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SINGULARITIES IN THE RELAXATION PERIODS IN THE
OXIDATION OF CO ON PLATINUM

V. I. Bykov, A. N. Gorban', and
T. P. Pushkareva

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When studying the process dynamics of chemical reactions the first problem is generally considered to be its limiting (for $t \rightarrow \infty$) conditions. For closed systems this problem has been solved for a fairly general case (see [1-3]); i.e., for $t \rightarrow \infty$ the system tends to a unique stationary point for fixed balance relationships, viz., the positive point of a detailed balance which is a stable "node" [4, 5]. A unique solution to this problem evidently does not exist for open systems: here a multiplicity of steady states [6, 7], autooscillations [8, 9], and more exotic limiting regimes [10, 11] are possible.

The singularities in the limiting behavior of the oxidation of CO on Pt have been studied in detail in [12-15]. However, besides a reply to the question "what will happen at $t \rightarrow \infty$?" it is also important to know how rapidly the limiting behavior is established. The slow establishment of chemical equilibrium, associated with delays in the reaction far from equilibrium (the induction periods) has been studied in chemistry since the time of van't Hoff [16]. At present, interest in slow relaxations arises from experiments [17-19] in which it was found that for certain chemical (including heterogeneous catalytic) reactions the reactant concentrations may slowly approach their limiting (steady-state) values, although the observed rate of reaction may remain fairly high. In the opinion of M. I. Temkin, who analyzed the relaxation period in the simplest case of a linear two-stage reaction involving one independent substance [20], such a situation is usually caused not by "intrinsic" relaxation processes which are determined directly by the reaction mechanism, but by "extrinsic"

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relaxation processes arising from reasons of a nonkinetic nature (the diffusion of the substances within the catalyst, a slow variation in its structure, etc.). The case of simple model reactions taking place in a flow reactor with ideal mixing has been discussed in [21, 22].

However, slow relaxations of a purely kinetic nature are possible.* This possibility has been demonstrated, for example, in [14, 23], where a kinetic model for the oxidation of CO on Pt, which corresponds to a nonlinear reaction mechanism, was studied numerically. As shown in [24, 25], slow relaxations of kinetic origin are associated with the presence of bifurcations (critical phenomena) in the system. A detailed mathematical analysis of this connection is given in [26, 27]. Our purpose is to study the singularities of the relaxation period in the oxidation of CO on Pt on varying the parameters over the range corresponding to real experimental conditions. Here we use the results of a parametric analysis of the steady states of a corresponding kinetic model over the real range of partial pressures and temperature presented in [12-15].

The non-steady-state kinetic model of a complex catalytic reaction for a constant composition of the gas phase has the form

$$\dot{x} = \sum_{j=1}^s \gamma_j \omega_j(x) = F(x), \quad (1)$$

where x is a vector for the concentration of the intermediate compounds, the vector γ_j has the coordinates $\gamma_{ji} = \beta_{ji} - \alpha_{ji}$ (β_{ji} , α_{ji} are the corresponding stoichiometric coefficients of the stages of a complex reaction mechanism), ω_j is the velocity of the j -th stage. The range of variation of x is a convex polyhedron D given by the conditions of nonnegativity of the concentration x_i and by the linear laws of conservation (balance relationships). The system (1) possesses the property that for any initial conditions $x(0) = x^0 \in D$ its solution $x(t) \in D$ for all $t \geq 0$. Generally, a number of parameters (temperature, partial pressures of the substances in the gas phase, rate constants of the stages, etc.) occur in the mathematical model (1). If they are signified by the vector α , then (1) is written in the form

$$\dot{x} = F(x, \alpha). \quad (2)$$

Since each solution to (2) is determined by fixing a specific value of α and the initial conditions, we shall therefore write that $x = x(t, \alpha, x^0)$. The steady-state (st.s) of system (2) is defined as the solution to the equation $F(x^*, \alpha) = 0$. The latter implicitly gives the dependence of x^* on α , which may be unique or not unique, respectively, in the cases of a unique st.s. or a multiplicity of them. In the second case x^* may vary "discontinuously," with a change in α - new st.s. may appear or old st.s. disappear. Such bifurcations are possible for even the simplest reactions involving stages of the interaction of different intermediate substances (e.g., see [7]). The possibility of critical phenomena for the oxidation of CO on Pt was shown on models in [12-15]. We may note that at that time quite recent experimental data characterizing the multiplicity of st.s. in a separate range of parameters [28] had not appeared.

In an analysis of the establishment processes it is not the rate of motion (\dot{x}) which plays the principal role but rather the time of establishment itself. For stable linear systems the relaxation period is introduced reasonably as $\tau = -1/\text{Re}\lambda$, where λ is an eigenvalue of the matrix for the right-hand sides of the system (2) containing the lowest real part with respect to the modulus (a "linear" relaxation period). It is clear that this characteristic is suitable in a nonlinear case only when representing a small vicinity of an equilibrium st.s. in which a linear approximation is valid with sufficient accuracy. Furthermore, for nonlinear systems the real parts of the eigenfunctions of the matrix of a linear approximation to a st.s. may not fully characterize the rate of relaxation, and the choice of time characteristic representing the rate of change of $x(t, \alpha, x^0)$ for $t \rightarrow \infty$ may be indeterminate [25, 26].

Let us introduce the necessary symbols and definitions. For the fixed initial conditions x^0 and set of parameters α let us indicate the ω -limited set of the solution to (2) $x(t, \alpha,$

*Where it is unnecessary we do not indicate what relaxes and in which direction; in these cases relaxation always means the tendency of the reactant concentrations (and, correspondingly, the rates of reaction) to their steady-state values.

x^0) by $\omega(x^0, \alpha)$. This set consists of points \tilde{x} such that $x(t, \alpha, x^0) \rightarrow \tilde{x}$ for a specific sequence $t_i \rightarrow +\infty$. We emphasize that for nonlinear systems the cluster of ω -limited points does not always consist of steady states [8-11].

Let $\varepsilon > 0$, $x^0 \in D$, $\alpha \in K$, $x(t, \alpha, x^0)$ be the solution to (2) with the initial condition $x(0) = x^0$. We define the relaxation period of this solution "with an accuracy ε " as

$$\tau(x^0, \alpha, \varepsilon) = \inf \{t \geq 0 : \rho(x(t', \alpha, x_0), \omega(x^0, \alpha)) < \varepsilon \text{ for } t' > t\}, \quad (3)$$

where $\rho(x, \omega) = \inf_{y \in \omega} \|x - y\|$ is the distance from the point to the set. According to the definition (3), $\tau(x, \alpha, \varepsilon)$ is the time to the final appearance of the trajectory in the ε -vicinity of its ω -limited set. The nature of the tendency of the solution to a limited set can naturally also be represented by other characteristics. For example, besides (3), the period of residence outside the ε -vicinity of the limited set is particularly important (for detail see [26] where six relaxation periods are considered; the period $\tau(3)$ corresponds to τ_3 from [26]). We shall say that for $x^0 \in D$, $\alpha \in K$ slow relaxations exist for the system (2) if such an $\varepsilon > 0$ is found for which $\tau(x^0, \alpha, \varepsilon)$ is not limited above in $D \times K$; for any $t_k > 0$ initial conditions $x^0 \in D$ and a value $\alpha \in K$ are found such that $\tau(x^0, \alpha, \varepsilon) > t_k$.

The necessary and sufficient conditions for the presence of slow relaxations for (2) have been obtained in [26, 27]. There are two possible reasons for slow relaxations corresponding to the period τ : the breakdown of semicontinuity below the function $\omega(x^0, \alpha)$: the existence of $x^0 \in D$, $\alpha \in K$ and $x^* \in \omega(x^0, \alpha)$ such that for certain $\delta > 0$ and sequences $x_i^0 \rightarrow x^0$, $\alpha_i \rightarrow \alpha$ for any $i = 1, 2, \dots$

$$\rho(x^*, \omega(x_i^0, \alpha_i)) > \delta; \quad (4)$$

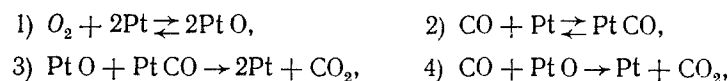
2) the existence in D for a certain $\alpha \in K$ of integral motions which are not positively stable according to Poisson [29], for which the α - and ω -limited sets intersect, i.e., the presence of $\alpha \in K$, $x^0 \in D$ such that $x(t, \alpha, x^0)$ is determinate and lies in D for all t (both positive and negative), x^0 does not belong to $\omega(x^0, \alpha)$ and sequences $t_i \rightarrow \infty$, $t_{jk} \rightarrow \infty$ are found such that

$$\lim_{i \rightarrow \infty} x(t_i, \alpha, x^0) = \lim_{j \rightarrow \infty} x(-t_{jk}, \alpha, x^0).$$

It is natural to call the first singularity e in the dynamics (the breakdown of semicontinuity below $\omega(x^0, \alpha)$) the bifurcation of a ω -limited set and the second the presence of loops (an unstable trajectory with intersecting α - and ω -limiting sets). The initial data (x^0) and (α) occur equally in the presented definition of bifurcation (4), in contrast to the traditional approach, in which only bifurcations with respect to a parameter are considered as a simple example of slow relaxation.

The behavior of the system (1) if the bifurcation of an ω -limited set is associated with the appearance of new st.s. may serve as a simple example of a slow relaxation. If the initial conditions x^0 fall in the range of attraction of a newly appearing st.s. (with a change in the parameters α) then the relaxation period from these initial conditions to the old st.s. tends to infinity as α approaches its bifurcation values. Another example is the behavior of a system close to the separatrixes dividing the region of attraction of the stable st.s. In this case bifurcation is associated with the ω -limited set varying discontinuously when the initial data are incident on the separatrix.

Both these situations, the appearance of new st.s. and the delay of the solution in the vicinity of the separatrix, may be realized in the specific reaction of the oxidation of CO on Pt. As in [12-15], let us consider a two-route mechanism for the reaction:



to which corresponds the non-steady-state kinetic model

$$\dot{x} = 2k_1 p_1 z^2 - 2k_{-1} x^2 - k_3 xy - k_4 p_2 x = P(x, y), \quad (5)$$

$$\dot{y} = k_2 p_2 z - k_{-2} y - k_3 xy = Q(x, y),$$

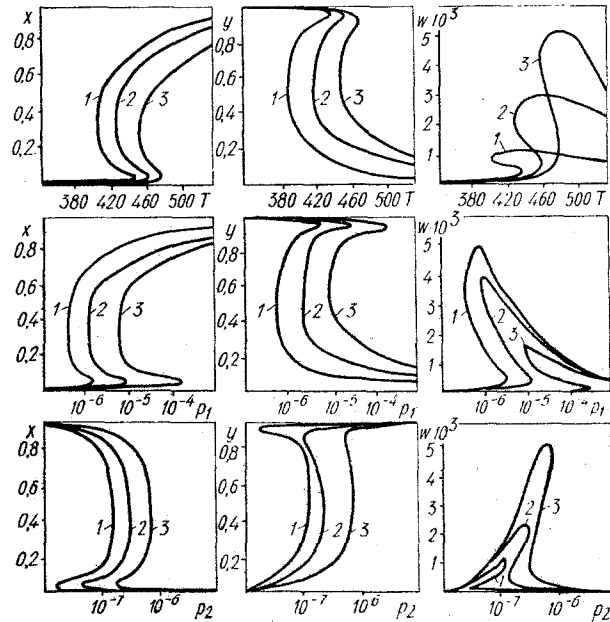


Fig. 1. Dependence of the steady-state values for the concentrations of surface substances x^* , y^* , and rates of reaction w^* on the parameters. a) $p_2 = 10^{-7}$; 1) $p_1 = 5 \times 10^{-5}$; 2) 8×10^{-6} ; 3) 3×10^{-6} ; b) $p_2 = 10^{-7}$; 1) $T = 410^\circ\text{K}$; 2) 450; 3) 470; c) $p_1 = 5 \times 10^{-4}$; 1) $T = 450^\circ\text{K}$; 2) 430; 3) 410.

where x , y , $z = 1 - x - y$ are the concentrations of PtO, PtCO, and Pt, respectively; p_1 , p_2 are the partial pressures of O_2 and CO; $k_i(T)$ are the rate constants of the reactions depending on the temperature T according to the Arrhenius law. In the system (5) p_1 , p_2 , and T occur as the parameters, and the phase variables are x and y . Their range of variation $D = \{x, y; x \geq 0, y \geq 0, x + y \leq 1\}$. The values of the preexponential factors and the activation energies occurring in $k_i(T)$ are presented in [15]. The limits of variation of p_1 , p_2 , and T were given by the inequalities $300^\circ\text{K} \leq T \leq 600^\circ\text{K}$, $10^{-8} \text{ torr} \leq p_1 \leq 10^{-3} \text{ torr}$, $10^{-8} \text{ torr} \leq p_2 \leq 10^{-6} \text{ torr}$, which correspond to the actual conditions of conducting an experiment [12].

Loops are absent for the dynamic system (5), while the ω -limited sets consist only of st.s. which are determined from the equations

$$P(x^*, y^*) = Q(x^*, y^*) = 0. \quad (6)$$

The solutions x^* , y^* to the system of algebraic equations (6) depend on the parameters p_1 , p_2 , and T . Over a wide range of variation of these parameters, (6) may have three solutions [15], i.e., the reaction being considered may have three values for the steady-state velocity $w^* = k_3 x^* y^* + k_4 p_2 x^*$. Examples of the dependence of the steady-state values of x^* , y^* , w^* on the parameters are presented in Fig. 1.

With a change in the parameters p_1 , p_2 , and T over a definite range two st.s. may appear or disappear in the model (5), being produced or removed at the point of bifurcation in a single, level st.s. (for a small variation in the parameters it either disappears from D or gives two new st.s.). This leads to the appearance of hysteresis with respect to the corresponding parameters in the x^* , y^* , $w^*(p_1, p_2, T)$ relationships (see Fig. 1). The range of multiplicity of the st.s. for the reaction being considered within the parameters (p_1 , p_2 , T) has been described in detail in [12, 14, 15].

The type of stability of the st.s. $(x^*, y^*) = (*)$ is determined by the roots of the characteristic equation

$$\lambda^2 - \sigma\lambda + \Delta = 0, \quad (7)$$

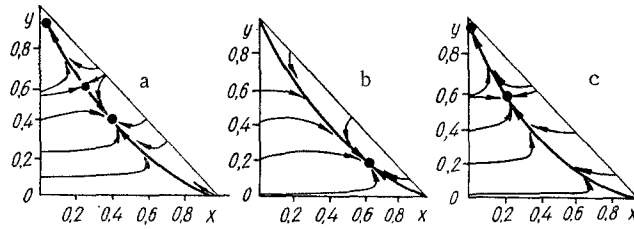


Fig. 2. Phase portrayal of the system (5) for $p_1 = 3 \times 10^{-6}$, $p_2 = 10^{-7}$; a) $T = 450^\circ\text{K}$; b) 470°K ; c) 448°K .

where

$$\sigma = \frac{\partial P}{\partial x} (*) + \frac{\partial Q}{\partial y} (*), \quad \Delta = \frac{\partial P}{\partial x} (*) \frac{\partial Q}{\partial y} (*) - \frac{\partial P}{\partial y} (*) \frac{\partial Q}{\partial x} (*).$$

In our case of (5) $\sigma < 0$ always; therefore, (*) is unstable if $\Delta < 0$. So the unstable st.s. is a saddle for which the roots (7) are real and of different sign (for determinacy we shall consider $\lambda_1 < 0$, $\lambda_2 > 0$). It is easy to show [13] that a unique st.s. is always stable (a stable node); if there are three st.s., then two of them are stable nodes and one is unstable (a saddle).

Phase portrayals of the system (5) give a clear idea of its dynamic behavior [23]. In Fig. 2 phase portrayals are presented of (5) corresponding to the cases of one and three st.s. In the first case the range of attraction of the st.s. is the whole polyhedron of the reaction D. However, if there are three st.s., then D is divided into two parts by the separatrices occurring in the saddle, viz., regions of attraction of two stable st.s. We may note that for our system (5) for any initial conditions $(x(0), y(0)) \in D$ not lying on the separatrix of the saddle, the solution $x(t)$, $y(t)$ is stabilized to one of the stable st.s.

The nature of the variation in the solution to (5) with the presence of three st.s. in time t is shown in Fig. 3. The system first tends rapidly to a certain "general main" (see the phase portrayal in Fig. 2) and then it approaches the st.s. along it more slowly. However, if the initial conditions $x(0)$, $y(0)$ are distributed in a certain ε -vicinity of the separatrix occurring in the saddle, then for the passage of a trajectory in the vicinity of an unstable st.s. another section of a slow variation in the solution appears.

As has already been indicated, with a change in the parameters a bifurcation of the st.s. may take place. It corresponds either to the merging of a node and a saddle and the appearance of a level st.s. of the saddle-node type, or the creation in D of a saddle-node and its splitting into a node and a saddle. A saddle-node type of st.s. has a region of attraction in D, this itself lying at the boundary of this region. The corresponding phase portrayal (5) is presented in Fig. 2c. The situation of the existence of a saddle-node is level-limiting between the cases with one and three rough st.s. The relaxation period τ may be as large as desired in the vicinity of the subsequent points $(x^0, y^0, \alpha) \in D \times K$ (and only in their vicinity): 1) α is a vector of the parameter values for which a level point of the saddle-node type exists in the system; (x^0, y^0) lies in the region of attraction of this saddle-node;

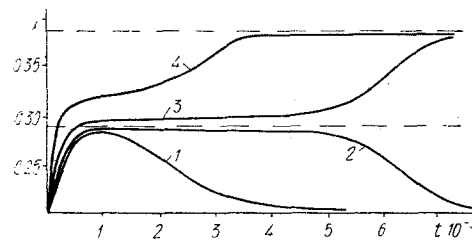


Fig. 3. Behavior of the solution $x(t)$ to the system (5) with time for $T = 450^\circ\text{K}$, $p_1 = 3 \times 10^{-6}$, $p_2 = 10^{-7}$, $x(0) = 0$: 1) $y(0) = 0.59$; 2) 0.60 ; 3) 0.61 ; 4) 0.62 .

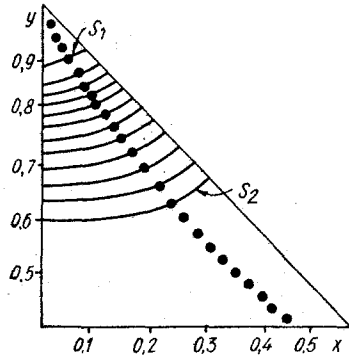


Fig. 4

Fig. 4. Geometrical position of the separatrix of a saddle on the phase portrayal: $p_1 = 3 \times 10^{-6}$, $p_2 = 10^{-7}$, S_1 corresponds to $T = 448^\circ\text{K}$, $S_2 = 468^\circ\text{K}$.

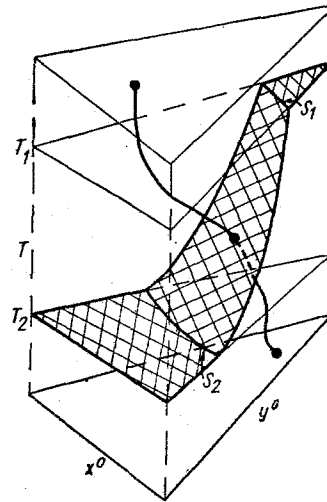


Fig. 5

Fig. 5. Surface of the singularities of the relaxation period.

2) α is a vector of the parameter values for which (x^0, y^0) lies on the separatrix of the saddle.

In the space $D \times K$ the multiplicity of these points forms a surface, the description of whose singularities makes it necessary to calculate the separatrix of the saddle for different parameter values and to search for the region of attraction of the level saddle-nodes. The slope of the direction into which the separatrices enter the saddle is equal to

$$\beta = \left(\lambda_1 - \frac{\partial P}{\partial x} (*) \right) / \frac{\partial P}{\partial y} (*) \quad (8)$$

In order to find the required separatrices numerically it is sufficient to integrate a system of ordinary differential equations of (5) in reciprocal time (replacing t by $-t$) with the initial conditions

$$x^0 = x^* \pm \varepsilon (1 + \beta^2)^{-1/2}, \quad y^0 = y^* \pm \varepsilon \beta (1 + \beta^2)^{-1/2}, \quad (9)$$

where β has been calculated in the st.s. (x^*, y^*) according to (8) and $\varepsilon > 0$ and is sufficiently small. It is necessary to integrate the system (5) up to the emergence of the solution $x(t), y(t)$ at the boundary of the region D .

With a change in one or other parameter, e.g., temperature T , in the region corresponding to the multiplicity of st.s. the separatrices being considered sweep a certain range D^* on the phase portrayal of D (it is hatched in Fig. 4). Apart from the boundaries of D this region is bounded by the separatrices S_1, S_2 of level st.s., these being saddle-nodes corresponding to bifurcations of the st.s., i.e., to the merging or appearance of two st.s. in the given case. For example, with a variation in temperature T over the range $[440^\circ\text{K}, 480^\circ\text{K}]$ (for fixed pressure values $p_1 = 3 \times 10^{-6}$, $p_2 = 10^{-7}$) the bifurcation of the st.s. takes place at $T_1 = 448^\circ\text{K}$, $T_2 = 468^\circ\text{K}$. With a monotonic increase in T the value of T_1 corresponds to the creating of new st.s. (level st.s. of the saddle-node type) which then gives two level st.s. in D (saddle and node). The bifurcation value of T_2 corresponds to the merging of two st.s. to the appearance of a level st.s., which for $T > T_2$ disappears from D . If T decreases monotonically, commencing from a certain value of $T > T_2$, then the sequence of bifurcations is similar to the previous one, a saddle-node is generated at first (first bifurcation), then it is broken down into two new st.s., one of which, unstable with a further variation in the parameter, merges (second bifurcation) with the previously existing st.s. and the only st.s. remaining is the stable one appearing with the first bifurcation. The geometrical position

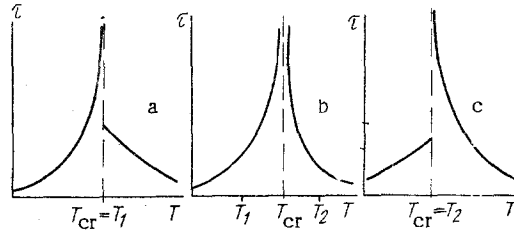


Fig. 6. Qualitative nature for the temperature dependence of the relaxation period.

of the st.s. on the phase portrayal of D is shown in Fig. 4 by the dotted line. The points lying outside D^* correspond to the stable st.s., while those within D^* correspond to unstable st.s.

According to the calculation made, the surface of the singularities in the relaxation period divides the space of the triplet (x^0, y^0, T) into two parts (Fig. 5). To each value of the initial data (x^0, y^0) corresponds a unique value of the parameter T in whose vicinity the solution to (5) emerging from (x^0, y^0) may relax as slowly as desired. Let us call this critical value of the temperature $T_{cr}(x^0, y^0)$. We may note that in the general case this surface may have folds and other singularities but in the example considered it is arranged fairly simply. If $T_{cr}(x^0, y^0) = T_1$ [i.e., (x^0, y^0) lies in the region of attraction of a saddle-node, which appears at $T = T_1$], then the slow relaxations from these initial conditions take place in the vicinity of T_1 for $T < T_1$ (Fig. 6). If $T_1 < T_{cr}(x^0, y^0) < T_2$, then slow relaxations are possible in the vicinity of $T_{cr}(x^0, y^0)$ both for $T > T_{cr}(x^0, y^0)$ and for $T < T_{cr}(x^0, y^0)$. However, if $T_{cr}(x^0, y^0) = T_2$, then slow relaxations exist in the vicinity of T_2 for $T > T_2$. Besides the surface of the singularities it is useful to know those dimensions of the region of initial data (for a given T) from which relaxation takes place more slowly than a given period τ_0 , i.e., to be able to calculate the following quantity:

$$\mu(T, \varepsilon, \tau_0) = \text{mes} \{(x^0, y^0) : \tau(x^0, y^0, T, \varepsilon) > \tau_0\},$$

where mes is a measure (area) of this region. For large τ_0 in the uneven case corresponding to the presence of three st.s., an estimate can be obtained from the equation

$$\lim_{\tau_0 \rightarrow \infty} \frac{\ln \mu(T, \varepsilon, \tau_0)}{\tau_0} = -\lambda, \quad (10)$$

where λ is a positive eigenfunction of the matrix for the linear approach of the right-hand sides of (5) to a saddle point. Equation (10) contains the eigenfunction of the Jacobi matrix for the right-hand sides of (5) not in a stable st.s. but in a saddle (unstable); we recall that for a "linear" relaxation time the rate of relaxation is determined from the eigenfunctions at a stable point to which relaxation takes place.

It should be noted that the retardation of the rate of change in the solutions $x(t)$, $y(t)$ when they pass in the ε -vicinity of a st.s. (*) does not necessarily take place also in the case where $(*) \in D$. For example, just before bifurcation ($T < T_1$) the system (6) has a pair of complex solutions which for $T = T_1$ merge into one st.s. $\in D$ which produces two new st.s. with a subsequent growth in T . The situation just after bifurcation corresponds to the merging of the st.s. $\in D$ into one level st.s., which then produces a pair of complex roots of (6) outside the region D . In both cases slow motions will be observed just before or just after bifurcation, in that part of the region D where st.s. should appear or only just disappear, since here the right-hand sides of the system (5) are small with respect to ε . Consequently, the st.s. which are nonphysical but lying in the vicinity of the region D affect the dynamics of the system. Such "out of this world" st.s. may have an effect on the actual course of events. A similar observation was made for the first time in [30]. The nature of the variation in the solutions to the system (5) in situations just before and just after bifurcation is analogous to that shown in Fig. 3. If the initial conditions of the system (5) are such that on tending to a unique stable st.s. the solutions pass through sections of the region D where P, Q are small (of the order of ε), then a retardation of the rate of change in $x(t)$, $y(t)$ will naturally be observed in this region.

Thus, the surface of the singularities in the period of relaxation to a st.s. has been constructed for a specific catalytic oxidation reaction. A knowledge of it enables us to isolate a region of slow establishment of st.s. (the vicinity of the surface of the ~~spe-~~ singularities) within the space of the initial compositions and parameters. The approach demonstrated may be found useful for studying and understanding the processes of slow ~~estab-~~ relaxation and induction periods.

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OSCILLATING CHEMICAL REACTIONS WITH THE PARTICIPATION
OF MACROCYCLIC NICKEL COMPOUNDS

K. B. Yatsimirskii, L. P. Tikhonova,
L. N. Zakrevskaya, and Ya. D. Lampeka

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Oscillating chemical reactions in which different substrates are oxidized by the bromate ion under a periodic regime may be of three types: 1) oxidation of organic substrates in the presence of catalysts — transition-metal compounds [1]; 2) oxidation of organic substrates in the absence of catalysts [2]; 3) oxidation of transition-metal complexes, serving as catalysts in reactions of the first type [3-5].

Catalysts for oscillating chemical reaction of the first type may be complex compounds able to undergo one-electron oxidation-reduction, and characterized by a value of the standard redox potential within 1.1-1.6 V. Up to the present, only a small number of such catalysts are known: cerium(III, IV)* and manganese(II, III) compounds in sulfuric acid solutions, and also complex compounds of iron(II, III) and ruthenium(II, III) with 2,2'-dipyridyl and 1,10-phenanthroline.

It has already been shown that compounds of iron(II) with phenanthroline are oxidized under fairly severe conditions by bromate ion under an oscillating regime without an organic reducing agent (third type reaction) [3]. We recently discovered a new class of transition-metal compounds, able to participate in oscillating chemical reactions of the first and third types. These compounds were copper(II) and nickel(II) complexes with macrocyclic tetraaza ligands [4-6]. In reactions of the third type with the participation of macrocyclic copper and, in particular, nickel complexes, in contrast to reactions with the participation of complex compounds of iron with 1,10-phenanthroline, stable reproducible concentration oscillations are observed. In the present work we describe the results of a study on oscillating chemical reactions of the oxidation of malonic acid by bromate ion with the participation of a macrocyclic tetraaza complex of nickel(II), and also the oxidation of this complex in the absence of malonic acid.

*In this case, the oxidation state of the metal-ion catalyst periodically changing in the course of the reaction is designated as M(n, n+1).

L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from *Teoreticheskaya i Éksperimental'naya Khimiya*, Vol. 18, No. 4, pp. 439-444, July-August, 1982. Original article submitted September 25, 1981.