COMPREHENSIVE

CHEMICAL KINETICS

EDITED BY

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VOLUME 32

KINETIC MODELS OF
CATALYTIC REACTIONS

COMPREHENSIVE CHEMICAL KINETICS

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Preface

This volume is concerned with providing an up-to-date and rigorous account of the dynamics of catalytic reactions. The authors' view of the detailed objectives and scope of the book are summarised in their preface which follows.

Oxford   R.G. Compton
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Authors' Preface

"Yet who would have thought the old man to have had so much blood in him?" This title, given by Prof. Rutherford Aris and his collaborator W.W. Farr to their recent paper [*Chem. Eng. Sci.,* 41 (1986) 1385], is a phrase used by Lady Macbeth (*Macbeth,* V, 1, 42–44). Fierce, isn't it? Apparently, they mean it to imply that traditional theoretical problems in the dynamics of chemical reactions, in particular the known problem of the dynamics of the continuous stirred tank reactor (CSTR), are far from being exhausted. Novel mathematical approaches provide new results oriented to physico-chemical comprehension. This current trend is confirmed by the present volume.

This book has been written by mathematicians and chemists, the collaborators of the Institutes of the Siberian Branch of the U.S.S.R. Academy of Sciences [The Institute of Catalysis (Novosibirsk), the Computing Centre (Krasnoyarsk) and the Tuva Complex Department (Kyzyl)]. It presents the results of 15 years activity of this Siberian team as reported in two earlier monographs (*Kinetic Models of Catalytic Reactions,* Nauka, Novosibirsk, 1983 and *Kinetics for Model Reactions of Heterogeneous Catalysis,* Nauka, Novosibirsk, 1984, both published in Russian). Unfortunately, these results are hardly known to English-speaking readers.

Compared with the above monographs, the book has been revised and completed. It accounts for the rapid development of events in the region of mathematical chemistry, which is at a crossroads where chemistry, physics, mathematics and chemical technology meet. Besides establishing a general theory permitting us to investigate the dependence of kinetic characteristics for complex reactions on the structure of the detailed mechanism, the book provides a comprehensive analysis of some concrete typical mechanisms for catalytic reactions, in particular for the oxidation of carbon monoxide on platinum metals. This reaction is a long-standing traditional object of chemical catalytic investigations. In fact, the book presents "three kinetics": (a) detailed, oriented to the elucidation of a detailed reaction mechanism according to its kinetic laws; (b) applied, with the aim of obtaining kinetic relationships for the further design of chemical reactors; and (c) mathematical kinetics whose purpose is the analysis of mathematical models for heterogeneous catalytic reactions taking place under steady- or unsteady-state conditions.

What unites the Siberian team? Primarily it is a common interest in the complex dynamics of catalytic reactions. The boundaries of this field are

extended and dynamic approaches are applied to a variety of chemical systems. The newest and, as it would seem, absolutely abstract mathematical results make it possible not only to answer questions that are traditionally interesting for chemists and physicists, but also to extend their list.

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Chapter 4

Introduction

This book embraces problems having both physicochemical and mathematical sense.

A widespread concept of "mathematical physics equations" includes primarily linear and quasi-linear partial differential equations. But what are "mathematical chemistry equations" and "mathematical chemistry" in general?

The concept of "mathematical chemistry" had been already used by M.V. Lomonosov [1] and later on in the 19th century by Du Bois-Reymond, but for a long time it became inapplicable, apparently due to the lack of a distinct field for its application. As a rule, it was, and has remained, preferable to speak about the application of mathematical methods in chemistry rather than about "mathematical chemistry". To our mind, it is now quite correct to treat mathematical chemistry as a specific field of investigation. Its equations are primarily those of chemical kinetics, i.e. ordinary differential equations with a specific polynomial content. We treat these equations relative to heterogeneous catalytic systems.

We will try to define the way in which the structure of a complicated chemical mechanism and its respective kinetic model are associated with the peculiarities of steady and non-steady kinetic relationships, i.e. how the elementary reactions with simple kinetic dependences lead to complicated kinetic behaviour.

Chapter 1 presents all the necessary information concerning linear algebra and the qualitative theory of differential equations in terms of which we construct and analyze kinetic models of heterogeneous catalytic reactions.

Chapter 2 describes the evolution in fundamental concepts of chemical kinetics (in particular, that of heterogeneous catalysis) and the "prehistory" of the problem, i.e. the period before the construction of the formal kinetics apparatus. Data are presented concerning the ideal adsorbed layer model and the Horiuti–Temkin theory of steady-state reactions. In what follows (Chapter 3), an apparatus for the modern formal kinetics is represented. This is based on the qualitative theory of differential equations, linear algebra and graphs theory. Closed and open systems are discussed separately (as a rule, only for isothermal cases). We will draw the reader's attention to the two results of considerable importance.

(1) Many kinetic problems of complex reactions in closed systems can be treated from the geometrical viewpoint. In due course it became possible for

analytical mechanics; now it can also be realized for chemical kinetics. Geometrical representation not only simplifies the interpretation, but also offers new possibilities, e.g. for planning experiments.

(2) Sets of quasi-steady-state equations can have several solutions, which correspond to several steady-state rate values of complex reaction in open systems (multiplicity of steady states). *It has been shown that the necessary condition here is the presence of an interaction step between various intermediates in the complex reaction mechanism*. Let us discuss this result in more detail.

Since the late 1930s (studies by D.A. Frank-Kamenetskii, Ya.B. Zeldovich and N.N. Semenov), it has been known that there exist multiple steady states of chemical systems due to the simultaneously occurring chemical, thermal, and diffusional processes [2]. It is so evident that it can be shown very simply. Thus, in a non-isothermal continuously stirred tank reactor (CSTR) the temperature dependence of the rates for heat release and heat removal are exponential and linear, respectively. These dependences can be balanced at more than one point, and it is this fact that accounts for several steady states. In non-isothermal cases one can also observe self-oscillations of the reaction rate (including first-order reactions). Generally speaking, in non-isothermal cases the critical effects of various types, i.e. multiple steady states and self-oscillations, have been thoroughly investigated both experimentally and theoretically as early as in the 1930s–1940s. A new fact to be accounted for was that similar effects had been found in a purely kinetic region, i.e. in isothermal conditions without a distorting effect of heat and mass transfer. At the present time a great number of experimental data have been accumulated for isothermal critical effects. Thus as early as in the 1950s, Boreskov et al. [3] established a critical effect for the kinetics of hydrogen oxidation on nickel catalysts. Under isothermal conditions with certain gas-phase compositions, a "downward jump" in the reaction rate is observed. The same gas composition accounts for drastically different reaction rates. It is just a case of multiple steady states. Also changeable (from first to zero) is the reaction order. Similar phenomena had also been found for the kinetics of CO oxidation and hydrogenation. Apparently, Davis [4] was the first to observe these phenomena (in the 1930s), but his experimental data were met with distrust. Finally, and more recently, after the development of a special electrothermographical technique Barelko and Merzhanov revealed the existence of critical effects being purely kinetic in nature [5]. They established that many complete catalytic oxidation reactions can lead to such kinetic "revolutions". For ammonia oxidation on platinum they observed hysteresis: the transition from "upper" to "lower" steady state and back takes place at different values of the reaction parameters. The kinetic dependences obtained by increasing and decreasing the parameters are different.

In the 1950s–1960s interesting experimental data were obtained for some homogeneous catalytic reactions. Late in the 1950s, Belousov established

isothermal self-oscillations for the catalytic oxidation of citric acid by bromate (catalyzed by cerium ions). For some time, Belousov's paper appeared in a small-circulation publication and was little read by chemists. It was thus largely ignored. On S.E. Shnol's initiative, Zhabotinskii et al. continued the investigation of this reaction. They showed experimentally that self-oscillations do exist due to the complex reaction chemistry and they constructed a qualitative mathematical model based on the "law of mass action" [6]. Keen interest was shown in the Belousov–Zhabotinskii reaction in particular and in chemical self-oscillations in general. Several hundred papers were devoted to the Belousov–Zhabotinskii reaction.

According to Zhabotinskii, a simplified reaction scheme in the system consisting of malonic acid (MA) + bromate and cerium ions is of the form

$$Ce^{3+} \xrightarrow[H^+]{BrO_3^-} Ce^{4+} \tag{1}$$

$$Ce^{4+} \xrightarrow{MA} Ce^{3+} \tag{2}$$

Reaction (1) yields products of BrO_3^- reduction (Br_2, HOBr) which brominate MA to form its bromine derivatives (BMA). Reaction (2) produces an inhibitor for reaction (1) acting as a feedback. If the system contains much Ce^{4+}, the amount of Br^- is also high and reaction (1) is hindered. Finally, the amount of Ce^{4+} falls to its lower critical value and the concentration of Br^- also decreases. Reaction (1) then proceeds at a high rate and everything begins again.

Self-oscillations have also been revealed for heterogeneous catalytic reactions. Hugo and Jakubith [7] and Wicke and co-workers [8] found self-oscillations for CO oxidation on platinum. In the period 1973–1975, M.G. Slinko and co-workers studied self-oscillations in hydrogen oxidation on nickel [9,10].

Belousov–Zhabotinskii experimental data became one of the starting points for Prigogine and his school in studying the complicated dynamic behaviour of "far from equilibrium" chemical systems. These investigations were reported in a series of monographs [11,12] and Prigogine has recently been awarded a Nobel prize.

To interpret isothermal critical effects quantitatively, Prigogine used mechanisms involving autocatalytic steps, i.e. a "brusselator" and an "oregonator". These names have been derived from "Brussels" + "oscillator" and "Oregon" + "oscillator", since various research groups worked in Brussels and Oregon. It must be emphasized that, as long ago as the 1940s, Zeldovich reported that an autocatalytic reaction under isothermal conditions can also lead to critical effects [13].

"Oregonator" and "brusselator" studied in detail by the Prigogine school were nevertheless extremely speculative schemes. A study of the behaviour of classical chemical kinetics equations assumed a high priority in order to select the structure responsible for the appearance of critical effects. The results of such a study, described in Chap. 3, can be applied to interpret critical effect experiments.

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For linear mechanisms we have obtained structurized forms of steady-state kinetic equations (Chap. 4). These forms make possible a rapid derivation of steady-state kinetic equations on the basis of a reaction scheme without laborious intermediate calculations. The advantage of these forms is, however, not so much in the simplicity of derivation as in the fact that, on their basis, various physico-chemical conclusions can be drawn, in particular those concerning the relation between the characteristics of detailed mechanisms and the observable kinetic parameters. An interesting and important property of the structurized forms is that they vividly show in what way a complex chemical reaction is assembled from simple ones. Thus, for a single-route linear mechanism, the numerator of a steady-state kinetic equation always corresponds to the kinetic law of the overall reaction as if it were simple and obeyed the law of mass action. This type of numerator is absolutely independent of the number of steps (a thousand, a million) involved in a single-route mechanism. The denominator, however, characterizes the "non-elementary character" accounting for the retardation of the complex catalytic reaction by the initial substances and products.

In Chap. 5 we present the results of our detailed study of steady- and non-steady-state characteristics for typical non-linear mechanisms and kinetic models. It appears that the known adsorption mechanism, i.e. the Langmuir–Hinshelwood mechanism, is the simplest one ensuring multiple steady states on the catalyst surface ("catalytic trigger"). If this mechanism is completed with a "buffer" step, it would be the simplest mechanism providing self-oscillations of the reaction rate ("catalytic oscillator"). It is advisable that approaches under development are applied for the interpretation of concrete catalytic reactions and primarily of the oxidation of simple molecules (H_2, CO) on metals. The investigations by Langmuir in the period 1910–1930 initiated the kinetics of heterogeneous catalysis. So far these reactions*, demonstrating an ever-increasing number of new non-trivial properties, have remained a traditional subject of investigation, as can be judged by the number of publications in the *Journal of Catalysis, Kinetica i Kataliz,* and *Surface Science.* It is for this reason that in Chap. 6 we present a detailed analysis of the kinetic model for the reaction of oxidation of CO on the Group VIII metals. Qualitative and numerical analyses reveal a great variety of steady-state and relaxational characteristics. The constructed kinetic models describe experimental data obtained under both deep vacuum (on Pt, Ir metals) and normal conditions (Pd-containing catalysts).

We have carried out the analysis of slow relaxations when the times to achieve steady states are much higher than those of separate reactions. It has been shown that they are caused not only by slow secondary processes but also by the closeness to the region of critical conditions. The general theory of slow relaxations permits us to interpret various peculiarities of

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*These reactions are known as the Mona Lisa of heterogeneous catalysis.

relaxation regimes found in the experiments, e.g. induction periods, "memory" effects, etc. We believe the theory described in Chap. 7 will be of interest for the mathematicians who deal with physico-chemical problems.

It is surprising that complicated dynamic behaviour proved to be characteristic of the simplest and quite ordinary kinetic models of catalytic reactions, namely of the Langmuir–Hinshelwood adsorption mechanism. We are possibly at the initial stage of interpreting the kinetics of complex reactions and the "Sturm und Drang" period has not yet been completed.

Thus we have described the contents of our book. But what has given impetus to its writing?

First, it is of common interest to unsteady processes and their models. Chemical unsteadiness must be taken into account in many cases. For example, studies with variations in catalyst activity, calculations of fluidized catalyst bed processes (when the catalyst grain "is shaking" in a flow of the reaction mixture and has no time to attain its steady state), analyses of relaxational non-stationary processes and problems of control. Unsteady state technology is currently under development [14,15], i.e. the technology involving programmed variation of the process parameters (temperature, flow rate, concentration). The development of this technology is impossible without distinct interpretation of the unsteady reaction behaviour.

Secondly, it is necessary to interpret critical effects recently discovered experimentally and which are of common interest. In the adjacent field, i.e. homogeneous catalysis, a great number of such facts have been accumulated for Belousov–Zhabotinskii reactions. These facts can be interpreted only in terms of the non-linear unsteady-state models.

Thirdly, it is the development of the theory of differential equations that provided chemical kinetics with a new powerful apparatus [16] to be put into operation. This apparatus is not only a convenient formal means. It will also be a base for a meaningful conceptional language.

The Soviet school of chemical kinetics has accumulated a unique experience in interpreting concrete catalytic reactions in terms of the stepwise mechanism concept. In the present book we have made an attempt to interpret this experience on the basis of modern formal kinetics of complex reactions. Since the authors have addressed the book to chemists and mathematicians, it is desirable that they both read the whole of the book.

References

1   M. Giua, Storia Della Chimia, Union Tipografico-Editrice Torinese, Torino, 1962.
2   D.A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, Nauka, Moscow, 1967 (in Russian).
3   G.K. Boreskov, M.G. Slinko and A.G. Filippova, Dokl. Akad. Nauk SSSR, 92 (1953) 353.
4   W. Davies, Philos. Mag., 17 (1934) 233; 19 (1935) 309.
5   V.V. Barelko and A.G. Merzhanov, Probl. Kinet. Katal., 17 (1973) 182.
6   A.M. Zhabotinskii, Concentration Self-oscillations, Nauka, Moscow, 1974 (in Russian).

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7   P. Hugo and M. Jakubith, Chem.-Ing.-Tech., 44 (1972) 383.

8   H. Beusch, P. Fieguth and E. Wicke, Chem. Ing. Tech., 44 (1972) 445.

9   V.D. Beljaev, M.M. Slinko, V.I. Timoshenko and M.G. Slinko, Kinet. Katal., 14 (1973) 810.

10   M.G. Slinko and M.M. Slinko, Catal. Rev. Sci. Eng., 17 (1978) 119.

11   P. Glansdorff and I. Prigogine, Thermodynamic Theory of Structure, Stability and Fluctuations, Wiley-Interscience, London, 1971.

12   G. Nicolis and I. Prigogine, Self-organization in Non-equilibrium Systems, Wiley-Interscience, New York, 1977.

13   Ya.B. Zeldovich, Zh. Tech. Fiz., 11 (1941) 493.

14   A. Baiker and W. Richarz, Chimia, 30 (1976) 502.

15   Yu.Sh. Matros, Unsteady Processes in Catalytic Reactors, Studies in Surface Science and Catalysis, Vol. 22, Elsevier, Amsterdam, 1985.

16   A.I. Volpert, Qualitative Methods for Chemical Kinetics Equations, Institut Khimicheskoi Fiziki, Akad. Nauk SSSR, Chernogolovka, 1976 (in Russian).

Chapter 1

Minimum Minimorum

1. Introduction

It is well established that most chemical reactions are complex in nature. For example, the oxidation of hydrogen described as

$$2\,H_2 + O_2 \;=\; 2\,H_2O$$
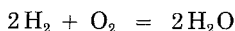
but, according to the modern conceptions, a detailed mechanism of the reaction is [1]

(1) $H_2 + O_2 \rightleftarrows 2\,OH$

(2) $OH + H_2 \rightleftarrows H_2O + H$

(3) $H + O_2 \rightleftarrows OH + O$

(4) $O + H_2 \rightleftarrows OH + H$

(5) $O + H_2O \rightleftarrows 2\,OH$

(6) $2\,H + M \rightleftarrows H_2 + M$

(7) $2\,O + M \rightleftarrows O_2 + M$

(8) $H + OH + M \rightleftarrows H_2O + M$

(9) $2\,OH + M \rightleftarrows H_2O_2 + M$

(10) $OH + O + M \rightleftarrows H_2O + M$

(11) $H + O_2 + M \rightleftarrows HO_2 + M$

(12) $HO_2 + H_2 \rightleftarrows H_2O_2 + H$

(13) $HO_2 + H_2 \rightleftarrows H_2O + OH$

(14) $HO_2 + H_2O \rightleftarrows H_2O_2 + OH$

(15) $2\,HO_2 \rightleftarrows H_2O_2 + O_2$

(16) $H + HO_2 \rightleftarrows 2\,OH$

(17) $H + HO_2 \rightleftarrows H_2O + O$

(18) $H + HO_2 \rightleftarrows H_2 + O_2$

(19) $O + HO_2 \rightleftarrows OH + O_2$

(20) $H + H_2O_2 \rightleftarrows H_2O + OH$

(21) $O + H_2O_2 \rightleftarrows OH + HO_2$

(22) $H_2 + O_2 \rightleftarrows H_2O + O$

(23) $H_2 + O_2 + M \rightleftarrows H_2O_2 + M$

(24) $OH + M \rightleftarrows O + H + M$

(25) $HO_2 + OH \rightleftarrows H_2O + O_2$

(26) $H_2 + O + M \rightleftarrows H_2O + M$

(27) $O + H_2O + M \rightleftarrows H_2O_2 + M$

(28) $O + H_2O_2 \rightleftarrows H_2O + O_2$

(29) $H_2 + H_2O_2 \rightleftarrows 2\,H_2O$

(30) $H + HO_2 + M \rightleftarrows H_2O_2 + M$

where M is a "third body", i.e. any substance, combining with which molecules exchange energy. In this case the number of steps is 30, but it can be even more! The question arises whether they all exist in reality? They do. It has long been known from experiments that hydrogen oxidation takes place through intermediates such as O, H, OH, etc. Their concentration is usually

low, but these intermediates are of essential importance for the reaction. Hence the reaction mechanism must include steps involving the participation of these substances.

To exemplify a complex mechanism of a heterogeneous catalytic reaction, we will consider the interaction of methane with steam on a nickel surface. Stoichiometric equations for this reaction are

$$CH_4 + H_2O = CO + 3H_2$$
$$CO + H_2O = CO_2 + H_2 \;.$$
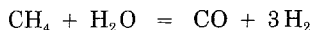
At the same time a probable detailed mechanism can be represented by

(1) $CH_4 + Z \rightleftarrows ZCH_2 + H_2$

(2) $ZCH_2 + H_2O \rightleftarrows ZCHOH + H_2$

(3) $ZCHOH \rightleftarrows ZCO + H_2$

(4) $ZCO \rightleftarrows Z + CO$

(5) $Z + H_2O \rightleftharpoons ZO + H_2$

(6) $ZO + CO \rightleftharpoons Z + CO_2$
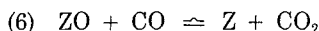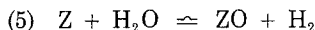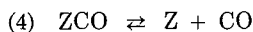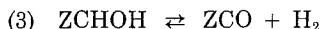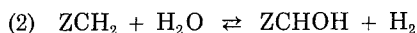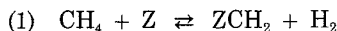
Here Z represents a catalyst surface site (active centre). The two final steps are in equilibrium, designated by the symbol $\rightleftharpoons$. "The natural classification" of simple (elementary) reactions by the number of molecules involved simultaneously in the reaction belongs to Van't Hoff. If the reaction involves one molecule (reaction $A \rightarrow B$), it is classified as first-order (monomolecular). In cases where two molecules take part in the reaction (e.g. $2A \rightarrow B$ or $A + B \rightarrow C$), the reaction is said to be second-order (bimolecular). With the participation of three molecules ($3A \rightarrow B$ or $2A + B \rightarrow C$), the reaction is specified as third-order (termolecular). The simultaneous interaction of more than three reactants is believed to be highly improbable.

The basic concept in chemical kinetics is the reaction rate. For elementary reactions it is the number of elementary acts in a chemical conversion per unit reaction volume or per unit reaction surface for unit time.

Any chemical reaction can be written in the general form as

$$\sum_i^{N_A} \alpha_i A_i \rightleftarrows \sum_i^{N_B} \beta_i B_i \tag{1}$$

where α_i and β_i are the stoichiometric coefficients for the initial substances A_i and reaction products B_i, respectively, and N_A and N_B are the number of initial substances and reaction products, respectively.

For simple reactions the above values are limited. Thus, α_i and β_i can only be equal to 0, 1, 2 or 3 (rarely).

Stoichiometric equations are free from these limitations. For example, the C_2H_4O oxidation reaction is

$$2\,C_2H_4O \,+\, O_2 \;=\; 4\,CO_2 \,+\, 4\,H_2O \tag{2}$$

Reactions in which the initial substance is simultaneously its product are rather rare. These "propagation" reactions were called auto-catalytic steps by Kondratiev and Nikitin. For example, one of the steps in the thermal dissociation of hydrogen is

$$H_2 + H \;\rightleftarrows\; H + H + H \tag{3}$$

As a rule, in simple reactions the initial substances and products are different and the reaction does not yield any of the initial substances.

In the case of gas-phase catalytic reactions, the reactants are, on the one hand, gaseous and, on the other hand, surface substances. The latter are on the surface of solid catalysts.

A simple catalytic reaction is described as

$$\sum_{i=1}^{N_A} \alpha_i A_i \,+\, \sum_{i=1}^{N_X} \alpha_i' X_i \;\rightleftarrows\; \sum_{i=1}^{N_B} \beta_i B_i \,+\, \sum_{i=1}^{N_Y} \beta_i' Y_i \tag{4}$$
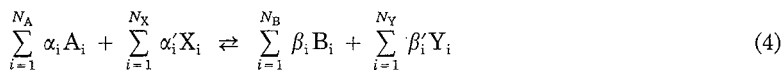
where A_i and B_i are the initial substances and products in the gas phase, respectively, α_i and β_i are their stoichiometric coefficients, X_i and Y_i are the surface substances, and α_i' and β_i' are their stoichiometric coefficients.

As usual, eqn. (4) is of the form

$$\alpha A \,+\, \sum_{i=1}^{N_X} \alpha_i' X_i \;\rightleftarrows\; \beta B \,+\, \sum_{i=1}^{N_Y} \beta_i' Y_i \tag{5}$$

Here α and $\beta = 1$ or 0, i.e. it is assumed that a simple catalytic reaction either involves the participation of only one molecule of gaseous substance (e.g. $CH_4 + Z \rightleftarrows ZCH_2 + H_2$) or it proceeds without the participation of these substances (e.g. $ZCHOH \rightleftarrows ZCO + H_2$). The stoichiometric coefficients α_i' and β_i' are assumed to equal 1, 2, or 3 (rarely) and $\Sigma\alpha_i'$ and $\Sigma\beta_i' \leqslant 3$.

The rate of a simple reaction as represented by eqns. (1) and (4) is determined from the difference between the rates of the direct and reverse reactions

$$w \;=\; w^+ - w^- \tag{6}$$

Under equilibrium, $w = 0$ and $w^+ = w^-$.

The dependence of the rates for the direct and reverse reactions on the concentration of the reactants is expressed in terms of the law of mass action as

$$w^+ \;=\; k^+ C_{A_1}^{\alpha_1} C_{A_2}^{\alpha_2} \ldots \;=\; k^+ \prod_{i=1}^{N_A} C_{A_i}^{\alpha} \tag{7}$$

$$w^- \;=\; k^- C_{B_1}^{\beta_1} C_{B_2}^{\beta_2} \ldots \;=\; k^- \prod_{i=1}^{N_B} C_{B_i}^{\beta_i} \tag{8}$$

where C_{A_i} and C_{B_i} are the concentrations of the initial substances and products, respectively and k^+ and k^- are rate coefficients for the direct and reverse reactions to determine a specific reaction rate, i.e. the rate when the concentrations of reactants are equal to unity. They fit the Arrhenius relationship and increase exponentially with temperature

$$k^+ = k_0^+ \exp\left(-E^+/RT\right) \tag{9}$$

$$k^- = k_0^- \exp\left(-E^-/RT\right) \tag{10}$$

Here k_0^+ and k_0^- are the pre-exponential factors, E^+ and E^- are the activation energies for the direct and reverse reactions, respectively, R is the universal gas constant, and T is the absolute temperature.

The ratio of the rate coefficients for the direct and reverse reactions can be used to define the equilibrium constant

$$K_{eq} = \frac{k^+}{k^-} \tag{11}$$

Homogeneous catalytic reactions fit the relationship

$$w = w^+ - w^- = -\frac{1}{\alpha_i V}\frac{dN_{A_i}}{dt} = \frac{1}{\beta_i V}\frac{dN_{B_i}}{dt} \tag{12a}$$

Here N_{A_i} and N_{B_i} are the concentrations of the substances in the system and V is the volume of the system.

Heterogeneous catalytic reactions fit the relationship

$$w = w^+ - w^- = -\frac{1}{\alpha_i S_{cat}} \cdot \frac{dN_{A_i}}{dt} = \frac{1}{\beta_i S_{cat}} \cdot \frac{dN_{B_i}}{dt} \tag{12b}$$

Here S_{cat} is the surface area of the catalyst for conversion.

For steps taking place without changing the number of moles, eqns. (12a) and (12b) take the usual form

$$w = w^+ - w^- = -\frac{1}{\alpha_i}\frac{dC_{A_i}}{dt} = \frac{1}{\beta_i}\frac{dC_{B_i}}{dt} \tag{13}$$

The reactions whose rates fit the mass action law can be called simple. This postulate is, however, inaccurate. One can meet complex reactions involving several steps, but which nevertheless fit the above law. According to Laidler, simple (elementary) reactions take place by overcoming one energy barrier (one barrier per elementary reaction).

Strange as it seems, there are one-step reactions in nature, e.g. first-order reactions of monomolecular decomposition

$$C_2H_5Br \rightarrow C_2H_4 + HBr$$

and

$$CH_3N_2CN_3 \rightarrow C_2H_6 + N_2$$
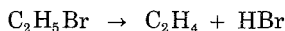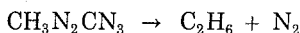
the second-order reactions

$$2\,NOI \;\rightarrow\; 2\,NO + I_2$$

and

$$CO + O_2 \;\rightarrow\; CO_2 + O$$
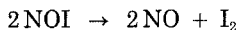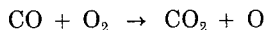
and the third-order reaction

$$2\,NO + O_2 \;\rightarrow\; 2\,NO_2$$
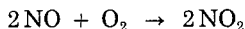
These cases are, however, exceptions rather than the rule. Most reactions are now considered to be multi-step and complex.

2. Chemical kinetics and linear algebra

A natural language accounting for the stoichiometry of chemcial reactions is that of linear algebra. Let us remind ourselves of its basic concepts.

A matrix is a rectangular array of numerals containing m rows and n columns. A general form of this m-by-n matrix is

$$\vec{A} \;=\; \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{m1} & a_{m2} & \cdots & a_{mn} \end{bmatrix}$$

Here a_{ij} are matrix elements and i is the row number and j the column number whose intercept provides a place for the element a_{ij}. If $m = 1, n > 1$, a one-row matrix $[a_1, a_2, \ldots a_n]$ is obtained. This is called a vector row. For $m > 1$ and $n = 1$ we have a one-column matrix called a vector column

$$\begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_m \end{bmatrix}$$

Matrices can be added and multiplied by some numerals and by each other. The latter operations are often used in formal chemical kinetics. The sum of two m-by-n matrices $\vec{A} = a_{ij}$ and $\vec{B} = b_{ij}$ gives a new m-by-n matrix, $\vec{C} = c_{ij}$, whose elements are determined by the equality $c_{ij} = a_{ij} + b_{ij}$. The sum of matrices is designated as $\vec{C} = \vec{A} + \vec{B}$.

A new matrix $k\vec{A} = [ka_{ij}]$ is the product of multiplying matrix $\vec{A} = [a_{ij}]$ by k. For this multiplication it is necessary to multiply every element of the matrix by k.

Let $\vec{A} = [a_{i,j}]$ be an m-by-n matrix and $\vec{B} = [b_{i,j}]$ be an n-by-p matrix, i.e.

the number of rows in matrix $\vec{B}$ is the same as the number of columns in matrix $\vec{A}$. Then the product of matrices $\vec{A}$ and $\vec{B}$ (designated as $\overline{AB}$) is called an m-by-n matrix, $\vec{C} = [c_{i,j}]$, whose elements are determined by the equalities

$$c_{ij} = a_{i1}b_{1j} + a_{i2}b_{2j} + \ldots + a_{in}b_{nj} \tag{14}$$

where $i = 1, 2, \ldots, m; j = 1, 2, \ldots, p$

The element $c_{i,j}$ of matrix $\vec{C}$, positioned at the intercept of the ith row and the jth column, is equal to the scalar product of the ith vector-row of matrix $\vec{A}$ and the jth vector column of matrix $\vec{B}$.

One must remember that the product $\vec{A}\vec{B}$ is defined only if the number of columns of matrix $\vec{A}$ is equal to the number of rows of matrix $\vec{B}$. If the rows and columns in matrix $\vec{A}$ interchange their places, it produces matrix $\vec{A}^{\mathrm{T}}$, which is called a matrix transposed with respect to matrix $\vec{A}$

$$\vec{A}^{\mathrm{T}} = \begin{bmatrix} a_{11} & a_{21} & \ldots & a_{m1} \\ a_{12} & a_{22} & \ldots & a_{m2} \\ \vdots & \vdots & & \vdots \\ a_{1n} & a_{2n} & \ldots & a_{mn} \end{bmatrix}$$

If the number of rows and columns is the same, the matrix is called square. This number is called a matrix order. The totality of elements $(a_{11}, a_{22}, \ldots a_{nm})$ of the square matrix is its main diagonal.

Each square matrix is assumed to correspond to a certain value (to be more precise, to a numerical function) which is called a matrix determinant. For a first-order matrix, i.e. the number of a_{ij}, the determinant is equal to this number itself

$$\det [a_{ij}] = a_{ij} \tag{15}$$

A second-order determinant is equal to

$$\det \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = a_{11}a_{22} - a_{21}a_{12} \tag{16}$$

A minor for element a_{ij} of matrix $\vec{A}$ is the determinant for the matrix obtained from matrix $\vec{A}$ with the ith row and jth column omitted. An algebraic complement for element a_{ij} of matrix $\vec{A}$ is its minor multiplied by $(-1)^{i+j}$. Matrix determinant amounts to the sum of the products of elements for some column (or row) with their algebraic complements.

An important concept is the matrix rank. The highest order of the non-zero determinant generated by a given matrix is designated as $\mathrm{rg}\vec{A}$. With a zero determinant the matrix is singular. The matrix whose elements along the main diagonal are equal to unity and all the rest are zero is called a unit or identity matrix. If some vector $\vec{Y}$ is a linear combination of vectors, it is called linear-dependent

$$\vec{Y} = K_1 \vec{Y}_1 + K_2 \vec{Y}_2 + \ldots + K_m \vec{Y}_m \tag{17}$$

The rank for a set of vectors is the maximum number of linearly independent vectors. If, from the total set of vectors, one chooses the combination containing the maximum number of linearly independent vectors it will be a basis. The matrix rank remains unchanged if one adds a row that is a linear combination of the other rows and if this row is cancelled.

It is very convenient to apply a matrix technique to solve sets of linear equations. The set of linear equations relative to the n unknowns x_1, x_2, $\ldots$, x_n is

$$\begin{cases} a_{11}x_1 + a_{12}x_2 + \ldots + a_{1n}x_n = b_1 \\ a_{21}x_1 + a_{22}x_2 + \ldots + a_{2n}x_n = b_2 \\ a_{m1}x_1 + a_{m2}x_2 + \ldots + a_{mn}x_n = b_m \end{cases} \tag{18}$$

In matrix representation it is

$$\overrightarrow{AX} = \vec{B} \tag{19}$$

If $\vec{B} = 0$, the system is called homogeneous.

But what is the field for the direct application of linear algebra concepts in chemical kinetics?

The chemical composition of substances is accounted for by the molecular matrix whose element a_{ij} is the atomic number of the ith element entering into the jth reactant molecule. Thus for the mixture of C, O_2, CO and CO_2, the molecular matrix is

$$\vec{A} = \begin{array}{c} \\ \end{array} \begin{array}{cc} C & O \\ \begin{bmatrix} 1 & 0 \\ 0 & 2 \\ 1 & 1 \\ 1 & 2 \end{bmatrix} & \begin{array}{l} C \\ O_2 \\ CO \\ CO_2 \end{array} \end{array} \tag{20}$$

The rows here correspond to the substances C, O_2, CO and CO_2 and the columns are the elements C and O.

Molecular masses of substances are determined by the equation

$$\vec{M} = \vec{A}\vec{M}_A \tag{21}$$

Here $\vec{M}$ is the vector column of the molecular masses of the substances, $\vec{A}$ is the molecular matrix and $\vec{M}_A$ is the vector column of the atomic masses. The size of matrix $\vec{A}$ is N-by-m, where N is the number of reactants in the system and m the number of chemical elements entering into the composition of reactants.

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A stoichiometric matrix is one whose elements are the stoichiometric coefficients of the reacting substances. Its rows correspond to the reactions and its columns are the reacting substances.

For the reactions

(1) $2\,C + O_2 = 2\,CO$

(2) $2\,CO + O_2 = 2\,CO_2$ \hfill (22)

(3) $C + O_2 = CO_2$

the stoichiometric matrix $\vec{\Gamma}$ is of the form

$$
\vec{\Gamma} = \begin{array}{c} \end{array}
\begin{array}{cccc} C & O_2 & CO & CO_2 \end{array}
$$

$$
\vec{\Gamma} = \left[\begin{array}{rrrr}
-2 & -1 & 2 & 0 \\
0 & -1 & -2 & 2 \\
-1 & -1 & 0 & 1
\end{array} \right] \begin{array}{c} 1 \\ 2 \\ 3 \end{array}
\tag{23}
$$

The stoichiometric coefficients of the initial substances for a given reaction are included with a negative sign. Those of the reaction products are positive. If a substance does not participate in a reaction, its stoichiometric coefficient is taken to be zero.

The size of a stoichiometric matrix is (s-by-N), where s is the number of reactions and N the number of reactants in the system. Stoichiometric equations for a complex reaction can be represented as

$$
\vec{\Gamma}\vec{a} = \vec{0}
\tag{24}
$$

Here $\vec{a}$ is the vector column of the reactants. Thus, the stoichiometric equations (22) can be obtained by multiplication

$$
\left[\begin{array}{rrrr}
-2 & -1 & 2 & 0 \\
0 & -1 & -2 & 2 \\
-1 & -1 & 0 & 1
\end{array} \right] \times
\left[\begin{array}{c}
C \\ O_2 \\ CO \\ CO_2
\end{array} \right] =
\left\{ \begin{array}{l}
-2\,C - O_2 + 2\,CO = O \\
-O_2 - 2\,CO + 2\,CO_2 = O \\
-C - O_2 + CO_2 = O
\end{array} \right.
$$

What requirements must the stoichiometric matrix $\vec{\Gamma}$ fit? Chemists choose stoichiometric coefficients such that, in each reaction, the number of atoms on the left-hand and right-hand sides are the same for every element. Hence the law of constant mass for atoms of a given type must hold over the reaction steps. In matrix representation, this requirement is of the form

$$
\vec{\Gamma}\vec{A} = 0
\tag{25}
$$

Let us multiply matrices (23) and (20)

$$
\begin{bmatrix} -2 & -1 & 2 & 0 \\ 0 & -1 & -2 & 2 \\ -1 & -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 2 \\ 1 & 1 \\ 1 & 2 \end{bmatrix} =
$$

$$
= \begin{bmatrix} (-2) \times 1 + (-1) \times 0 + 2 \times 1 + 0 \times 1 & (-2) \times 0 + (-1) \times 2 + 2 \times 1 + 0 \times 2 \\ 0 \times 1 + (-1) \times 0 + (-2) \times 1 + 2 \times 1 & 0 \times 0 + (-1) \times 2 + (-2) \times 1 + 2 \times 2 \\ (-1) \times 1 + (-1) \times 0 + 0 \times 1 + 1 \times 1 & (-1) \times 0 + (-1) \times 2 + 0 \times 1 + 1 \times 2 \end{bmatrix} = 0
$$

We obtain a matrix in which all the elements are zero (a zero matrix). Hence the stoichiometric matrix is written correctly.

The size of the matrix $\vec{\Gamma}\vec{A}$ obtained by multiplying matrices $\vec{\Gamma}$ (s-by-N) and $\vec{A}$ (N-by-m) is (s-by-m). If this matrix is multiplied by the vector column of atomic masses $\vec{M}_A$ then, taking into account eqn. (21), we obtain

$$
\vec{\Gamma}\vec{A}\vec{M}_A = \vec{\Gamma}\vec{M} = \vec{0} \tag{26}
$$

This is the equation for the law of mass conservation over steps.

Equation (25) makes it possible to construct correctly the stoichiometric matrix $\vec{\Gamma}$ for a given number of substances and, hence, molecular matrix $\vec{A}$. Among the rows of this matrix one can find those that are linearly dependent. Thus, in matrix (23), the third row will be obtained if one adds the two upper rows and multiplies the sum by 1/2.

The rank of matrix $\vec{\Gamma}$ can never be above $N - m$, where m is the number of chemical elements in the system. This holds due to the fact that there always exist m linearly dependent columns of matrix $\vec{\Gamma}$ set by eqn. (25)

$$
\text{rg } \vec{\Gamma} \leqslant N - m \tag{27}
$$

The rank of matrix $\vec{A}$ is

$$
\text{rg}\vec{A} = \min (N, m) \tag{28}
$$

As a rule, $\text{rg}\vec{A} = m$, then the rank for a stoichiometric matrix is determined as

$$
\text{rg } \vec{\Gamma} \leqslant N - \text{rg}\vec{A} \tag{29}
$$

This relationship is called the Gibbs stoichiometric rule.

For example, for the mixture of reactants C, O_2, CO, CO_2, $N = 4$, $\text{rg}\vec{A} = 2$ [see eqn. (20)]. Then $\text{rg}\vec{\Gamma} \leqslant 2$; hence in matrix (23) any two rows are linearly independent.

Substances corresponding to the linearly independent columns of matrix $\vec{\Gamma}$ are called the key substances; the remainder are referred to as non-key substances. It is evident that the number of key substances is equal to the

rank of a stoichiometric matrix. For the $C + O_2 + CO + CO_2$ mixture one can choose any two substances to be the key substances.

In the general case, the solution of the problem of constructing a stoichiometric matrix using eqn. (25) is ambiguous. In principle, one can obtain multiple sets of stoichiometric equations involving those that will be linearly dependent. If stoichiometry is expected to be more than a simple "bookkeeping" of material components in a chemical system it is necessary to impose some physico-chemical restrictions, primarily on the number of reacting substances in each elementary reaction (it must be $\leqslant 3$). Then the number of possible variants is sharply reduced. So far several computation algorithms to construct stoichiometric matrices have been developed. The computer derives chemical equations taking into account the physical limitations specified. It is evident that these algorithms will be effective to describe chemical conversions in complex multi-component mixtures. In simple cases their application would be senseless.

3. Unsteady- and steady-state kinetic models

The kinetics of chemical reactions is studied in laboratory reactors. These reactors can be divided into several groups, taking into account whether they belong to closed or open systems. Closed systems can exchange energy with the environment but do not exchange substance. Open systems exchange either substance and energy or only substance.

A laboratory catalytic reactor that is a closed system, is said to be a static system. The kinetic model for complex reactions taking place in the reactor is of the form

$$\vec{\dot{c}} \equiv \frac{\mathrm{d}\vec{c}}{\mathrm{d}t} = \vec{\Gamma}^{\mathrm{T}} \vec{w}(\vec{c}) \tag{30}$$

Here $\vec{c}$ is the vector column of substance concentrations, $\vec{\Gamma}^{\mathrm{T}}$ is the transposed stoichiometric matrix, and $\vec{w}(\vec{c})$ is the vector column of reaction rates determined from eqns. (6)–(8). It is an unsteady-state kinetic model.

Let us write such a model for the catalytic reaction of methane with steam on a nickel catalyst. Its detailed mechanism has been given above.

The stoichiometric matrix is

	CH_4	H_2O	H_2	CO	CO_2	Z	ZCH_2	$ZCHOH$	ZCO	ZO	
$\vec{\Gamma} =$	-1	0	1	0	0	-1	1	0	0	0	1
	0	-1	1	0	0	0	-1	1	0	0	2
	0	0	1	0	0	0	0	-1	1	0	3
	0	0	0	1	0	1	0	0	-1	0	4
	0	-1	1	0	0	-1	0	0	0	1	5
	0	0	0	-1	1	1	0	0	0	-1	6

The transposed matrix is

$$\bar{\Gamma}^{\mathrm{T}} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & -1 & 0 \\ 1 & 1 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 & -1 & 1 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 \end{bmatrix}$$

and the vector column of reaction rates is

$$\vec{w} = \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ w_6 \end{bmatrix}$$

After multiplying matrix $\bar{\Gamma}^{\mathrm{T}}$ by the vector column of the reaction rates, $\vec{w}$, we obtain an unsteady-state kinetic model

$$\frac{d[CH_4]}{dt} = -w_1 \qquad\qquad \frac{d[H_2O]}{dt} = -w_2 - w_5$$

$$\frac{d[H_2]}{dt} = w_1 + w_2 + w_3 + w_5 \qquad\qquad \frac{d[CO]}{dt} = w_4 - w_6$$

$$\frac{d[CO_2]}{dt} = w_6 \qquad\qquad \frac{d[Z]}{dt} = -w_1 + w_4 - w_5 + w_6$$

$$\frac{d[ZCH_2]}{dt} = w_1 - w_2 \qquad\qquad \frac{d[ZCHOH]}{dt} = w_2 - w_3$$

$$\frac{d[ZCO]}{dt} = w_3 - w_4 \qquad\qquad \frac{d[ZO]}{dt} = w_5 - w_6$$

For a closed system the laws of mass conservation for various atoms must be met

$$\vec{A}^T \vec{c} \ = \ \vec{C} \tag{31}$$

where $\vec{A}$ is the molecular matrix; $\vec{c}$ the vector column of substance concentrations, and $\vec{C}$ the vector column for the numbers of the different atoms.

Thus, for the $H_2 + O_2 + H_2O$ mixture

$$\vec{A} \ = \ \begin{array}{cc} H & O \\ \begin{bmatrix} 2 & 0 \\ 0 & 2 \\ 2 & 1 \end{bmatrix} & \begin{array}{c} H_2 \\ O_2 \\ H_2O \end{array} \end{array} \qquad \vec{A}^T \ = \ \begin{bmatrix} 2 & 0 & 2 \\ 0 & 2 & 1 \end{bmatrix} \qquad \vec{c} \ = \ \begin{bmatrix} c_{H_2} \\ c_{O_2} \\ c_{H_2O} \end{bmatrix}$$

$$\vec{A}^T \vec{c} \ = \ \vec{C} \ = \ \begin{bmatrix} 2 & 0 & 2 \\ 0 & 2 & 1 \end{bmatrix} \times \begin{bmatrix} c_{H_2} \\ c_{O_2} \\ c_{H_2O} \end{bmatrix} \ = \ \begin{bmatrix} 2c_{H_2} + 2c_{H_2O} \\ 2c_{O_2} + c_{H_2O} \end{bmatrix}$$

Consequently, $C_H = 2c_{H_2} + 2c_{H_2O}$, $C_O = 2c_{O_2} + c_{H_2O}$, and C_H and $C_O =$ total amounts of O and H atoms in the system. It is evident that the equations of type (31) must fit any stoichiometry of complex reactions.

The most popular catalytic reactor which is an open system is a gradientless apparatus. The principle of its operation is to pass a reaction mixture through a system with a catalyst under intense stirring. In this case the space velocity is lower than the stirring rate.

A mathematical model for the unsteady-state heterogeneous catalytic reaction in a gradientless reactor is

$$V_g \dot{\vec{c}} \ = \ V_c f(\vec{c}, \vec{x}) + v_0 \vec{c}_0 - v\vec{c} \tag{32}$$

$$\dot{\vec{x}} \ = \ g(\vec{c}, \vec{x}) \tag{33}$$

where $\vec{c}$ is the vector of substance concentrations in the gas phase, $\vec{x}$ the vector of substance concentrations on the catalyst surface, $f(\vec{c}, \vec{x})$ and $g(\vec{c}, \vec{x})$ the vector functions of kinetic relationships derived according to the surface action law, V_c and V_g the volumes of the catalyst and the gas phase in the reactor, respectively, v_0 and v the inlet and outlet flow rates of the reaction mixture, and $\vec{c}_0$ the vector of the inlet concentrations of reactants in the gas phase. For a closed catalytic system, $v_0 = v = 0$. Equations (32) and (33) represent the unsteady-state model for a continuously stirred tank reactor.

On the basis of their heterogeneity, reactants are divided into two groups: gas-phase substances having concentration $\vec{c}$ and surface substances with concentration $\vec{x}$.

It is possible to classify substances in the other ways. Thus, one can discriminate "observable" and "unobservable" substances depending on whether their concentration is or is not controlled in the experiment. Then substances are classified as "removable" and "non-removable" from the system when exchanging with the environment and, finally, initial substan-

ces and products on the one hand and intermediates on the other. The latter do not enter into the stoichiometric equations of complex reactions. The above classifications, however, depend to a considerable extent on experimental techniques. As far as the final stoichiometric equation is concerned, their choice is not ideal. After all one can arrive at a simple result: substances can be present both in the gas phase and on the catalyst surface. In most cases the latter are "unobservable" and "non-removable" and it is these substances that are not recommended to be included in the final reaction equations.

Concentrations of gaseous substances must satisfy the state equation

$$\sum_{i=1}^{N} c_i = \frac{P}{RT} \tag{34}$$

where P is the pressure of the gas mixture, T the absolute temperature, and R the universal gas constant.

The concentrations of the surface substances are related by the equation

$$\sum_{i=1}^{n} b_{ij} x_i = c_j \tag{35}$$

Here $b_{ij} =$ the number of j-type active sites entering into the ith substance. In most cases it is assumed that there exists only one type of active site, hence the linear law of conservation, eqn. (35), is unique.

As a rule $b_{ij} = 1$. For the reaction of methane with water vapour, eqn. (35) can be rewritten as

$$x_Z + x_{ZCH_2} + x_{ZCHOH} + x_{ZCO} + x_{ZO} = c_Z$$

(here $c_Z = 10^{14}$–10^{15} molecules cm^{-2}).

Now if the concept of surface coverage, i.e. dimensionless concentrations $\Theta_i = x_i/c_z$, is introduced, we obtain

$$\sum_{i=1}^{n} \Theta_i = 1 \tag{36}$$

provided that there is only one type of active site and $b_{ij} = 1$.

After achieving the steady state, eqns. (32) and (33) transform into

$$V_c f(\vec{c}, \vec{x}) + v_0 \vec{c}_0 - v\vec{c} = 0 \tag{37}$$

$$g(\vec{c}, \vec{x}) = 0$$

The steady state for a closed system is equilibrium. From eqn. (37) we obtain

$$\frac{v\vec{c} - v_0 \vec{c}_0}{V_c} = f(\vec{c}, \vec{x}) = \vec{W} \tag{38}$$

Equations (36) and (37) represent the steady-state model. After achieving

the steady-state, eqn. (38) is used to determine W, the steady-state rate for concentration variations of gas-phase substances, experimentally.

If one suggests that, in the course of the experiment, the flow rate of the reaction mixture varies insignificantly, $v \approx v_0$, then eqns. (32) and (38) can be written as

$$V_g \dot{\vec{c}} = V_c f(\vec{c}, \vec{x}) + v(\vec{c}_0 - \vec{c}) \tag{39}$$

$$\frac{v(\vec{c}_0 - \vec{c})}{V_c} = f(\vec{c}, \vec{x}) = \vec{W} \cdot \tag{40}$$

One must note the significant peculiarity of mechanisms and models for catalytic reactions. The sequence of steps in the detailed mechanism always contains at least one cycle of intermediate substances, i.e. a catalytic cycle. It means that substances containing active catalytic sites are both consumed and formed. This can be confirmed by the stoichiometric matrix for the reaction of methane with water vapour.

4. Steady-state reaction theory

Most catalytic reactions take place under steady conditions. In the 1950s and 1960s Horiuti and Nakamura [2] and Temkin [3] developed a steady-state reaction theory. Reactions are called steady-state provided that, with constant concentrations of gas-phase substances, the concentrations of substances on the catalyst surface are also unchanged. An example is provided by the conditions observed in a gradientless reactor. A mathematical model for a steady-state reaction is given by the algebraic set of equations (36) and (37). Of importance is the concept of the pseudo-steady-state hypothesis. Qualitatively it is specified as "matching" intermediates to a reactor gas mixture. With varying concentrations of reactants in the gas phase, the concentrations of intermediates change so that, in practice, they do not differ from the values corresponding to the steady reaction conditions with constant concentrations of gaseous substances amounting to given instantaneous concentrations. In this case a mathematical reaction model takes the form of the algebraic-differential set

$$V_g \dot{\vec{c}} = V_c f(\vec{c}, \vec{x}) + v_0 \vec{c}_0 - v \vec{c} \tag{41}$$

$$g(\vec{c}, \vec{x}) = 0 \tag{42}$$

Subset (42) treated under the assumption of constant concentrations of gas-phase substances is the set of pseudo-steady-state equations

$$g(\vec{x}) = 0 \tag{43}$$

Pseudo-steadiness is one of the most essential characteristics for catalytic reactions. In what follows this concept is specified more rigorously on the

basis of the differential equation theory. It is necessary because studying quasi-steady-state equations (the method of quasi-steady-state concentrations) is the most popular approach in the formal kinetics of complex reactions.

For the steady-state reaction theory it is not important whether the reaction is steady or pseudo-steady. Only the fact that the formation and consumption rates of intermediates are equal is of importance.

Horinti has introduced the concepts of "independent intermediates", "stoichiometric number", "reaction route" and "independent reaction routes" that have been extensively used in the steady-state reaction theory. Let us clarify them by a model izomerization reaction with a detailed mechanism

$$A + Z \; \rightleftarrows \; AZ \qquad 1$$
$$AZ \; \rightleftarrows \; BZ \qquad 1 \qquad\qquad (44)$$
$$BZ \; \rightleftarrows \; B + Z \qquad 1$$

In this case there are three intermediates AZ, BZ, and Z, the latter being an active catalytic site. Their surface coverages are related by at least one balanced relationship

$$\Theta_Z + \Theta_{AZ} + \Theta_{BZ} = 1 \qquad\qquad (45)$$

As a rule, this relationship is unique. According to eqn. (45), the number of linearly independent intermediates, I, will be lower then their total number, I_{tot}, by unity

$$I = I_{tot} - 1 \qquad\qquad (46)$$

To obtain stoichiometric equations for the reaction steps (brutto-equations) that do not involve intermediates, one must add the steps of the detailed mechanism, first multiplying them by the numbers specified. For the simple mechanism of eqns. (44) these numbers equal unity and are placed on the right-hand side of the equations of the reaction steps. Horiuti specified these numbers as stoichiometric numbers (not to confuse them with stoichiometric coefficients, which indicate the number of molecules of a reacting substance). Stoichiometric numbers must fit the equation

$$\vec{\nu}^T \vec{\Gamma}_{int} = 0 \qquad\qquad (47)$$

Here $\vec{\nu}^T$ is the transposed matrix of stoichiometric numbers and $\vec{\Gamma}_{int}$ is the matrix of stoichiometric coefficients for intermediates. Elements of the latter are taken to be negative if substance is consumed in a given reaction step, positive if it is formed, and zero if substance is not involved in the reaction step. Multiplication of matrix $\vec{\nu}^T$ (P-by-s) by matrix $\vec{\Gamma}_{int}$ (s-by-I_{tot}) gives the matrix $\vec{\nu}^T \vec{\Gamma}_{int}$ whose size is (P-by-I_{tot}) (s is the number of steps).

The vector column for the matrix of stoichiometric numbers $\vec{\nu}$ (s-by-P) is called the route of a complex reaction. The rank of matrix $\vec{\Gamma}_{int}$ cannot be

above $(s - P)$ where P is the number of linearly independent routes. It does take place due to the fact that, according to eqn. (47), there are P linearly dependent rows and usually

$$\text{rg}\vec{\Gamma}_{\text{int}} = s - P \tag{48}$$

On the other hand, with a unique law of conservation with respect to catalyst

$$\text{rg}\vec{\Gamma}_{\text{int}} = I = I_{\text{tot}} - 1 \tag{49}$$

After substituting eqn. (49) in eqn. (48), we obtain

$$P = s - I_{\text{tot}} + 1 \tag{50}$$

This relationship to determine the number of linearly independent routes is called Horinti's stoichiometric rule.

For isomerization reaction (44), $I = 3 - 1 = 2$, hence $P = 1$. This reaction is a one-route reaction.

Let us now consider a more complex case. A detailed mechanism for the synthesis of vinyl chloride on a mercuric chloride + medical charcoal catalyst can be represented by the sequence of steps

$$
\begin{array}{lcc}
 & \text{I} & \text{II} \\
HgCl_2 \cdot HCl + C_2H_2 \rightleftarrows HgCl_2 \cdot C_2H_2 \cdot HCl & 1 & 0 \\
HgCl_2 \cdot HCl + HCl \rightleftarrows HgCl_2 \cdot 2HCl & 0 & 1 \\
HgCl_2 \cdot C_2H_2 \cdot HCl + HCl \rightarrow HgCl_2 \cdot HCl + C_2H_3Cl & 1 & 0 \\
HgCl_2 \cdot 2HCl + C_2H_2 \rightarrow HgCl_2 \cdot HCl + C_2H_3Cl & 0 & 1 \\
\hline
C_2H_2 + HCl = C_2H_3Cl &
\end{array}
\tag{51}
$$
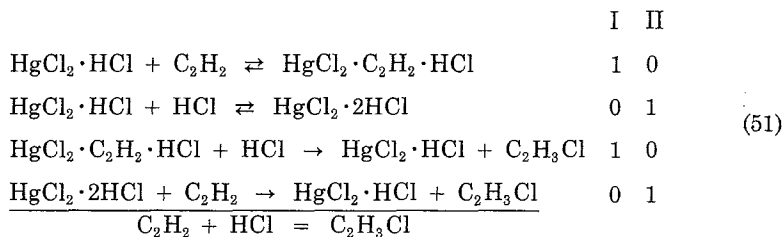
For this mechanism the initial catalytic centre is $HgCl_2 \cdot HCl$ and the surface coverage of coal by pure mercuric chloride is neglected. Here we have three intermediates. They are $HgCl_2 \cdot HCl$, $HgCl_2 \cdot 2HCl$ and $HgCl_2 \cdot C_2H_2 \cdot HCl$ ($s = 4$, $P = 4 - 3 + 1 = 2$). Consequently, two independent reaction routes are observed. Vector columns of stoichiometric numbers are given to the right of the step equations.

Each step of the mechanisms detailed above involves no more than one molecule of some intermediate. Such mechanisms are called linear.

Let us now consider an example of a non-linear mechanism, including a reaction that involves two molecules of some intermediates. The probable reaction mechanism for ammonia synthesis on an iron catalyst can be represented as

$$
\begin{array}{ll}
Z + N_2 \rightleftarrows ZN_2 & 1 \\
ZN_2 + H_2 \rightleftarrows ZN_2H_2 & 1 \\
ZN_2H_2 + Z \rightleftarrows 2ZNH & 1
\end{array}
\tag{52}
$$

$$\underline{ZNH + H_2 \rightleftarrows Z + NH_3 \quad 2}$$

$$N_2 + 3H_2 = 2NH_3$$
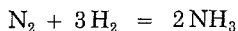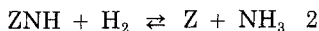
Step 3 is non-linear. There are four intermediates in this reaction, $P = 4 - 4 + 1 = 1$. In this case, unlike the one-route reaction of eqn. (44), the stoichiometric numbers are not all equal. Routes are vectors and they can be treated with the same operations as vectors. They can be multiplied by arbitrary numbers. If vector $\vec{a}$ (1;1;1), which is a route for the detailed mechanism (44) and leads to the stoichiometric equation $A = B$, is multiplied by an arbitrary number m, the vector $m\vec{a}$ is obtained. This vector is also a reaction $mA = mB$.

It is evident that the choice of stoichiometric numbers is ambiguous. In principle, one can obtain an infinitive number of routes by obtaining them as linear combinations of routes entering into the basic route.

But what are the real routes of a chemical reaction? A mechanism for a complex reaction is described completely by its set of steps, whereas its set of routes cannot be chosen adequately. It is of importance to understand that reaction steps are real, whereas reaction routes are one of the ways to represent chemical "book-keeping".

Steady-state reaction theory gives an answer to an important question, namely that if one knows a kinetic law for some elementary reaction, in what way can an equation for the complex reaction rate be derived?

Let us introduce a concept of reaction run over a given route [4]. Reaction run is determined as the disappearance of molecules of the initial substances and the appearance of those of the products whose amount is determined by the coefficients of the stoichiometric equation corresponding to a given route. Reaction rate $\vec{v}_{(p)}$ over the route P is specified as the number of the respective runs per unit time or unit surface. The rates of individual steps, w^+ and w^-, are always positive, whereas $\vec{v}_{(p)}$ can also be negative depending on the stoichiometric chemical equation.

Let us write the steady-state condition for the steps

$$\vec{v}\vec{v}_{(p)} = \vec{w} \tag{53}$$

Here $\vec{v}_{(p)}$ is the vector column of the rates over the reaction routes and $\vec{w}$ the vector column for the rates of the steps. So the rate of every step is represented as a linear combination of the rates over the reaction routes.

The sense of condition (53) reduces to the fact that the formation rate of intermediates is equal to their consumption rate. For unit time in a unit volume or on a unit surface there form $\vec{\Gamma}_{int}^{T}\vec{w}$ molecules for an intermediate. Note that the $\vec{\Gamma}_{int}^{T}$ matrix size is (I_{tot}-by-s). After substituting $\vec{w}$ from eqn. (53), we obtain

$$\vec{\Gamma}_{int}^{T}\vec{w} = \vec{\Gamma}_{int}^{T}(\vec{v}\vec{v}_{(p)}) = (\vec{\Gamma}_{int}^{T}\vec{v})\vec{v}_{(p)} \tag{54}$$

According to eqn. (47), $\vec{\Gamma}_{int}^{T}\vec{v} = 0$. Hence $\vec{\Gamma}_{int}^{T}\vec{w} = 0$ also, as was to be shown.

Let us derive the basic equation for the steady-state reaction theory [3]. For this purpose we will use the identity

$$(w_1 - w_{-1})w_2 w_3 \ldots + w_{-1}(w_2 - w_{-2})w_3 \ldots + w_{-1}w_{-2}(w_3 - w_{-3}) \ldots$$
$$+ \ldots = w_1 w_2 w_3 \ldots - w_{-1}w_{-2}w_{-3} \ldots \quad (55)$$

Expressing $(w_1 - w_{-1})$, $(w_2 - w_{-2})$, etc., by the equation

$$w_s - w_{-s} = \sum_{p=1}^{P} v_s^{(p)} v_{(p)}$$

gives

$$(v_1^{(1)} v_{(1)} + v_1^{(2)} v_{(2)} + \ldots)w_2 w_3 \ldots + w_{-1}(v_2^{(1)} v_{(1)} + v_2^{(2)} v_{(2)} + \ldots)w_3 \ldots +$$
$$+ w_{-1}w_{-2}(v_3^{(1)} v_{(1)} + v_3^{(2)} v_{(2)} + \ldots) \ldots + \ldots$$
$$= w_1 w_2 w_3 \ldots + w_{-1} w_{-2} w_{-3} \ldots$$

Dividing both sides of the above equality by $w_1 w_2 w_3 \ldots$ and rearranging the terms gives

$$v_{(1)} \left(\frac{v_1^{(1)}}{w_1} + \frac{w_{-1} v_2^{(1)}}{w_1 w_2} + \frac{w_{-1} w_{-2} v_3^{(1)}}{w_1 w_2 w_3} + \ldots \right)$$
$$+ v_{(2)} \left(\frac{v_1^{(2)}}{w_1} + \frac{w_{-1} v_2^{(2)}}{w_1 w_2} + \frac{w_{-1} w_{-2} v_3^{(2)}}{w_1 w_2 w_3} + \ldots \right) + \ldots$$
$$= 1 - \frac{w_{-1} w_{-2} w_{-3} \ldots}{w_1 w_2 w_2 \ldots} \quad (56)$$

It is this equation that is the basic equation for the steady-state reaction theory. It holds irrespective of the order of numbering the steps, which is confirmed by

$$v_{(1)} \left(\frac{v_{s_1}^{(1)}}{w_{s_1}} + \frac{w_{-s_1} v_{s_2}^{(1)}}{w_{s_1} w_{s_2}} + \frac{w_{-s_1} w_{-s_2} v_{s_3}^{(1)}}{w_{s_1} w_{s_2} w_{s_3}} + \ldots \right)$$
$$+ v_2 \left(\frac{v_{s_1}^{(2)}}{w_{s_1}} + \frac{w_{-s_1} v_{s_2}^{(2)}}{w_{s_1} w_{s_2}} + \frac{w_{-s_1} w_{-s_2} v_{s_3}^{(2)}}{w_{s_1} w_{s_2} w_{s_3}} + \ldots \right)$$
$$= 1 - \frac{w_{-s_1} w_{-s_2} w_{-s_3} \ldots \ldots}{w_{s_1} w_{s_2} w_{s_3} w_{s_4} \ldots \ldots}$$

Here the steps are numbered not by the numerals 1, 2, etc., but by double indices to show that the sequence of steps can be chosen arbitrarily.

If at least one of the reaction steps is irreversible, the term $(w_{-s_1} w_{-s_2} w_{-s_3} \ldots / w_{s_1} w_{s_2} w_{s_3} \ldots)$ on the right-hand side of eqn. (57) disappears.

To obtain a dependence of the rates over the P independent routes on the concentration of gas-phase substances, it is necessary to have a set of $s = P + I$ equations, eqn. (57), which contain I independent intermediates entering into the equation for the reaction rates w_s and w_{-s}.

This technique is not recommended for very simple mechanisms (e.g. linear mechanisms with two intermediates). In these cases one should derive a set of pseudo-steady-state equations. It will be a set of algebraic equations

that are linear with respect to the intermediates. Their concentrations and hence the step rates can easily be determined. For really complex reactions (primarily multi-route reactions), one cannot omit special algorithms simplifying the derivation of kinetic equations.

A significant simplification of the algorithm is associated with applying chemical kinetic methods taken from the graphs theory. A graph is a geometrical scheme consisting of a set of points connected by lines. It can be a complex electric scheme, a railway network, a plan of constructional works or finally, a complex chemical reaction.

Graph theory as a mathematical discipline was elaborated by Euler. In 1736 he published his article in which he proved the insolubility of a problem of keen interest to the citizens of Königsberg: whether it is possible to visit all the seven bridges over the River Preigel, crossing each bridge only once. This problem on the Königsberg bridges was unique for more than 100 years. Only in the middle of the 19th century was the interest in the graph theory reawakened. The famous four colours problem was formulated. In this it is necessary to paint different countries in such a way that neighbours are coloured differently. For a long time the problems of "commivoyager", "five queens", "jealous husbands", "Attila's horse", "Hanoi tower", etc. enriched the "science collection" section of popular magazines. Only in the last thirty years has graph theory entered a new period: it has been extensively applied in electrical engineering, economics, biology, psychology and chemical kinetics.

King and Altman [5] and Temkin developed a method to represent a reaction mechanism as a graph. Its nodes are intermediates and its edges are steps. Reaction directions are marked by arrows on the edges.

A graph corresponding to the detailed mechanism for the isomerization reaction (44) is represented as
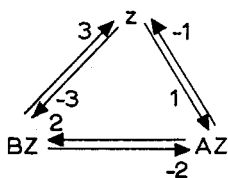
A detailed mechanism for vinyl chloride synthesis, eqn. (51), is accounted for by the graph
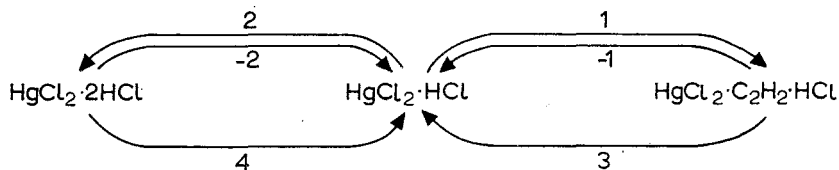
A graph circle is a final sequence of the edges in which no node except the starting point occurs twice. A graph for the isomerization reaction has one circle, whereas that for vinyl chloride synthesis contains two circles. Every route of a chemical reaction corresponds to a graph's circle and vice versa. The number of independent reaction routes is equal to the number of elements in the basis of circles. It permits us to determine independent reaction routes from the graph type.

Let us specify definitions that are necessary for further description. A tree is any sequence of the graph edges containing no circles. A spanning tree (maximal tree) is a sequence of edges going through all the nodes of the initial graph. It suffices to add at least one edge to the spanning tree so as to obtain a circle. Spanning trees of nodes are specified in this way if they enter this node. Spanning trees characterize routes of conversions due to which a given intermediate is formed from a combination of the others. Thus, for an izomerization reaction we have the following spanning trees.

Spanning trees of node Z
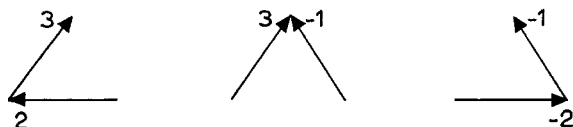
Spanning trees of node AZ
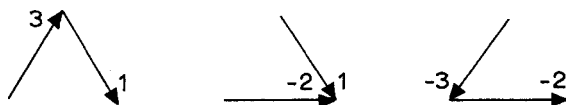
Spanning trees of node BZ
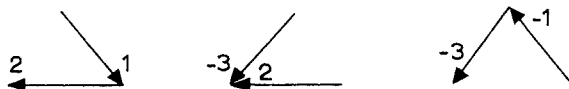
Consequently the one-route isomerization reaction has n nodes and n steps. It can easily be shown that n spanning trees enter in every node and the total number of spanning trees is n^2. For the mechanism under consideration $n = 3$ and the overall number of spanning trees will be nine. Edge weights are obtained if the rates of steps (direct and reverse) corresponding to the graph's edge are divided by the concentrations of reacting intermediates.

$$b_s^+ = \frac{w_s^+}{x_i^+} \tag{58}$$

$$b_s^- = \frac{w_s^-}{x_i^-} \tag{59}$$

Here b_s^+ and b_s^- are the edge weights for the direct and reverse steps and x_i^+

and x_i^- the concentrations of the intermediates for the direct and reverse steps, respectively. This characteristic is also called a frequency, a kinetic coefficient or probability. The physico-chemical sense of the edge weight is simple. It is a step rate with unit concentration of reacting intermediate.

Step weights for the isomerization mechanisms are

$$
\begin{aligned}
b_1 &= k_1[A] & b_{-1} &= k_{-1} \\
b_2 &= k_2 & b_{-2} &= k_{-2} \\
b_3 &= k_3 & b_{-3} &= k_{-3}[B].
\end{aligned} \tag{60}
$$

Spanning tree weights are equal to the product of its constituent edge weights. Let us determine the weights for the spanning trees entering into different nodes.

For node Z

$$
B_{Z,1} = b_2 b_3, \qquad B_{Z,2} = b_3 b_{-1}, \qquad B_{Z,3} = b_{-2} b_{-1} \tag{61}
$$

For node AZ

$$
B_{AZ,1} = b_3 b_1, \qquad B_{AZ,2} = b_1 b_{-2}, \qquad B_{AZ,3} = b_{-3} b_{-2} \tag{62}
$$

For node BZ

$$
B_{BZ,1} = b_1 b_2, \qquad B_{BZ,2} = b_2 b_{-3}, \qquad B_{BZ,3} = b_{-1} b_{-3} \tag{63}
$$

The overall spanning tree weight of the nodes is

$$
\begin{aligned}
\text{Z:} \quad B_z &= b_2 b_3 + b_3 b_{-1} + b_{-2} b_{-1} \\
\text{AZ:} \quad B_{AZ} &= b_3 b_1 + b_1 b_{-2} + b_{-3} b_{-2} \\
\text{BZ:} \quad B_{BZ} &= b_1 b_2 + b_2 b_{-3} + b_{-1} b_{-3}
\end{aligned} \tag{64}
$$

The overall spanning tree weight of the graph is

$$
B = B_Z + B_{AZ} + B_{BZ} \tag{65}
$$

Let us write a formula that will considerably simplify the derivation of kinetic equations for complex reactions

$$
x = \frac{B_X}{B} \tag{66}
$$

Here x is the intermediate concentration, B_X the overall weight of node spanning trees corresponding to a given substance and B the total spanning tree weight for a graph.

Equation (66) (Mazon law in electrical engineering) was used [6] to calculate steady-state rates of complex fermentation reactions. Recently [7], the correctness of this equation has been confirmed.

With known concentrations of intermediates one can readily determine the required rate of any step. For a one-route mechanism this rate is just the rate over the route. For example,

$$
w = k_2[AZ] - k_{-2}[BZ] \tag{67}
$$

Since $k_2 = b_2$ and $k_{-2} = b_{-2}$, eqn. (67) can be rewritten as

$$w = b_2[\text{AZ}] - b_{-2}[\text{BZ}] \tag{68}$$

Then

$$
\begin{aligned}
w &= \frac{b_2 B_{\text{AZ}} - b_{-2} B_{\text{BZ}}}{B} \\[2mm]
&= \frac{b_2(b_3 b_1 + b_1 b_{-2} + b_{-3} b_{-2}) - b_{-2}(b_1 b_2 + b_2 b_{-3} + b_{-1} b_{-3})}{B} \\[2mm]
&= \frac{b_1 b_2 b_3 - b_{-1} b_{-2} b_{-3}}{b_1 b_2 + b_2 b_3 + b_3 b_1 + b_{-1} b_{-2} + b_{-2} b_{-3} + b_{-3} b_{-1} + b_1 b_{-2} + b_2 b_{-3} + b_3 b_{-1}} \tag{69}
\end{aligned}
$$

Substituting step weights from eqn. (60) into eqn. (69) gives

$$w = \frac{k_1 k_2 k_3[\text{A}] - k_{-1} k_{-2} k_{-3}[\text{B}]}{k_1[\text{A}](k_2 + k_3 + k_{-2}) + k_{-3}[\text{B}](k_{-1} + k_{-2} + k_2) + k_2 k_3 + k_{-1} k_{-2} + k_3 k_{-1}} \tag{70}$$

Let us analyze the structure of eqn. (70). Its numerator can be written as $K^+[\text{A}] - K^-[\text{B}]$, where $K^+ = k_1 k_2 k_3$ and $K^- = k_{-1} k_{-2} k_{-3}$. In this form, it corresponds to the brutto-equation of the reaction A = B obtained by adding all the steps of the detailed mechanism with unit stoichiometric numbers. The numerator is a kinetic equation for the brutto-reaction A = B considered to be elementary and fitting the mass action law. The denominator accounts for the "non-elementary character" due to the inhibition of the complex catalytic reaction rate by the initial substances and products.

If all the steps are irreversible ($k_{-1} = k_{-2} = k_{-3} = 0$), eqn. (70) is simplified considerably to

$$w = \frac{k_1 k_2 k_3[\text{A}]}{k_1[\text{A}](k_2 + k_3) + k_2 k_3} \tag{71}$$

The same algorithm can also be effectively used for complex multi-route reactions.

A graph for a linear mechanism of any complexity can always be represented such that every independent route will have a step that belongs only to this route. Then the rate of this step w_s, is equal to that over the qth route, $v_{(q)}$

$$v_{(q)} = \frac{(b_s^+ B_i - b_s^- B_{i+1})}{B} \tag{72}$$

Here b_s^+ and b_s^- are the weights of the edges corresponding to the direct and reverse reactions of the sth step, respectively, B_i and B_{i+1} are the overall weights for the spanning trees of the ith and $(i + 1)$th graph nodes, respectively, accounting for the intermediates with the indices i and $(i + 1)$ of the sth step and B is the overall spanning tree weight of the graph.

Recently, structurized forms for steady-state kinetic equations have been obtained that can be written directly from the reaction graph [7–9]. Equation (69) is a particular case for these structurized forms.

What does the application of the graph theory give? In the introduction to his book Zykov [10] says: "Let us admit frankly: graph theory is not a revolution in science and the appearance of this apparatus in the mathematical arena is not an encroachment on mathematical fundamentals and does not introduce any ideas that pass the comprehension of most contemporaries nor wait for their complete recognition by our descendants". His words can be amplified by the fact that, in physical chemistry, graphs have not proved revolutionary. Nevertheless it is a very useful method of representation. Reaction mechanism is as if it were created for geometrical representation. When drawing direct and inverse arrows in reaction equations, chemists did not know that in this way they draw a map, a graph of complex chemical reaction. Concepts of the graph theory, namely "route", "circle", "basis of circles" correspond in the most natural way to those of chemical kinetics. And it is not surprising that various authors are starting to use graphs practically in chemical and biochemical kinetics.

5. Elements of qualitative theory of differential equations

It is not our aim here to give a complete description of the fundamentals of a qualitative theory. This can be found in the literature [11–18]. This section is only a short list of the basic concepts, i.e. a kind of a dictionary.

"Complex" behaviour of chemical reactions over a period of time can be described only in terms of unsteady-state kinetic models. As a rule they are sets of ordinary differential equations of the type

$$\frac{d\vec{c}}{dt} = f(\vec{c}, \vec{k}) \tag{73}$$

Here $\vec{c}$ is the vector of variables and $\vec{k}$ the vector of parameters. Usually the right-hand side of eqn. (73) does not contain the time variable, t, in the explicit form. Such systems are called autonomous.

The phase space of eqn. (73) is the space of vectors $\vec{c}$. Its points are specified by the coordinates $c_1, \ldots, c_n$. The set of phase space points is the set of all possible states of the system. Phase space can be not only the whole vector space but also a certain part. Thus in chemical kinetic equations, variables are either concentrations or quantities of substances in the system. Their values cannot be negative. It is therefore natural to restrict ourselves to the set of those $\vec{c}$ all the components of which are not negative, i.e. $c_i \geqslant 0$. In what follows we shall refer to these $\vec{c}$ values as non-negative. Hence positive are those $\vec{c}$ values all the components of which are positive, i.e. $c_i > 0$.

Chemical kinetic equations possess the following properties. For any non-negative initial conditions, $\vec{c}_0$, the only solution of eqn. (73) that exists is $\vec{c}(t, \vec{k}, \vec{c}_0)$. At the initial moment it takes values of $\vec{c}_0$, i.e. $\vec{c}(0, \vec{k}, \vec{c}_0) = \vec{c}_0$.

Its solution is determined over the whole of the positive time half-axis $t \in [0, \infty)$, is a continuous and differentiable function of t, $\vec{k}$, $\vec{c}_0$ and is non-negative at $t \geqslant 0$.

In chemical kinetics it is natural to consider the solutions of eqn. (73) for $t \geqslant 0$ on the positive half-axis $[0, \infty)$. Generally speaking, the function $\vec{c}(t, \vec{k}, \vec{c}_0)$ can also be determined for negative values of t, but in this case concentrations can take negative values, i.e. they have no physical sense.

A phase semi-trajectory (positive) will be called a curve in the phase space whose points are the values of $\vec{c}(t, \vec{k}, \vec{c}_0)$ with fixed $\vec{k}$, $\vec{c}_0$ and $t \in [0, \infty)$. If $\vec{c}(t, \vec{k}, \vec{c}_0)$ is also determined (and has a physical sense) for $t \in (-\infty, 0]$ one must speak about negative semi-trajectories, i.e. values of $\vec{c}(t, \vec{k}, \vec{c}_0)$ for $t \in (-\infty, 0]$ and a whole trajectory, i.e. $\vec{c}(t, \vec{k}, \vec{c}_0)$ values for $t \in (-\infty, \infty)$. Movements of the point over the phase trajectory or semi-trajectory account for the variations in the reactor mixture composition during the reaction. Since the equation $\vec{c} = \vec{c}(t, \vec{k}, \vec{c}_0)$ has only one solution, every point of the phase space is passed by one and only one, of the phase trajectories which neither intersect nor merge. A particular case of the phase trajectory is a rest point (a singular point), i.e. $\vec{c}(t, \vec{k}, \vec{c}_0) \equiv \vec{c}_0; \vec{f}(\vec{c}_0, \vec{k}) = \vec{0}$. If movement starts from the rest point, the system will remain there. For a closed chemical system, i.e. the system that does not exchange substance with the environment, the rest point is called an equilibrium state. For open systems it is called a steady state. There exist specific trajectories, e.g. limit cycles, that are closed. These specific points and trajectories have special fields of application. The totality of phase trajectories is characterized by the phase portrait. It is the advantage of the qualitative analysis that it can be used to represent a phase portrait for the set of equations without its solution since, in many cases, an analytical solution cannot be obtained and the possibilities of computing methods are also limited. A special problem is to establish the number of rest points. It will be discussed in what follows primarily as applied to heterogeneous catalytic reactions.

Important are the concepts of an ω-limit (ω in the sense of the last one, i.e. "from α to ω") point and an ω-limit set. The point $\vec{c}_1$ is called the ω-limit for the solution of eqn. (73) $\vec{c}(t, \vec{k}, \vec{c}_0)$ if the approach of this solution to $\vec{c}_1$ will be arbitrarily close after the arbitrarily high period of time. It means that there exists a sequence $\{t_1, \ldots, t_n, \ldots\}$, $t_n \to \infty$, such that $\vec{c}(t_n, \vec{k}, \vec{c}_0) \to \vec{c}_1$. The set of the whole of ω-limit points for $\vec{c}(t, \vec{k}, \vec{c}_0)$ is called an ω-limit set and is designated as $\omega(\vec{k}, \vec{c}_0)$. In the simplest case, $\omega(\vec{k}, \vec{c}_0)$ can consist only of one rest point [Fig. 1(a)]. This set itself can be a closed trajectory, i.e. a limit cycle [Fig. 1(b)]. A detailed analysis has been carried out for the systems with two variables (on the plane) [11–14]. Hitherto three-dimensional systems had not been analyzed. In 1963, Lorenz [19] established that the seemingly simple set of three equations

$$\dot{c}_1 = \sigma(c_1 - c_2)$$

$$\dot{c}_2 = -c_2 + rc_1 - c_1 c_3$$
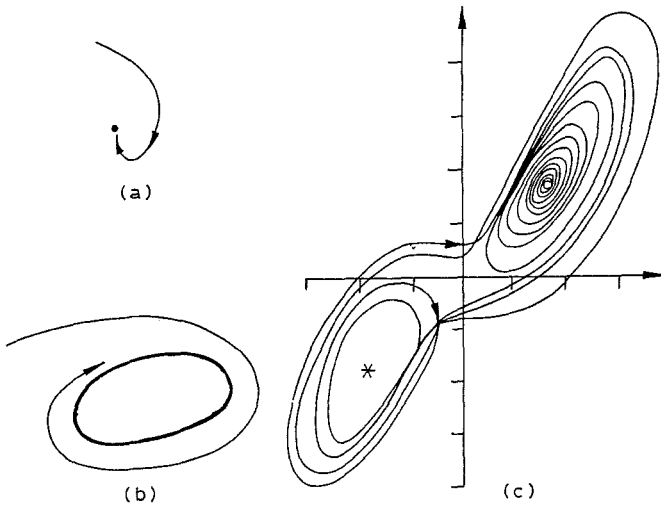
Fig. 1. Examples of ω-limit sets. (a) Rest point; (b) limit cycle; (c) Lorenz attractor [projection on the (c_1, c_3) plane, $\sigma = 10$, $r = 30$, $b = 8/3$].

$$\dot{c}_3 = - bc_3 + c_1 c_2$$

(where σ, r and b are parameters) has a limit set of unexpectedly complex character. The behaviour of this phase trajectory is illustrated in Fig. 1(c). This limit set was called a Lorenz attractor. Limit sets similar to Lorenz attractors are called strange attractors.

An important problem of the qualitative analysis is to elucidate the structure of ω-limit sets. Unfortunately, there is no commonly accepted method to solve this problem. The exception is likely to be two cases studied extensively, i.e. two-dimensional and multi-dimensional systems but near the rest point. In the latter case one must first establish whether the rest point is stable and, in particular, whether it is ω-limiting for the initial data that are close to it. The concept of stability is of great importance for the qualitative theory, and hence it must be considered in more detail. There exists local stability, i.e. to sufficiently low perturbations, and global stability, i.e. to perturbations of a given value or (often) of an arbitrary value. These types of stability do not coincide. Having proved the local stability of the system, i.e. the existence of such ε with which the system with perturbations lower than this ε remains stable, we cannot yet say that the system is stable in the global sense. It can be illustrated by the simple mechanical analogy of a ball at the bottom of a cup. If the walls of the cup are infinitely high, at any deviation the ball will roll down to the bottom (the asymptotic global stability). If the cup size is infinite, at small deviations the ball will return to its initial position (the asymptotic local stability) but with a

considerable displacement the ball will slip out of the cup (i.e. there is no asymptotic global stability).

Let us give accurate definitions. Let $\vec{c}(t, \overline{k}, \vec{c}_0)$ be a solution for eqn. (73) which satisfies the initial condition $\vec{c}(t_0) = \vec{c}_0$. This solution is called stable (according to Lyapunov) if for any infinitesimal $\varepsilon > 0$ there exists values of $\delta > 0$ such that the inequality

$$|\vec{c}_0 - \vec{\overline{c}}_0| < \delta \tag{74}$$

results in

$$|\vec{c}(t, \overline{k}, \vec{c}_0) - \vec{c}(t, \overline{k}, \vec{\overline{c}}_0)| < \varepsilon \tag{75}$$

Here $\vec{c}_0$ and $\vec{\overline{c}}_0$ are systems variable at time $t = 0$ in the unperturbed and perturbed cases, respectively.

The solution $\vec{c}(t, \overline{k}, \vec{c}_0)$ is called asymptotically stable if it is stable according to Lyapunov and there exists values of $\delta > 0$ such that the inequality (74) results in

$$|\vec{c}(t, \overline{k}, \vec{c}_0) - \vec{c}(t, \overline{k}, \vec{\overline{c}}_0)| \to 0 \quad \text{at } t \to \infty \tag{76}$$

Since rest points are particular cases of the phase trajectories $\vec{c}(t, \overline{k}, \vec{c}_0) \equiv \vec{c}_0$, the above definitions of stability according to Lyapunov are also valid for them. A rest point is stable according to Lyapunov if, for any $\varepsilon > 0$ there exists values of $\delta > 0$ such that after a deviation from this point within δ, the system remains close to it (within the ε value) for a long period of time. A rest point is asymptotically stable if it is stable according to Lyapunov and there exists values of $\delta > 0$ such that after the deviation from this point within δ the system tends to approach it at $t \to \infty$.

Many other definitions for stability are known and they do not always look alike. Each of them characterizes a required property of the solution under study. Though the Lyapunov definition of stability seems to be the most natural, in many cases it cannot be used. No stability definition can fit every real case. Some other versions of this concept are given in ref. 20 in which further references can be found.

So far we have defined the local stability ("there exists such δ as . . ."). Now let us define the global stability for rest points. The rest point $\vec{c}_0$ is called globally asymptotically stable (as a whole) within the phase space D if it is stable according to Lyapunov, and for any initial conditions $\overline{d}_0 \in D$ the solution $\vec{c}(t, \overline{k}, \overline{d}_0)$ tends to approach $\vec{c}_0$ at $t \to \infty$.

In what way is an unsteady kinetic model investigated to elucidate whether the rest point is locally stable? In this case a combination of approaches, which can be called a "rite", is used:

(1) To linearize the system: (a) to introduce new variables $\vec{\xi} = \vec{c} - \vec{\overline{c}}$ that are equal to the discrepancies between the current concentrations $\vec{c}$ and the concentrations $\vec{\overline{c}}$ at a rest point; (b) in eqn. (73) to go from $\vec{c}$ to $\vec{\xi}$; and (c) to expand the right-hand side into a series over the powers of $\vec{\xi}$ and to discard

the non-linear terms. The linearized system obtained is represented in the vector form by

$$\frac{\overrightarrow{d\xi}}{\overrightarrow{dt}} = \vec{P}\vec{\xi} \tag{77}$$

where $\vec{P}$ is the matrix of partial derivatives

$$\vec{P} = \frac{\partial \vec{f}(\vec{c}, \vec{k})}{\partial \vec{c}}\Bigg|_{\vec{c}=\vec{\overline{c}}} \tag{78}$$

or in the coordinate form

$$\frac{d\xi_i}{dt} = \sum_j \frac{\partial f_i(c, k)}{\partial c_j}\Bigg|_{\vec{c}=\vec{\overline{c}}} \xi_j \tag{79}$$

(2) To obtain a characteristic equation. It is of the form

$$\det(\vec{P} - \lambda \vec{I}) = 0 \tag{80}$$

where $\vec{I}$ is the unit matrix.

(3) To investigate the roots of the characteristic equation.

The stability of the rest point for eqn. (73) depends on the roots of the characteristic equation. The rest point is asymptotically stable if the real parts of all the roots in eqn. (80) are negative. It is unstable if the real part of at least one of the roots is positive. In the case where some roots in eqn. (80) are purely imaginary and the rest of them have a negative real part, the stability cannot be established by using only linear approximations. In this case the rest point of eqn. (77) is stable but not asymptotic.

Let us illustrate the sense of the "rite" by investigating the stability of a system with two variables. Let us take the system

$$\dot{c}_1 = P(c_1, c_2)$$
$$\dot{c}_2 = Q(c_1, c_2) \tag{81}$$

After introducing the variables $\xi_1 = c_1 - \overline{c}_1$ and $\xi_2 = c_2 - \overline{c}_2$, the linearized system (81) is of the form

$$\frac{d\xi_1}{dt} = a_{11}\xi_1 + a_{12}\xi_2; \frac{d\xi_2}{dt} = a_{21}\xi_1 + a_{22}\xi_2; \tag{82}$$

$$a_{11} = \frac{\partial P(c_1, c_2)}{\partial c_1}\Bigg|_{\vec{\overline{c}}}; \qquad a_{12} = \frac{\partial P(c_1 c_2)}{\partial c_2}\Bigg|_{\vec{\overline{c}}};$$

$$a_{21} = \frac{\partial Q(c_1, c_2)}{\partial c_1}\Bigg|_{\vec{\overline{c}}}; \qquad a_{22} = \frac{\partial Q(c_1, c_2)}{\partial c_2}\Bigg|_{\vec{\overline{c}}} \tag{83}$$

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A solution for eqn (82) is found in the form

$$\xi_1 = A_e{}^{\lambda t}$$
$$\xi_2 = Be^{\lambda t}$$

(84)

After substituting eqn. (84) in eqn. (83) and reducing by $e^{\lambda t}$, we obtain

$$\lambda A = a_{11}A + a_{12}B$$

(85)

$$\lambda B = a_{21}A + a_{22}B$$

(86)

From eqn. (86) we can write

$$A = -B\frac{a_{22} - \lambda}{a_{21}}$$

(87)

and substituting this into eqn. (85) gives

$$[(a_{11} - \lambda)(a_{22} - \lambda) - a_{12}a_{21}]\, B = 0$$

(88)

For $B \neq 0$ we have

$$\lambda^2 - (a_{11} + a_{22})\,\lambda - a_{12}a_{21} + a_{11}a_{22} = 0$$

(89)

It is just the characteristic equation. According to eqn. (80) it can be written as

$$\begin{vmatrix} a_{11} - \lambda & a_{12} \\ a_{21} & a_{22} - \lambda \end{vmatrix} = 0$$

(90)

From eqn. (89) we obtain

$$\lambda_{1,2} = \frac{a_{11} + a_{22}}{2} \pm \sqrt{\left(\frac{a_{11} + a_{22}}{2}\right)^2 + a_{21}a_{12} - a_{11}a_{22}}$$

(91)

According to the theory of linear differential equations, the overall solution for eqn. (82) is found in the form

$$\xi_1 = C_{11}e^{\lambda_1 t} + C_{12}e^{\lambda_2 t}$$
$$\xi_2 = C_{21}e^{\lambda_1 t} + C_{22}e^{\lambda_2 t}$$

(92)

Here C_{ij} is determined by the initial conditions.

The analysis of characteristic roots λ determines not only the local stability (in the small) of a singular point for system (81), but also the character of motion near it, i.e. its type. Let us investigate the linear equation (82). For this purpose we will consider the following cases separately.

(1) The roots of the characteristic equation (89) are real.

Here several variants are possible.

(a) $\lambda_1 < 0$, $\lambda_2 < 0$, and $\lambda_1 \neq \lambda_2$. The solution of eqn. (82) is a sum of the exponents $\xi_1 = C_{11}e^{\lambda_1 t} + C_{12}e^{\lambda_2 t}$ and $\xi_2 = C_{21}e^{\lambda_1 t} + C_{22}e^{\lambda_2 t}$, decreasing with time. Consequently the zero solution (a rest point) is stable. This singular
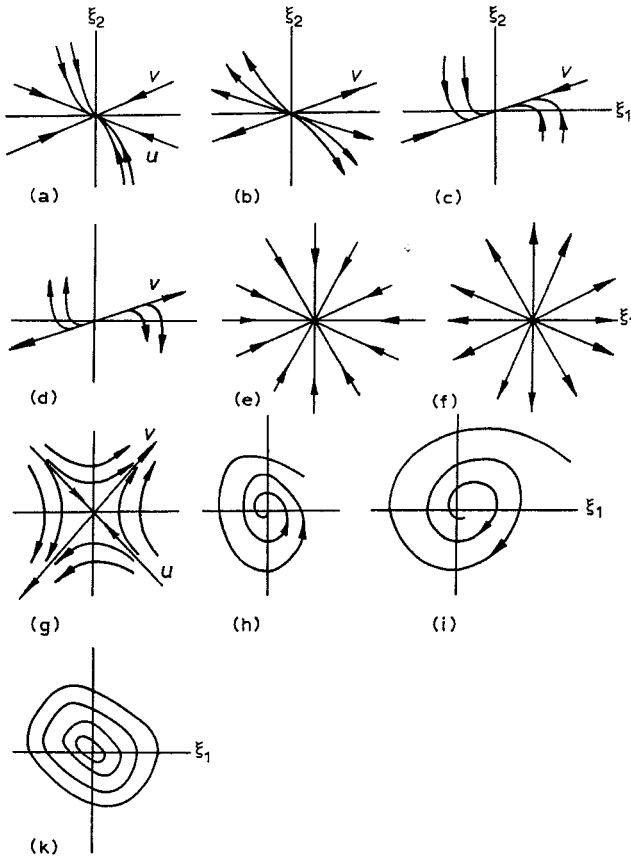
Fig. 2. Types of stationary points on the plane. (a), (c), (e) Stable nodes; (b), (d), (f) unstable nodes; (g) saddle point; (h) stable focus; (i) unstable focus, (k) whirl.

point is called a stable node. The character of trajectories near a stable node is illustrated in Fig. 2(a), where u is a straight line specified by the equation

$$\frac{\xi_1}{\xi_2} = \frac{C_{11}}{C_{21}}$$

and v is a straight line specified by the equation

$$\frac{\xi_1}{\xi_2} = \frac{C_{12}}{C_{22}}$$

In this case, to be specific we assume that $\lambda_1 < \lambda_2$.

(b) $\lambda_1 > 0$, $\lambda_2 > 0$, and $\lambda_1 \neq \lambda_2$ (here, to be specific we assume that $\lambda_1 > \lambda_2$).

Phase trajectories extend far from the singular point. It is an unstable node [Fig. 2(b)].

(c) $\lambda_1 = \lambda_2 = \lambda$, $\lambda < 0$. Two different cases exist, either the matrix (83) is diagonal

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = \begin{bmatrix} \lambda & 0 \\ 0 & \lambda \end{bmatrix}$$

or it can be reduced to the form

$$\begin{bmatrix} \lambda & 1 \\ 0 & \lambda \end{bmatrix}$$

by the linear transformation of variables. In the former case the solution is of the form $\xi_1 = A e^{\lambda t}$, $\xi_2 = B e^{\lambda t}$ and the trajectories behave as shown in Fig. 2(3). In the latter case

$$\xi_1 = C_{11} e^{\lambda t} + C_{12} t e^{\lambda t}; \ \xi_2 = C_{21} e^{\lambda t} + C_{22} t e^{\lambda t}$$

The character of trajectories is illustrated in Fig. 2(c) where v is a straight line specified by the equation $\xi_1 / \xi_2 = C_{12}/C_{22}$. In both cases the rest point is also called a stable node.

(d) $\lambda_1 = \lambda_2 = \lambda$, $\lambda > 0$. This case differs from the previous one in reversing the direction of motion. Phase trajectories extend far from the singular point [Fig. 2(d), (f)] which is called an unstable node.

(e) The roots have opposite signs (e.g. $\lambda_1 > 0$, $\lambda_2 < 0$). The general solution is the sum of exponents with opposite signs. The singular point is unstable, since with time the term with a positive exponent will be predominant. This singular point is called a saddle [Fig. 2(g)]. There are only two trajectories moving over which it is possible to enter this point. Consequently, in terms of more strict terminology, it should be treated as semi-stable.

(2) *The roots have an imaginary part.*

To analyze this case, eqns. (82) must be reduced to one second-order equation. Differentiating the first equation and eliminating ξ_2 gives

$$\frac{d^2 \xi_1}{dt^2} + 2\delta \frac{d\xi_1}{dt} + \omega_o^2 \xi_1 = 0 \tag{93}$$

where

$$2\delta = (a_{11} + a_{22}), \ \omega_o^2 = a_{11} a_{22} - a_{12} a_{21} \tag{94}$$

Let us write eqn. (91) in the form

$$\lambda_{1,2} = -\delta \pm (\delta^2 - \omega_o^2)^{1/2} \tag{95}$$

Since the roots have imaginary parts, $\omega_o^2 - \delta^2 = \omega^2 > 0$ and

$$\lambda_{1,2} = -\delta \pm i\omega \tag{96}$$

One can readily show that the solution for eqn. (93) is of the form

$$\xi(t) = e^{-\delta t}(c_1 \cos \omega t + c_2 \sin \omega t)$$

Here the following cases are possible.

(a) $\delta > 0$. The solution $\xi(t)$ is in the form of damped oscillations. Phase trajectories are converging spirals and the singular point is a stable focus [Fig. 2(h)].

(b) $\delta < 0$. Phase trajectories are diverging spirals. The singular point is an unstable focus [Fig. 1.2(i)].

(c) $\delta = 0$. The solution is undamped oscillations with frequency ω. Phase trajectories are enclosed ellipses [Fig. 2(k)]. The singular point is called a whirl. It is the non-rough point, i.e. even with insignificant variations in the parameters, the phase picture alters. For the rough point, the phase picture is not affected by small variations of parameters. The above terms (rough and non-rough) were introduced by Andronov et al. [11, 12].

Closed trajectories around the whirl-type non-rough points cannot be mathematical models for sustained self-oscillations since there exists a wide range over which neither amplitude nor self-oscillation period depends on both initial conditions and system parameters. According to Andronov et al., the stable limit cycles are a mathematical model for self-oscillations. These are isolated closed-phase trajectories with inner and outer sides approached by spiral-shape phase trajectories. The literature lacks general approaches to finding limit cycles.

There exists the concept of "Bendikson criterion". If, for eqn. (81), the expression

$$\frac{\partial P(c_1, c_2)}{\partial c_1} + \frac{\partial Q(c_1, c_2)}{\partial c_2}$$

does not change its sign in a certain region of the phase plane, this region contains no closed-phase trajectories.

In principle, to study the local stability of a stationary point from a linear approximation is not difficult. Some difficulties are met only in those cases where the real parts of characteristic roots are equal to zero. More complicated is the study of its global stability (in the large) either in a particular preset region or throughout the whole phase space. In most cases the global stability can be proved by using the properly selected Lyapunov function (a so-called second Lyapunov method). Let us consider the function $V(\vec{c})$ having first-order partial derivatives $\partial V/\partial c_i$. The expression

$$\sum_i \frac{\partial V}{\partial c_i} \dot{c}_i = \sum \frac{\partial V}{\partial c_i} f_i(\vec{c}, \vec{k}) \tag{97}$$

will be referred to a derivative V of eqn. (73) and denoted by $\dot{V}$. This expression can be treated as a derivative V of the solution of eqn. (73)

$$\frac{d}{dt} V(\vec{c}(t)) = \sum_i \frac{\partial V}{\partial c_i} \dot{c}_i = \sum_i \frac{\partial V}{\partial c_i} f_i(\vec{c}, \vec{k}) \qquad (98)$$

The second Lyapunov method implies that one uses V values which have maxima at the rest point under study whose derivative [eqn. (98)] is not positive ($\dot{V} \leqslant 0$) in the vicinity of this point and zero values are admitted only at this point.

From the various versions of this method we will choose only one. Let $\dot{V} \leqslant 0$ and, only at the rest point under study $\vec{\bar{c}}$, $\dot{V} = 0$. Then let V have its minimum, $V(\vec{\bar{c}}) = V_{min}$ at the point $\vec{\bar{c}}$ and for some $\varepsilon > V_{min}$ the set specified by the inequality $V(\vec{c}_o) < \varepsilon$ is finite. Then for any initial conditions $\vec{c}_o$ from this set the solution of eqn. (73) is $\vec{c}(t, \vec{k}, \vec{c}_o) \to \vec{\bar{c}}$ at $t \to \infty$. $V(\vec{c})$ is called a Lyapunov function. The arbitrary function whose derivative is negative because of the system is called a Chetaev or sometimes a dissipative function. Physical examples are free energy, negative entropy, mechanical energy in systems with friction, etc. Studies of the dissipative functions can often provide useful information about a given system. A modern representation for the second Lyapunov method, including a method of Lyapunov vector functions, can be found in ref. 20.

In addition to Lyapunov functions, it is also useful to investigate ω-invariant sets. The set $\tilde{S}$ in the phase space is called ω-invariant provided that, for any solution of eqn. (73), $\vec{c}(t)$ due to $\vec{c}(t_o)$ lies within $\tilde{S}$, i.e. $\vec{c}(t_o) \in \tilde{S}$, it follows that for any $t_1 > t_o$, $\vec{c}(t_1) \in \tilde{S}$. The ω-invariant set is a type of "bag": once entered there at some moment of time, the solution will not leave at any subsequent moment. It is evident that, for any dissipative function, the V-set specified by the inequality $V(\vec{c}) < \varepsilon$ is ω-invariant. Let $V(\vec{c}(t_o)) < \varepsilon$, but due to dissipativity for any $t_1 > t_o$ $V(\vec{c}(t_1)) \leqslant V(\vec{c}(t_o))$ and certainly $V(\vec{c}(t_1)) < \varepsilon$. In what follows, however, we will meet ω-invariant sets that are not associated with any differentiated dissipative function. The simplest example of an ω-invariant set is a positive semi-trajectory.

Along with all its points, any ω-invariant set has a positive semi-trajectory coming from it. Therefore among the ω-invariant sets containing a given point a positive semi-trajectory coming from it will be minimal. We believe it will be of interest for systems, depending on parameters, to investigate ω-invariant sets that are independent of them (or of a certain part of the parameters). Here the minimum ω-invariant sets containing the point $\vec{c}_o$ will no longer be semi-trajectories. These sets [designated here as $V(\vec{c}_o)$] consist of those points $\vec{\bar{c}}$ for which there exist such moments of time $t_1 > 0$, and the function $\vec{k}(t)$ on the section $[0, t_1]$, taking values within the region of parameters for the initial eqn. (73) such that the solution $\vec{c}(t)$ for the equation

$$\frac{d\vec{c}}{dt} = \vec{f}(\vec{c}, \vec{k}(t)) \qquad (99)$$

with the initial conditions $\vec{c}(0) = \vec{c}_o$, at the initial moment of time takes the value $\vec{\tilde{c}}$: $\vec{c}(t_1) = \vec{\tilde{c}}$. In other words, among the ω-invariant sets that are independent of a certain series of parameters and contain a given point, the minimum set consists of those $\vec{\tilde{c}}$ into which the solution of type (99) equations with the initial conditions $\vec{c}(0) = \vec{c}_o$ can fall at a positive moment of time. In this case the parameters of which $V(\vec{c}_o)$ must be independent can be arbitrary time functions. In constructing $V(\vec{c}_o)$ we deal with so-called differential inclusions: the derivative $\overline{dc}/dt$ in eqn. (99) has not been specified. We preset only the set to which it belongs. A theory of differential inclusions has been developing largely for the application to problems of automatic monitoring and control when the information about some object is incomplete. We will not need the data accumulated in this field since differential inclusions in kinetics are rather specific.

An important property of the systems having a convex finite ω-invariant set is as follows. Any closed convex finite ω-invariant set has a steady-state point. This follows from the known Brower fixed-point theorem (see, for example, ref. 21), that has been extensively used in various fields of mathematics to prove theorems concerning the existence of solutions.

In conclusion of our short excursion into the qualitative theory of differential equations, we shall discussed the often-used term "bifurcation". It is ascribed to the systems depending on some parameter and is applied to point to a fundamental reconstruction of phase portrait when a given parameter attains its critical value. The simplest examples of bifurcation are the appearance of a new singular point in the phase plane, its loss of stability, the appearance (birth) of a limit cycle, etc. Typical cases on the plane have been discussed in detail in refs. [11, 12, and 14]. For higher dimensions, no such studies have been carried out (and we doubt the possibility of this).

Wherever possible, a qualitative analysis of equations must precede numerical simulation. However, particularly for dimensions greater than 2, it is not always possible to carry out a complete analysis without a computer. Therefore a tendency has recently developed to apply numerical calculations to "guess" qualitative peculiarities. A reasonable strategy for complicated cases is to combine numerical experiments and their "qualitative" interpretation.

6. Relaxation in catalytic reactions

Let us consider the catalytic isomerization reaction whose steady-state kinetic model has already been considered in the previous section. Its detailed mechanism is of the form: (1) $A + Z \rightleftarrows AZ$; (2) $AZ \rightleftarrows BZ$; (3) $BZ \rightleftarrows B + Z$. Under the assumption of constant concentrations of substances in the gas phase, it will be written as

$$\frac{d[Z]}{dt} = -k_1[A][Z] + k_{-1}[AZ] + k_3[BZ] - k_{-3}[B][Z]$$

$$\frac{d[AZ]}{dt} = k_1[A][Z] - k_{-1}[AZ] - k_2[AZ] + k_{-2}[BZ] \tag{100}$$

$$\frac{d[BZ]}{dt} = k_2[AZ] - k_{-2}[BZ] - k_3[BZ] + k_{-3}[B][Z]$$

where the concentrations [A] and [B] are the parameters.

A solution is found to be $[Z] = ae^{-\lambda t}$, $[AZ] = be^{-\lambda t}$, $[BZ] = ce^{-\lambda t}$. We obtain

$$-\lambda ae^{-\lambda t} = -k_1[A]ae^{-\lambda t} + k_1be^{-\lambda t} - k_3ce^{-\lambda t} - k_{-3}[B]ae^{-\lambda t}$$

$$-\lambda be^{-\lambda t} = k_1[A]ae^{\lambda t} - k_{-1}be^{-\lambda t} - k_2be^{-\lambda t} + k_{-2}ce^{-\lambda t} \tag{101}$$

$$-\lambda ce^{-\lambda t} = k_2be^{-\lambda t} - k_{-2}ce^{-\lambda t} - k_3ce^{-\lambda t} + k_{-3}[B]ae^{-\lambda t}$$

Dividing eqns. (101) by $e^{-\lambda t}$

$$a(k_1[A] + k_{-3}[B] - \lambda) - bk_{-1} - ck_3 = 0$$

$$-ak_1[A] + b(k_{-1} + k_2 - \lambda) - ck_{-2} = 0 \tag{102}$$

$$-ak_{-3}[B] - bk_2 + c(k_3 + k_{-2} - \lambda) = 0$$

The set of equations (102) can be represented as a matrix. Elements of the whole of its columns have co-factors a, b and c, respectively. Dividing the columns by these

$$\begin{vmatrix} k_1[A] + k_{-3}[B] - \lambda & -k_{-1} & -k_3 \\ -k_1[A] & k_2 + k_{-1} - \lambda & -k_{-2} \\ -k_{-3}[B] & -k_2 & k_3 + k_{-2} - \lambda \end{vmatrix} = 0 \tag{103}$$

It is just the characteristic eqn. (80) for a given case. Let us write the determinant of matrix (103) as a sum of the products for the elements of the first row with their algebraic complement

$$(k_1[A] + k_{-3}[B] - \lambda) \cdot \begin{bmatrix} k_2 + k_{-1} - \lambda & -k_{-2} \\ -k_2 & k_3 + k_{-2} - \lambda \end{bmatrix} +$$

$$+ k_{-1} \cdot \begin{vmatrix} -k_1[A] & -k_2 \\ -k_{-3}[B] & k_3 + k_{-2} - \lambda \end{vmatrix} - k_3 \cdot \begin{vmatrix} -k_1[A] & k_2 + k_{-1} - \lambda \\ -k_{-3}[B] & -k_2 \end{vmatrix} = 0 \tag{104}$$

whence it follows

$$\lambda^3 - \lambda^2(b_1 + b_2 + b_3 + b_{-1} + b_{-2} + b_{-3}) + (B_Z + B_{AZ} + B_{BZ}) = 0 \tag{105}$$

We obtain three characteristic roots

$$\lambda_0 = 0$$

$$\lambda_1 + \lambda_2 = b_1 + b_2 + b_3 + b_{-1} + b_{-2} + b_{-3} \tag{106}$$

$$\lambda_1 \lambda_2 = B_Z + B_{AZ} + B_{BZ}$$

It is interesting that the product of the characteristic roots is the sum of the whole of the trees in the graph for this reaction mechanism [see eqns. (60) and (64)].

Since one of the roots is zero, we obtain

$$[Z](t) = [\overline{Z}] + \alpha_1 e^{\lambda_1 t} + \alpha_2 e^{\lambda_2 t}$$

$$[AZ](t) = [\overline{AZ}] + \beta_1 e^{\lambda_1 t} + \beta_2 e^{\lambda_2 t} \tag{107}$$

$$[BZ](t) = [\overline{BZ}] + \gamma_1 e^{\lambda_1 t} + \gamma_2 e^{\lambda_2 t}$$

Here $[\overline{Z}]$, $[\overline{AZ}]$ and $[\overline{BZ}]$ are the steady-state concentrations of the respective substances: $[\overline{Z}] = [Z](t)$, $[\overline{AZ}] = [AZ](t)$, $[\overline{BZ}] = [BZ](t)$ at $t \to \infty$.

One must remember one important thing. The values of λ determining relaxation are not rate constants as such. In general, the characteristic roots λ are rather complex functions of these constants.

Any dynamic system becomes stable eventually and comes to the rest point, i.e. attains its equilibrium or steady state. For closed systems, a detailed equilibrium is achieved at this point. This is not so simple as it would seem, as substantiated by a principle of the thermodynamics of irreversible processes. At a point of detailed equilibrium not only does the substance concentration remain unchanged ($dc/dt = 0$), but also the rate of each direct reaction is balanced by that of its associated reverse counterpart ($\omega_{+i} = w_{-i}$).

A necessity to apply this principle will be illustrated by a simple example. Let us take a triangle of the reactions

$$\tag{108}$$

Note that the reaction $C \rightleftarrows A$ is a combination of $A \rightleftarrows B$ and $B \rightleftarrows C$. Mechanism (108) corresponds to the kinetic model

$$\frac{d[A]}{dt} = -(k_1 + k_{-3})[A] + k_{-1}[B] + k_3[C]$$

$$\frac{d[B]}{dt} = -(k_{-1} + k_2)[B] + k_{-2}[C] + k_1[A]$$

$$\frac{d[C]}{dt} = -(k_{-2} + k_3)[C] + k_2[B] + k_{-3}[A] \tag{109}$$

At equilibrium all the derivatives are equal to zero. From eqns. (109) one can readily obtain

$$[\overline{A}] = \frac{(k_{-1}[\overline{B}] + k_3[\overline{C}])}{k_1 + k_{-3}} \tag{110}$$

$$[\overline{B}] = \frac{(k_{-2}[\overline{C}] + k_1[\overline{A}])}{k_{-1} + k_2} \tag{111}$$

$$[\overline{C}] = \frac{(k_2[\overline{B}] + k_{-3}[\overline{A}])}{k_{-2} + k_3} \tag{112}$$

Here $[\overline{A}]$, $[\overline{B}]$ and $[\overline{C}]$ are the equilibrium concentrations of the respective substances. After eliminating $[\overline{C}]$ from eqns. (110) and (111), it can easily be determined that

$$\frac{[\overline{B}]}{[\overline{A}]} = \frac{k_1 k_{-2} + k_{-3} k_{-2} + k_1 k_3}{k_2 k_3 + k_{-1} k_{-3} + k_{-1} k_{-2}} \tag{113}$$

By analogy

$$\frac{[\overline{C}]}{[\overline{B}]} = \frac{k_1 k_2 + k_{-3} k_{-1} + k_{-3} k_2}{k_{-2} k_1 + k_{-2} k_{-3} + k_1 k_3} \tag{114}$$

$$\frac{[\overline{A}]}{[\overline{C}]} = \frac{k_2 k_3 + k_{-1} k_3 + k_{-1} k_{-2}}{k_1 k_2 + k_{-3} k_{-1} + k_{-3} k_2}$$

The form of eqns. (113) and (114) is rather strange, since ratios of equilibrium concentrations must equal equilibrium constants.

$$\frac{[\overline{B}]}{[\overline{A}]} = \frac{k_1}{k_{-1}} = K_{p1}$$

$$\frac{[\overline{C}]}{[\overline{B}]} = \frac{k_2}{k_{-2}} = K_{p2} \tag{115}$$

$$\frac{[\overline{A}]}{[\overline{C}]} = \frac{k_3}{k_{-3}} = K_{p3}$$

After multiplying these relationships, we obtain a new equation

$$K_{p1} K_{p2} K_{p3} = \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}} = 1 \tag{116}$$

This equation imposes limitations on kinetic model parameters. Whence

$$k_{-3} = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \tag{117}$$

After substituting eqn. (117) into eqn. (113), we obtain

$$\frac{[\overline{B}]}{[\overline{A}]} = \frac{k_1 k_{-2} + k_1 k_3 + k_{-2}(k_1 k_2 k_3 / k_{-1} k_{-2})}{k_3 k_2 + k_3 k_{-1} + k_{-1} k_{-2}}$$

$$= \frac{k_1 (k_{-2} k_{-1} + k_3 k_{-1} + k_2 k_3)}{k_{-1}(k_3 k_2 + k_3 k_{-1} + k_{-1} k_{-2})}$$

$$= \frac{k_1}{k_{-1}} = K_{p1} \tag{118}$$

Thus to fit ordinary equilibrium relationships, system parameters should be related by an equation of the eqn. (117) type. It was Wegscheider in 1902 who first noted this fact in his study of a reaction that is more complex than the above, i.e. (1) $A_1 \rightleftarrows A_2$; (2) $A_3 \rightleftarrows A_4$; (3) $A_2 + A_3 \rightleftarrows A_1 + A_4$.

Detailed equilibrium must occur in closed systems, whereas in open systems, particularly in those that are far from being in equilibrium due to their exchange with the environment, the situation is much more complicated. Primarily, steady-state solutions can be multiple, i.e. the rates of substance formation and consumption can be balanced on many points.

For several cases, e.g. for linear pseudo-steady-state equations (linear mechanisms), the steady state is certain to be unique. But for non-linear mechanisms and kinetic models (which are quite common in catalysis, e.g. in the case of dissociative adsorption), there may be several solutions. Multiplicity of steady-states is associated with types of reaction mechanisms.

Fairly recently it has been established that a set of pseudo-steady-state equations for complex catalytic reactions can have several solutions only when their detailed mechanisms involve as one step an interaction between various intermediates [22]. The simplest catalytic mechanism possessing this property is an adsorption mechanism. For example

$$O_2 + 2\,Pt \rightarrow 2\,PtO$$
$$CO + Pt \rightarrow Pt\,CO \tag{119}$$
$$PtO + PtCO \rightarrow 2\,Pt + CO_2$$

Let us write pseudo-steady-state equations for mechanism (119)

$$2k_1[O_2](1 - [PtO] - [PtCO])^2 - k_3[PtCO][PtO] = 0 \tag{120a}$$

$$k_2[CO](1 - [PtO] - [PtCO]) - k_3[PtCO][PtO] = 0 \tag{120b}$$

The value $1 - [PtO] - [PtCO]$ is equal to the concentration of unoccupied sites on the Pt surface.

The system (120) with certain value so the parameters can have several steady-state solutions, i.e. so-called boundary solutions

$$[PtO] = 1, [PtCO] = 0$$
$$[PtO] = 0, [PtCO] = 1$$

In the former case the whole of the surface is covered by oxygen, in the latter case it is covered by CO. Here the reaction rate is zero. Other solutions also exist. After subtracting eqn. (120b) from eqn. (120a), we obtain

$$2k_1[O_2](1 - [PtO] - [PtCO])^2 = k_2[CO](1 - [PtO] - [PtCO]) \quad (121)$$

whence

$$[Pt] = 1 - [PtO] - [PtCO] = \frac{k_2[CO]}{2k_1[O_2]} \quad (122)$$

The reaction rate is

$$W = k_2[CO][Pt] = \frac{k_2{}^2[CO]^2}{2k_1[O_2]} \quad (123)$$

There are two steady states with this reaction rate since eqns. (120a) and (120b) are symmetrical with respect to [PtO] and [PtCO]. The analysis indicates that the steady states with non-zero rates are observed only when the conditions

$$2k_1[O_2] > k_2[CO]$$
$$k_3(2k_1[O_2] - k_2[CO])^2 > 8k_1[O_2]\,k_2{}^2[CO]^2 \quad (124)$$

are met.

Thus there exist four steady-state solutions two of which are stable and the other two unstable.

$$W = \frac{k_2^2[CO]^2}{2k_1[O_2]}$$

provided that the conditions (124) are met and the initial state of the surface is within the attraction region of the internal stable study state and

$$W = 0$$

for the remaining cases.

With fixed [CO], and increasing [O$_2$] the steady-state reaction rate W is initially zero (the overall surface is covered with CO) and it can then jump to the value $k_2{}^2[CO]^2/2k_1[O_2]$. With further increase in [O$_2$], the reaction rate varies inversely with [O$_2$]. In turn, with constant [O$_2$] the reaction rate rises quadratically with increasing [CO] and then "jumps" down to zero values. This example indicates that rather simple but non-linear schemes can be characterized by complex dynamic behaviour. In radiophysical terms, scheme (119) can be called a simple catalytic trigger since, in this case, there exist two stable steady states.

The kinetic model accounting for the adsorption mechanism (119) cannot have rate self-oscillations since, in this case, Bendikson criterion is met

$$\frac{\partial}{\partial[PtO]}\left(\frac{d[PtO]}{dt}\right) + \frac{\partial}{\partial[PtCO]}\left(\frac{d[PtCO]}{dt}\right) < 0 \quad (125)$$

If one wants to describe the observed experimental rate self-oscillations, mechanism (119) must be completed by a step with at least one more intermediate or the rate constants for the steps must be assumed to be dependent on the concentrations [22, 23].

The above kinetic models are based on the surface action law that is absolutely analogous to the mass action law for volume reactions in ideal systems. In this case a model of "an ideal adsorbed layer" acts, which is valid under the following assumptions:

(1) the catalyst is homogeneous, i.e. all its components are energetically the same, and the chemisorption energy is independent of the surface coverage with various substances;

(2) the catalyst is stable and its properties do not depend on the composition of the reaction and its effect on the catalyst; and

(3) the energy distribution in the system is equilibrium.

A large number of experiments (calorimetric, isotopic, etc.), however, indicate the considerable energy inhomogeneity of catalysts. On the other hand, the literature reports numerous experimental data testifying to the fact that catalysts themselves significantly change under the effect of reaction media. This was especially emphasized by Boreskov [24].

Boudart [25] noted that "though the non-ideal nature of all real catalytic surface has been convincingly proved, it remains unclear what form their associated equations must take". Boreskov [24] states: "One can note a striking contradiction between multiple cases of inhomogeneous real catalysts and the small portion of kinetic equations accounting for their inhomogeneity". Apparently, the "ideal adsorption layer" model wherein the catalyst surface is treated as a chessboard, in several cases proves to be too simplified. Great efforts are to be made to construct physically substantiated models that will account for the complex totality of all the processes taking place in the "reaction mixture–catalyst" systems.

References

1   V.I. Dimitrov, Simple Kinetics, Nauka, Novosibirsk, 1982 (in Russian).
2   J. Horiuti and T. Nakamura, Z. Phys. Chem. N.F., 11 (1957) 358.
3   M.I. Temkin, Dokl. Akad. Nauk SSSR, 152 (1963) 156.
4   M.I. Temkin, Zh. Vses. Khim. Ova., 20 (1975) 7.
5   E. King and C. Altman, J. Phys. Chem., 60 (1956) 1375.
6   M.V. Volkenshtein and B.N. Goldshtein, Biokhimiya, 31 (1966) 541; Dokl. Akad. Nauk SSSR, 170 (1966) 913.
7   V.A. Evstigneev and G.S. Yablonskii, Kinet. Katal., 20 (1979) 1549.
8   G.S. Yablonskii and V.I. Bykov, Kinet. Katal., 18 (1977) 1561.
9   V.A. Evstigneev, G.S. Yablonskii and V.I. Bykov, Dokl. Akad. Nauk SSSR, 245 (1979) 871.
10 A.A. Zykov, Finite Graphs Theory, Nauka, Novosibirsk, 1969 (in Russian).
11 A.A. Andronov, E.A. Leontovich, I.I. Gordon and A.G. Maier, Qualitative Theory of Second-Order Dynamic System, Nauka, Moscow, 1966 (in Russian).

12   A.A. Andronov, E.A. Leontovich, I.I. Gordon and A.G. Maier, Theory of Bifurcation of Dynamic Systems on a Plane, Wiley, New York, 1973.
13   A.A. Andronov, A.A. Vitt and S.E. Khaikin, Theory of Oscillations, Fitzmatgiz, Moscow, 1959 (in Russian).
14   V.I. Arnold, Additional Chapters of the Theory of Ordinary Differential Equations, Nauka, Moscow, 1978 (in Russian).
15   N. Minorsky, Nonlinear Oscillations, Van Nostrand, Princeton, NY, 1962.
16   N.N. Bogoljubov and U.A. Mitropolskii, Asymptotic Methods in the Theory of Non-linear Oscillations, Nauka, Moscow, 1974 (in Russian).
17   B.D. Hassard, N.D. Kazarinoff and J.-H. Wan, Theory and Applications of Hopf Bifurcation, Cambridge University Press, London, 1981.
18   M. Kubicek and M. Marek, Computational Methods in Bifurcation Theory and Dissipative Structures, Springer-Verlag, New York, 1983.
19   E.N. Lorenz, J. Atmos. Sci., 20 (1963) 130.
20   A.A. Martynjuk and R. Gutovskii, Integral Inequalities and Stability of Motion, Naukova Dumka, Kiev, 1979 (in Russian).
21   M.A. Krasnoselskii and P.P. Zabrejko, Geometrical Methods of Nonlinear Analysis, Nauka, Moscow, 1975 (in Russian).
22   M.G. Slin'ko, V.I. Bykov, G.S. Yablonskii and T.A. Akramov, Dokl. Akad. Nauk SSSR, 226 (1976) 876.
23   M.G. Slin'ko and M.M. Slin'ko, Catal. Rev. Sci. Eng., 17 (1978) 119.
24   G.K. Boreskov, Kinet. Katal., 13 (1972) 543.
25   M. Boudart, Usp. Khim., 43 (1974) 317 (in Russian).