later, an active interest was shown in more realistic two-dimensional adsorption systems [24—27]. Taking into account the multi-site nature of adsorbed molecules and lateral interactions was extended to the kinetics of adsorption—desorption processes of one-dimensional ($d = 1$ [28]) and two-dimensional systems on the open surface and in pores [29—31].

At the same time, it became clear that the statistical description of large molecules can take into account the different orientations of an adsorbate. Each orientation of a molecule is characterized by its value of the binding energy with the surface, and it can be considered a sort of a certain species; therefore, taking into account different orientations of the molecules, even for a one-component system, is reduced to the theory of adsorption of a mixture of species of different sizes. The role of different molecular orientations is best illustrated for a molecule shaped as a "rigid rod". In addition to the horizontal and vertical positions of the rod, different orientations of the adsorbate in the plane of the surface should be distinguished. Moreover, as the density of the adsorbate increases, an ordered arrangement of molecules having the same vertical orientation of their long axes becomes preferable [32]. The problem of calculating the adsorption of large molecules (blocking more than one adsorption site) is one of the most difficult problems of statistical thermodynamics to date.

1.3. Isotherms for a Nonuniform Surface

A very important area in the mid-1930s was associated with work on the generalization of the Langmuir isotherm for a uniform surface to cover the case of adsorption on nonuniform surfaces. Langmuir himself constructed an isotherm when considering adsorption equilibrium on nonuniform surfaces [33] using unnormalized contributions from different areas of the surface. For a "crystalline" surface with a small number of different areas and "amorphous" surfaces with a large number of different areas characterized by a continuous change in adsorption capacity, he expressed the coverage as

$$\theta = \sum_{q=1}^{t} \frac{a_q P}{1 + a_q P} \quad \text{and} \quad \theta = \int \frac{a_q P}{1 + a_q P} ds, \qquad (1)$$

where t is the number of crystalline areas and s is a parameter that characterizes the relative fraction of q-areas of the surface.

The value of s is related to the q-type of the site via the normalized distribution function f_q, which characterizes the fraction of the surface covered with q-type sites; that is, $ds = f_q dq$ or $ds = f(Q)dQ$ if a rule is set that determines the relationship between the adsorbate

binding energy Q on the q-type surface site. Then the integral expression (1) can be rewritten as

$$\theta = \int_{Q_{\max}}^{Q_{\min}} f(Q) \frac{a_Q P}{1 + a_Q P} dQ. \tag{2}$$

Equation (2) underlies the statistics of all processes on nonuniform surfaces without taking into account lateral interactions. In this regard, one of the first works on the use of the normalized uniform energy distribution function $f(Q)$ for the adsorption site was the work by Temkin in 1934. These equations of adsorption—quasi-logarithmic $\theta = \dfrac{1}{f} \ln \dfrac{1 + a_1 P}{1 + a_0 P}$ for a full range of surface coverages and logarithmic $\theta = \dfrac{1}{f} \ln(a_1 P)$ for medium surface coverages ($a_1 P \gg 1$ and $a_0 P \ll 1$)—appeared as a footnote in [34]. Here, a_0 and a_1 are the adsorption coefficients for the most weakly bound and strongly bound sites, respectively. $f = (Q_{\max} - Q_{\min})/RT$ is a parameter of the linear distribution function of sites over energies. The complete derivation of isotherms was given in the form of the author's insert in his article [35]. Temkin himself published his isotherm in his article much later [1, 2] (the work [2], in fact, was his doctoral dissertation).

The description of adsorption using the integral distribution functions of various types of sites (Eq. (2)) became the most common approach in those years. As an example, we point out the work published simultaneously [36], in which the same integral description was used to find the energy distribution function of the adsorption sites, which corresponds to the Freundlich isotherm $aP = \theta^n$. The possibilities of using the integral description for explaining experimental isotherms were also analyzed in [37].

For catalytic processes, the possibility of studying reactions on surfaces with specified properties is especially important. Modeling the structure and chemical composition of the surface reveals the role of each factor. In this regard, experiments on the effect of steps, breaks of steps [38, 39], and surface composition of alloys [40—43] on catalytic activity are very informative. Thus, the presence of steps on Pt(III) leads to an increase in the rate of hydrogen isotope exchange by two orders of magnitude, and the activity of bimetallic catalysts may exceed the activity of the active component itself [44]. Experiments on model surfaces made it possible to concretize the ideas proposed earlier in the Taylor theory of active sites [45], the Balandin multiplet theory [46], and the Kobozev theory of active ensembles [47].

It is interesting that a similar "insert" appeared later in the work of Langmuir [48], who invited Tonks to a large review titled "Monolayers on Solids" that included a description of the adsorption of large species indicated above. The part by Tonks was later published as a separate work [49]. (These examples show that the formulation of ideas can refer to different links.)

The physical meaning of the distribution functions of adsorption sites for ideal reaction systems is an example of taking into account strong interactions between the components of the adsorption system and the surface atoms of the adsorbent. The condition of independence of the influence of each adsorption site makes it possible to simplify the task greatly and consider each adsorption site independently of others (although the latter is not always a good approximation, especially in the case of strong mutual influence of adsorbates). Today, when interest in the field of heterogeneous catalysis has greatly shifted toward the processes occurring on nonmetallic catalysts (oxides, sulfides, zeolites, metal complexes, etc.) and polyfunctional systems, the question of the distribution functions of the adsorption sites over energy remains relevant. These questions began to be developed long time ago [50—55]. Their essence is reduced to the transition from one-dimensional energy distribution functions (Eq. (2)) to multidimensional distribution functions $f(Q_1, ..., Q_n)$, where n is the number of components, since different components of mixtures change their binding energy with the surface in different ways on adsorption sites of different types.

1.4. The Model of a Ionic Melt

Another example of using ideal models for describing strong interactions is the ionic melt model proposed by Temkin in the mid-1940s [5, 6]. Strong ion interactions lead to a very strong correlation between positively and negatively charged ions, which prefer to form structures that are most close to neutral compounds if they form strictly ordered structures. Thus, the theory of ideal ionic melts was proposed [5, 6] and came into widespread acceptance. This model assumes the presence of an ideal ordered solution in which cations and anions form two interpenetrating sublattices without mixing. This leads to a structure in which there are only ions and each of them is surrounded by ions of only a different kind. All ions of the same sign are equivalent in size and energy of interaction with ions of the other sign. Therefore, only the concentrations of ions in different sublattices play the main role. This model was included in all textbooks on metallurgical processes (see, e.g., [56]). It was reformulated for metallurgical slags [57] and formed the basis for the statistical thermodynamics of ionic solutions/melts for applications to practically important metallurgical slags. Later, Temkin's ideas were actively developed in the form of models of regular ionic solutions and slags.

Now, more detailed models of regular solutions or more accurate ones that take into account interactions between the components of melts are considered. For example, Pak et al. [58] studied the influence of second nearest neighbors in a strictly regular model of

melts on the thermodynamic functions of a solution for a number of oxides in order to analyze phase diagrams. The modern development of techniques for modeling phase diagrams led to the creation of Calphad software packages [59], and a theory was developed in [60] for calculating the surface tension at phase interfaces in ordered solutions, including ionic melts and slags.

2. ELEMENTARY STAGESS OF SURFACE PROCESSES

Currently, the rates of elementary surface processes are calculated based on the theory of absolute reaction rates (TARR). This theory was proposed for the gas phase by Eyring [61]. TARR uses the concept of an activated complex (AC) or transition state which is in equilibrium with the initial reactants. The rate of the bimolecular reaction A + B is expressed as

$$U_{AB} = K_{AB} n_A n_B,$$

$$K_{AB} = \varkappa \frac{kT}{h} \frac{F_{AB}^*}{F_A F_B} \exp(-E_{AB}/kT), \qquad (3)$$

where n_i is the concentration of reactant i (the number of molecules of type i per unit volume); K_{AB} is the rate constant expressed through the height of the thermodynamic barrier E_{AB}, the product of statistical sums (sums for inner states) of the original molecules F_A and

F_B, and the statistical sum AC F_{AB}^* calculated for all degrees of freedom, except for the "reaction path"; $\varkappa$ is the transmission coefficient, which in most cases can be taken equal to 1; $k_B T$ is the product of the Boltzmann constant and the absolute temperature T; and h is Planck constant.

TARR determines the magnitude of the preexponential factor in the Arrhenius equation for homogeneous reactions. This allows us to refine the results of earlier theories according to which this factor should be equal to the number of collisions for bimolecular reactions and the frequency of atomic vibrations in a molecule for monomolecular reactions.

2.1. TARR for Surface Processes on Uniform Surfaces

TARR was developed by Temkin for processes on uniform surfaces [14]. This work is classical and has been included in many textbooks [62–64].

The rates of elementary stages for ideal reaction systems are described for mono- (U_i) and bimolecular (U_{ij}) reactions as follows:

$$U_i = K_i \theta_i, \quad U_{ij} = K_{ij} \theta_i \theta_j, \qquad (4)$$

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

$$K_{ij} = K_{ij}^0 \exp(-E_{ij}/k_B T),$$

$$K_{ij}^0 = \varkappa (k_B T/h\sigma)\left(F_{ij}^*/F_i F_j\right), \qquad (5)$$

K_{ij}^0 is the preexponential factor in the rate constant, k_B is the Boltzmann constant, σ is a numerical coefficient depending on the units of measure of concentrations. If the surface area does not change during the reaction, it is convenient to measure the concentration of species as the degree of surface coverage θ_i, which characterizes the surface fraction occupied by component i.

TARR theory made it possible to significantly advance the calculations of the rates of adsorption processes compared with the collision model used by Langmuir [33]. The statistical sums of the initial reagents and AC in formula (5) make it possible take into account the contributions of the internal degrees of freedom.

For the gas phase, the independent consideration of the translational, rotational, and vibrational motions of reagents and AC is justified [61, 65]: $F_i = F_i^{tran} F_i^{rot} F_i^{vib}$. In [14], this multiplicative representation was extended to surface processes in the absence of lateral interactions. At present, the expression similar to the representation of F_i statistical sums is extended to any states of the reaction system. Despite its approximate nature, it makes it possible to take into account the factor of degeneration of one or another degree of freedom (translational, vibrational, and/or rotational) depending on the bond energy with the surface.

Later, Temkin's TARR for uniform surfaces was also generalized by him to nonuniform surfaces for the description of interactions between adsorbed molecules, adsorption equilibrium, and the kinetics of heterogeneous processes [2]. His consideration of surface nonuniformity also became a classic work [62–64].

2.2. Consideration of Lateral Interactions

When considering lateral interactions in adsorption and kinetics on nonuniform surfaces [2], Temkin used the virial theorem by analogy with the work of Langmuir describing the dipole–dipole interactions in the Cs/W system [66]. The Temkin equations were written without specifying the type of the potential in order to extend the application to a wider range of coverages compared with the work by Langmuir, which was valid for relatively low coverages. As a result, equations were constructed in the mean field approximation, in which there were no correlation effects between interacting species.

It should be noted that, by that time, there were already equations for the equilibrium and kinetics of

adsorption and desorption within the framework of the collision model [67]. In the collision model, the state of adsorbed species is almost completely unrelated to the state of the gas phase molecules; therefore, there is no transition state in this model, which is a necessary concept for TARR. The consistent consideration of AC properties has not been performed for a long time, which was a challenge to the theory. Numerous attempts to overcome this problem are described in detail in the review [68].

2.3. Cluster Approach

By 1972, a situation had arisen where the theory of correlation functions [69, 70], which was more flexible than the method of partition functions, made it possible to reflect the local correlations of interacting species, was used to solve the problem of considering the properties of AC. These methods were used in the framework of the impurity approach [71, 72] to problems in the Ising model. It was proposed to use an impurity approach to calculating the rate of the elementary process assuming that AC is an impurity to the reactants in the reaction system [73]. This approach took into account the statistical nature of the distribution of the impurity and the entire spectrum of correlations between the adsorbed species, but the association of AC with the impurity excluded the dynamic nature of the elementary process assumed in TARR [2, 14, 61, 65].

In the work by Fejanin [73], the concentration of AC was expressed as $C_m = \exp(-\beta\varepsilon_{AC}) \langle U_m \rangle$, where ε_{AC} is the activation energy for the appearance of AC; $\beta = 1/(k_B T)$;

the average value $\langle U_m(f) \rangle = 1 - \theta_f + J'_m \sum_{k=0}^{z} \frac{x^k}{k!} F_k(f)$

was obtained by averaging over all local configurations of neighbors near different states of the central impurity site; J'_m is the ratio of statistical sums of AC and the initial reactant (species in desorption and vacancies in adsorption); $x = \exp[\beta(\varepsilon^* - \varepsilon)] - 1$, where ε is the energy of interaction between neighboring adsorbed species; ε^* is the energy of interaction of AC with the neighboring species. Functions F_k reflect the spectrum of probabilities of various configurations of a neighboring species that participates in the elementary process.

This version of the theory was reported on April 23, 1973 at a meeting of specialists in Moscow at the seminar "Theoretical Problems of Diffusion Kinetics" and on October 31, 1973 at the Leningrad Seminar "Theory of Surface Phenomena" (Fedyanin V.K. and Tovbin Yu.K. "Kinetics of monomolecular adsorption and desorption on a uniform surface"). However, at the laboratory seminar (at that time Fedyanin worked in the Temkin's laboratory, and Tovbin worked in the Laboratory of Mathematical Modeling) Temkin emphasized the need to reflect the dynamic nature of the presence of AC in the reaction system, and not as

a stable species with a small concentration. Therefore, in [74], this model was presented as a comparison of the contributions of two terms of the sum of U: $(1 - \theta_f)$ and $J'_m \sum_{k=0}^{z} \frac{x^k}{k!} F_k(f)$. The contribution of the first term could vary from zero to unity. The contribution of the second term, containing the factor known in TARR as the frequency factor, which is in J'_m and proportional to $k_B T/h$ is much greater than unity. Therefore, the contribution of the first term can be neglected. All calculations were carried out using this simplified formula and an experiment on the desorption of potassium atoms from the surface of tungsten was described [75], which reflected the influence of lateral interactions.

Thus, a dilemma has arisen: either a Temkin model with no correlation effects, but with the dynamic nature of AC in the system of species with lateral interactions or an impurity approach based on correlation functions with a full correlation spectrum. A different construction of theory was required. Full agreement between the co-authors was achieved 5 years later, when it was possible to reformulate the impurity model so that it reflected the dynamic nature of AC [76, 77]. In the second version, $C_m = \exp(-\beta\varepsilon_{AC}) \langle n_f U_m \rangle$, where n_f is the filling number of site f with adsorbed species ($n_f = 1$ for species A and $n_f = 0$ for a vacancy). Then the process binding to the initial species in site f automatically reflected the state of filling the site and the only possible course of the process (either adsorption or desorption). As a result, we managed to keep all the probability calculation technique from the work by Tyablikov and Fedyanin [72], and the physical meaning was preserved as in Eyring and Temkin's theory.

On this basis, a "cluster approach" was developed for atomic–molecular processes in any condensed phases [78, 79], and it was extended to any number of components in the mixture. The essence of this alternative approach [78, 79] to the Bogolyubov method for homogeneous systems [69] was the initial consideration of locally inhomogeneous systems, when the exact system of equations for the full spectrum of local correlations was built for each local cluster and then the calculation of all cluster distributions of system components was made consistent for the entire volume. This required the use of approximate methods for calculating local distributions of molecules, but the method of description was the same for the entire system.

2.4. Today's State of the Theory

Currently, the kinetic theory of atomic–molecular processes in condensed phases based on the cluster approach reflects the following physical factors: (1) nonuniformity of the surface or volume of solids, (2) the mutual influence of adsorbed and absorbed species or the components of the solution, (3) differ-

ent sizes of species and blocking several adsorption site by the reactants, (4) limited rates of reactant mobility, (5) surface and/or volume restructuring in solids, (6) external fields, and (7) high pressures in the gas phase. The idea of the ordering of components in solutions (as in ionic melts) was extended to the reaction systems [80] and used in surface processes [81, 82]. It is important to note that expressions for calculating the rates of different types of stages are consistent with each other and the expression for the rate of each stage takes into account all the above-mentioned real properties of the system throughout the entire range of densities and temperatures. These issues are described in more detail in the monograph [79] and publications [83–85].

The model of two-dimensional electron gas proposed by Temkin in [86] should be mentioned. It gives the same concentration dependences for the isotherm and heat of adsorption, as the model for taking into account lateral interactions in the mean field approximation taking into account surface nonuniformity at medium coverages. He kept returning to it up to his review article [87]. The main idea was the linear dependence of the kinetic energy of the electron gas as the isolated zone of the surface states was covered. However, subsequent more detailed studies have not confirmed its validity. This concerns the consideration of the effects of screening electrons of a two-dimensional system [88–90] and numerous subsequent works on quantum chemical calculations of the electronic states of a surface. The model [86] admits a simple generalization to the kinetics of surface processes, but, in fact, presents a phenomenological description of effects that are different from the direct correlation effects of nearest neighbors.

3. GENERAL QUESTIONS OF THE DESCRIPTION OF CONDENSED PHASES

It is necessary to outline a range of issues related to the description of condensed phases using examples of surface processes in dense monolayers and in volume of a gas. These include (3.1) the work on the description of the catalytic process of high-pressure ammonia synthesis [91], (3.2) the difference in interpretations of taking into account the nonideality of the reaction medium in the works of Temkin [2, 91] and the Eyring school [65] and the requirement for theories to satisfy the concept of self-consistency in the description of the rates of elementary stages, and (3.3) the equilibrium states of the reaction system [2, 91].

3.1. Ammonia Synthesis at High Pressures

In describing the process of ammonia synthesis at high pressures, a qualitatively new concept of the compressibility of the adsorption layer was introduced [91]. Under these conditions, the concept of pressure

related to the gas phase should be replaced by fugacity, and the rate constants in the rates expressions of elementary reactions should be modified to take into account the effect of adsorption equilibrium shift on the catalyst surfaces. Temkin [91] took into account the nonideality of the gas phase, the nonideality of the system of adsorbed species, the influence of the nonideality of adsorbed species on the kinetics of the elementary stages, and the catalyst surface nonuniformity. The inclusion of these factors [91] made it possible to obtain a final expression for the rate of ammonia synthesis, in which the self-consistency in the description of the rates of the elementary stages in the equilibrium of the reaction system was fulfilled.

3.2. Consideration of Nonideal Reaction Medium

It should be recalled that, in the Eyring theory, when switching to nonideal systems, it was recommended to introduce activity coefficients for both reagents and AC for the considered stage. The reaction rate is written in the form of mass action law $U_{AB} = K_{AB}^* n_A n_B$ (3), but for nonideal reaction systems, the rate constants of elementary stages are written as $K_{ij}^* = K_{ij} \alpha_i \alpha_j / \alpha_{ij}^* \exp(-E_{ij}/k_B T)$, where $\alpha_i = a_i/n_i$ is the activity coefficient of reactant i, α_{ij}^* is the activity coefficient of the AC, K_{ij} is the reaction rate constant in the ideal system.

By definition, the activity in thermodynamics a_i depends on all concentrations of solution components and on all their molecular properties, including the intermolecular interaction energies [92]. Therefore, the rate constant is "hooked" on to all the physicochemical properties of the reaction system through the activity coefficients [93, 94]. Additional contradictions are related to the fact that, in the case of a lack of equilibrium, the very notion "chemical potential" μ_i does not exist, and the value of the activity coefficient of AC (α_{ij}^*) cannot always be determined and justified. For its construction, averaging over all possible states of the environment (over all configurations and sorts of neighboring molecules) is required, while a change of a neighbor changes the reaction conditions. The way out of this situation is possible only through direct consideration of molecular interactions and the rejection of thermodynamic bonds.

In this respect, Temkin's work [2, 91] was geared to the inclusion of direct model constructions reflecting the interactions of AC with its neighbors in order to avoid the use of thermodynamic relations. As indicated above, the problem of correct consideration of the nonideality of reaction systems in the entire range of densities remained unsolved for a long time. To illustrate the contrast between the Temkin concept (the absence of the AC activity coefficient) and the
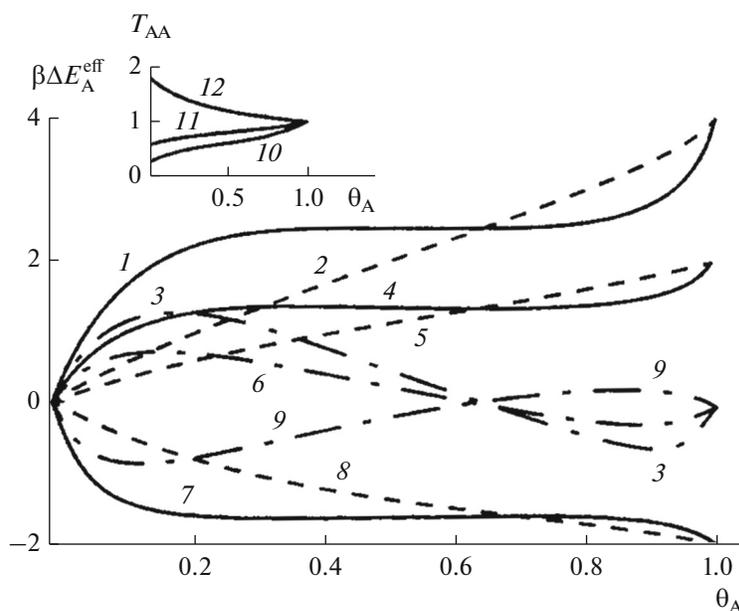
Fig. 1. Effective activation energies for the rates of (*1, 4, 7*) slow and (*2, 5, 8*) fast monomolecular reactions, (*3, 6, 9*) their difference $\beta[\Delta E_A^{eff}(\text{slow}) - \Delta E_A^{eff}(\text{fast})]$ and (*10–12*) the $T_{AA} = t_{AA}^*/t_{AA}$ function (inset) at $s = 2$, $\beta\varepsilon_{AA} = 1$ and various ratios $\varepsilon_{AA}^*/\varepsilon_{AA}$: (*1–3, 10*), 0.5 (*4–6, 11*), and 1.5 (*7–9, 12*).

Eyring concept (the presence of the AC activity coefficient) we give two examples of these two ways of taking into account the influence of the environment for the isothermal and nonisothermal desorption process. For the simplest one-component system, the "medium" is represented by other molecules A, and relaxation (establishment of equilibrium) consists in the redistribution of molecules around AC during their migration.

Figure 1 shows the calculated rates of the fast and slow monomolecular reactions and $-\ln\eta_A$, where $\ln\eta_A = -\ln(U_A(\text{slow})/U_A(\text{fast})) = \beta[\Delta E_A^{eff}(\text{slow}) - \Delta E_A^{eff}(\text{fast})]$, $\beta\Delta E_A^{eff} = -\ln(U_A/U_A^{ideal})$ for the entire range of variation of the density of reagent A [95]. These calculations correspond to the rate of nondissociative desorption on a square lattice ($z = 4$). Here, the effective activation energies characterize the degree of deviation of the reaction rate in a nonideal reaction system from the ideal one. The inset to Fig. 1 shows the concentration dependences of the relationship $T_{AA} = t_{AA}^*/t_{AA}$ (where t_{AA} and t_{AA}^* are the probabilities of finding species A near another species A and near AC, respectively), which characterize local changes in the distributions of components A due to their migration under the influence of AC for a slow reaction. This ratio tends to unity at $\theta \geq 1$, and the maximum effect of AC is manifested at small θ: $T_{AA} = \theta\exp(\beta\delta\varepsilon_{AA})$. For a fast reaction, $T_{AA} = 1$ for all θ.

Figure 1 shows a qualitative difference in the concentration dependences of the reaction rates for differ-

ent medium relaxations: in the absence of relaxation, $\ln U_A(\text{fast})$ changes almost linearly with increasing θ, and during equilibrium relaxation of the medium, $\ln U_A(\text{slow})$ changes dramatically in the $\theta < 0.2$ and $\theta > 0.8$ regions and remains almost constant at $0.2 < \theta < 0.8$. This general property of the influence of the nature of the relaxation of the medium is also preserved for other situations: the monomolecular and bimolecular stages in solutions that were studied in [95]. It forms the basis for analyzing the experimental concentration dependences of the logarithms of the reaction rates in a wide range of concentrations.

Thermal desorption curves in Fig. 2 are given for slow (a) and fast (b) relaxation of the medium [96]. Curves are presented for different initial surface coverages: (*1*) 0.99, (*2*) 0.7, (*3*) 0.5, and (*4*) 0.3. Thermal desorption curves are obtained by linear heating of the surface according to the law $T = T_0 + bt$, where b is the heating rate (K/s), T_0 is the initial temperature for which at the initial moment of time the initial surface coverage is θ_0. The differential equation $d\theta/dT = -U_d$ is solved, where U_d is the desorption rate for a given initial coverage $\theta_{t=0} = \theta_0$.

The parameters of the curves in Fig. 2a were obtained from experimental data for the CO–Pt system [68, 79] using the model from [76, 77]. The same parameters according to the Eyring concept are given in Figs. 2b. Comparison of the effective activation energy of the process in Fig. 2c, where curve *1* corresponds to Fig. 2a, and curve *2* corresponds to Fig. 2b shows that the strong repulsion of CO molecules leads
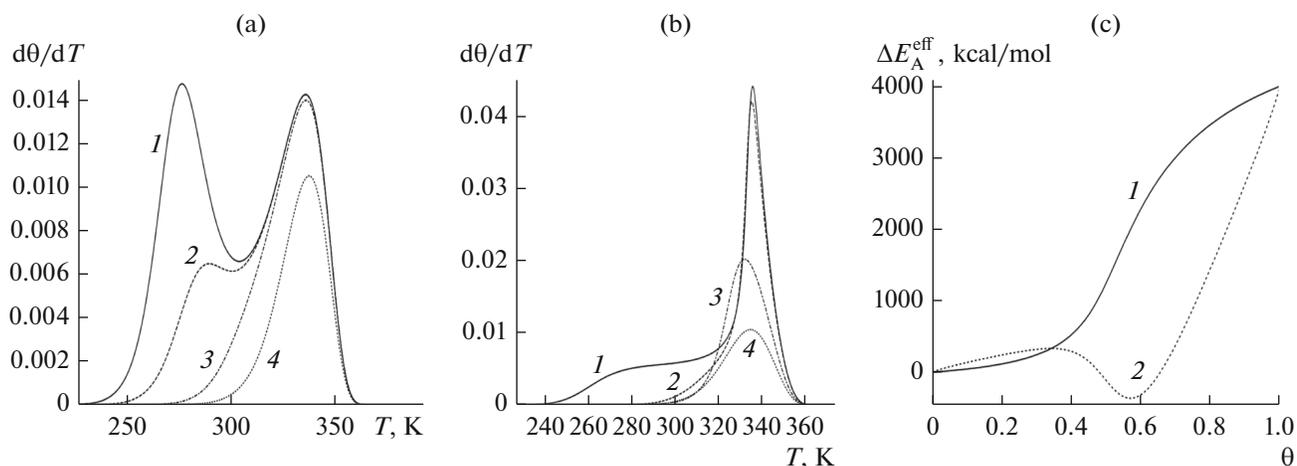
Fig. 2. Thermal desorption curves for the CO−Pt system for (a) fast and (b) slow process of monomolecular desorption at different initial coverages θ_0: (*1*) 0.99, (*2*) 0.7, (*3*) 0.5, and (*4*) 0.3 [96]. (c) The concentration dependence of the effective activation energy ΔE_A^{eff} due to the influence of lateral interactions calculated for monomolecular desorption at $T = 300$ K in the case of (*1*) fast and (*2*) slow processes.

to splitting the thermal desorption curve. According to the Eyring scheme, a characteristic curve is obtained for a first-order phase transition corresponding to the case of strong attraction of species in the system (which qualitatively distorts the physical meaning of the parameters of interaction between species). These examples show that the Temkin's concept is physically correct, and the Eyring's concept is not.

3.3. The Concept of Self-Consistency in the Description of Rates of Elementary Stages

The concept of a self-consistency in the description of the rates of kinetic processes and equilibrium in nonideal and nonuniform systems used in [2, 91] is key to the relationship between equilibrium and kinetics as a limiting transition in time. This means that the equilibrium distribution of molecules in the reaction system should follow from the condition of equality of the rates in the forward and reverse directions of the elementary reaction. In the kinetic theory of gases, all new proposed approaches are checked against this condition. In the condensed phases, this is not done for many reasons (primarily due to the lack of the equation of state in dense liquid, adsorption, and solid phases).

It was noted above that a rough description of the effects of correlation does not allow us to construct correct expressions for the rates of elementary stages. In [97−102], different versions of taking into account interactions between species on uniform and nonuniform surfaces were analyzed. The proof of the fulfillment of the self-consistency condition for the general case of taking into account the surface nonuniformity and lateral interactions in the quasichemical approximation was given in [68] (see also [103−105]). It was

proven that the theory provides a self-consistent description of dynamics and equilibrium on all spatial scales for any densities, temperatures, intensities of lateral interactions and external fields only if the correlation effects are taken into account at least for the short-range order. Otherwise, the self-consistency condition is violated; therefore, the molecular/mean field approximation, the chaotic approximation, and the density functional theory cannot be used to describe the dynamics in dense phases.

However, it is necessary to point out that the concept of self-consistency is necessary, but not sufficient. The presence of self-consistency does not automatically mean the correctness of the equations for the rates of stages, since the equations for isotherms may also be incorrect at the same time. As an example, we point out mean field approximation, chaotic approximation, and density functional for any one- and two-site stages on a uniform surface, as well as for single-site stages on a nonuniform surface in the mean field approximation, since it levels out all nonuniformities of the system [106]. The same applies to the Temkin equations of 1941 and 1950 that used the same approximation. For a nonuniform surface, equations [2] do not allow the splitting of the thermal desorption curves, which are indicated by experiments [68, 79, 107]. This disadvantage is due to the lack of consideration for correlation effects. Finally, this applies to all cases of the use of the mass action law equation, when it does not reflect the physical state of the system, due to the interactions between the components of the reaction system.

It should be noted that in the discussed processes, at the atomic−molecular level, the rates of the stages relate to any degrees of deviations from the equilib-

rium state, and not only to small deviations, as assumed in the Onsager approach [108, 109]. The concept of self-consistency imposes a restriction on the method of constructing equations for the stages at this microscopic level (although formally it is completely transferred to more detailed level-by-level kinetics in Pauli-type equations [110, 111]).

In the development of Temkin's ideas on the dynamic nature of the elementary act of any interaction of particles and Bogolyubov's ideas on a unified method for calculating the distribution of particles [69], a "cluster approach" was developed for inhomogeneous systems of any density (any phases) both in equilibrium and in kinetics with any degrees of deviations from equilibrium [79, 112, 113]. The master equation for the evolution of the total distribution function of the system $P(\{I\}, \tau)$ that is at time τ in the state $\{I\}$, $\{I\} \equiv \left\{\gamma_f^j\right\} \equiv \gamma_1^i, ..., \gamma_M^i$ (where γ_f^j refers to the occupied state i of site f, and braces refer to the complete list of sites of the system M) due to the realization of elementary processes α has the form:

$$\frac{d}{d\tau} P(\{I\}, \tau) = \sum_{\alpha, \{I\}} [W_\alpha(\{II\} \to \{I\}) P(\{II\}, \tau)$$
$$- W_\alpha(\{I\} \to \{II\}) P(\{I\}, \tau)], \tag{6}$$

where $W_\alpha(\{I\} \to \{II\})$ is the probability of realization of the elementary process α as a result of which the system passes from state $\{I\}$ to state $\{II\}$ by the time τ. The sum over α is the sum over all possible transitions for all realizable states of the system.

The probabilities W_α of transitions α obey the condition of detailed balance

$$W_\alpha(\{I\} \to \{II\}) \exp(-\beta H(\{I\}))$$
$$= W_\alpha(\{II\} \to \{I\}) \exp(-\beta H(\{II\})), \tag{7}$$

where $H(\{I\})$ is the full energy of the system in state $\{I\}$. In the equilibrium state $P(\left\{\gamma_f^i\right\}, \infty \to \tau) = \exp(-\beta H(\left\{\gamma_f^i\right\}))/Q$, where $Q = \sum_{\{I\}} \exp(-\beta H(\left\{\gamma_f^i\right\}))$ is the statistical sum of the system over all variables of the system.

It should be noted that, by the early 1980s, in the Glauber kinetic equations (master equations) used to describe spin systems and crystal growth processes, phenomenological probabilities of transitions W_α between different states of spins, molecules, or systems were usually used [68, 114]. Only in 1982, the requirement was first formulated for the transition probabilities W_α in the Glauber and/or Pauli equations on the basis of the master equation to satisfy the theory of chemical reactions and/or scattering [112, 113] and the condition of self-consistency that Temkin so actively used. This is currently a generally accepted idea.

This principle made three levels consistent: the quantum level for calculating energy, the dynamic level for an elementary act, and the statistical level for calculating the probabilities of particular configurations of neighbors, and the third level determines the first two.

Currently, the cluster approach has the same level generality of application as thermodynamics [115]: the self-consistent description of equilibrium and non-equilibrium processes in three states of matter and at phase boundaries is possible.

In the modern theory, the key role belongs to the correlation effects of interacting adsorbed species on the surface or atoms inside a solid catalyst or adsorbent with their spatial distribution. In the latter case, the effects of correlation form adsorption and catalytic sites, and their description is necessary for describing processes on complex nonmetal catalysts [116, 117]. The rate equations [79, 112, 113] form the basis for modeling the formation of various types of catalysts and provide methods for constructing multidimensional distribution functions $f(Q_1, ..., Q_n)$ of an adsorption site for multicomponent reaction systems [118, 119]. Thus, the idea of the important role of strong correlations of the interacting components of solids goes from the model of ionic melts to the models of the formation of modern catalytic and polyfunctional systems.

CONCLUSIONS

Statistical thermodynamics of ideal systems allowed Temkin to obtain his classical results at the beginning of the formation of physical chemistry in the 1930−40s. The same rigorous methods of statistical thermodynamics are necessary for the further development of modern physical chemistry, the theory of kinetic processes, and catalysis.

The theory of absolute reaction rates for all homogeneous and inhomogeneous surfaces (in the absence of lateral interactions) should be named after Temkin since he was its real author.

As mentioned above, today in the field of heterogeneous catalysis, interest is strongly shifted toward processes that occur on nonmetallic catalysts and polyfunctional systems. Their detailed kinetic description is extremely difficult due to the problems of determining the nature of the activation sites. Nevertheless, the previously developed approaches can be applied to describe complex systems by generalizing the distribution functions of adsorption sites for various components in the reaction mixtures. Such models, of course, can be applied to all multistage heterogeneous catalytic reactions and when modeling the processes of outer and inner mass and heat transfer in heterogeneous catalysis. The current state of the theory of adsorption and kinetics of surface processes makes it possible to take into account various physicochemical factors of reaction systems at the same time.

The concept of a self-consistent description of reaction rates and equilibrium used by Temkin is key in any complex situations outside the applicability of

the models of ideal reaction systems as well. The use of condensed phase methods made it possible to obtain a solution to the problem of self-consistent temporal and equilibrium description of the distribution of interacting species over sites of uniform and nonuniform lattices, and this makes it possible to solve many problems describing processes at gas–solid interfaces. Various studied processes (adsorption, absorption, diffusion of species, and surface reactions) indicate the fundamental role of cooperative effects that are due to the interaction between the components of the reaction system in the kinetics of these processes. Modern theory can be used for practically important catalytic processes, since they form the basis for studying changes in the catalyst activity related to thermal stability, sintering, poisoning, etc.).

Close tasks arise when studying the nature of surface segregation of alloys in vacuum and gas phase, in crystal growth from the gas phase and crystal sublimation, during the formation and removal of protective films, during surface etching and the impact of species with different energies on it, etc.

The formulated general self-consistency conditions indicate how to achieve self-consistency in all condensed phases.

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Translated by Andrey Zeigarnik