

On the Scientific Heritage of Mikhail Isaakovich Temkin

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Abstract—The article presents a retrospective of the main scientific works of an outstanding physical chemist M.I. Temkin (1908–1991) on the kinetics of catalytic reactions and chemical engineering, as well as other branches of physical chemistry. The historical significance of theoretical studies by Professor M.I. Temkin for the development of modern ideas on catalytic kinetics is shown and their development and application in modern scientific practice is discussed.

Keywords: Temkin, kinetics, complex reactions, catalysis, mass transfer

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“On October 1, 1991, Mikhail Isaakovich Temkin, a prominent physical chemist and a world-famous scientist, passed away.” This was the beginning of the obituary [1] co-authored by researchers who worked with Mikhail Temkin for a long time in the Laboratory of Chemical Kinetics at Karpov Physico-Chemical Institute (Fig. 1) and by myself, who started to work in the laboratory in early 1986.

Since then, two more times I returned to the analysis of the research work by Mikhail Temkin (or Tyoma, as many called him treading in Academician A.N. Frumkin’s steps). These were a rather formal listings of the main works by Mikhail Temkin [2] and a less formal description of the personality of my thesis advisor [3] or, as they say in Germany, *Doktorvater*. The last article contained a number of anecdotal his-

torical details reflecting the difficult fate and personality of Professor Temkin. Not everything, of course, was mentioned there. I remember, for example, my sophomore year at the Department of Chemical Engineering of the Mendeleev Moscow Institute of Chemical Technology. At a lecture on physical chemistry devoted to the Temkin–Schwartzman method for calculating the temperature dependence of the Gibbs energy or equilibrium constants (Fig. 2), I was very surprised to hear from the lecturing professor-electrochemist that coefficients M in the equations were thus called after Misha (nickname for Mikhail) Temkin. The lecturer was apparently displeased by the inventor of the method.

One could only guess that, at some point in his scientific career, that lecturer of mine had to face the mocking disposition of Professor Temkin, who sometimes made undiplomatic comments on the level of scientific works that he did not like.

A few years later, when I began to work in the Temkin’s laboratory, he told various stories about his scientific life, lectures by Nikolay Zelinsky at the Moscow State University, scientific stay with Michael Polanyi in Manchester and encounters with Hugh Taylor, overnight stays in Leningrad with Nikolay Semenov who was developing his theory of chain reactions at that time, collaboration with Alexander Frumkin, conflicts with Nikolay Kobozev who was Temkin’s diploma thesis advisor, translation of Linus Pauling’s lectures from English into Russian during his visit to Moscow, somewhat clouded relationships with Veniamin Levich and Georgii Boreskov, and Temkin’s opinion on the work of Aleksey Balandin and Juro Horiuti, and so on.



V.L. Kuchaev M.I. Temkin N.V. Kul'kova F.S. Shub

Fig. 1. M.I. Temkin with senior research scientists of the Laboratory of Chemical Kinetics at the Karpov Institute.

29. Величина M_n для вычисления термодинамических функций по методу Темкина и Шварцмана

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ - T (\Delta a M_0 + \Delta b M_1 + \Delta c M_2 + \Delta d M_3 + \Delta c' M_{-2})$$

ΔH_{298}° – стандартный тепловой эффект

$$\Delta S_{298}^\circ = \sum (n_i S_{298}^\circ)_{\text{прод}} - \sum (n_i S_{298}^\circ)_{\text{исх}}$$

$$\Delta a \text{ (соответственно } \Delta b, \Delta c, \Delta d, \Delta c') = \sum (n_i a)_{\text{прод}} - \sum (n_i a)_{\text{исх}}$$

$$M_n = \ln \frac{T}{298,15} + \frac{298,15}{T} - 1$$

$$M_n = \frac{T^n}{n(n+1)} + \frac{298,15^{n+1}}{(n+1)T} - \frac{298,15^n}{n} \text{ (при } n \neq 0)$$

T	M_0	$M_1 \cdot 10^{-3}$	$M_2 \cdot 10^{-6}$	$M_{-2} \cdot 10^8$	$M_3 \cdot 10^{-9}$
300	0,0000	0,0000	0,0000	0,0000	0,00000
400	0,0392	0,0130	0,0043	0,0364	0,00144
500	0,1133	0,0407	0,0149	0,0916	0,00553
600	0,1962	0,0759	0,0303	0,1423	0,01246
700	0,2794	0,1153	0,0498	0,1853	0,02257
800	0,3597	0,1574	0,0733	0,2213	0,03630
900	0,4361	0,2012	0,1004	0,2521	0,05411

Fig. 2. The Temkin–Schwartzman method [4].

Temkin loved to tell stories. Since he had been working with the same team for many years, it was not surprising that he enjoyed telling stories to his one and only graduate student, who also unfortunately, turned out to be the last one.

In this article, I do not want to recall these real or perhaps somewhat confabulated stories and legends that create a certain halo around Temkin's name or to list all known details about the works of Mikhail Temkin again. This has been done already [2, 3].

Instead, it seems appropriate to make a feeble attempt to reflect Temkin's scientific heritage in the context of its development and current scientific trends, although I understand the subjectivity of such analysis. Definitely, this is difficult to do for any disciple. To be objective in estimating the impact of someone's research supervisor, it is necessary to distance mentally and physically from him or, alternatively, it should take a long time making it possible to rethink the teacher's research work. This time has probably come. Another challenge is how to discuss the development of the research ideas of the Temkin's school. Sheer reproduction of the ideas of a scientific leader who founded a scientific school usually leads only to popularization of such ideas, often in a rather simplified form. In the case of Mikhail Isaakovich, It would be ideal to discuss what has been done over the past 30 years in the kinetics of heterogeneous catalytic processes that do not automatically follow from Temkin's system of knowledge. This should be done separately and first attempts have already been made [5].

In addition, it seems interesting to analyze the situation and the environment in which Temkin worked, and to do so, I have to talk about what the Karpov Physico-Chemical Institute or Karpov Institute for short was and who were Temkin's teachers.

Karpov Institute occupied a special place in the system of Soviet science. This was due to the fact that the institute operated under the Ministry of Chemical Industry, not being a typical applied research institute. The first director of the Karpov Institute, initially the Central Chemical Laboratory, was Academician Aleksei Bach, who returned from many years of emigration. Bach was the first scientific advisor of then young Mikhail Temkin, who had just started to work at the Karpov Institute after graduating from the Moscow State University in 1931 and had a reputation as a prodigy. The style of scientific work of the Bach's laboratory and the whole institute was a combination of fundamental science and practice. In the Soviet Union, the development of the chemical industry required the creation of specialized research organizations focused on specific chemical and technological problems. Some of these institutes (Institute of Nitrogen Industry, Institute of Plastics, Institute of Artificial Fibers, Coal Institute, Institute of Special Chemistry, etc.) were formed by split-off from the Karpov Institute. This allowed the employees to focus on the theoretical problems of physical chemistry without losing their connection with industry. This was, perhaps, the unique feature of the Karpov Institute, which was neither a typical applied research nor a typical institute within the Academy of Sciences of USSR. To some extent, the experience of the Karpov Institute was repeated by the Institute of Catalysis (Siberian Branch of the USSR Academy of Sciences), which is not surprising, since founders of that Institute G.K. Borekov and M.G. Slinko worked for many years at the Karpov Institute (Fig. 3).

Karpov Institute had several departments that studied various aspects of physical chemistry: catalysis, kinetics, structure of matter, and quantum chemistry, synthesis and properties of polymers, electro-

chemistry and corrosion, surface phenomena, aerosols, radiation chemistry and even the theoretical foundations of chemical technology. A characteristic feature of the Karpov Institute that influenced the scientific activity of Temkin, who worked in the same laboratory all his life, was basic science inextricably linked with the solution of practical problems.

Operating within the Ministry of Chemical Industry affected the choice of processes studied by Temkin. When preparing this article, I carefully looked once again at the entire list of publications by Temkin trying to focus on a purely chemical component: catalytic reactions, which kinetics was studied in the Laboratory of Chemical Kinetics at the Karpov Institute. Work on the kinetics of ammonia synthesis certainly brought him the main fame. This is described by the Temkin–Pyzhev equation:

$$r = k' P_{N_2} \left(\frac{P_{H_2}^3}{P_{NH_3}^2} \right)^m - k'' \left(\frac{P_{NH_3}^2}{P_{H_2}^3} \right)^{1-m}, \quad (1)$$

where r is the rate, k' , k'' , and m are constants, and P_i are the reactant pressures. It was derived on the basis of the idea that the reaction rate is determined by nitrogen adsorption on the energetically nonuniform surface. Temkin continued to work on the kinetics of ammonia synthesis for many years, and its contribution to the study of this reaction is beyond any doubt. Thus, in the introduction to the article on ammonia synthesis [6] Michel Boudart wrote about Temkin's work of 1940:

The three seminal ideas in this early work of Temkin are powerful because of their generality. The first one is that adsorption of nitrogen is rate determining, with a clear notion of the now accepted meaning of the rate determining step. The second one is the virtual pressure or fugacity of adsorbed nitrogen, a concept of great importance to the understanding of catalytic cycles at the steady-state. Indeed, it implies that the active adsorbed intermediates are not necessarily in equilibrium with fluid phase species, as assumed in conventional Langmuir–Hinshelwood kinetics. The third idea is the kinetic description of the catalytic surface as a non-uniform one. The last was systematized later by Temkin's school both in theory and application to a large number of important catalytic reactions. The importance of Temkin's theory of kinetics on non-uniform surfaces is not so much in its formalism to fit kinetic data, but in the deeper kinetic understanding of how any catalyst works and how to select the catalyst with the fastest turnover rate [3].

Like the kinetic concepts of Christiansen and Horiuti, those of Temkin were far ahead of their common acceptance by the catalytic community. Even today, more than fifty years after the Temkin–Pyzhev paper, the idea of fugacity of adsorbed species is not appreciated by the majority of workers in catalytic kinetics.



Fig. 3. Employees of the Karpov Institute at the May Day demonstration: V.M. Cherednichenko, M.G. Slinko, G.L. Borekov, N.V. Kul'kova, L.I. Luk'yanova (from the private archive of N.V. Kul'kova).

The life work of Temkin is inseparably linked to ammonia synthesis. It illustrates vividly how so many of the general concepts in heterogeneous catalysis have originated and still are tested in the study of ammonia synthesis.

In addition to ammonia synthesis, several other processes for the production of syngas from natural gas, including methane steam reforming and water-gas shift reaction, should be noted.

Some reactions that were studied in the Temkin's laboratory were also associated with large-scale processes in the chemical industry, such as ethylene oxide and methanol synthesis and ammonia oxidation. Fewer works were devoted to reactions required in the production of basic organic synthesis, namely the synthesis of acrylonitrile or ethanol by ethylene hydration. Most likely, this is due to the fact that this type of work was concentrated in another laboratory of Karpov Institute, namely the Laboratory of Organic Catalysis led by Professor A.I. Gel'bsteyn.

In the 1970s and 1980s, there was a need for the scientific support for the practical work of the State Institute for Nitrogen Industry (GIAP) for the production of caprolactam. Hence, Temkin's interest in the synthesis of hydroxylamine sulfate, hydrogenation of benzoic acid, phenol, and benzene (the topic of my PhD dissertation). Since I was a graduate of the Department of Chemistry and Technology of Organic Synthesis, this subject was closer to me, and its development first at the Karpov Institute and later in other places in the 1990s was associated with hydrogenation of substituted aromatic compounds, including substituted phenols, which made it possible to discuss the issues of stereo- and enantioselectivity. The kinetic analysis of the above reactions was no longer due directly to their industrial implementation, and Tem-

kin once told me when writing a project on this topic that in his work he tried to avoid studying the kinetics of fine organics synthesis.

Indeed, in addition to already mentioned above there are relatively few reactions that have been studied in the Temkin's laboratory, including carbon monoxide chlorination, ethylene hydrogenation, and formic acid decomposition. Perhaps this is all. It is interesting that some of these works, such as the hydrogenation of aromatic hydrocarbons or the decomposition of formic acid, turned out to be in demand many years later due to new problems associated with the catalytic conversion of biomass components, in particular lignin and hemicelluloses.

One can only guess what could be Temkin's contribution to the study of more complex multi-route reactions with interesting chemistry, which would include analysis of selectivity, chemoselectivity, regioselectivity, enantioselectivity, solvent effects, structure sensitivity, size ratio of large organic molecules and nanoscale catalysts, reactions on zeolites with the acid site distribution and pore sizes comparable to the size of molecules, quantitative description of the concentration diffusion in zeolites, catalysis on bifunctional catalysts, understanding the surface diffusion between sites of different types. This list can be continued.

As can be seen from the above list of reactions, there is nothing in it associated with oil refining, and, therefore, with analysis of transformations in multi-component mixtures, which again was determined by the Temkin's place of work, the Karpov Institute, which was part of the structure of the Ministry of Chemical Industry. At that time, another ministry was responsible for petrochemistry and oil refining.

The very first work by Temkin was done under the guidance of Professor N.I. Kobozev [7] and was devoted to oxidation of nitric oxide by ozone. Relations between them were ruined in the early 1950s, when scientific discussions of Kobozev's theory of active ensembles turned into open confrontation, which manifested itself during the All-Union Workshop on Heterogeneous Catalysis in the Chemical Industry [8]. Other teachers in the Karpov Institute were Academician A.N. Bach [9] and Academician A.N. Frumkin with whom Temkin had a long history of collaborative research [10]. The Temkin isotherm

$$\theta = \frac{1}{f} \ln(a_0 p), \quad (2)$$

which is often used for the description of adsorption processes, was obtained by electrochemical measurements by A.N. Frumkin and A.I. Slygin for the hydrogen equilibrium on platinum [11]. On Frumkin's request, Temkin solved the problem of finding such a distribution of the adsorption coefficient $a = a(s)$ over the number s of sites on a nonuniform surface so that the overall Langmuirian equilibrium adsorption on

the sites of all types be close to the logarithmic isotherm:

$$\theta = \int_0^1 \frac{a_s p}{1 + a_s p} ds. \quad (3)$$

Frumkin and Slygin [11] actually acknowledged Temkin's contribution to the development of theoretical ideas about the logarithmic isotherm:

"...Such calculations were carried out by Temkin at our request on the basis of his theory. Details of these calculations will be published elsewhere. Temkin found values for the heat of hydrogen adsorption on platinum varying from 23600 to 10100 cal as the surface was covered...."

A more general solution leads to a quasi-logarithmic adsorption isotherm:

$$\theta = \frac{1}{f} \ln \frac{1 + a_0 p}{1 + a_1 p}, \quad (4)$$

where f is the nonuniformity parameter and constants a_0 and a_1 refer to the strongest and weakest sites of adsorption [12].

In the textbook by Ross [13] it is stated *"...the so-called Temkin equation was first derived by Slygin and Frumkin, but was popularized by Temkin and Pyzhev in connection with their work on the decomposition of ammonia over platinum and tungsten surfaces."* It is difficult to say where this statement came from, since it was Temkin who linked the logarithmic isotherm and a linear decrease in the heat of adsorption with increasing coverage [12]. Temkin wrote [12] that his goal was to solve an integral equation of type (3) and that *"at one time, the author, at the suggestion of Frumkin, solved this problem with reference to the logarithmic isotherm,"* and Zeldovich was busy working on a similar problem for the Freundlich isotherm. The identification of who was the first is not the goal of this article—the more so the physical validity of even nonuniformity of the surface (approximately equal number of different sites) is not obvious. Despite the ambiguity of the physical grounds for the uniform distribution of the surface nonuniformity, and its inconsistency with today's ideas of active sites, the Temkin isotherm (sometimes called the Tempkin isotherm) turned out to be quite popular and is still used because of its simple form.

Temkin derived the equation for the kinetics of ammonia synthesis using the model of biographical (intrinsic) nonuniformity, and applied the same approach to the two-step sequence of catalytic reactions. Even for such a two-step scheme, the derivation of equation is rather complicated [14]. Although the concept of biographical nonuniformity was later extended to more complex linear mechanisms [15] consisting of three or more steps, the very structure of the model with a difficult-to-explain even nonuniformity clearly did not contribute to its widespread use

data of the International Critical Tables for the diffusion constant. All experiments were duplicated, results agreeing within 5 per cent.

The following values of D were obtained for the diffusion of heavy water from ~ 3 mol. per cent solution into ordinary water.

$$D = 1.1 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1} \text{ at } 0.0^\circ \text{ C.}$$

$$D = 2.5 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1} \text{ at } 28.0^\circ \text{ C.}$$

Hence the constants are of the usual order of magnitude, contrary to the result of Orr and Thomson.

My thanks are due to Prof. M. Polanyi for the use of the micropycnometer apparatus and for much valuable discussion.

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¹ NATURE, 134, 776; 1934.
² Z. phys. Chem., A, 186, 254; 1933.

Diffusion of Heavy Water into Ordinary Water

Fig. 4. Excerpt from the article by M.I. Temkin in *Nature*, 1935.



V.M. Pyzhev

M.I. Temkin

Fig. 5. M.I. Temkin's co-workers in the late 1930s.

even for single-route reactions. Already in 1941 Temkin himself considered an alternative to surface heterogeneity, namely, the adsorption layer with the mutual influence of adsorbed molecules [12]. Later, he developed a model of surface electron gas [14], which was later extended to the adsorption of multicomponent mixtures and the kinetics of catalytic reactions [16], including kinetics with catalyst deactivation [17].

I believe that Temkin's collaboration with Polanyi, one of the founders of the modern theory of chemical kinetics, in Manchester in 1934 had a significant impact on Temkin's scientific work in general. It was there that Temkin performed and published an article in *Nature* as the sole author and acknowledged fruitful discussions of the results with Polanyi (Fig. 4). In Manchester Temkin also met Horiuti, who also

worked for Polanyi. Horiuti was yet another prominent specialist in the field of heterogeneous catalytic kinetics with whom Temkin had been in scientific contact for many decades.

Upon returning from Manchester, Temkin began to apply transition state theory to catalytic reactions that led to the publication of a number of fundamental works in this field [18, 19].

As noted above, at the same time the equation for the kinetics of ammonia synthesis [20] was derived, which is often referred to in the literature as the Temkin-Pyzhev equation (Fig. 5).

One of the interesting concepts put forward to explain the kinetics of ammonia synthesis was the concept of virtual fugacity. Michel Boudart in his article "Virtual Pressure and Virtual Fugacity in Catalysis

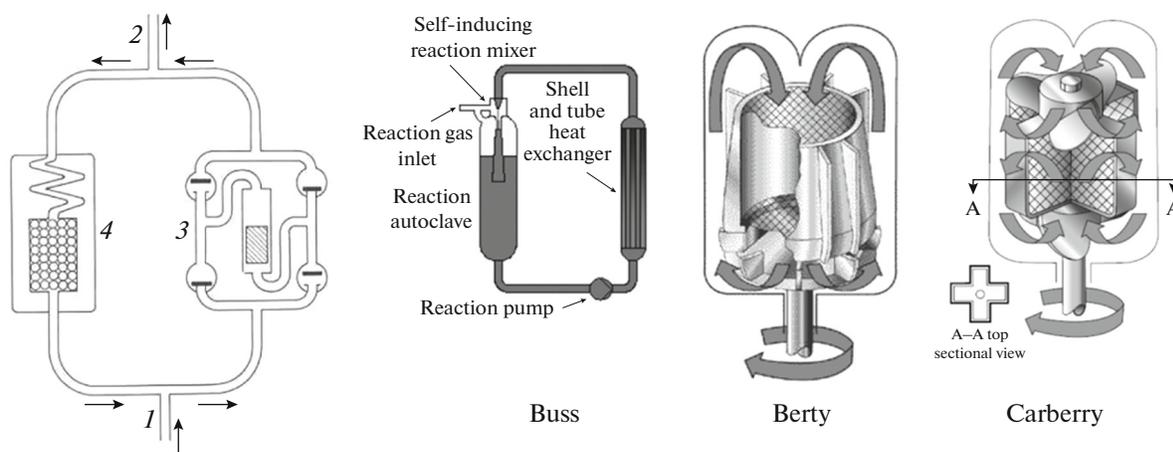


Fig. 6. Gradientless reactors (on the left, Temkin–Kiperman–Luk’yanova loop reactor [30]).

and Electrocatalysis” (*Catalysis Letters*, 1989, volume 3, page 111) gives the following comments on this concept:

“In catalytic reactions, the concept of *virtual pressure* or *virtual fugacity* of a reactant or product was first conceived fifty years ago by Temkin and Pyzhev in connection with ammonia synthesis and decomposition [2]. If we write the

$$v_d/v_a = [N_2]_v/[N_2]_{ss}, \quad (5)$$

where $[N_2]_{ss}$ is the actual pressure (or fugacity) of N_2 in the reacting system at the steady state and $[N_2]_v$ is the virtual pressure (or fugacity) of N_2 defined as the pressure or fugacity of N_2 that would be necessary to reach a surface concentration $[N^*]_{ss}$ prevailing during the steady-state of the reaction, if N_2 were in equilibrium with the surface.”

I would like to note that an interest in the thermodynamic equilibrium between the phases manifested in that work and other publications of the 1940s [21–24] remained with Temkin for a very long time, and for many decades he returned to similar thermodynamic problems [25]. His attention to the kinetics of ammonia synthesis did not weaken, which led to the appearance of a number of works, including those published over decades, including the 1990s [26–28]. Two of them [27, 28] discuss transient processes, namely the establishment of a steady state in flow and circulating flow reactors.

Since the discussion of Temkin’s scientific heritage in this article is not intended to list his works in chronological order, I would like to bounce over to a theme, which is more of engineering rather than a physicochemical nature. In fact, it is quite rare for a physical chemist with a fundamental-science university education like Temkin’s to be interested in the issues of laboratory or industrial reactors, mass transfer in two- and three-phase systems, and diffusion in porous media. This is more likely to be expected from

scientists with a background in chemical engineering. However, in 1957, Temkin published papers on the application of ammonia synthesis kinetics in technological calculations [29] that discussed the role of diffusion in grains. In the same year, a flow circulation gradientless reactor was described by him [30]. In such a reactor, due to the high circulation rate, the conversion per pass is very low and there are no axial and radial gradients. These features of the flow circulation reactor make it possible to avoid integration when analyzing the reaction rate, since the reactor operates in a differential mode. Similar reactors (Fig. 6) have become very popular both in the laboratory practice and in industry (the Buss loop reactor).

Another interesting work related to reactors was published together with Kul’kova [31] and contained a description of a single-pellet string reactor (Fig. 7), or, as it is called, the Temkin reactor (Fig. 8). In this reactor, individual pellets are separated by an inert material. Recently, several papers have appeared where such a reactor was used for catalyst screening [32, 33].

I would like to mention other works by Temkin that refer to engineering chemistry: diffusion of gases [34, 35] and liquids in porous catalysts [36, 37], the calculation of the catalyst efficiency factor [38, 39], and the calculation of the mass transfer coefficient in liquid–solid systems [40],

$$\beta_{Ls} = 1.0 \left(\frac{\varepsilon D^4}{v d_{cat}^2} \right)^{1/6}, \quad (6)$$

and gas–liquid systems [41],

$$\beta_{g-l} = 1.0 \left(\frac{\varepsilon D^4}{v d_{bubbles}^2} \right)^{1/6}. \quad (7)$$

Equations (5) and (6) were derived from the analysis of experimental data using the relationships between the Sherwood number and the Reynolds and Schmidt numbers under the assumption that the

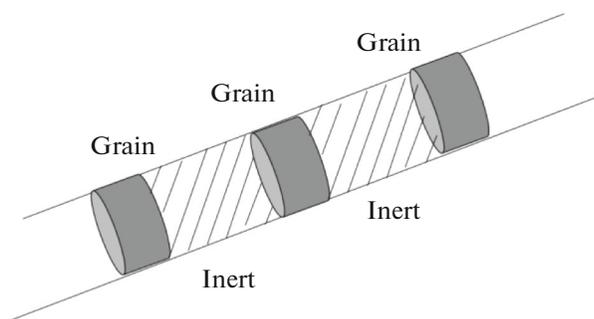


Fig. 7. One-row Temkin–Kul’kova reactor.

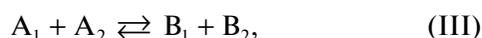
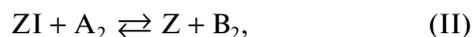
Reynolds number is determined according to the Kolmogorov theory from the dissipation energy. An equation of the form (5) is very convenient for modeling mass transfer and is still actively used in engineering calculations [42]. Its application requires knowledge of the dissipation energy, and the last of the Temkin’s published scientific papers was devoted just to the quantitative determination of the dissipation energy in shaking reactors [43].

Temkin’s studies that connected the elementary reactions at active sites of the catalyst with mass transfer processes at the grain and reactor levels received further development to some extent in the scientific work of his Karpov Institute’s colleague, Mikhail Slinko, who developed at the Karpov Institute and at the Institute of Catalysis in Novosibirsk a spatiotemporal hierarchical approach to obtaining mathematical models of catalytic systems starting from the molecular level [44]. Now this approach is actively applied and further developed by D. Vlachos and co-workers [45].

To some extent, Temkin’s work can be considered as the basis for what became known as microkinetic modeling [46]. When studying the detailed kinetics of heterogeneous catalytic reactions using transition state theory taking into account surface nonuniformity, Temkin together with Horiuti, whom he knew from his work with Polanyi, developed in the 1960s (Fig. 9) the theory of multi-route steady-state complex reactions [47, 48]. The rate equation for a steady-state multistep reaction

$$r = \frac{\prod_{i=1}^s r_{+i} - \prod_{i=1}^s r_{-i}}{\sigma_1 r_{+2} \dots r_{+s} + r_{-1} \sigma_2 r_{+3} \dots r_{+s} + r_{-1} r_{-2} \dots \sigma_s}, \quad (8)$$

despite its relatively complex form can be used for multistep reactions of catalysis by organometallic complexes [49]. A specific case of the multistep mechanism is a two-step scheme [50] with one intermediate species:



where Z is a site, I is a surface intermediate, A_1 and A_2 are initial reactants, and B_1 and B_2 are products. It has become quite widespread, partly due to its popularization by Boudart [51]. A rather simple rate equation for a two-step scheme,

$$r = \frac{k_1 P_{A_1} k_2 P_{A_2} - k_{-1} P_{B_1} k_{-2} P_{B_2}}{k_1 P_{A_1} + k_2 P_{A_2} + k_{-1} P_{B_1} + k_{-2} P_{B_2}}, \quad (9)$$

was used by Temkin for the analysis of the optimal catalyst [52] and the principles of the Balandin’s multiple theory [53].



(10) DE 20 2009 003 014 U1 2010.08.26

(12)

Gebrauchsmusterschrift

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DE	198 61 355	B4
DE	198 50 233	A1
DE	101 17 274	A1
WO	06/0 83 437	A2
WO	02/0 81 075	A1
WO	98/07 026	A1

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Bezeichnung: Temkin-Screening-Reaktor

Fig. 8. Patent of Sued-Chemie (Germany) for a single-row Temkin reactor.



M.I. Temkin

Fig. 9. Employees of the Laboratory of Chemical Kinetics in 1963.

Later, the two-step scheme was used to analyze the influence of structure sensitivity [54], solvent effect [55], and maxima in the Hammett-type dependencies [56].

A recent example of the application of the theory of multi-route steady-state reactions for the thermodynamic analysis of empty (blank) routes for the partial oxidation of methane can be mentioned [57].

The development of the theory of complex multi-route reactions and a need to simulate kinetic data using numerical methods motivated the creation of computer programs for kinetic simulations at the Karpov Institute [58]. The application of the theory of complex reactions to the kinetic and mechanistic description of reactions based on understanding its chemistry, inevitably led to the application of the transition state theory for calculating the rate constants [58]. Later, this approach was used and widely popularized by J. Dumesic [59], Boudart's disciple. It should be noted that the kinetic studies of heterogeneous catalytic reactions in the Soviet Union and in Europe in the 1960–70s were conducted mostly by specialists in physical chemistry in collaboration with mathematicians and process engineers. In the United States, heterogeneous catalysis was mainly studied at the departments of chemical engineering, where, since the 1940s, the purely engineering Hougen–Watson approach dominated for decades. In this sense, the contribution of Dumesic significantly changed the situation not only in the United States, but throughout the world, since the so-called microkinetic modeling with extensive use of theory and quantum chemical calculations became quite popular for the quantitative

description of catalytic reactions [59–62]. For many heterogeneous–homogeneous processes, this approach is, in fact, the only possible [63–65].

Such a creative development of the theory of complex reactions for solving practical problems requires the use of many methods of surface studies, which were not available during Temkin's active work. It should be noted, however, a very interesting series of works carried along these lines at the Karpov Institute back in the 1960s on the study of the heats of adsorption by calorimetric methods [66, 67].

Of the other Temkin's publications on the kinetics of catalytic reactions, I would like to mention probably the first use of membrane catalysis to determine the possible chain nature of catalytic reactions [68, 69] and the use of graph theory to visualize complex reactions [70].

Such graphical methods were further developed thanks to Oleg Temkin, Mikhail Temkin's namesake [71], while other aspects of the kinetics of heterogeneous catalytic reactions are being developed by the current Karpov Institute staff under the leadership of A.K. Avetisov [72–76], who is the head of the Laboratory of Chemical Kinetics since M.I. Temkin left, and by G.S. Yablonsky who also continues the glorious traditions of the Soviet school of kinetics of catalytic processes [77].

This article is mainly devoted to Temkin's research in the field of kinetics of heterogeneous catalysis in a broad sense, including the issues of thermodynamics, phase equilibrium, and mass transfer. In conclusion, I

would like to say a few words about Temkin's work that was completely unrelated to catalysis.

In the post WW2 years, Temkin lectured at the Department of Physical Chemistry of the Moscow Institute of Steel and collaborated with Dr. Schwartzman, with whom the Temkin–Schwartzman method mentioned at the beginning of this article was developed [78]. This collaboration mainly concerned some problems of theoretical metallurgy, namely the description of the thermodynamic properties of slag systems. Temkin formulated the main principles of the theory of oxide melts, which consisted in the fact that such melts (slags) are ionic systems. Temkin's work [79] is still considered fundamental for the thermodynamic treatment of slags and ionic salts [80]. I felt this in my own experience, when, many years ago, lecturing a course on chemical kinetics at Åbo Akademi University, I received an unusual request from a Finnish graduate student D. Lindberg, now a professor, to make a copy of this article by Temkin, albeit in Russian.

In another fundamental work by Temkin and Schwartzman of that period [81], he formulated the principle of the thermodynamic description of carbon solutions in iron, which initiated the whole direction of the application of thermodynamics to the problems of metallurgy.

To finish this small article, which can be viewed not only as an analysis of Temkin's scientific heritage, but also as a memory of my scientific teacher, I would like to mention Temkin's collaboration with Prof. Blumenfeld, the founder of the largest school of biophysicists. They considered a possible mechanism for the formation of adenosine triphosphate in oxidative phosphorylation [82]. One time L. Blumenfeld worked at the Karpov Institute and was a disciple of the famous theoretician Yakov Syrkin. Blumenfeld dedicated the following friendly lines to Mikhail Temkin:

Let generations yet unborn be envious,
When we were Temkin's graduates,
He used to drink cherry brandy with us.
That's what remember all the mates.

I fully subscribe to these lines.

REFERENCES

- Shub, F.S., Kul'kova, N.V., Kuchaev, V.L., and Murzin, D.Yu., *Zh. Fiz. Khim.*, 1992, vol. 66, p. 586.
- Murzin, D.Yu. and Kul'kova, N.V., *Kinet. Katal.*, 1995, vol. 36, p. 3.
- Murzin, D.Yu., *J. Mol. Catal. A.: Chem.*, 2010, vol. 315, p. 105.
- Kratkii spravochnik fiziko-khimicheskikh velichin* (Short Handbook on Physicochemical Values), Mishchenko, K.P. and Ravidelya, A.A., Eds., Leningrad: Khimiya, 1974.
- Murzin, D.Yu., *Langmuir*, 2010, vol. 26, p. 4854.
- Boudart, M., *Top. Catal.*, 1994, vol. 1, p. 405.
- Kobozev, N.I., Temkin, M., and Fraiberg, S., *Zh. Obshch. Khim.*, 1933, vol. 3, p. 534.
- Geterogennyi kataliz v khimicheskoi promyshlennosti* (Heterogeneous Catalysis in Chemical Industry), Moscow: Goskhimizdat, 1955, p. 471.
- Temkin, M.I. and Bakh, A.N., *Zh. Fiz. Khim.*, 1934, vol. 5, p. 809.
- Temkin, M.I. and Frumkin, A.N., *Zh. Fiz. Khim.*, 1955, vol. 29, p. 1513.
- Frumkin, A.N. and Shlygin, A.I., *Dokl. Akad. Nauk SSSR*, 1934, vol. 2, p. 173.
- Temkin, M.I., *Zh. Fiz. Khim.*, 1941, vol. 15, p. 296.
- Ross, J., *Contemporary Catalysis*, Amsterdam: Elsevier, 2018, p. 386.
- Temkin, M.I., *Adv. Catal.*, 1979, vol. 28, p. 173.
- Snagovskii, Yu.S. and Avetisov, A.K., *Dokl. Akad. Nauk SSSR*, 1971, vol. 196, p. 878.
- Murzin, D.Yu., *Ind. Eng. Chem. Res.*, 1995, vol. 34, p. 1208.
- Murzin, D.Yu., and Avetisov, A.K., *Chem. Eng. Sci.*, 1998, vol. 53, p. 2469.
- Temkin, M., *Acta Physicochim. URSS*, 1938, vol. 8, p. 141.
- Temkin, M.I., *Acta Physicochim. URSS*, 1940, vol. 13, p. 733.
- Temkin, M. and Pyzhev, V., *Zh. Fiz. Khim.*, 1939, vol. 13, p. 851.
- Temkin, M., *Acta Physicochim. URSS*, 1944, vol. 19, p. 163.
- Temkin, M., *Zh. Fiz. Khim.*, 1943, vol. 17, p. 269.
- Temkin, M., *Zh. Fiz. Khim.*, 1943, vol. 17, p. 414.
- Temkin, M., *Acta Physicochim. URSS*, 1945, vol. 20, p. 713.
- Temkin, M.I., *Khim. Prom-st.*, 1991, p. 610.
- Temkin, M.I., *Khim. Prom-st.*, 1990, p. 292.
- Kuchaev, V.L., Shapatina, E.N., Shub, F.S., and Temkin, M.I., *Kinet. Katal.*, 1991, vol. 32, p. 1107.
- Kuchaev, V.L., Shapatina, E.N., Zyskin, A.G., and Temkin, M.I., *Kinet. Katal.*, 1991, vol. 32, p. 1098.
- Temkin, M.I., *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva*, 1957, vol. 2, p. 219.
- Temkin, M.I., Kiperman, S.L., and Luk'yanova, L.I., *Dokl. Akad. Nauk SSSR*, 1950, vol. 74, p. 763.
- Temkin, M.I. and Kul'kova, N.V., *Kinet. Katal.*, 1969, vol. 10, p. 461.
- Götz, D., Kuhn, M., and Claus, P., *Chem. Eng. Res. Des.*, 2015, vol. 94, p. 594.
- <http://www.wraconferences.com/wp-content/uploads/2016/11/ILS-ERTC-Presentation-V3b-2.pdf>.
- Cherednichenko, V.M. and Temkin, M.I., *Zh. Fiz. Khim.*, 1957, vol. 31, p. 157.
- Temkin, M.I., *Kinet. Katal.*, 1981, vol. 22, p. 1365.
- Temkin, M.I., *Kinet. Katal.*, 1990, vol. 31, p. 1458.
- Khomenko, A.A., Shub, F.S., and Temkin, M.I., *Kinet. Katal.*, 1990, vol. 31, p. 1467.
- Temkin, M.I., *Kinet. Katal.*, 1983, vol. 24, p. 1270.
- Temkin, M.I., *Kinet. Katal.*, 1984, vol. 25, p. 478.
- Temkin, M.I., *Kinet. Katal.*, 1977, vol. 18, p. 493.

41. Temkin, M.I. and Kul'kova, N.V., *Khim. Prom-st.*, 1989, p. 862.
42. Salmi, T. and Russo, V., *Chem. Eng. J.*, 2019, vol. 356, p. 445.
43. Murzin, D.Yu., Konyukhov, V.Yu., Kul'kova, N.V., and Temkin, M.I., *Kinet. Katal.*, 1992, vol. 33, p. 728.
44. Slin'ko, M.G., *Kinet. Katal.*, 1969, vol. 10, p. 957.
45. Salciccioli, M., Stamatakis, M., Caratzoulas, S., and Vlachos, D.G., *Chem. Eng. Sci.*, 2011, vol. 66, p. 4319.
46. Reuter, K., *Catal. Lett.*, 2016, vol. 146, p. 541.
47. Temkin, M.I., *Dokl. Akad. Nauk SSSR*, 1963, vol. 152, p. 156.
48. Temkin, M.I., *J. Res. Inst. Catal., Hokkaido University*, 1968, vol. 16, p. 355.
49. Murzin, D.Yu. and Salmi, T., *Catalytic Kinetics*, Amsterdam: Elsevier, 2016, p. 572.
50. Temkin, M.I., *Dokl. Akad. Nauk SSSR*, 1965, vol. 161, p. 160.
51. Boudart, M. and Djega-Mariadassou, G., *Kinetics of Heterogeneous Catalytic Reactions*, Princeton: Princeton University Press, 1984, p. 242.
52. Temkin, M.I., *Kinet. Katal.*, 1984, vol. 25, p. 299.
53. Temkin, M.I., *Kinet. Katal.*, 1986, vol. 27, p. 533.
54. Murzin, D.Yu., *J. Mol. Catal. A: Chem.*, 2010, vol. 315, p. 226.
55. Murzin, D.Yu., *Catal. Sci. Technol.*, 2016, vol. 6, p. 5700.
56. Murzin, D.Yu., *Mol. Catal.*, 2017, vol. 433, p. 321.
57. Avetisov, A.K., Kuchaev, V.L., and Murzin, D.Yu., *AIChE J.*, 2006, vol. 52, p. 4273.
58. Ostrovskii, G.M., Zyskin, A.G., and Snagovkii, Yu.S., *Int. Chem. Eng.*, 1989, vol. 29, p. 435.
59. Dumesic, J.A., Rudd, D.F., Aparicio, L.M., Rekoske, J.E., and Treviño, A.A., *The Microkinetics of Heterogeneous Catalysis*, Washington: ACS, 1993.
60. Gu, G.H., Wittreich, G.R., and Vlachos, D.G., *Chem. Eng. Sci.*, 2019, vol. 197, p. 415.
61. Rellan-Pineiro, M. and Lopez, N., *ACS Sustainable Chem. Eng.*, 2018, vol. 6, p. 16169.
62. Chen, Z., Wang, H., Su, N.Q., Duan, S., Shen, T., and Xin, X., *ACS Catal.*, 2018, vol. 8, p. 5816.
63. Alexiadis, V.I., Thybaut, J.W., Kechagiopoulos, P.N., Chaar, M., van Veen, A.C., Muhler, M., and Marin, G.B., *Appl. Catal., B*, 2014, vols. 150–151, p. 496.
64. Deutschmann, O., *Catal. Lett.*, 2015, vol. 145, p. 272.
65. Sinev, M.Yu., *Russ. J. Phys. Chem. B*, 2007, vol. 1, p. 412.
66. Ostrovskii, V.E., Karpovich, I.R., Kul'kova, N.V., and Temkin, M.I., *Zh. Fiz. Khim.*, 1963, vol. 37, p. 2596.
67. Ostrovskii, V.E. and Temkin, M.I., *Kinet. Katal.*, 1966, vol. 7, p. 529.
68. Temkin, M.I. and Apel'baum, L.O., *Problemy Fiz. Khim.*, 1958, vol. 1, p. 4.
69. Temkin, M.I. and Apel'baum, L.O., *Problemy Kinet. Katal.*, 1960, vol. 10, p. 392.
70. Temkin, M.I., *Dokl. Akad. Nauk SSSR*, 1965, vol. 165, p. 615.
71. Zeigarnik, A.V. and Temkin, O.N., *Kinet. Catal.*, 1999, vol. 40, p. 484.
72. Zyskin, A.G., Avetisov, A.K., and Christiansen, L., *Theor. Found. Chem. Eng.*, 2002, vol. 36, p. 461.
73. Kuchaev, V.L., Shapatina, E.N., Zyskin, A.G., Avetisov, A.K., and Christiansen, L., *Kinet. Catal.*, 2003, vol. 44, p. 827.
74. Zyskin, A.G. and Avetisov, A.K., *Russ. J. Electrochem.*, 2009, vol. 45, p. 996.
75. Avetisov, A.K. and Zyskin, A.G., *Russ. J. Phys. Chem. A*, 2018, vol. 92, p. 1107.
76. Avetisov, A.K., Rostrup-Nielsen, J.R., Kuchaev, V.L., Bak Hansen, J.-H., Zyskin, A.G., and Shapatina, E.N., *J. Mol. Catal. A: Chem.*, 2010, vol. 315, p. 155.
77. Marin, G.B., Yablonsky, G.S., and Constales, D., *Kinetics of Chemical Reactions: Decoding Complexity*, 2nd ed., Wiley, 2019.
78. Temkin, M.I. and Shvartsman, L.A., *Usp. Khim.*, 1948, vol. 17, p. 259.
79. Temkin, M., *Acta Physicochim. URSS*, 1945, vol. 20, p. 411.
80. Pelton, A.D., *Miner. Process. Extr. Metall., Trans. Inst. Min. Metall.: Sect. C*, 2005, vol. 114, p. 172.
81. Temkin, M.I. and Shvartsman, L.A., *Zh. Fiz. Khim.*, 1949, vol. 23, p. 755.
82. Blyumenfel'd, L.A. and Temkin, M.I., *Biofizika*, 1962, vol. 7, p. 731.

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