

Simplest Non-linear Mechanisms of Catalytic Reactions Producing Critical Phenomena

1. Critical phenomena in heterogeneous catalytic reactions (experiment, models)

The discovery of isothermal critical effects in heterogeneous catalysis has radically changed the situation there. In recent years several surveys [1–20] have been devoted to these effects in various catalytic reactions and models used for their treatment. The possibility of the existence of a multiplicity of steady states in reactions carried out over catalytic fibres has been known for more than 70 years. It was Liljenroth [21] who first established this phenomenon in NH_3 oxidation over Pt and analyzed its stability. Later, Tamman [22], Davies [23], Frank-Kamenetskii [24], and Buben [25] performed experimental and theoretical studies of the jumpwise increase in the oxidation rate of hydrogen, carbon monoxide, and hydrocarbons on Group VIII metals. In the 1950s, when studying hydrogen oxidation over nickel, palladium, and platinum, Boreskov et al. [26, 27] found that, in a certain range of reaction parameters, the same gas phase composition is associated with sharply differing values of the steady-state reaction rate. It is this effect that is called a multiplicity of steady states in a catalytic reaction. Later, similar effects along with self-oscillations of the reaction rate were observed in various catalytic reactions, e.g. CO hydrogenation [28], hydrogen oxidation [29–41], oxidation of ammonia [42–45] and ethylene [46–48], and others [49–62].

Critical effects in CO oxidation over Pt catalysts were obtained [33, 34, 63–85] in various catalytic systems: over wires, foils and gauzes, on single pellets and fixed beds, in isothermal and adiabatic reactors (differential and integral). The literature also reported the oscillating behaviour of the homogeneous oxidation of CO [86, 87].

We must emphasize one essential peculiarity: until recently practically the whole of the critical effects in CO oxidation (and in the other catalytic oxidation reactions) were obtained at normal (~ 760 torr) or almost normal pressures. In ultrahigh-vacuum experiments, these effects have been observed*, and have induced scepticism. Over the last several years the situa-

* Self-oscillations of the rate in high-vacuum experiments have been found only for the platinum-catalyzed reactions ($\text{NO} + \text{CO}$) [61] and ($\text{CO} + \text{O}_2$) [88].

tion has changed since some data were obtained at $p \approx 10^{-8}$ to 10^{-7} torr [89–92], which can be interpreted as a multiplicity of steady states or at least a high parametric sensitivity of the reaction rate. For example, Tataurov and Ivanov [89] found a hysteresis of the reaction rate on increasing and decreasing the temperature with a 5 min exposure at every temperature value ($p_{O_2}/p_{CO} = 6$). But on increasing the time exposure (up to 30–60 min), this hysteresis appeared to be “false”. They observed a prolonged (above 50 min) time for the achievement of the steady state with a low reaction rate. This is ascribed [89] to both the slow formation of a surface oxide and the total retardation of the reaction rate with decreasing temperature. A quantitative analysis of these data will be carried out in what follows.

Taylor et al. [90], when studying the oxidation of CO over Ir (110), also found hysteresis on decreasing and increasing the temperature. This hysteresis is ascribed primarily to the non-linear kinetic dependences of the conversions of surface substances [90]. However, in our opinion, this hysteresis is also most likely to be “false” since temperature variations of catalyst were sufficiently high ($\sim 1.25 \text{ K s}^{-1}$) and the steady state could hardly be achieved.

It is interesting that, in the experiments by Taylor et al. [90] after the repetition of the same standard experimental run (increase and then decrease of temperature), the hysteresis peculiarities of kinetic curves were preserved but not reproduced quantitatively. Apparently, this is also associated with the fact that the time to achieve a steady state was insufficient. It could also be due to the slow mass transfer processes between surface and bulk.

Some data concerning sharp jumps in the dependence of the steady-state rate on the temperature and partial pressures of CO and O₂ are reported in refs. 91 and 92. The latter study is of interest since the authors obtained a region for the multiplicity of steady-state rates; every value of the parameter (in their case it was the partial pressure of CO) was maintained for a long time (up to an hour). We believe it is only in this study that the “real” hysteresis has been established. The long time to go from a metastable state with a high reaction rate to a steady state with a low reaction rate is ascribed by the authors [92] to the formation of well-ordered structures of CO adsorbed on the Pt surface.

Most of the critical effects in oxidation reactions over Pt metals were observed under isothermal conditions. Hence the complex dynamic behaviour can be directly due to the structure of the detailed catalytic reaction mechanism, specifically to the laws of physico-chemical processes in the “reaction medium–catalyst” systems. The types and properties of mathematical models to describe critical effects are naturally dependent on those physico-chemical prerequisites on which these models are often based [4, 9]. Let us describe the most important factors used in the literature to interpret critical effects.

(a) The presence of the step for the interaction between various inter-

mediates in the detailed catalytic reaction mechanisms, the competition of adsorption and interaction steps and the reversible change in the number of active surface centres in the course of the reaction [93–111].

(b) Variations in the rate constants under the influence of the surface coverages or the concentration in a thin subsurface layer of catalyst [3, 4, 15, 28–32, 112–121].

(c) Superheating in the thin surface layer of catalyst [66, 67, 122–125].

(d) Branching chain processes on the catalyst surface [5, 17, 35, 36, 41–44, 126–130].

(e) Homogeneous continuation of the heterogeneous catalytic reaction (reaction outcome in the gas volume) [86, 131–135].

(f) Phase transformations on the catalyst surface [136, 137], including the formation and decomposition of surface and subsurface oxides during the reaction [37, 47–49, 85, 118]; structural transformations of the catalyst surface and its reconstruction as a result of the reaction [138–145].

(g) Interaction of kinetic and diffusional processes [71, 145–151].

(h) The effect of heat- and mass-transfer processes [6–8, 11, 12, 33, 63, 65, 76–80, 118, 119, 148–161].

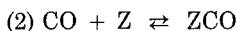
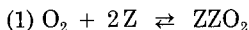
It was Wicke and co-workers [33, 34] who were the first to observe critical effects in CO oxidation over Pt/Al₂O₃ and Pt wires. (Approximately at the same time, similar results were obtained by Hugo and Jakubith [64].) When the reaction is carried out at a gas temperature $T = 453$ K in an air + 1% CO mixture, self-oscillations in the formation rate of CO₂ and the catalyst temperature (with a 2–3 K oscillation amplitude) and also hysteresis behaviour of the steady-state rate with varying CO concentration and gas-phase temperature are observed. An important conclusion drawn by Wicke and co-workers [33, 34] is that the reason for this dynamic behaviour of the reaction consists in the complex chemical mechanism of the processes on the catalyst surface. Neither external nor internal diffusion and thermal processes can be responsible for the critical phenomena [34]. The authors [34] believe that the non-linear rates of intermediate formation and decomposition on the catalyst surface can lead to the multiplicity of steady states. But Wicke did not carry out a systematic analysis of the models corresponding to his concepts. The model investigated in ref. 34 was simplified but not substantiated. It was based on the adsorption mechanism including a step of oxygen dissociative adsorption on a doubled centre, molecular adsorption of CO, and an interaction step between these adsorbed substances. It was suggested that oxygen adsorption is in equilibrium and at the same time the concentration of O₂ZZ is negligible. If these suggestions are valid, the formation rate of CO₂ is described by

$$W_{\text{CO}_2} = kP_{\text{O}_2}[\text{ZCO}](1 - [\text{ZCO}])^2$$

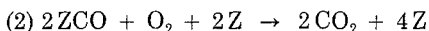
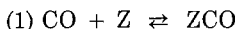
It must be noted that the assumptions concerning the equilibrium adsorption of O₂ and the low concentration of O₂ZZ hold only at sufficiently high temperatures. But in the region of critical effects, oxygen adsorption is

practically irreversible and its surface concentration can be sufficiently high [37, 66, 85]. In addition, Wicke did not in practice give a mechanism as a combination of steps. To reconstruct this combination using the kinetic dependence of W_{CO_2} given in ref. 34 is difficult.

Wicke's line was continued by Eigenberger [7, 105–107] who applied the same concepts. His first publication on this subject [105] appeared in 1976. He formulated a mechanism of CO oxidation over Pt metals



Using the assumption about the equilibrium adsorption of oxygen, Eigenberger represented this mechanism by the still simpler autocatalytic scheme



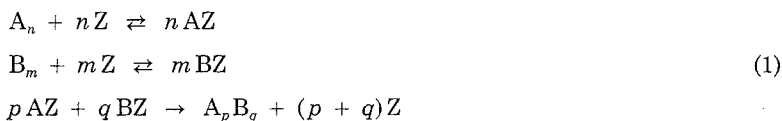
This scheme interpreting the multiplicity of steady states is practically identical to various autocatalytic systems used by Prigogine and his school ("brusselator", "oregonator") to interpret critical effects in homogeneous reactions. An important contribution of Eigenberger is that he used a "buffer step" to describe self-oscillations in the catalytic reaction rate. To modify the Wicke scheme, he added reversible formation steps of unreactive forms of oxygen [105–107]. It is these steps acting as "feedbacks" (binding–releasing of unoccupied sites) that permitted Eigenberger to describe quantitatively the rate self-oscillations obtained in Hugo and Jakubith's experiments [64]. It is interesting that the latter suggested a reversible slow transition between two forms (bridged and linear) of adsorbed CO, which can be treated as a buffer step.

Later, a comprehensive qualitative and numerical study of the above mechanism was performed but without Eigenberger's simplifying suggestions about the equilibrium adsorption of oxygen and low concentrations of O_2ZZ (these suggestions were necessary to reduce the complete system of three ordinary differential equations to a set of two equations) [162]. The analysis and comparison of the results calculated according to the complete [162] and "simplified" models [107] show that this simplification is not always correct and can essentially change the system dynamics up to the change of the number and stability type of steady states.

Studies of CO oxidation over $\text{Pt}/\text{Al}_2\text{O}_3$ [72–74] showed that oscillations are observed only in the presence of admixed hydrocarbons or water. If the reaction mixture is thoroughly purified, self-oscillations vanish. These data are evidently an argument in favour of the fact that reversible formation steps of non-reactive species play a special role in the appearance of self-oscillations. In accordance with the assertions of Marshneva et al. [163, 164],

these steps can also be the steps of the reversible adsorption of reaction products since the removal of CO_2 from the gas phase always leads to the stopping of self-oscillation processes. But some special experiments (e.g. refs. 85 and 165) show that self-oscillations also exist when the reaction mixture has been thoroughly purified. Apparently, at present we cannot make a final conclusion.

The Wicke and Eigenberger models are models for an ideal adsorption layer. They have been examined at the Institute of Catalysis, Siberian Branch of the U.S.S.R. Academy of Sciences [93–104, 108, 109] independently of Wicke and Eigenberger (the first publications refer to 1974). It was shown [93–96] that, for the detailed mechanisms of catalytic reactions either with the steps that are linear with respect to intermediates or with non-linear steps (but containing no interactions between various intermediates), the steady state of the reaction is unique and stable (autocatalytic steps are assumed to be absent). Thus the necessary condition for the multiplicity of steady states is the presence of steps for the interaction between various intermediates in the detailed reaction mechanism [93–100]. Special attention in these studies was paid to the adsorption mechanism of the general type permitting the multiplicity of steady states [102–104]



Various modifications of this mechanism are often used to describe catalytic oxidation reactions. The simplest version of this mechanism providing the multiplicity of steady states is that with $n = 2$, $m = p = q = 1$ (the simplest catalytic trigger). Studies of its dynamic properties assuming that the adsorption steps are irreversible, were made by Yablonskii et al. [97, 98, 166]. The dynamic behaviour of the mathematical models corresponding to these mechanisms is studied comprehensively in this chapter. Catalytic mechanisms with various buffer steps but without Eigenberger's simplifying assumptions have been studied in detail [108, 109]. Sufficient conditions under the fulfilment of which simple kinetic models constructed in accordance with the law of acting surfaces have self-oscillational solutions were obtained. The Ivanova general algorithm [167, 168] has been applied [109] which allowed the authors, according to the type of chemical reaction mechanisms, to judge which mechanism can be used to interpret the experimental critical effects found.

Comprehensive experimental and theoretical investigations of self-oscillations in oxidation reactions were begun in the 1970s by Slinko and co-workers (hydrogen oxidation on Ni and Pt). Their experimental methods are the optimal combination of electrothermography (ETM) with continuous measurements of the contact potential difference (CPD) between the catalyst and a reference electrode. It permitted them to observe simultaneously

the reaction rate and variations in the adsorbed layer composition on catalyst surfaces [29–32]. The specificity of the mathematical models elaborated by Slinko et al. to describe the dynamic behaviour of reactions [4, 30, 32, 112–115, 117] is taking into account the contribution of the substances adsorbed and dissolved in the subsurface layer to the catalytic properties of metals. On the one hand, it takes into account the dependence of activation energies for the reactions of the detailed mechanism on the adsorbed layer composition. The existence of this dependence has been confirmed by a large number of recent experimental data (see ref. 169). On the other hand, in several cases [32, 112] slow exchange processes between the catalyst surface and the bulk and also the dependence of reaction activation energies on the substance concentrations in the subsurface layer [115] have been taken into consideration. Models accounting for the latter dependence provide complex chaotic self-oscillations observed in experiments [4, 32]. The methods and the models elaborated by Slinko et al. have been extended to the other reactions, in particular that of CO oxidation. It is for this reaction that Pikios and Luss [116] and Ali and Hugo [120] later used the dependence of activation energies on the surface composition.

In 1973, Dauchot and Van Cakenberghe [66], when studying CO oxidation, established self-oscillations in the temperature of a Pt wire and in the photocurrent on a Si electrode covered with a Pt film. The authors [66] ascribed the photocurrent oscillations to oscillations in the composition of the adsorbed layer on the Pt film. They have proved experimentally that, in the region where the reaction rate is proportional to $P_{\text{CO}}/P_{\text{O}_2}$, the surface is covered by chemisorbed oxygen, whereas at high values of $P_{\text{CO}}/P_{\text{O}_2}$ the surface contains largely chemisorbed CO inhibiting the reaction. They interpreted self-oscillations in terms of the adsorption mechanism, according to which heat released during the reaction leads to a drastic increase in the surface coverage by oxygen. When the surface is almost completely covered by oxygen the reaction stops and the surface slowly cools. In this case the conditions for the simultaneous adsorption of CO and O₂ are once again created. Mathematical models corresponding to this thermokinetic hypothesis for the generation of self-oscillations have been studied [122–125]. The variables in these models are the concentrations of adsorbed oxygen and CO and the temperature of catalyst surface; the gas temperature is assumed to be constant. Though the calculated oscillations [122] of oxygen coverage have periods close to those for the oscillations of photocurrent [66], the amplitudes for the temperature oscillations of the catalyst surface obtained by using this model are too high (200–300 K) to speak about the fairly good agreement between calculation and experiment. Besides, it is likely that this model cannot describe oscillations with long periods (tens of minutes). This fact has caused some criticism [170].

Barelko et al. [5, 35, 42–44, 69, 70, 126, 127] investigated isothermal critical effects in several reactions of complete oxidation on Pt using a compensa-

tion electrothermograph developed by the group [171] which permitted them to eliminate the effect of a thermal factor.

To interpret critical effects, a phenomenological model of the branched reaction was suggested. The essence of this model consists in the fact that the reaction on the active catalyst centre is accompanied by energy release leading to the formation of new active centres. Active centres are the adsorbed atoms from the metal crystal lattice or the vacancies formed as a result of this transformation adsorption. They can be destroyed due to the return of adatoms into the lattice, its sublimation, etc. [35]. On the basis of this model, Barelko et al. interpreted the dynamics of reaction ignition and extinction, memorizing effects, different temperatures for the ignition and extinction, and inhibiting effects. A direct proof for the validity of this hypothesis would be a measurement of the super-equilibrium concentration for adsorbed metal atoms when catalytic reactions take place on the metal surface. Later, this hypothesis concerning the change in the number of active centres during the reaction was used in some theoretical studies [130, 172]. The Barelko hypothesis confirms the phenomenon of catalytic corrosion [128] that had been given special attention by Jensen and Ray [138, 139]. These authors believe that the reason for self-oscillations in various catalytic systems is of a physical rather than of a chemical nature. The suggested model of "fuzzy wire" was based on several experimental data, in particular the fact that the preliminary thermal treatment of a Pt fibre leads to the formation of rough porous protrusions on the surface on which a catalytic process takes place. Large temperature fluctuations arise on the surface of these formations. Every such formation is suggested to be an independent oscillator. A mathematical model corresponding to this hypothesis is a complex system of integrodifferential equations. The model provides a good qualitative (and partly quantitative) agreement between the calculated and experimental complex oscillations in the oxidation reactions of butane and cyclohexane. It is useful to describe chaotic non-isothermal oscillations, but it can hardly be used (as the authors themselves claim [138]) to interpret isothermal oscillations with long periods (oxidation of CO, H₂, etc.). (The periods of isothermal self-oscillations of the rate can differ considerably: they can amount to minutes [33, 34, 75, 85] or seconds [63, 73, 81, 85].)

In several recent studies an assumption is made concerning the homogeneous-heterogeneous mechanisms of oxidation reactions as a reason for critical effects, in particular in the oxidation of cyclohexane over zeolites [131] and of CO over Pd [132-134] and V [135] catalysts. Berman and Elinek [131] have established in their experiments that cyclohexane oxidation over zeolites follows a mixed homogeneous-heterogeneous mechanism. Studies of the mathematical reaction model written down in accordance with the law of mass action showed that the system can have from one to three steady states. When the steady state is unique, there exists a region of parameters

in which this state is unstable. In this case, limit cycles arise. The model describes qualitatively fluctuations in the amplitude and period of reaction rate oscillations with varying cyclohexane concentration. Calculated values for the period and average rate are close to experimental data. It is interesting that, in the case of multiplicity, the lower steady state (with a low reaction rate) is characterized by a very low concentration of radicals in the gas phase whereas, in the upper steady state (with a high reaction rate), the surface concentration of intermediates is low. It indicates that homogeneous-heterogeneous processes are unstable. Stable performance is observed only for either heterogeneous or homogeneous oxidation [131]. Unstable behaviour, when the reaction extends into gas volume, was also observed in CO oxidation [132-135]. However, so far no models that would be similar to that suggested by Berman and Elinek to describe cyclohexane oxidation over zeolites [131] have been constructed. The main difficulty here is the lack of information about the formation steps of radicals.

Berman and Krylov [136, 137] showed that phase transformations over catalyst surfaces can account for the existence of several steady states in the kinetic regions. Two-dimensional phases on a catalyst surface can form either during the adsorption of one reactant or under the competing adsorption of two reactants. Wicke et al. [10, 83, 84] ascribe the critical effect in the isothermal oxidation of CO over Pt to the reversible formation of its two-dimensional clusters on the Pt surface. The reaction is assumed to follow an adsorption mechanism. In this case CO can adsorb on two types of Pt active centre (α and β) whereas oxygen can be adsorbed only on β . The number of β reactive centres is approximately 1/4 of the total number. The unstable behaviour of the reaction rate is due to the competition between CO adsorption promoting the growth of clusters and desorption and interaction of adsorbed substances. The latter processes are also enhanced by the growth of CO clusters. However, models accounting for the organization and growth of surface clusters have so far been insufficiently developed.

Riekert in his theoretical investigation [173] showed that, in oxidation reactions over metals, critical effects can arise if, under reaction conditions, the existence of both a pure metal surface and a subsurface oxide that can contact with the reactants is thermodynamically possible.

The process of catalyst oxidation and reduction can be treated as a reversible phase transition [136]. It is to this process that the authors of recent investigations [37, 47-49, 85] ascribe critical effects. When studying kinetic self-oscillations in the oxidation of hydrogen over nickel [37] and measuring CPD, the authors established that the reaction performance oscillates between the states in which oxygen is adsorbed either on the reduced or on the oxidized nickel surface. Vayenas et al. [47-49], by using direct measurements of the electrochemical activity of O_2 adsorbed on Pt, showed that the isothermal self-oscillations of the ethylene oxidation rate over Pt are due to the periodic formation and decomposition of subsurface Pt oxides. A mathemati-

cal model for this reaction is based on the mechanism which includes the steps of oxygen adsorption, subsurface oxide formation, and impact interaction between gaseous ethylene and oxygen in the adsorbed and dissolved states [48]. The parameters of this model were determined from independent measurements. It appeared that this model can describe fairly well all the experimental characteristics of the oscillation and steady-state performance of this reaction [48].

The properties of the rate oscillations in the oxidation of CO over Pt, Pd, and Ir were examined comprehensively in experiments by Turner et al. [85] who suggested that the reaction follows an adsorption mechanism. Studies of the reaction model written in accordance with the law of acting surfaces show the existence of regions of multiplicity for the curves $W_{\text{CO}_2}(T)$ at a fixed ratio of reactant partial pressures $P_{\text{CO}}/P_{\text{O}_2}$ and $W_{\text{CO}_2}(P_{\text{CO}}/P_{\text{O}_2})$ at a fixed temperature T , which was already known [166, 174–176]. Experimental data indicate that self-oscillations take place between two stable branches of the kinetic curves in the region of hysteresis [85].

Thus the adsorption mechanism has given boundaries for the reaction rate within which self-oscillations take place. But this mechanism by itself does not account for the existence of self-oscillations (it will be discussed in detail in what follows). The analysis of their experimental data led Turner et al. [85] to the conclusion that the fluctuations in the catalyst temperature and CO partial pressure cannot cause self-oscillations. They ascribe these self-oscillations to the slow process of the formation and removal of subsurface oxygen due to which the surface catalytic activity changes [85]. This effect is accounted for by the suggestion concerning the blocking of chemisorption sites for O_2 and CO by the oxide formed. These active sites are released owing to the slow interaction of subsurface oxygen with chemisorbed CO. Slow oxidation and reduction of the surface metal film induces transitions between two stable branches of the kinetic curves in the region of multiplicity. These assumptions permitted Turner et al. [85] to remain in the framework of the validity for the hypothesis of an ideal adsorption layer.

Qualitative studies of this dynamic model with three variables, i.e. surface concentrations of CO and the two forms of oxygen (surface and subsurface), showed [170] the possibility of interpreting self-oscillations in this catalytic system. Recently a comprehensive analysis of this model [170] has been carried out [177]. Sales et al. [178, 179] determined experimentally the parameters for the oxidation and reduction of the Pt subsurface layer. The application of these parameters and those for the CO oxidation over Pt that are close to the values measured in high-vacuum experiments, made it possible to perform the quantitative reproduction, by using the model [180], of almost the whole of the experimentally observed characteristics for the self-oscillations in the reaction rate of CO oxidation over Pt.

During the last decade, the models have been extensively applied, accounting for the biographical inhomogeneity of catalyst surfaces and the

formation of spatio-temporal waves and dissipative structures due to the catalytic reaction [181, 182]. Chang [183] represented a catalyst surface as a set of uniform domains. His model can describe fluctuations in the catalyst activity as a result of the biographical inhomogeneity, non-uniformity of transfer coefficients, and local oscillations in the substance flow. A macroscopically measured value (e.g. steady-state reaction rate) is the result of averaging over various domains. The theory [183] interprets the existence of "soft" hysteresis for the observed values. The author gives their simple classification and predicts new types of hysteresis. Chang's results [183] were used to interpret the experimental data of Barelko [43] for NH_3 oxidation over Pt. In ref. 184, spatially inhomogeneous states of the catalyst are modelled through its representation as a system of separate particles-microreactors opened for heat and mass transfer and mutual interactions.

The studies of Ertl and co-workers showed that the reason for self-oscillations [142, 145, 185-187] and hysteresis effects [143] in CO oxidation over Pt(100) in high vacuum ($\sim 10^{-4}$ Torr) is the existence of spatio-temporal waves of the reversible surface phase transition $\text{hex} \leftrightarrow (1 \times 1)$. The mathematical model [188] suggests that in each of the phases an adsorption mechanism with various parameters of CO and O_2 adsorption/desorption and their interaction is realized, and the phase transition is modelled by a semi-empirical method via the introduction of discontinuous non-linearity. Later, an imitation model based on the stochastic automat was used [189] to study the qualitative characteristics for the dynamic behaviour of the surface.

Yeates et al. [190] made an attempt to generalize the Ertl results for polycrystalline Pt and the other Pt single crystal planes at almost atmospheric pressures. The results [190] indicate that the oscillational performance of CO oxidation can be due to at least two different mechanisms. At low pressures ($\sim 10^{-4}$ Torr), for Pt(100) the self-oscillations of the reaction rate result from the reversible phase transition $\text{hex} \leftrightarrow (1 \times 1)$ [142] but at higher pressures and for Pt single crystals differing from Pt(100) as well as for polycrystalline Pt, the authors [190] believe that a more probable model is similar to that suggested elsewhere [170]. The model was modified [190] by the introduction of an empirical temperature dependence of the reaction rate. Later, Aluko and Chang [191] added the heat balance equation and could describe temperature oscillations of the catalyst. This approach makes it possible to eliminate the disadvantage of thermokinetic models [170]: due to the slow process of surface oxidation/reduction the model [191] describes oscillations with sufficiently long (~ 10 min) periods. The conclusions [190] were confirmed in an experiment by Lindstrom and Tsotsis [192]. It must be noted, however, that Kaul and Wolf [193] observed wave propagation over supported Pt and Pd catalysts under non-isothermal self-oscillational CO oxidation at atmospheric pressure.

Note that an interesting tendency has recently been observed: the literature reports studies of the dynamics for the models of an ideal adsorption

layer [107, 170, 178, 194–200]*. In particular, simple models of heterogeneous catalytic reactions including auto-catalytic steps were examined [197, 198]. The appearance of these studies is symptomatic: “ideal” models compared with complicated “real” models provide a more reliable basis for the qualitative interpretation of complex dynamics. They have not yet exhausted all their possibilities.

We have used CO oxidation on Pt to illustrate the evolution of models applied to interpret critical effects in catalytic oxidation reactions. All the above models use concepts concerning the complex detailed mechanism. But, as has been shown previously, critical effects in oxidation reactions were studied as early as the 1930s. For their interpretation primary attention is paid to the interaction of kinetic dependences with the heat-and-mass transfer law [146]. It is likely that in these cases there is still more variety in dynamic behaviour than when we deal with purely kinetic factors. A theory for the non-isothermal continuous stirred tank reactor for first-order reactions was suggested in refs. 152–155. The dynamics of CO oxidation in non-isothermal, in particular adiabatic, reactors has been studied [77–80, 155]. A sufficiently complex dynamic behaviour is also observed in isothermal reactors for CO oxidation by taking into account the diffusion both in pores [71, 147–149] and on the surfaces of catalyst [201, 202]. The simplest model accounting for the combination of kinetic and transport processes is an isothermal continuously stirred tank reactor (CSTR). It was Matsuura and Kato [157] who first showed that if the kinetic curve has a maximum peak (this curve is also obtained for CO oxidation [158]), then the isothermal CSTR can have several steady states (see also ref. 203). Recently several authors [3, 76, 118, 156, 159, 160] have applied CSTR models corresponding to the detailed mechanism of catalytic reactions.

In a recent survey [19] it was noted that a realistic model for catalytic oxidation reactions must include equations describing the evolution of at least two concentrations of surface substances and account for the slow variation in the properties of the catalyst surface (e.g. oxidation–reduction). For the synchronization of the dynamic behaviour for various surface domains, it is necessary to take into consideration changes in the concentrations of gas-phase substances and the temperature of the catalyst surface. It is evident that, in the hierarchy of modelling levels, such models must be constructed and tested immediately after kinetic models. On the one hand, the appearance of such models is associated with the experimental data on self-oscillations in reactors with noticeable concentration variations of the initial substances and products (e.g. ref. 74); on the other hand, there was a gap between the comprehensively examined non-isothermal models with simple kinetics and those for the complex heterogeneous catalytic reactions

* As a rule, the authors of the above studies did not know of the results of such investigations performed in the U.S.S.R., particularly our results. Consequently, “rediscoveries” appeared, primarily in analyzing the models of adsorption and impact mechanisms [195, 196].

in which the concentrations of the initial substances and products were suggested to be unchanged. A theoretical analysis of the model for the isothermal CSTR in the case of the Langmuir–Hinshelwood mechanism has been carried out [159, 160]. It appeared that algebraic non-linearities of mechanism (1) and the mass exchange with the environment are sufficient for the appearance of the multiplicity of steady states and periodic solutions. The analysis of the data for typical conditions of catalytic oxidation reactions [160, 204] showed that the CSTR model contains a small parameter $\varepsilon = \tau_r/\tau_s$ (τ_s and τ_r are the characteristic times of mass exchange and reaction, respectively) at derivatives of the concentrations of surface substances. Hence relaxation consists of the regions of rapid motion determined by the surface dynamics and slow motion when the surface is quasi-stationary with respect to the gas phase. Since mechanism (1) provides a multiplicity of steady states [102–104] in the kinetic region, the manifold slow motions has topological peculiarities (folds); under certain conditions it leads to relaxational oscillations [159, 160]. A possibility of complex isothermal multipeak oscillations in CSTR for mechanism (1) supplemented by a buffer step has been reported [160]. These oscillations appear to be due to the superposition of slow oscillations in the buffer intermediate and of fast “reactor” oscillations. An algorithm to search for complex oscillations consisting in the analysis of quasi-steady-state algebraic equations for slow subsystems has been reported by Chang and Aluko [205]. Theoretical and experimental studies of the CSTR dynamics and self-oscillations in the ($O_2 + CO + 1-C_4H_8$) system over Pt/Al_2O_3 have been carried out [206–210]. Morton and Goodman [206] repeated the result of Chang and Aluko [160]. It was shown that self-oscillations are possible in the system without a buffer step. The Hopf bifurcation leading to the appearance of self-oscillations for mechanism (1) is possible at $m \neq n$, $n < p$ or $m > q$. These conditions correspond to the previously obtained [102, 103] necessary conditions for the multiplicity of steady states in the kinetic region. Taking into account the interaction of 1-butene with active sites of the catalyst permitted Mukesh et al. [208, 209] to obtain multipeak self-oscillations. A theoretical analysis for the model of the catalytic oxidation of H_2 in CSTR was performed by Ivanova et al. [211, 212]. Polizopoulos and Takoudis [213] obtained criteria for the multiplicity of steady states for a two-step reaction in CSTR (with desorption according to the law $k_d\theta \exp\{-\alpha\theta\}$).

It is the necessity to interpret critical effects observed in experiment that is a stimulus for the elaboration of a totality of various models accounting for various steps of complex catalytic processes. So far research workers have not come to a unified viewpoint about the factors causing critical effects, but most of them ascribe the complex dynamic behaviour of reactions by the kinetic peculiarities of their mechanism. In principle, a “complete” model of catalytic reactions can be suggested that would include the following principal characteristics: (1) a detailed reaction mechanism; a hypothesis about an ideal adsorbed layer; (2) biographical inhomogeneity of the cat-

alyst surface; (3) induced catalyst inhomogeneity; the dependence of rate constants on the adsorbed layer composition; (4) the existence of diffusion processes for reactants into catalyst bulk; the dependence of rate constants on the bulk concentration of reactants; (5) the existence of diffusion processes for adsorbed substances over the catalyst surface; (6) phase and structural transformations; (7) a possibility for the reaction to extend into a gas phase; (8) the existence of non-isothermal conditions on the surface; (9) surface-to-bulk energy transfer, and (10) taking into account the hydrodynamic picture in CSTR and the heat transfer parameters. It is evident that such a complete model would be extremely complicated for studying its properties. It is most natural to investigate the properties of a system of some particular models accounting for various properties of complex catalytic processes.

It can be stated that, at the very beginning of the construction of models for heterogeneous-catalytic reactions, a "bifurcation" took place: models were separated into "real" (most of all) and "ideal". These models cannot, however, be opposed; they must supplement each other. We cannot ignore the essential dependences of reaction parameters on the surface composition and state of the catalyst (see ref. 169) even if the significance of these dependences has not yet been clarified. This demand is satisfied by the model suggested by Creighton et al. [199] to describe the critical effects obtained in deep vacuum. The authors [199] applied a semi-empirical dependence of the CO sticking coefficients on the surface composition and temperature.

On the other hand, we cannot refuse simple models of the ideal layer. The knowledge of the dynamic properties of this layer is a basis for the qualitative interpretation of complicated real situations.

The aim of the present chapter is a comprehensive investigation of the kinetic characteristics of various non-linear catalytic reaction mechanisms. The objects under examination will be typical non-linear mechanisms on the one hand and, on the other, detailed mechanisms for catalytic oxidation reactions, primarily CO oxidation over metals (see Chap. 6).

2. The "parallel" adsorption mechanism

The general results in Chap. 3 permit us to claim that critical effects can be interpreted qualitatively in terms of the ideal adsorbed layer model. Detailed mechanisms applied to interpret these phenomena must necessarily include a step of interaction between various intermediates (naturally, in the absence of the auto-catalytic steps).

It is evident that such steps are not involved in linear mechanisms, including the two-step mechanism



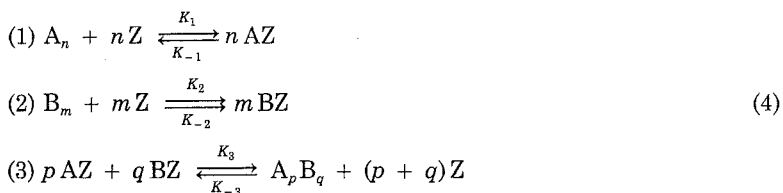
studied comprehensively by Temkin [214] and then Boudart [215]. Nor are they contained in the impact mechanism



In kinetic models corresponding to schemes (2) and (3), the steady state is unique and stable. These mechanisms involve the participation of two intermediates.

Let us consider a more complex case, i.e. mechanisms with three intermediates.

The simplest detailed mechanism having a step of interaction between various intermediates includes three steps*



This is an adsorption mechanism (we call it a "parallel" adsorption mechanism, since the adsorption of reactants follows two independent routes; in what follows we will consider one more adsorption mechanism that is "consecutive").

The unsteady-state kinetic model corresponding to mechanism (4) assuming constant concentrations of the initial substances and products A_n , B_m , A_pB_q is of the form

$$\begin{aligned} \dot{x} &= nk_1z^n - nk_{-1}x^n - pk_3x^py^q + pk_{-3}z^{p+q} \\ \dot{y} &= mk_2z^m - mk_{-2}y^m - qk_3x^py^q + qk_{-3}z^{p+q} \\ x + y + z &= C_z \end{aligned} \quad (5)$$

where $x = [AZ]$, $y = [BZ]$, $z = [Z]$ are the concentrations of substances on the catalyst surface, $k_1 = K_1[A_n]$, $k_2 = K_2[B_m]$, $k_3 = K_3$, $k_{-1} = K_{-1}$, $k_{-2} = K_{-2}$, $k_{-3} = K_{-3}[A_pB_q]$, $K_{\pm i}$, $i = 1, 2, 3$ are the rate constants for the direct and reverse reactions in mechanism (4), $n, m, p, q \geq 1$ are the stoichiometric coefficients, and C_z is the total number of active centres per unit surface of catalyst.

System (5) is an autonomous set of two non-linear differential equations.

* Hypothetically, it is possible that a two-step mechanism exists involving the participation of three intermediates: (1) $AB + 2Z \rightarrow AZ + BZ$; (2) $AZ + BZ \rightarrow C + 2Z$. This scheme (a disproportion mechanism) is extremely rare. In addition, it satisfies the principle of complex balancing [216-218]. Hence the steady state here is unique and stable.

The reasons for non-linearity here are first, the step of interaction between intermediates AZ and BZ, and second, the step of adsorption-desorption of the initial substances A_n and B_m .

Studies [96, 98, 102] of the number of steady-state points in eqns. (5) belonging to the reaction polyhedron (simplex) \bar{S}

$$\bar{S} = \{(x, y): x \geq 0, \quad y \geq 0, \quad x + y \leq C_2\}$$

showed that a sufficient condition for the uniqueness of the internal steady state (i.e. of the state in which none of the concentrations x, y, z is equal to zero) is the relationship

$$n = m \geq p, q \quad (6)$$

When this condition is not satisfied, a multiplicity of steady states (Table 1)

TABLE 1

Steady states of the adsorption mechanism

Reversibility of adsorption steps	Kinetic order of steps	
	$n = m$	$n \neq m$
<i>Two boundary steady states</i>		
$k_{-1} = 0$ $k_{-2} = 0$	At $qk_1 \neq pk_2$, internal steady states are absent, and at $qk_1 = pk_2$ there is a singular line of steady states.	Two internal steady states can exist.
<i>One boundary steady state</i>		
$k_{-1} \neq 0$ $k_{-2} = 0$ (or $k_{-1} = 0$, $k_{-2} \neq 0$, but it must be redesigned: $n \leftrightarrow m$, $p \leftrightarrow q$, $k_1 \leftrightarrow k_2$)	At $pk_2 \geq qk_1$, internal steady states are absent, and at $pk_2 < qk_1$ the existence of one ($n \geq p$) and two ($n < p$) internal steady states is possible.	There can be two ($n > m$), one or three ($n < m, m \geq p$), two or four ($n < m, m < p$) internal steady states.
<i>No boundary steady states</i>		
$k_{-1} \neq 0$ $k_{-2} \neq 0$	If $n = m \geq p, q$, there is a unique internal steady state; multiplicity of steady states can arise when this condition is not satisfied.	There can be several internal steady states.

in the catalytic reaction corresponding to mechanism (4) is possible. For its realization, the following conditions are necessary: (a) the kinetic orders of the steps must be in a definite ratio and (b) the parameters of the model must satisfy definite inequalities.

The reversibility of the adsorption steps in mechanism (4) affects the total number of steady states. As can be seen from Table 1, if two adsorption steps are reversible, boundary steady-state points are absent. Irreversibility of one adsorption step leads to the appearance of one boundary steady-state point in which the concentration of the reversibly adsorbing substance is equal to zero and the irreversibly adsorbing substance occupies all active sites of the catalyst surface. In the case where both adsorption steps are irreversible, there exist two boundary steady-state points: $(x = 0, y = C_2)$ and $(x = C_2, y = 0)$. In the latter case, at equal kinetic orders of the adsorption steps ($n = m$) a multiplicity of steady-state solutions is possible, i.e. at $pk_2 = qk_1$ (non-rough case) there exists a singular line of steady states connecting two boundary steady-state points. It can manifest itself in the unreproducibility of experimental data in a certain range of the parameters.

Thus the presence of steps for the interaction between various intermediates in the detailed mechanisms is only a necessary condition for the multiplicity of steady states in catalytic reactions. A qualitative analysis of the dynamic system (5) for mechanism (4) showed that the existence of several stable steady states with a non-zero reaction rate needs the following additional conditions: (a) the stoichiometric coefficients of intermediates must fit definite relationships ensuring the kinetic competition of these substances [violation of conditions (6)]; (b) the system parameters must satisfy definite inequalities.

We believe that it is not necessary to consider the overall kinetic order of steps above three in mechanism (4). We have analyzed comprehensively [97, 102, 103] all the possible versions for mechanism (4) assuming that the stoichiometric coefficients n, m, p , and q can amount to 1 or 2, $p + q \leq 3$, and $k_{-3} = 0$. The principal results of this analysis are listed in Table 2. By using the method of general analysis and the Sturm and Descartes theorem concerning the number of positive roots in the algebraic polynomial (ref. 219, pp. 248 and 255), we could show that there exist four detailed mechanisms providing the possibility of obtaining three steady states with a non-zero catalytic reaction

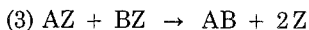
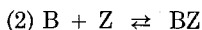
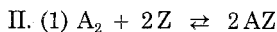
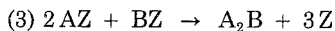
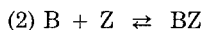
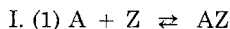
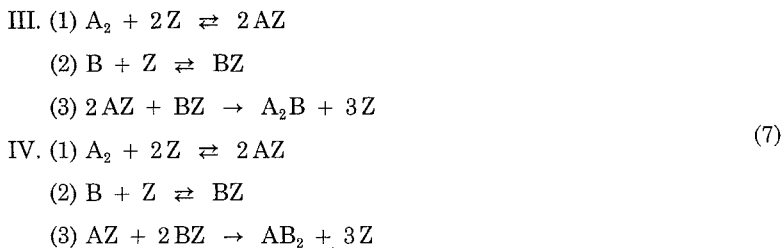


TABLE 2

Necessary conditions for the existence and the number of surface steady states of the catalyst depending on the kinetic orders and reversibility of steps in mechanism (4)

Kinetic orders of steps	Parameters			
	I ($k_{-i} = 0$, $i = 1, 2, 3$)	II ($k_{-1} \neq k_{-2}$ $= k_{-3} = 0$)	III ($k_{-2} \neq k_{-1}$ $= k_{-3} = 0$)	IV ($k_{-1} \neq 0$, $i = 1, 2$)
1 $n = 1$ $m = 1$ $p = 1$ $q = 1$	Two boundary steady-state points (s.p.); at $k_1 = k_2$ there exists a variety of s.p.	One boundary and at $k_1 > k_2$ one internal s.p.	One boundary and at $k_2 > k_1$ one internal s.p.	One internal s.p. and no boundary s.p.
2 $n = 2$ $m = 2$ $p = 1$ $q = 1$	Refer to I.1	Refer to II. 1, but with $k_1 > k_2$	Refer to III.1 but with $k_2 > k_1$	Refer to IV.1
3 $n = 2$ $m = 2$ $p = 2$ $q = 1$	Refer to I.1 but with $k_1 = 2k_2$	Refer to II.1 but with $k_1 > 2k_2$	Refer to III.1 but with $2k_2 > k_1$	Refer to IV.1
4 $n = 1$ $m = 1$ $p = 2$ $q = 1$	Refer to I.3	One boundary and at $k_1 > 2k_2$ two internal s.p.	One boundary and at $2k_2 > k_1$ one internal s.p.	One or three internal s.p. and no boundary s.p.
5 $n = 2$ $m = 1$ $p = 1$ $q = 1$	Two boundaries and at $2k_1 > k_2$ two internal s.p. are possible	One boundary and at $2k_1 > k_2$ two internal s.p. are possible	One boundary and at $2k_1 > k_2$ one or three internal s.p.	Refer to IV.4
6 $n = 2$ $m = 1$ $p = 2$ $q = 1$	Refer to I.5 but with $k_1 > k_2$	Refer to II.5 but with $k_1 > k_2$	Refer to III.5 but with $k_1 > k_2$	Refer to IV.4
7 $n = 2$ $m = 1$ $p = 1$ $q = 2$	Refer to I.5 but $4k_1 > k_2$	Refer to II.5 but with $4k_1 > k_2$	Refer to III.5 but with $4k_1 > k_2$	Refer to IV.4



Thus if the multiplicity of steady states for the catalyst surface manifesting itself in the multiplicity of steady-state catalytic reaction rates has been found experimentally and for its interpretation a three-step adsorption mechanism of type (4) and a hypothesis about the ideal adsorbed layer are used, the number of concrete admissible models is limited (there are four). It can be claimed that some types of adsorption mechanism have "feedbacks", but for the appearance of the multiplicity of steady states these "feedbacks" must possess sufficient "strength". The analysis of these cases (mechanisms 4-7 in Table 2) shows that, to achieve multiplicity, the reaction conditions must "help" the non-linear step.

Hence we have managed to obtain the simplest detailed mechanisms providing a possibility to achieve several (in this case three) steady-states of the catalyst surface. These are three-step adsorption mechanisms (7) whose parameters satisfy definite inequalities. Using the radiophysical terminology, these mechanisms can be called the simplest catalytic triggers. It is these mechanisms that must be used to interpret experiments in which critical effects are observed.

A special study must be carried out for the dynamic properties of model (5) and primarily for the stability of its steady states. Stability "in-the-small" is determined by the signs of the eigenvalues λ for the characteristic equation of the system matrix linearized near the steady state. It was shown [103] for system (5) that the steady states are either stable nodes ($\lambda_1 < 0, \lambda_2 < 0$) or the saddle points (e.g. $\lambda_1 < 0, \lambda_2 > 0$). Near the stable steady state, the system behaviour in time is known to be of the exponential character ($\sim \Sigma \exp \{\lambda_i t\}$). Saddle points are unstable since the trajectories of the motion from any point of the saddle neighbourhood move away from it. There are only two trajectories entering the saddle: they are separatrices accounting for $\lambda_i \leq 0$ ($i = 1$ or 2). We have also proved [103] the following properties: (a) the trajectories of system (5) beginning at the reaction simplex S do not leave it; (b) system (5) has no foci and unstable nodes; (c) the limit cycles and closed curves consisting of the trajectories of system (5) are absent; (d) the attraction regions of stable nodes are separated by the curves consisting of separatrices and saddle points; one separatrix always starts from the boundary of the simplex $x + y = C_2$ and the other goes from either the boundary $x = 0$ or $y = 0$; (e) if at $x = 0$ ($y = 0$) there are no steady-state

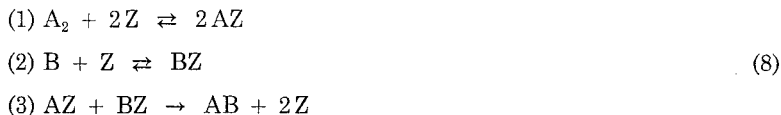
points, then the steady-state point of system (5) with the minimum value of x (or y) is stable.

These properties characterize both the type and the stability of steady-state points in system (5). If the steady-state point is unique, it is stable. If there are several steady states, then at least one of them is unstable. Stable and unstable steady states alternate.

The most important conclusion resulting from the properties (b) and (c) is that system (5) has no oscillation (either damping or non-damping). Thus if experiments have revealed these phenomena, for their interpretation one must use models that are more complicated than system (5). It is necessary to use models with more than two intermediates or to utilize models in which the rate constants of the elementary reactions depend on the concentrations of the intermediates.

3. Steady-state characteristics of the simplest mechanism permitting multiplicity of catalyst steady states

Let us carry out a comprehensive analysis of steady-state kinetic dependences for catalytic reactions following the adsorption mechanism



This is the only mechanism from mechanisms (7) in which the total kinetic order with respect to intermediates for every step is no greater than two. Scheme (8) enters as a component into the detailed mechanisms of oxidation reactions over metals. In particular, many researchers describe CO oxidation over platinum metals by the type (8) mechanism.

Let us start our investigation with the case when the adsorption steps in mechanism (8) are irreversible [166]. The unsteady-state kinetic model is then of the form

$$\dot{x} = 2k_1 P_{A_2} (1 - x - y)^2 - k_3 xy \quad (9)$$

$$\dot{y} = k_2 P_B (1 - x - y) - k_3 xy$$

where x , y , and $(1 - x - y)$ are the dimensionless concentrations of the substances AZ, BZ, and Z, respectively, P_{A_2} and P_B are the partial pressures of observed substances assumed to be constant, and k_i are the rate coefficients. The steady state of the surface is determined by the solution for a system of algebraic equations corresponding to (9)

$$2k_1 P_{A_2} (1 - x - y)^2 - k_3 xy = 0 \quad (10a)$$

$$k_2 P_B (1 - x - y) - k_3 xy = 0 \quad (10b)$$

Here there always exist two boundary steady states ($x = 1, y = 0$) and ($x = 0, y = 1$). The former corresponds to the complete surface coverage with substance A_2 and the latter by substance B. In both cases the steady-state reaction rate $W = k_3xy = 0$. But besides boundary steady states, there can also exist internal steady states. After subtracting eqn. (10b) from eqn. (10a), we obtain

$$1 - x - y = \frac{k_2 P_B}{2k_1 P_{A_2}} \quad (11)$$

The expression (11) makes physical sense if $2k_1 P_{A_2} > k_2 P_B$. In the steady state the reaction rate takes the form

$$\begin{aligned} W_{\text{ads}} &= k_2 P_B (1 - x - y) = \frac{k_2^2 P_B^2}{2k_1 P_{A_2}} \\ &= k_3 xy \end{aligned}$$

hence

$$xy = \frac{k_2^2 P_B^2}{2k_1 P_{A_2} k_3}$$

On the other hand

$$xy = x \left(1 - x - \frac{k_2 P_B}{2k_1 P_{A_2}} \right)$$

The quadratic equation

$$\frac{k_2^2 P_B^2}{2k_1 P_{A_2} k_3} = x \left(1 - x - \frac{k_2 P_B}{2k_1 P_{A_2}} \right) \quad (12)$$

has two positive solutions at

$$k_3 (2k_1 P_{A_2} - k_2 P_B)^2 \geq 8k_1 P_{A_2} k_2^2 P_B^2 \quad (13)$$

In the region where $2k_1 P_{A_2} > k_2 P_B$, condition (13) will be written as

$$\frac{2k_1 P_{A_2}}{1 + 2\sqrt{2k_1 P_{A_2}}/k_3} > k_2 P_B \quad (14)$$

It is interesting that by taking into account eqn. (11), the inequality (13) can be written as $(x - y)^2 > 0$, where x and y are the concentrations of AZ and BZ in the internal steady-state points. This condition seems to be trivial, but it gives possibilities for the following statement. If the catalytic reaction mechanism is of type (8) with irreversible adsorption steps and the experimental data have revealed one steady state with a non-zero reaction rate, i.e. $W_{\text{ads}} = k_3xy$ and, hence, $x \neq 0, y \neq 0$, and $x \geq y$ (or vice versa) then already from this one fact it follows that (a) there exist two boundary steady states ($x = 1, y = 0$) and ($y = 1, x = 0$) with a zero reaction rate and one

of these states is stable; and (b) there is one more internal but unstable steady state in which the reaction rate is equal to that in the stable internal steady state. This sufficiently obvious fact has not been noted by the several authors who have studied the reaction model of CO oxidation [194, 195].

In the plane of the parameters (P_{A_2} , P_B) the inequality (14) specifies the region in which there exists a multiplicity of steady states. For example, it is satisfied by the set of parameters $k_1 P_{A_2} = k_2 P_B = 1$, $k_3 = 10$. It can be shown that, independently of the ratio $k_2 P_B / k_1 P_{A_2}$, the boundary steady state ($x = 0$, $y = 1$) is stable whereas ($x = 1$, $y = 0$) is unstable. Among two internal steady states located symmetrically with respect to the line $x = y$, stable will be the state with a higher value of x and $x \geq y$.

A steady-state reaction rate can be represented as

$$W_{\text{ads}} = \begin{cases} \frac{k_2 P_B^2}{2k_1 P_{A_2}} & \text{if (14) is satisfied and the initial} \\ & \text{conditions for the dynamic system (9) lies in the} \\ & \text{attraction region of the internal stable steady states} \\ 0 & \text{in all other cases} \end{cases}$$

The dependences $W(P_{A_2})$ and $W(P_B)$ of the steady-state rate for the reactions following the adsorption mechanism (8) are represented in Fig. 1(a) and (b). At a fixed P_B , the curve $W_{\text{ads}}(P_{A_2})$ has two branches (zero and non-zero) corresponding to the reaction rates in the boundary and the internal steady-state points. In the range $P_{A_2} = 0$ to $(k_2/2k_1)P_B$, the catalyst surface is completely covered by BZ and $W_{\text{ads}} = 0$. On further increasing P_{A_2} , a jump-wise rise in the reaction rate up to the value of W_{ads}^+ is possible. This value then decreases in inverse proportion to P_{A_2} . In the case in which P_{A_2} is fixed, the rate rises quadratically with increasing P_B and then "drops" on to the branch of zero rates that exists at any P_B value.

We can write down relationships to determine critical values for the parameters at which a transition from one branch of the curve for the dependence of the steady-state reaction rate to the other becomes possible. For example, at fixed k_3 and P_{A_2} , the critical value of P_B is determined by the equation

$$P_B = \frac{2k_1}{k_2} P_{A_2} \left[1 + \left(\frac{8k_1 P_{A_2}}{k_3} \right)^{1/2} \right]^{-1} \quad (15)$$

The critical rate value corresponding to eqn. (15) will be

$$W_{\text{ads}}^+ = 2k_1 P_{A_2} \left[1 + \left(\frac{8k_1 P_{A_2}}{k_3} \right)^{1/2} \right]^{-2} \quad (16)$$

Also fulfilled are the simple relationships

$$\lim_{P_B \rightarrow \infty} \max_{P_{A_2}} W_{\text{ads}}^+ = \lim_{P_{A_2} \rightarrow \infty} \max_{P_B} W_{\text{ads}}^+ = \frac{k_3}{4} \quad (17)$$

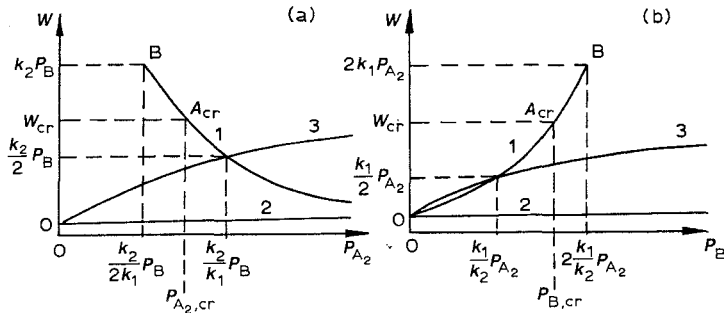


Fig. 1. Dependence of steady-state reaction rate on partial pressures P_{A_2} (a) and P_B (b). 1, W_{ads}^+ (non-zero branch); 2, W_{ads} (zero branch); 3, W_{im} ; A_{cr} = critical point of drop in steady-state reaction rate; B = limit value of A_{cr} .

$$\lim_{k_3 \rightarrow \infty} \max_{P_{A_2}} W_{ads}^+ = k_2 P_B \quad (18)$$

$$\lim_{k_3 \rightarrow \infty} \max_{P_B} W_{ads}^+ = 2k_1 P_{A_2}$$

Figure 1 also represents $W_{im}(P_{A_2})$ and $W_{im}(P_B)$ for the reaction that follows the impact mechanism



A simple analysis of the kinetic model corresponding to mechanism (19) shows that, in this case, the steady state of the surface is always unique and $W_{im}(P_{A_2})$ and $W_{im}(P_B)$ are of monotonic character

$$W_{im} = k_2 P_B (1 - z^*)$$

where

$$z^* = \frac{k_2 P_B}{4k_1 P_{A_2}} \left[\left(1 + \frac{8k_1 P_{A_2}}{k_2 P_B} \right)^{1/2} - 1 \right]$$

$$\lim_{P_B \rightarrow \infty} W_{im}(P_{A_2}, P_B) = 2k_1 P_{A_2}$$

$$\lim_{P_{A_2} \rightarrow \infty} W_{im}(P_{A_2}, P_B) = k_2 P_B$$

Figure 2 represents three-dimensional kinetic dependences in the " $W \times P_{A_2} \times P_B$ " coordinates for the impact (a) and adsorption (b) mechanisms. In our opinion, an analogy between the surface peculiarities in Fig. 2(b) with those examined and classified in catastrophe theory [220, 221] can be claimed.

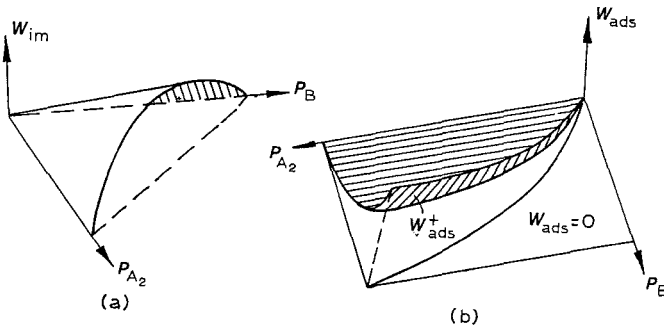


Fig. 2. Kinetic dependence of $W(P_{A_2}, P_B)$ for (a) impact and (b) adsorption mechanisms.

Regions of different kinetic behaviour can be vividly represented by the diagrams of steady states that are constructed in the " $P_i \times P_j$ " and " $P_i \times T$ " coordinates. We will apply these diagrams in what follows when studying CO oxidation over Pt.

The effect of step reversibility. A suggestion about the reversibility of adsorption steps for A_2 in the impact mechanism (19) does not lead to any essentially new results. Kinetic curves $W_{im}(P_{A_2})$ and $W_{im}(P_B)$ have the same type as those with saturation.

The case will be different for the adsorption mechanism. The kinetic model corresponding to mechanism (8) with reversible adsorption steps is represented as [222]

$$\dot{x} = 2k_1P_{A_2}(1-x-y)^2 - 2k_{-1}x^2 - k_3xy \equiv P(x, y) \quad (20)$$

$$\dot{y} = k_2P_B(1-x-y) - k_{-2}y - k_3xy \equiv Q(x, y)$$

From $Q(x, y) = 0$ we have

$$y = \frac{k_2P_B(1-x)}{k_2P_B + k_{-2} + k_3x} \quad (21)$$

$$1-x-y = \frac{(k_{-2} + k_3x)(1-x)}{k_2P_B + k_{-2} + k_3x}$$

After substituting eqns. (21) into $P(x, y) = 0$, we obtain

$$2k_1P_{A_2}(k_{-2} + k_3x)^2(1-x)^2 = x(k_2P_B + k_{-2} + k_3x) \cdot [k_2P_Bk_3(1-x) + 2k_{-1}x(k_2P_B + k_{-2} + k_3x)] \quad (22)$$

Let us write eqn. (22) as $f(x) = g(x)$, where $f(x)$ and $g(x)$ are the formation and consumption rates of AZ, respectively (Fig. 3). The steady-state concentrations x are the points of interception of $f(x)$ and $g(x)$. On the section $[0, 1]$ these functions have at least one intercept, since $f(0) > 0$, $g(0) = 0$ and

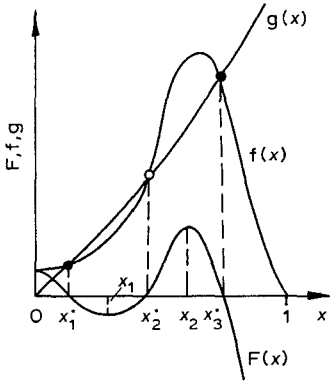


Fig. 3. Qualitative shape of formation $f(x)$ and consumption $g(x)$ of AZ functions. $F(x) = f(x) - g(x)$.

$f(1) = 0, g(1) > 0$. Hence there exists at least one steady state, but it is also possible that there will be three steady states. A necessary and sufficient condition for their appearance will be (see Fig. 3)

$$f(x) = g(x)$$

$$\left. \frac{df(x)}{dx} \right|_{x_{st}} > \left. \frac{dg(x)}{dx} \right|_{x_{st}} \tag{23}$$

The inequality from eqns. (23) will simultaneously be the condition of instability of the middle steady state. Its physical sense is evident: a derivative of the formation rate for AZ must be higher than that of the derivative of the consumption rate for the same substance.

The analysis of the characteristic roots for the linearized system shows that if the steady state is unique, it is stable; but if there are three steady states (x_1, x_2, x_3) the outer ones (x_1, x_3) are stable, whereas the middle one (x_2) is unstable.

The equation $f(x) = g(x)$ is a fourth-order algebraic equation, hence to write down the conditions (23) in the explicit form for the general case is difficult. An explicit form of the multiplicity criterion for eqns. (23) solutions can be obtained, e.g. from the simple demand for eqns. (23) to account for the inflexion point x^* for the $f(x)$ function. Then from $f''_{xx}(x^*) = 0$ we obtain

$$x^* = \frac{1}{2 \times 3^{1/2}} \left[3^{1/2} - 1 - \frac{k_{-2}}{k_3} (3^{1/2} + 1) \right] \tag{24}$$

It is evident that $x^* > 0$. Then

$$\frac{k_{-2}}{k_3} \leq \frac{3^{1/2} - 1}{3^{1/2} + 1} \approx 0.227 \tag{25}$$

The inequality (25), implying a demand for the sufficiently weak reversibility of the adsorption step of B, is a necessary condition for the multiplicity of steady-state solutions. To a necessary and sufficient condition for multiplicity, we must substitute eqn. (24) into the inequality from (23), but the expression obtained will be extremely cumbersome.

The conditions determining a region for the existence of several steady states can be obtained by different methods and can be of different forms. Thus for the more simple case $k_{-1} = 0$, an inequality can be obtained from eqns. (23) determining a boundary for the multiplicity of internal steady states

$$\frac{b_1}{9a_3^2} (a_2^2 - 3a_1a_2) \geq \left(b_0 - \frac{1}{3} b_1 \frac{a_2}{a_3} \right)^2 \quad (26)$$

where

$$a_1 = 2k_1 P_{A_2} k_{-2}^2 + k_2 P_B k_3 (k_2 P_B + k_{-2}) - 4k_1 P_{A_2} k_{-2} k_3$$

$$a_2 = 4k_1 P_{A_2} k_{-2} k_3 - k_3^2 (2k_1 P_{A_2} - k_2 P_B)$$

$$a_3 = 2k_1 P_{A_2} k_3^2$$

$$a_0 = -2k_1 P_{A_2} k_{-2}^2$$

$$b_1 = \frac{2}{3} a_1 - \frac{2a_2^2}{9a_3}$$

$$b_0 = a_0 - \frac{a_1 a_2}{9a_3}$$

With the fulfilment of condition (26), the system (20) has three internal steady states. For the case under consideration ($k_{-1} = 0$) there also exists a boundary steady state ($x = 1, y = 0$). The analysis of condition (26) shows that the multiplicity of steady states will be realized with other conditions being constant at relatively low temperatures (the desorption rate is low) and low values of P_B , high P_{A_2} , and also at sufficiently high k_3 .

Steady-state kinetic curves $W(P_B)^*$ for the adsorption mechanism (8), taking into account the reversibility of adsorption steps, are illustrated in Fig. 4(a), (b). At a given value of k_{-1} with increasing k_{-2} [Fig. 4(a)], the region of multiplicity for steady states diminishes and at some value of k_{-2} it vanishes completely. With increasing k_{-2} , the kinetic curve can achieve a maximum and finally take the form of that with saturation. A similar effect is observed with the reversibility of the first step at a given value of k_{-2} [Fig. 4(b)]. But the parametric sensitivity here is lower than in the former case.

* For the calculations [222], the fixed parameters were $k_1 = k_2 = 1, k_3 = 10$, whereas the values of P_{A_2}, P_B, k_{-1} and k_{-2} were varied over a wide range.

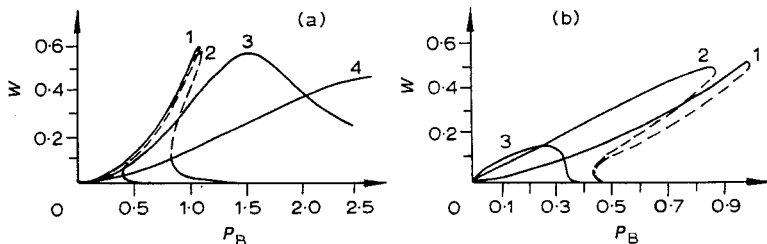


Fig. 4. Dependence of steady-state reaction rate on partial pressure P_B . $P_{A_2} = 1$. Dashes here and hereafter are the corresponding values in unstable steady state. (a) $k_{-1} = 0.01$. 1, $k_{-2} = 0.01$; 2, $k_{-2} = 0.1$; 3, $k_{-2} = 1.0$; 4, $k_{-2} = 7.0$. (b) $k_{-2} = 0.01$. 1, $k_{-1} = 0.05$; 2, $k_{-1} = 3.0$; 3, $k_{-1} = 200.0$.

The same situation is also observed in the kinetic curves $W(P_{A_2})$ [Fig. 5(a), (b)]. Note that the types of hysteresis for $W(P_{A_2})$ and $W(P_B)$ differ. The former hysteresis is characterized by a "counterclockwise" direction and the direction of the latter is "clockwise". Typical temperature dependences for the adsorption mechanism constructed at various values of k_{-1}^0 and activation energies $E_1 = E_2 = 0$; $E_{-1} = 60$, $E_{-2} = 30$ and $E_3 = 10$ kcal mol $^{-1}$ are represented in Fig. 6. Kinetic curves $W(P_{A_2}, P_B)$ in the three-dimensional space are given in Fig. 7 which also represent the projection of a steady-state rate "cusp"* to the plane of the P_{A_2} and P_B parameters. It is this projection that is the above diagram of steady states. Thus we have isolated a region for the multiplicity of steady states. In a similar way, three-dimensional plots $W(P_{A_2}, T)$ and $W(P_B, T)$ can be constructed.

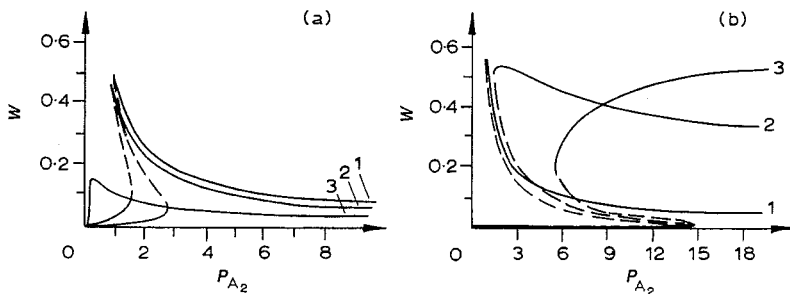


Fig. 5. Dependence of steady-state reaction rate on partial pressure P_{A_2} . $P_B = 1$. (a) $k_{-1} = 0.01$. 1, $k_{-2} = 0.05$; 2, $k_{-2} = 0.1$; 3, $k_{-2} = 1.0$. (b) $k_{-2} = 0.01$. 1, $k_{-1} = 0.05$; 2, $k_{-1} = 5.0$; 3, $k_{-1} = 200.0$.

* This concept has been borrowed from the "catastrophe theory". Nowadays this theory has been extensively developed [220]. Strictly speaking, it is the theory of the peculiarities of differentiable mappings [221].

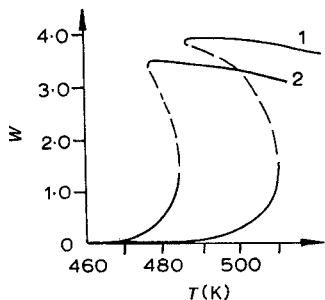


Fig. 6. Temperature dependence of steady-state reaction rate. $P_{A_2} = P_B = 1$. $k_{-1} = 0.01$. 1, $k_{-2} = 0.1$; 2, $k_{-2} = 0.5$.

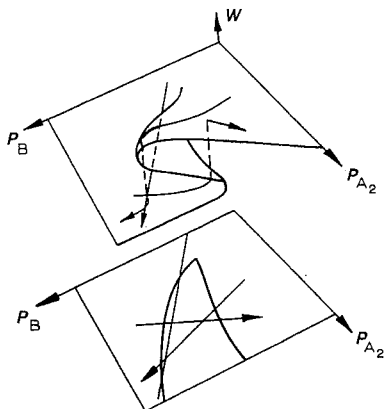


Fig. 7. Steady-state reaction rate surface at $T = \text{const.}$

4. Relaxation characteristics of the "parallel" adsorption mechanism

Let us now examine the behaviour of the solutions for the dynamic system (20) in time and analyze the system trajectories in the phase pattern. This analysis permits us to characterize peculiarities of the unsteady-state behaviour (in particular to establish whether the steady state is stable or unstable), to determine its type (focus, node, saddle, etc.) and to find attraction regions for stable steady states, singular lines, etc.

For numerical studies [223] of system (20) corresponding to the three-step mechanism (8) its parameters were taken to be $k_1 = k_2 = 1$, $k_3 = 10$, $k_{-1} = 0.01$, and $k_{-2} = 0.1$. Values of P_{A_2} and P_B were varied over a wide range. A sequence of phase portraits for reaction (8) with one or three steady

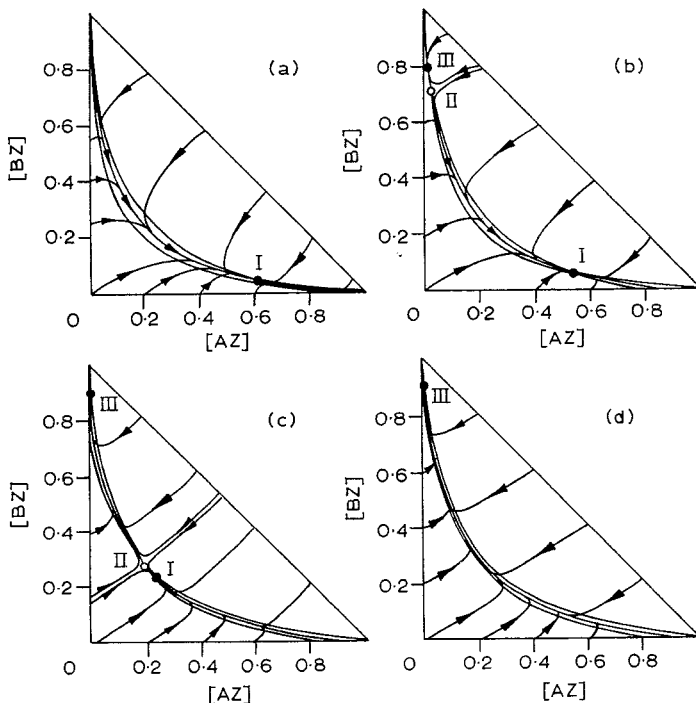


Fig. 8. Phase patterns of system (20) at various values of P_B . $P_{A_2} = 1$, $k_1 = k_2 = 1$, $k_3 = 10$, $k_{-1} = 0.01$, $k_{-2} = 0.1$ (s^{-1}). (a) $P_B = 0.7$; (b) $P_B = 0.8$; (c) $P_B = 1.1$; (d) $P_B = 1.2$.

states depending on the parameter P_B ($P_{A_2} = 1$) is represented in Fig. 8(a)–(d). At low P_B , the steady state is unique [Fig. 8(a)]. From all initial surface compositions we come to this state which is characterized by practically complete AZ coverage ($x \approx 1$, $y \approx 0$) and a low reaction rate. With increasing P_B , there arise two more steady states [Fig. 8(b)]. One is stable (III) and the other is unstable (II). Now the phase portrait has two attraction regions corresponding to two stable steady states. The trajectory comes into one or another steady state depending on the region in which the initial conditions are set. These regions are separated by the separatrices entering into saddle II. With increasing P_B , the attraction region for the steady state III grows and stable and unstable steady states I and II converge [Fig. 8(c)]. Finally, at some bifurcational value of P_B , they merge. But at high P_B there exists once again only one steady state III [Fig. 8(d)]. In this state the surface is covered with BZ ($x \approx 0$, $y \approx 1$) and the reaction rate is low.

Similar alterations in the phase portrait also take place with increasing P_{A_2} . The only difference is that at low P_{A_2} the unique steady state is charac-

terized by practically complete BZ surface coverage, whereas at high P_{A_2} the dominating substance on the surface is AZ. At mean P_{A_2} there are two stable steady states (with their characteristic attraction regions) and one unstable steady state in the middle of them.

Transient characteristics $x(t)$ and $y(t)$ demonstrate various time scales. The trajectories are often characterized by the fast initial region and the slow motion in the neighbourhood of some general trajectory ("mainstream") towards a steady state. In the case when the phase portrait is characterized by several steady states, the trajectory can rapidly enter into the neighbourhood of the unstable steady state and then it slowly relaxes towards one of the stable states. The general trajectory ("mainstream") near which a slow motion takes place lies in the region between two null clines, $\dot{x} = 0$ and $\dot{y} = 0$. It is evident that, in this region, the relaxation of system (20) towards the steady state that is an intercept of the null clines will be slower the narrower this region becomes with variation of the parameter. When the variable parameter is close to the bifurcation value, the narrowing of the region will be particularly distinct.

To interpret various time scales found in numerical experiments, it is necessary first of all to determine the difference in the eigenvalues of the system matrix linearized in the steady-state neighbourhood. Figure 9 presents $\lambda_1(P_B)$ and $\lambda_2(P_B)$ which can easily be calculated as solutions of the quadratic equation. (In the general case λ is a complex function of the model parameters.) Different λ values can be the reason for the time separation. Indeed, λ_1 and λ_2 differ but their difference is no more than an order of magnitude. But there is another case that is less trivial. In the region of critical effects in which the parameter achieves its bifurcation value, one of the roots becomes positive (after passing through zero) [Fig. 9(c)]. It is in this region of the parameters that the time to achieve a steady-state τ , sharply increases when going from one branch of the steady-state kinetic curve to the other (Fig. 10). But far from steady state in the general case, we cannot judge the character of relaxation according to the λ_i values since here it can be affected by the non-linear properties of the system.

In several experiments, in particular the study by Temkin and co-workers [224] of the kinetics in ethylene oxidation, slow relaxations, i.e. the extremely slow achievement of a steady-state reaction rate, were found. As a rule, the existence of such slow relaxations is ascribed to some "side" reasons rather than to the purely kinetic ("proper") factors. The terms "proper" and "side" were first introduced by Temkin [225]. As usual, we classify as slow "side" processes variations in the chemical or phase composition of the surface under the effect of reaction media, catalyst deactivation, substance diffusion into its bulk, etc. These processes are usually considered to require significantly longer times to achieve a steady state compared with those characterizing the performance of chemical reactions. The above numerical experiment, however, shows that, when the system parameters attain their bifurcation values, the time to achieve a steady state, τ , sharply increases.

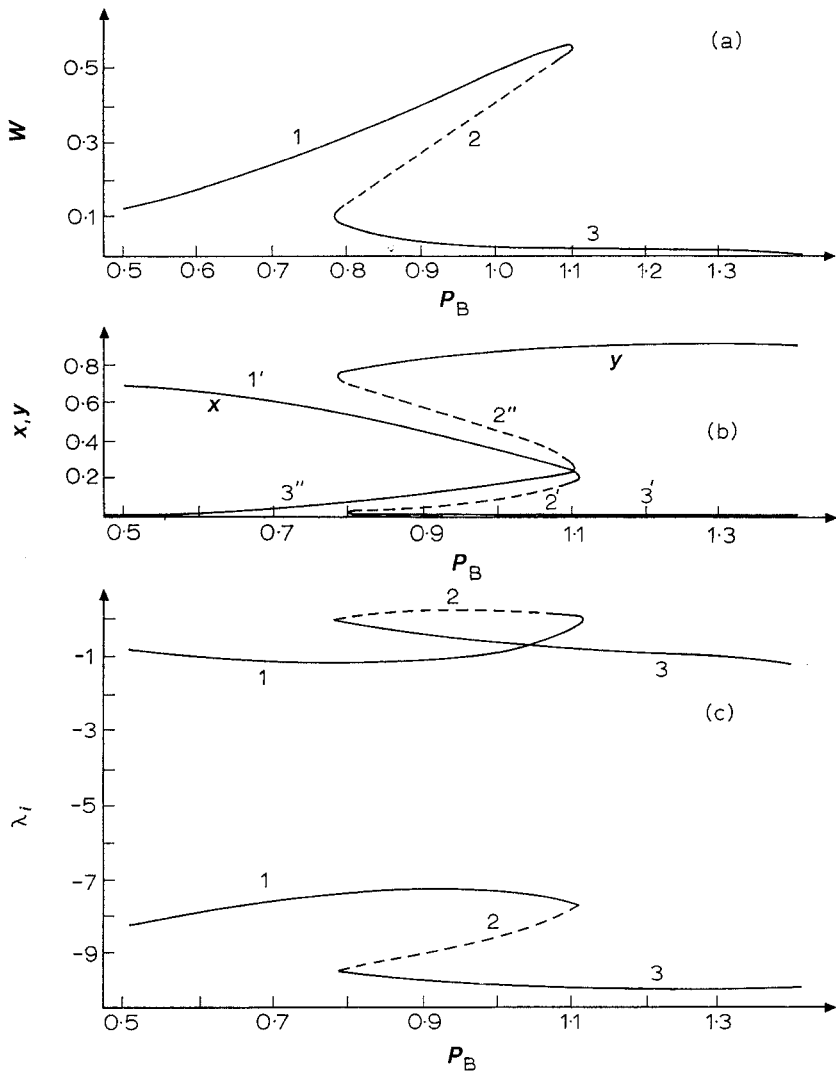


Fig. 9. (a) Steady-state reaction rate $W(P_B)$; (b) surface concentration of substances $x(P_B), y(P_B)$; (c) eigenvalues $\lambda_1(P_B)$ and $\lambda_2(P_B)$ of characteristic equation of system (20). For the values of the parameters, see Fig. 8.

This increase cannot be ascribed to the "side" reasons that have not been included into the reaction model. Similar increases of τ_* , namely long induction periods for the "ignition" and "quenching" of the reaction, were observed by Barelko et al. [5, 42-44, 46, 69] in the oxidation of simple molecules

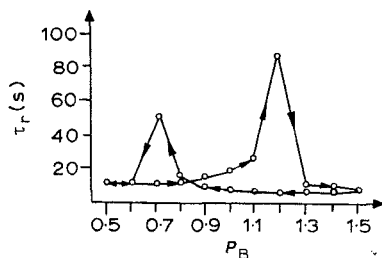


Fig. 10. Variations of time to achieve steady states, τ_r , with consecutive stepwise variations of P_B . The relaxation time, τ_r , was determined from the condition for the final entry of system (20) trajectory into the 5% neighbourhood of stable steady state.

(CO, H₂, NH₃, C₂H₄) over Pt. For details refer to the description of CO oxidation given below.

The results of the numerical experiment for system (20) necessitated a general mathematical investigation of slow relaxations in chemical kinetic equations. This study was performed by Gorban' et al. [226–228] who obtained several theorems permitting them to associate the existence of slow relaxations in a system of chemical kinetic equations (and, in general, in dynamic systems) with the qualitative changes in the phase portrait with its parameters (see Chap. 7).

Let us consider the concept of "relaxation" in more detail since no accurate definition for it has been given previously. The term "relaxation" is often used for the process by which either an equilibrium or a steady state is achieved in the system, and the relaxation time is treated as the time to achieve complete or partial thermodynamic equilibrium. It is evident that, in this context, the difference between "equilibrium" and "steady state" is insignificant. The concept of "relaxation time" is often used for the time during which a certain function characterizing the deviation from the equilibrium or the steady state diminishes by e (≈ 2.718) times compared with its initial value. It is evident, however, that this definition is only correct for one-dimensional linear systems. For multi-dimensional linear systems, a spectrum of relaxation times must be used. For non-linear systems, the application of these definitions is correct only in the neighbourhood of a singular point.

Classification of various relaxation times and their strong definitions have been reported [227, 228].

Let the phase portrait of the system be characterized by some set of ω -limit points. The concepts of an " ω -limit point" and an " ω -limit set" have been extensively used in the theory of dynamic systems. The thing is that the trajectory does not necessarily enter into a steady state. In the general case (as well as in the case of chemical kinetic equations), the existence of limit cycles is possible. The letter ω is a symbol for the region of the phase space into which at $t \rightarrow \infty$ the trajectory tends ("from α to ω "). Let \vec{x}_0 be a vector

of the initial compositions and \vec{k} be a set of rate constants. We can then introduce $\tau_1(\vec{x}_0, \vec{k}, \varepsilon)$ which is the time from $t = 0$ to the first entry of the trajectory $\vec{x}(t)$ into the ε neighbourhood of the ω -limit set, and $\tau_3(\vec{x}_0, \vec{k}, \varepsilon)$ which is the time until the final entry of the trajectory into the above neighbourhood.

We will also have $\tau_2(\vec{x}_0, \vec{k}, \varepsilon)$, which is the time of $\vec{x}(t)$ residence outside this neighbourhood. In particular cases, τ_1 , τ_2 and τ_3 coincide (Fig. 11).

The concept of slow relaxation refers to the case in which, for a given $\varepsilon > 0$ and arbitrary $t > 0$, there exist such \vec{x}_0 and \vec{k} values (lying in a given region having physical significance) as $\tau_{1(3)}(\vec{x}_0, \vec{k}, \varepsilon) > t$. It was established [226–228] that this type of slow relaxation is observed when, and only when, the phase portrait undergoes bifurcations.

Slow relaxations can be exemplified by the system behaviour corresponding to the adsorption mechanism (8) when the parameters \vec{k} are close to their bifurcation values.

Qualitative peculiarities for the dependence of the relaxation time on the system parameter are represented in Fig. 12. The most peculiar is the "critical slowing down" in the neighbourhood of bifurcation parameters. Here the relaxation rate is considerably lower than that of the slowest reaction and, in principle, it can be infinitesimal. A numerical experiment provides similar results (Fig. 13).

For the simplest three-step adsorption mechanism (4) at $n = 2$, $m = 1$ and $p = q = 1$, a retardation in the relaxation rate is observed in the region ("hole") between two null clines

$$\dot{x} = 2k_1 p_{A_2} (1 - x - y)^2 - k_3 xy = 0 \quad (27)$$

$$\dot{y} = k_2 p_B (1 - x - y) - k_3 xy = 0 \quad (28)$$

In this case adsorption steps are assumed to be irreversible. These isoclines are the second-order curves with a common axis of symmetry $x = y$. If there

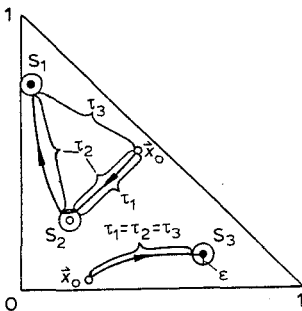


Fig. 11. Relaxation times τ_1 , τ_2 and τ_3 .

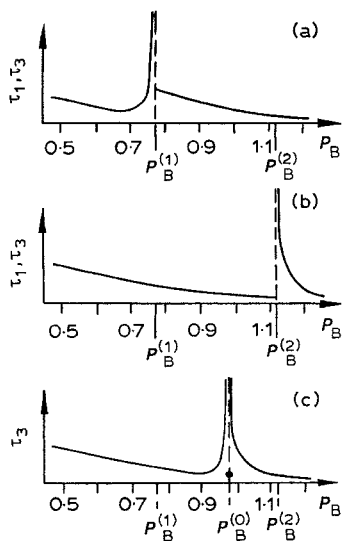


Fig. 12. Qualitative peculiarities for the dependences of relaxation times τ_1 and τ_3 on P_B . (a) $(x_o, y_o) \in V_1$; (b) $(x_o, y_o) \in V_2$; (c) $(x_o, y_o) \in V_3$. V_1 , V_2 , and V_3 are the attraction regions determined by separatrices of saddle-node points of various steady states.

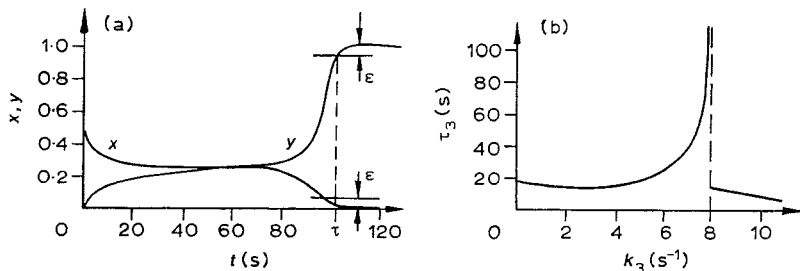


Fig. 13. Achievement of steady state for system (9) when relaxing from the initial state $(x_o = 0.5, y_o = 0)$ at $k_3 = 7.9$ (a) and dependence $\tau_3(k_3)$ at $\varepsilon = 0.05$. $k_1 P_{A_2} = 1, k_2 P_B = 1$ (s^{-1}).

are no internal steady states, the isocline $\dot{y} = 0$ over the whole of its length in the reaction simplex S is localized closer to the boundary $x + y = 1$ compared with $\dot{x} = 0$ [Fig. 14(a)]. Unrough internal steady state is generated on the line of equal concentrations $x = y$ [Fig. 14(b)]. It is in this region of surface coverages that, when the parameters become close to their bifurcation values, the time of relaxation towards steady state I from the initial conditions belonging to the attraction region formed under bifurcations of a two-fold equilibrium state III–IV type "saddle node", grows infinitely (Fig.

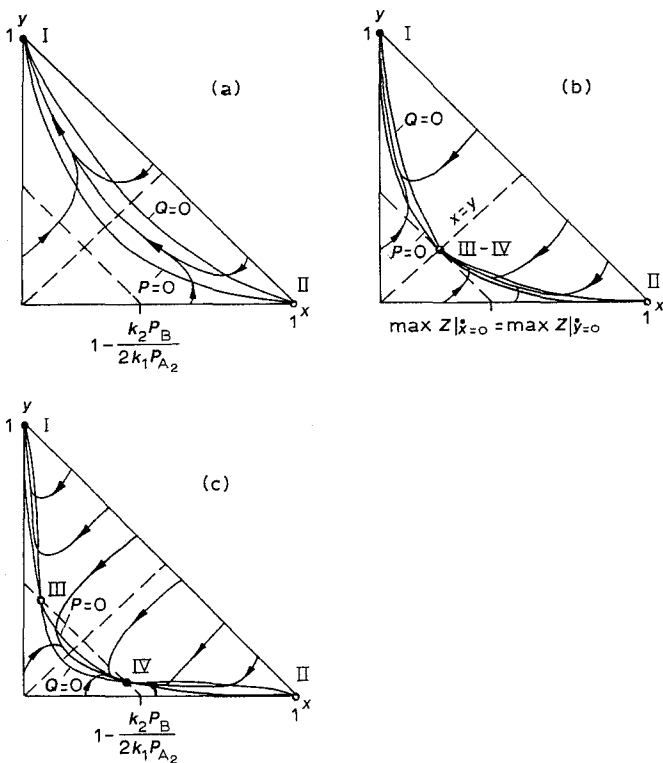


Fig. 14. Possible cases for mutual disposal of the null clines for system (9) in reaction simplex S .

13). This is due to the fact that the relaxation rate at a narrow place, i.e. the region of "condensing trajectories" [229], tends to zero more rapidly than the length of the trajectory where the relaxation is retarded. These properties, which can easily be obtained from the analysis of eqns. (27) and (28), make it possible to obtain the inequality [230]

$$\max z|_{y=0} \geq \max z|_{x=0}$$

This inequality is the necessary and sufficient condition for the multiplicity of steady states for the proper kinetic model. In addition, from the form of $\dot{x}|_{y=0}(z)$ and $\dot{y}|_{x=0}(z)$ we can also obtain sufficient conditions for the multiplicity of steady states [Fig. 14(b)]

$$\max z|_{y=0} \geq \frac{k_2 p_B}{2k_1 p_{A_2}}$$

$$\max z|_{x=0} \geq \frac{k_2 p_B}{2k_1 p_{A_2}}$$

In this case it is necessary to fulfil the condition $k_2 p_B / (2k_1 p_{A_2}) < 1$. If these conditions are expressed through the reaction parameters and are combined, we obtain

$$1 + 2\beta - 2(\beta^2 + \beta)^{1/2} \geq (2\alpha^{1/2} + 1)^{-1} \geq \frac{\beta}{\alpha} \quad (29)$$

where $\alpha = 2k_1 p_{A_2} / k_3$ and $\beta = k_2 p_B / k_3$ are the criteria characterizing the competition between the adsorption steps, on the one hand, and the interaction step on the other. Adsorption steps lead to the binding of unoccupied surface centres of the catalyst whereas the interaction step promotes their release. If the latter step is sufficiently strong and the adsorption steps of different substances are characterized by different kinetic laws, the system can have critical effects.

A bifurcation diagram on the plane of (α, β) criteria is represented in Fig. 15. An equation for the solid curve corresponds to the equality in eqn. (29).

We have already mentioned the sharp difference in the relaxation times outside the region between the null clines (~ 1 s) and inside it (as high as hundreds of seconds). The motion outside this region depends on the "fastest" reaction. Inside this region the relaxation rate is dependent on the complicated complex of rate constants, and in the general case we cannot suggest that the reaction rate is limited by some reaction. The common trajectory near which the relaxation is retarded is no more than a specific trajectory that is a separatrix going from the unstable into the stable steady

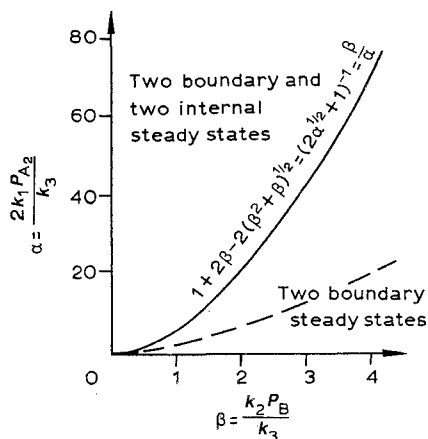


Fig. 15. Bifurcational diagram of system (9). In the region between the solid and broken curves, an effect of "critical slowing down" is possible.

state. These effects are also observed when the unstable steady state lies outside the physical region for the system determination [231].

Let us consider the kinetic model corresponding to the mechanism (8) at $k_{-1} \neq 0$ and $k_{-2} = 0$

$$\dot{x} = 2k_1 p_{A_2}(1 - x - y)^2 - 2k_{-1}x^2 - k_3xy$$

$$\dot{y} = k_2 p_B(1 - x - y) - k_3xy$$

Let us take $k_1 p_{A_2} = k_2 p_B = 1 \text{ s}^{-1}$, $k_3 = 0.5 \text{ s}^{-1}$ and $k_{-1} \neq 0$. Besides the boundary steady state ($x = 0, y = 1$), there always exists a real-valued steady state lying outside the physical region of determination ($0 < k_{-1} < 1$; its coordinates will be $x > 1, y < 0$).

Localization of this steady state as a point of intercept for the null clines $\dot{x} = 0$ and $\dot{y} = 0$ as a function of the k_{-1} value is shown in Fig. 16. At low k_{-1} this point is localized sufficiently close to the region of probable initial conditions (at $k_{-1} = 0$ it becomes a boundary steady state). It is the proximity of the initial conditions to the steady state outside the reaction polyhedron that accounts for the slow transition regime. Note that, besides two real-valued steady states, the system also has two complex-valued steady states. At bifurcation values of the parameters, the latter become real and appear in the reaction simplex as an unrough internal steady state. The proximity of complex-valued roots of the system to the reaction simplex also accounts for the generation of slow relaxations.

Similar results can also be obtained for the more simple mechanism

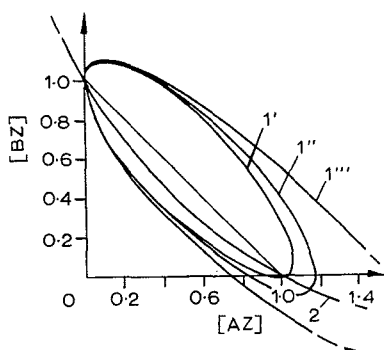
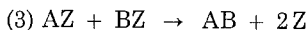
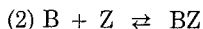
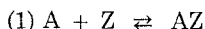


Fig. 16. Steady states and null clines for system (20) with varying k_{-1} ($k_1 p_{A_2} = k_2 p_B = 1 \text{ s}^{-1}$, $k_{-2} = 0, k_3 = 0.5 \text{ s}^{-1}$). 1, $[AZ] = 0$; 1', $k_{-1} = 10^{-3} \text{ s}^{-1}$; 1'', $k_{-1} = 10^{-2} \text{ s}^{-1}$; 1''', $k_{-1} = 10^{-1} \text{ s}^{-1}$; 2, $[BZ] = 0$.

Thus the effect of slow relaxations can also be noticeable in the case when the steady state inside the reaction polyhedron is unique and stable as a whole (all positive solutions tend to it at $t \rightarrow \infty$). For this purpose it suffices that the "external" (non-physical) steady state is close to the polyhedron boundary and the initial conditions localize on the opposite side of the boundary (inside the polyhedron).

We believe this fact to be of general importance. As a rule, chemical kinetic equations are non-linear and must have several steady-state solutions, not all of which have physical meaning (negative and complex-valued steady-state solutions may arise). But as we have shown, slow transition regimes can also be observed in the case where the steady-state solutions having no physical meaning are localized close to the reaction polyhedron. It is evident that the same situation can also arise in closed systems where the point of detailed equilibrium is always unique. Thus to interpret the dynamics of chemical reactions (in particular the reasons for the occurrence of induction periods) in the physically determined region of compositions, we can obtain the necessary information from the localization of all steady states in the system, including non-physical ones.

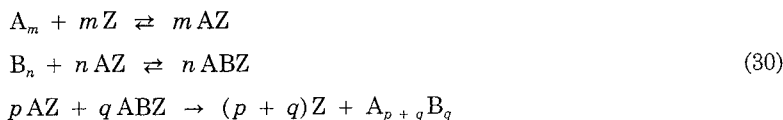
In conclusion, let us emphasize that our investigation has revealed a great variety of relaxation effects caused by the complex reaction kinetics, i.e. the effects are of purely kinetic origin.

Even for the linear mechanisms with a sufficiently large number of reactions, the relaxation time can be considerably higher than the characteristic time of the reaction [100]. This is possible when the eigenvalue of the system that is minimum with respect to its modulus has a non-zero imaginary part, i.e. it is necessary that the slowest relaxation process is of damping oscillation character. As far as the non-linear mechanisms are concerned, such a situation already arises in a small number of reactions. If the system has bifurcations (critical effects), there arise slow relaxations of the kinetic origin with the strict significance specified previously. These relaxations can take place infinitely slower than those of the slowest reactions taken separately. The kinetic model of the three-step adsorption mechanism is the simplest case demonstrating slow relaxations of the kinetic origin.

5. Analysis of "consecutive" adsorption mechanisms

Let us examine one more simple three-step mechanism whose steady-state characteristics are also of the hysteresis type. In what follows we will show that their type differs considerably from the previous one. It is the mechanism including steps of "consecutive" adsorption: one gas-phase substance is adsorbed on unoccupied sites and is then joined by a second gaseous substance, whereupon the two intermediates interact. In the general form this

mechanism can be represented by [232]



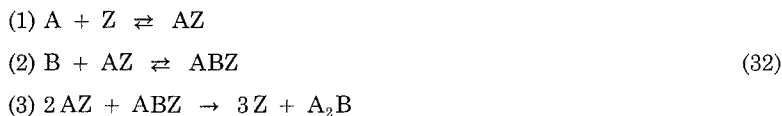
This mechanism is a constituent of the mechanisms for various catalytic reactions, e.g. for NH_3 oxidation [233].

A kinetic model of mechanism (30) for the subsystem of the intermediates AZ, ABZ, and Z, assuming constant concentrations of the observed substances A_m , B_n , and $A_{p+q}B_q$, is

$$\begin{aligned} \dot{x} &= mk_1(1-x-y)^n - mk_{-1}x^m - nk_2x^n + nk_{-2}y^n - pk_3x^py^q \\ &\equiv P(x, y) \\ \dot{y} &= nk_2x^n - nk_{-2}y^n - qk_3x^py^q \\ &\equiv Q(x, y) \end{aligned} \quad (31)$$

Here x , y , and $(1-x-y)$ are the concentrations of the surface substances AZ, ABZ, and Z, respectively, k_i are the rate constants (partial pressures A_m and B_n enter as cofactors), m , n , p , and q are the stoichiometric coefficients, and the functions $P(x, y)$ and $Q(x, y)$ are determined, as usually, in the reaction simplex $\bar{S} = \{(x, y): x \geq 0, y \geq 0, x + y \leq 1\}$. The initial conditions $x_0 = x(0)$, $y_0 = y(0)$ are set in \bar{S} . By analogy with the above, we can show that all the trajectories $x(t)$ and $y(t)$ starting in \bar{S} do not leave it. The latter provides the existence of at least one steady state for eqns. (31).

The simplest mechanism type (30) admitting a multiplicity of steady states is represented as [223, 232]



i.e. $m = n = q = 1$ and $p = 2$. Steady states are determined from eqns. (31): $P(x, y) = 0$ and $Q(x, y) = 0$. From the second equation of (31) we obtain

$$y = \frac{k_2x}{k_{-2} + k_3x^2}$$

Then the first equation of (31) can be transformed into the form

$$F(x) = x^3 - ax^2 + bx - c = 0$$

where $a = k_1k_3/k$, $b = (k_1k_2 + k_1k_{-2} + k_{-1}k_{-2})/k$, $c = k_1k_{-2}/k$, and $k = k_3(k_1 + k_{-1} + 3k_2)$. A necessary and sufficient condition for the existence of three solutions can be obtained if we demand that, at the points of extremum $x^{(1)}$ and $x^{(2)}$ of the functions $F(x)$, the condition $F(x^{(1)}) < 0$,

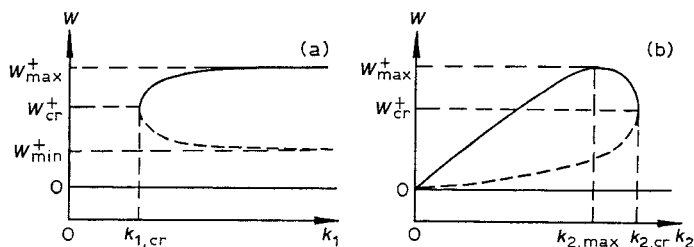


Fig. 17. Steady-state reaction rate as a function of (a) k_1 and (b) k_2 . The broken lines are unstable steady states.

$F(x^{(2)}) > 0$ is fulfilled. This condition is of the form

$$4(a^2 - 3b)(b^2 - 3ac) > (ab - 9c)^2 \quad (33)$$

In the simplest case, when $k_{-1} = k_{-2} = 0$, the fulfilment of (33) is necessary and sufficient for the fact that, along with a boundary steady state, the system has two internal steady states with a non-zero reaction rate $W = k_3 x^2 y$. Finally, we obtain the simple expression

$$k_3 > 4k \left(1 + 3 \frac{k_2}{k_1} \right) \quad (34)$$

The qualitative character of dependences $W(k_1)$ and $W(k_2)$ is shown in Fig. 17. Hysteresis for $W(k_1)$ is characterized by the existence of such a critical value of $k_{1,cr}$, as at all $k_1 > k_{1,cr}$, the steady-state rate has three essentially different values. We can write down in the explicit form the limit values of W at $k_1 \rightarrow \infty$ [W_{max}^+ , W_{min}^+ in Fig. 17(a)] and also W_{cr} corresponding to $k_{1,cr}$. For $W(k_2)$ [Fig. 17(b)] we can also calculate $k_{2,cr}$ and W_{cr} . An illustrative example of the qualitative character of the functional dependence $W(k_1, k_2)$ in three-dimensional space is given in Fig. 18. The bottom part of Fig. 18 shows the projection of the steady-state rates "fold" to the plane of the parameters at which the system has several steady states.

When the steps in mechanism (32) are reversible ($k_{-1}, k_{-2} > 0$), it can easily be shown that the qualitative character of $W(k_1)$ and $W(k_2)$ [Fig. 17(a), (b)] is preserved. Unlike the above catalytic trigger, in this case the multiplicity of steady states can also be observed at $k_1 \rightarrow \infty$ ($[A] \rightarrow \infty$), i.e. the region of parameters in which there are three steady states is infinite.

Dynamic studies can be performed as previously. We will only note that, like eqns. (5), the system (31) has no limit cycles. In addition, the unique steady state is always stable. If there are three steady states ($x_1 < x_2 < x_3$), two are stable (x_1 and x_3) and one (the middle steady state x_2) is unstable.

A comparative analysis of steady-state characteristics for "consecutive" and "parallel" three-step adsorption mechanisms with two independent intermediates shows that, to interpret the multiplicity of steady states, the

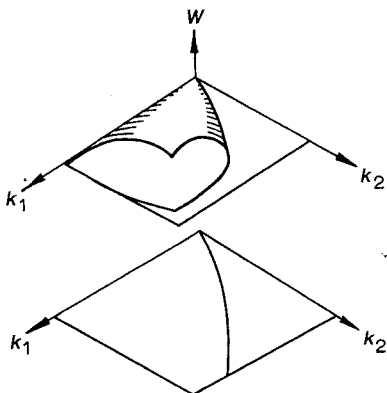


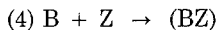
Fig. 18. Three-dimensional kinetic dependence for the "consecutive" adsorption mechanism.

former needs stronger non-linearity of the kinetic model. In the case under consideration, for the appearance of several steady states the step of interaction between the adsorbed substances must be three-molecular. For the parallel adsorption mechanism it can be obtained in terms of bimolecular reactions. If we restrict ourselves only to these reactions, the consecutive adsorption mechanism cannot be applied to interpret critical effects. On the other hand, if the experimental data are characterized by a practically infinite hysteresis of the steady-state rate [Fig. 17(a)], the detailed mechanism must involve a totality of steps of type (30). But neither "parallel" nor "consecutive" adsorption mechanisms with two independent intermediates can describe self-oscillations. For this purpose a more complicated model must be used.

6. Models of kinetic self-oscillations in heterogeneous catalytic reactions

In terms of the law of acting surfaces and without any additional assumptions, we will consider a simple kinetic model characterized by rate self-oscillations.

Let us complicate mechanism (4). It is known that many gases can be adsorbed on the catalyst surface in several (at least two) forms, one of which is unreactive. This case is observed, for example, in CO adsorption over Pt. By analogy with ref. 105, let us complete mechanism (8) by a buffer step



where (BZ) is an intermediate that does not participate in the main reaction.

This completed mechanism is accounted for by the kinetic model [108]

$$\dot{x} = 2k_1z^2 - 2k_{-1}x^2 - k_3xy \equiv P(x, y, q) \quad (35a)$$

$$\dot{y} = k_2z - k_{-2}y - k_3xy \equiv Q(x, y, q) \quad (35b)$$

$$\dot{q} = k_4z - k_{-4}q \equiv R(x, y, q) \quad (35c)$$

where z , x , y , and q are the surface concentrations of Z, AZ, BZ, and (BZ) on the catalyst, respectively, and partial pressures of gaseous A₂ and B enter as factors in the corresponding constants. The steady-state points for eqns. (35) are determined as a solution of the system of algebraic equations

$$P(x, y, q) = Q(x, y, q) = R(x, y, q) = 0 \quad (36)$$

Let us suggest that the first two equations $P = Q = 0$ in eqn. (36) set in the implicit form $x = x(q)$, $y = y(q)$, and $z = z(q)$. Then in accordance with eqn. (36) the equation $R = 0$ can be represented as

$$\begin{aligned} z(q) &= \alpha q \\ \alpha &= \frac{k_{-4}}{k_4} \end{aligned} \quad (37)$$

Hence the steady-state points for eqns. (35) correspond to the points of intersection in the (z, q) plane of the curve $z = z(q)$ and the straight line $z = \alpha q$ in eqn. (37). These points depend only on the ratio k_4 to k_{-4} , rather than their absolute value. It will be shown in what follows that the latter accounts for the dynamic characteristics of eqns. (35). The curve $z(q)$ is plotted in accordance with the solutions of the equations $P(x, y, q) = Q(x, y, q) = 0$ with respect to x and y , where q is ranging within $0 \leq q \leq 1$ according to the formula $z(q) = 1 - x(q) - y(q) - q$. These values of $x(q)$ and $y(q)$ are the steady-state points of the system corresponding to mechanism (8). We have selected above a region of the parameters for this mechanism in which there exist three steady states. In this region, the curve $z(q)$ can be of a typical S-shaped form (Fig. 19). Thus the concentration of unoccupied centres can change jumpwise at a certain concentration of the unreactive substance. (Note that similar results can be obtained when studying dynamic properties of the adsorption mechanism complicated by the catalyst deactivation.) The analysis for the stability of the steady-state point in the reduced system (35a)–(35b) where q acts as a parameter, indicates (see Sect. 3) that the unique steady state is stable. If the number of steady states amounts to three ($z_1 < z_2 < z_3$) the two outer (z_1 and z_3) are stable and the middle (z_2) is unstable. Studies of the stability character for the steady state of the complete system (35) show that this property of instability can be preserved at sufficiently low values of k_4 and k_{-4} . In this case system (35) can also have an unique steady state. As usual, the solution of (35) was considered in the reaction simplex.

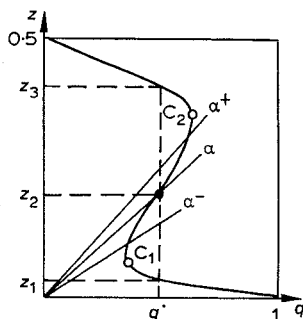


Fig. 19. The shape of the $z(q)$ curve.

$$\bar{S} = \{(x, y, q): x \geq 0, \quad y \geq 0, \quad q \geq 0, \quad x + y + q \leq 1\}$$

Let $(x^*, y^*, q^*) = (*)$ be a steady-state solution for eqns. (35). The analysis of stability for $(*)$ provides the characteristic equation

$$\lambda^3 + \sigma\lambda^2 + \delta\lambda + \Delta = 0$$

where $\sigma = -\text{tr}A$, $\delta = A_{11} + A_{22} + A_{33}$, $\Delta = -\det\bar{A}$, $\bar{A} = \|a_{ij}\|$ ($i, j = 1, 2, 3$) is the matrix of the corresponding linearized system at the point $(*)$, and A_{ii} ($i = 1, 2, 3$) are the principal minors of \bar{A} . In our case, matrix \bar{A} is non-positive [$a_{ij} < 0$, $(*) \in S$]. Hence it has a non-positive eigenvalue, i.e. a real-valued eigenvalue, $\lambda_1 \leq 0$. The character of the other two, i.e. λ_2 and λ_3 , is determined by the relationship between σ , δ , and Δ , moreover $\sigma > 0$. It can be shown that

$$\frac{dz(q)}{dq} - \alpha = -\frac{\Delta}{A_{33}}$$

where A_{33} reduces to zero at the points c_1 and c_2 in the curve $z(q)$ (Fig. 19), is negative between these points and positive outside the c_1, c_2 section. This relationship suggests that, for the case represented in Fig. 19, the value of Δ is sign-constant, namely $\Delta > 0$. Hence a necessary and sufficient condition for the instability of $(*)$ is the inequality $\delta < 0$. At $\delta < 0$, $(*)$ is stable, at $\delta = 0$ it corresponds to bifurcation values of the parameters (the transition of the real part of eigenvalues λ_2 and λ_3 through zero). From $\delta < 0$ for the fixed α we can obtain the inequality $k_4 < k_4^*$ for k_4 . Similarly, from $\delta < 0$ for a fixed k_4 we can obtain the limitations $\alpha^- < \alpha < \alpha^+$ for α (Fig. 19). Thus when k_1, k_{-1}, k_2, k_{-2} , and k_3 are properly chosen, in the space of the k_4 and k_{-4} parameters a region with the unique unstable steady state for (35) can be found.

Calculations were carried out at $k_1 = 2.5$, $k_2 = 1.0$, $k_3 = 10$, $k_{-2} = 0.1$, $k_4 = 0.0675$, and $k_{-4} = 0.022 \text{ s}^{-1}$, ensuring the uniqueness and instability of $(*)$. Fragments of the projection of the phase space (x, y, q) to the respective

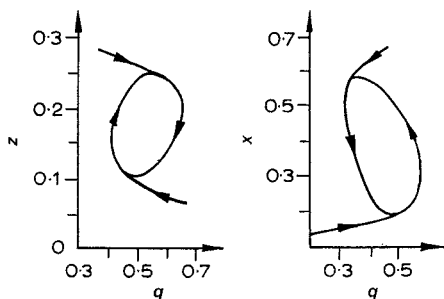


Fig. 20. Limit cycles on (x, z, q) phase space projections.

phase planes are represented in Fig. 20. A comparison with Fig. 19 shows that the oscillations are observed in the regions of phase coordinates close to the hysteresis in the curve $z(q)$. The shape of the limit cycles in Fig. 20 is considerably dependent on k_4 and k_{-4} . The lower k_4 and k_{-4} , the closer the shape of the limit cycle to the hysteresis in the $z(q)$ curve. Self-oscillations of the reaction rate $W = k_3xy$ with time are shown in Fig. 21. The broken line marks the W value in the unstable steady state (*) corresponding to this self-oscillation performance. Varying k_4 at a fixed ratio of α shows that, with increasing k_4 up to the limit values of k_4^* , the frequency of oscillation grows at an almost constant amplitude. At $k_4 > k_4^*$, the oscillations vanish "jump-wise" and the system stabilizes to the steady state (*)

Thus the mechanism formed by steps (1)–(4) can be called the simplest catalytic oscillator. [Detailed parametric analysis of model (35) was recently provided by Khibnik et al. [234]. The two-parametric plane $(k_2, k_{-4}/k_4)$ was divided into 23 regions which correspond to various types of phase portraits.] Its structure consists of the simplest catalytic trigger (8) and linear "buffer", step (4). The latter permits us to obtain in the three-dimensional phase space oscillations between two stable branches of the S-shaped kinetic characteristics $z(q)$ for the adsorption mechanism (1)–(3). The reversible reaction (4) can be interpreted as a slow reversible poisoning (blocking) of

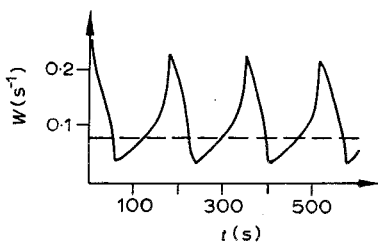
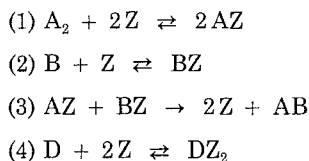


Fig. 21. Self-oscillations of reaction rate according to model (35).

the active catalyst surface. In the model examined, the self-oscillations of the reaction rate take place as a combination of the "fast" system of steps (1)–(3) (a typical adsorption mechanism) leading to a sharp change in the number of unoccupied sites of the surface, and the "slow" reversible step (4), ensuring self-oscillations of their concentrations. "Buffer" step (4) can also be represented by the other (but not every) reversible step with a hanging vertex. This step can also be non-linear. It is of importance that only k_4 and k_{-4} are sufficiently low and, by analogy with Fig. 19, the model parameters provide a unique intersection of the proper S-shaped curve at the point of its middle unstable branch $c_1 c_2$.

At the beginning of this chapter, we mentioned that Ivanova [167, 168], by using the Clark algorithm [235], had recently found sufficiently general conditions to ensure steady state uniqueness. Additionally, she formulated the instability conditions for this steady state.

Let us apply her method to study kinetic models for several adsorption mechanisms having buffer steps [109, 236]. For example, let us take the mechanism



The rank of the matrix of stoichiometric coefficients amounts to 3; the system has one law of conservation $C_1 + C_2 + C_3 + 2C_4 = C$, where C_1, C_2, C_3 , and C_4 are the concentrations of Z, AZ, BZ, and DZ_2 , respectively. On the tetrahedron boundary $C_1 \geq 0, C_2 \geq 0, C_3 \geq 0, C_1 + C_2 + C_3 \leq C$, there is only one steady-state point $(0, C, 0)$ that is unstable. All the trajectories for the respective system of differential equations enter into the interior of this tetrahedron. The coefficients a_2 and a_3 of the characteristic polynomial $P(\lambda)$ at the steady-state point (C_1, C_2, C_3) are of the form

$$\begin{aligned} a_2 &= \left\{ \frac{W_3^+ W_2^-}{C_1 C_2 C_3} \left[\frac{W_3^+}{W_2^-} (C_2 - C_3) + C_1 + C_2 + C_3 \right] \right. \\ &+ \frac{W_2^- W_4^+}{C_1 C_2 C_3 C_4} \left[\frac{W_3^+}{W_2^-} (C_2 + 3C_3 + 4C_4 + C_1) + (4C_4 + C_1)C_3 \right] \\ &\left. + C_2(C_2 + C_3 + 4C_4) \right\} \\ a_3 &= \frac{W_3^+ W_2^- W_4^+}{C_1 C_2 C_3 C_4} \left(\frac{W_3^+}{W_2^-} C_2 + C_1 + C_2 + C_3 + 4C_4 - 2k_1 \frac{C_1^2}{k_{-2}} \right) \end{aligned}$$

where $W_i^{+,-}$ are the rates of the individual reactions.

It follows from the steady-state equation for C_1 that $k_4 C_1^2 = k_{-4} C_4$. Conse-

quently, if the inequality $2k_4k_{-2} > k_{-4}k_1$ is fulfilled, then $a_3 < 0$ at every steady-state point, hence it is unique. If, in this case, the parameters are chosen so that $C_3 > C_2$ and $W_3^+/W_2^- > 0$ and W_4^+ is sufficiently low, then $a_2 < 0$.

The calculations show that, at values of the parameters fitting the above conditions, the system will have self-oscillations. If in the mechanism examined, step (4) is substituted by $AZ \rightleftharpoons DZ$, then coefficients a_2 and a_3 take the form

$$a_2 = \frac{W_3^+ W_2^-}{C_1 C_2 C_3} \left[\frac{W_3^+}{W_2^-} (C_2 - C_3) + C_1 + C_2 + C_3 \right] + \frac{W_4^+ W_2^-}{C_1 C_2 C_3 C_4} \left[\frac{W_3^+}{W_2^-} \{3(C_2 + C_4)C_3 + C_1(C_2 + C_3 + C_4)\} \right] + (C_1 + C_3)(C_2 + C_4)$$

$$a_3 = \frac{W_3^+ W_4^+ W_2^-}{C_1 C_2 C_3 C_4} \left[\frac{W_3^+}{W_2^-} (C_2 + C_4 - C_3) + C_1 + C_2 + C_3 + C_4 \right];$$

Here we can also find a region of the parameters providing self-oscillations of the reaction rate.

All the above mechanisms can be called the simplest catalytic oscillators. In all these mechanisms self-oscillations of the reaction rate are realized due to the combination of the fast system of steps (adsorption mechanism) leading to the sharp change in the number of unoccupied surface sites and of the "slow" reversible step ensuring self-oscillations of their concentration. If the parameters of the "buffer" step are sufficiently small compared with those of the main mechanism, all these oscillations will be typically relaxational.

Let us state the conclusions of this section. We have shown that, in terms of the law of acting surfaces (without any additional assumptions), it is possible to construct sufficiently simple kinetic models for the qualitative interpretation of self-oscillations in the rates of heterogeneous catalytic reactions.

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